Addressable Rubidium vapor cells for optical and electrical read-out of Rydberg excitations

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Zusammenfassung

In den letzten Jahren hat die Quanteninformationstechnologie an Bedeutung gewonnen, unter anderem da sie die Möglichkeit bietet bestimmte mathematische Probleme effizienter als klassische Computer zu berechnen. Quantenmechanische Systeme, die für solche Anwendungen geeignet sind basieren meist auf Einzelphotonen, die die Quanteninformation übertragen und ein System in das die quantenmechanische Information geschrieben, gespeichert und wieder ausgelesen werden kann. Erfolgsversprechende Ansätze für Einzelphotonenquellen oder Quantengatter sind zum Beispiel Quantenpunkte, Stickstoff-Fehlstellen in Diamant oder Atom- und Ionenfallen [1].

Eine weitere Möglichkeit zur Realisierung könnten Rydbergatome bieten [2, 3, 4]. Die Wechselwirkung zwischen zwei nah beieinanderliegenden Rydbergatomen ist so stark, dass durch die Verschiebung der Rydberg-Energieniveaus eine Blockade von weiteren Anregungen um ein bestehendes Rydbergatom entsteht. Innerhalb dieses Blockaderadius kann immer nur ein Rydbergatom angeregt werden, obwohl das Volumen viele Grundzustandsatome enthält. Dieser Blockaderadius kann, abhängig vom Rydbergzustand, mehrere Mikrometer groß sein. Dieser Effekt kann für die deterministische Erzeugung oder Detektion von Einzelphotonen genutzt werden [5]. Quantengatter [6, 7] und Einzelphotonenquellen [8] auf Basis von Rydbergatomen wurden bereits in ultrakalten Experimenten gezeigt.

Da ultrakalte Experimente immer sehr aufwendig sind wäre es für die industrielle Nutzung einfacher, wenn Quanteninformationsverarbeitung mit Rydbergatomen in kleinen, handlichen Dampfzellen realisiert werden könnte, was auch die Skalierbarkeit vereinfacht. Eine vielversprechende Realisierung solcher Dampfzellen wurde in [9, 10] vorgeschlagen. Sie besteht aus einer Anordnung von einzeln adressierbaren Mikrozellen die jeweils kleiner als der Rydbergblockaderadius sein müssen. Jede von diesen Zellen entspricht dann einem Quantenbit. Die kohärente Anregung von Rydbergatomen in 1 µm dünnen Dampfzellen konnte bereits realisiert werden indem durch geschickte Wahl des Rydbergzustands Wechselwirkungen zwischen der Glasoberfläche und den Rydbergatomen gezielt vermieden wurden [10]. Um die Kohärenz der Anregung trotz der hohen thermischen Geschwidigkeit der Atome zu erhalten muss der Anregungsprozess auf wenige Nanosekunden begrenzt werden [11]. Die Detektion von Einzelphotonen von Rydbergatomen in thermischen Dampfzellen muss noch gezeigt werden. Die Adressierbarkeit und die Schaltung der Transmission mit Hilfe von elektrischen Feldern wurde in [12] gezeigt und ist auch Teil dieser Arbeit.

Eine ähnliche Anwendung für Dampfzellen mit thermischen Atomen ist die Definition von Basisgrößen in der Physik. Durch die Ununterscheidbarkeit von Atomen sind Definitionen von Basisgrößen wie der Sekunde, die an atomare Eigenschaften wie z.B. Übergangsfrequenzen zwischen atomaren Niveaus gekoppelt sind in hohem Maße reproduzierbar und genau [13]. Dies wurde unter anderem in miniaturisierten Atomuhren gezeigt, die aus Dampfzellen bestehen und bei oder oberhalb der Raumtemperatur betrieben werden [14].

Solche Alkali-Dampfzellen können außerdem für die Magnetometrie oder zum detektieren von elektrischen und magnetischen Feldern verwendet werden [15, 16]. Hier wird die hohe Sensitivität der Atome auf Felder ausgenutzt. Sie bieten den Vorteil, dass für Sensoren auf atomarer Basis keine Kalibrierung notwendig ist und die Atome im Gegensatz zu Festkörper-basierten Sensoren nicht altern. Atomare Konstanten, wie die Polarisierbarkeit oder Übergangsmatrixelemente können berechnet werden. Manche dieser Objekte, wie z.B. Atomuhren werden bereits industriell hergestellt. Die Herstellung von solch kleinen Atom-Dampfzellen erfolgt ähnlich wie in der Halbleiterindustrie auf Basis der Waferstrukturierung. Alle bisher realisierten kommerziellen Produkte basieren allerdings auf der Verwendung von Alkaliatomen in niedrig angeregten Zuständen. Im Gegensatz dazu, und im Hinblick auf der Verwendung von mikroskopischen Dampfzellen mit Rydbergatomen für Quanteninformationstechnologie, sind die Anforderungen für Rydbergatome deutlich höher. Insbesondere muss der Druck in solchen Zellen wesentlich niedriger sein, da ansonsten keine Rydberganregung möglich ist. Für eine Anordnung von einzeln adressierbaren Mikrozellen können entweder die einzelnen Zellen direkt in das Glas strukturiert werden [17], oder einzelne Zellen können durch eine Anordnung von Elektroden, ähnlich wie Pixel in Flüssigkristall-Bildschirmen angesprochen werden. Durch Anlegen von elektrischen Feldern an jedem einzelnen Pixel werden die Energieniveaus der Atome aus der Resonanz geschoben und damit die Transmission des atomaren Dampfes gesteuert. Dampfzellen mit Dünnschicht-Strukturen können nicht wie herkömmliche Alkali-Dampfzellen durch Verschmelzen hergestellt werden, da die Dünnschicht-Strukturen sonst zerstört werden. Deswegen musste eine neue Fabrikationsmethode gefunden werden um Zellen mit Dünnschicht-Strukturen herzustellen, die für Rydberg-Spektroskopie geeignet sind.

In dieser Arbeit wurden Methoden entwickelt um Elektroden in Dünnschicht-Technik in Alkali-Dampfzellen zu implementieren und mit Rydberg-Spektroskopie zu charakterisieren. Eine Methode ist das verkleben von zwei beschichteten Glasplatten mit einem Glasrahmen [12]. Der verwendete Klebstoff muss eine niedrige Ausgasrate besitzen, da sich sonst der Druck in der Zelle zu schnell erhöht und Rydberg-Spektroskopie aufgrund von Kollisionsverbreiterung nicht mehr möglich ist. Selbst bei unserem verwendeten Klebstoff (Epotek 377) mit sehr geringer Ausgasrate wurde eine Erhöhung des Hintergrunddrucks in der Zelle beobachtet, was die Verwendbarkeit unserer geklebten Zellen auf 4 Wochen einschränkte (Kapitel 4). Um eine längere Lebensdauer zu erreichen und die Zerfallsrate der Rydbergatome weiter zu verkleinern wurde doppelseitiges anodisches Bonden zur Herstellung der Zellen eingeführt (Kapitel 1.3, 2). Dieses Verfahren beruht darauf zwei Substrate, bevorzugt ein siliziumbeschichtetes Substrat und ein natriumhaltiges Glassubstrat, auf eine Temperatur zu erhitzen, bei der die Natrium-Ionen in dem Glassubstrat beweglich werden. Wird dann eine Hochspannung über der Grenzfläche angelegt, so dass sich die Natrium-Ionen von der Grenzfläche wegbewegen, lassen sie gebundene Sauerstoffatome im Glas zurück, die sich dann mit den Silizium-Atomen des zweiten Substrats auf molekularer Ebene verbinden. Hierdurch wird eine hermetische Verbindung zwischen den beiden Substraten hergestellt. Mit dieser Methode konnte eine Rubidium-Dampfzelle realisiert werden, deren Hintergrunddruck über mehrere Monate stabil ist und zusätzlich Dünnschicht-Elektroden aus Chrom enthält [18]. Diese Zellen sind außerdem für Temperaturen bis mindestens 230 °C geeignet ohne eine irreversible Kollisionsverbreiterung der Rydberg-Signale, was besonders für dünne Zellen wichtig ist (Kapitel 4).

Implementierte Elektroden in Alkali-Dampfzellen bieten außerdem die Möglichkeit die Rydberg-Population direkt als einen Ionisierungsstrom über

die Elektroden zu detektieren (Ref. [19], Kapitel 5). Dies ist vergleichbar mit der gezielten Ionisierung und Detektion von einzelnen Ionen über Multi-Channel-Plates in Vakuum-Kammern. Diese können aber nicht in Dampfzellen eingesetzt werden. Stattdessen konnte in unseren Experimenten gezeigt werden, dass die kontinuierliche und unvermeidliche Ionisation der Rydbergatome durch Kollisionen mit einem Hintergrundgas, oder auch Rubidium-Grundzustandsatomen, ausreichend ist um einen Rydberg-Ionisationsstrom zu erzeugen. Die entstandenen Ladungen müssen hierfür über Elektroden in der Zelle nach außen abfließen können. Es wurde gezeigt, dass die Amplitude des gemessenen Ionisationsstroms direkt proportional zur Rydbergpopulation ist. Die Messung der Population kann zusammen mit der optisch ausgelesenen Transmission zusätzliche Information über das System liefern. Abhängig von den Parametern wie Atomdichte, Rabi-Frequenzen und Zerfallsrate des Rydbergzustands kann diese Methode sogar ein besseres Signal-zu-Rausch-Verhältnis liefern als die Transmission. Dies ist z.B. bei hoher optischer Dichte der Fall, wenn die Transmission des Probe-Lasers zu schwach ist um detektiert zu werden, oder bei hoher Zerfallsrate des Rydbergzustands aufgrund der hohen Anzahl der stattfindenden Kollisionen.

Die implementierten Elektroden wurden außerdem genutzt um elektrische Felder anzulegen und die Stark-Verschiebung des Rydberg-Zustands zu vermessen (Kapitel 6). Hierbei wurde beobachtet, dass sich eine im Mittel konstante Raumladungsdichte in der Zelle befindet die das konstante Feld eines Plattenkondensators in ein annähernd lineares Feld deformiert. Durch die Mittelung des betrachteten Signals entlang der Laser-Propagationsachse wird effektiv die Summe über verschiedene elektrische Felder beobachtet. Dadurch konnte zwar keine räumliche Verteilung, aber eine Häufigkeitsverteilung der vorhandenen Felder bestimmt werden. Die Ursache für die hohe Anzahl an Raumladungen ist der photoelektrische Effekt durch den blauen Anregungslaser auf der Glasoberfläche, die mit einer dünnen Schicht Rubidium benetzt ist. Dies konnte durch die Bestimmung der Austrittsarbeit des Prozesses eindeutig bestimmt werden. Die Vermeidung dieser Raumladungen könnte durch eine Drei-Photonen-Rydberganregung mit drei roten bzw. infraroten Lasern anstatt einer Zwei-Photonen-Anregung mit einem roten und einem blauen Laser erreicht werden um die Homogenität der elektrischen Felder in Dampfzellen zu erhöhen.

Um ein ganzes Array an einzeln ansteuerbaren Pixeln mit maximaler Homogenität des elektrischen Felds zu erreichen wäre es vorteilhaft transparente Elektroden zu verwenden. Standardmäßig wird für Flüssigkristallbildschirme und Solarzellen Indium-Zinnoxid oder Aluminium-Zinkoxid verwendet. Allerdings reagiert Rubidium mit diesen Oxiden, was in schwarzem, nicht mehr transparrentem, Rubidiumoxid resultiert und damit nicht mehr verwendet werden kann. Eine mögliche Alternative ist dotierter Diamant. Dieser ist allerdings nur schwer auf bestehende Substrate zu integrieren, da er nur auf bestimmten Materialien gewachsen werden kann. Aus diesem Grund wurde in dieser Arbeit Graphen als mögliches transparentes leitfähiges Elektrodenmaterial für Alkali-Dampfzellen untersucht indem eine Graphen-Flocke auf die strukturierten Elektroden transferiert wurde. Mit zwei solchen strukturierten Glassubstraten wurde dann eine Zelle mit anodischem Bonden hergestellt und mit Rubidium befüllt. Graphen behält sowohl seine hohe Transparenz für sichtbares Licht, als auch seine hohe elektrische Leitfähigkeit auch nachdem es längere Zeit Rubidium-Dampf ausgesetzt war (Kapitel 7). Ein Nebeneffekt ist, dass Rubidium bevorzugt auf der Graphen-Oberfläche adsorbiert wird. Aus Messungen des photoelektrischen Effekts wurde eine um 100-fach erhöhte Rubidium-Benetzung auf Graphen verglichen mit der reinen Glasoberfläche beobachtet. Diese Adsorption macht sich auch im Raman-Spektrum von Graphen bemerkbar, wo zusätzlich zu den charakteristischen Raman-Peaks ein zusätzlicher Peak sichtbar ist, der vermutlich durch die Rubidium-Kohlenstoff-Verbindung zustande kommt. Dieser Effekt könnte sich als Dotierung von Graphen mit Rubidium für elektronische Bauteile wie z.B. Graphenbasierte Transistoren als nützlich erweisen.

Im Hinblick auf Sensoren auf Basis von Rydberg-Atomen wurde die Methode aus [15] zur nicht-invasiven Detektion von Mikrowellen mit Hilfe von Rydbergatomen erweitert auf eine räumliche Detektion (Ref. [20], Kapitel 8). Hierbei wird ausgenutzt, dass die Übergangsfrequenzen zwischen zwei benachbarten Rydbergzuständen im Mikrowellenbereich liegen. Bei Anregung eines Rydberg-Zustands macht sich eine resonante Kopplung zum benachbarten Zustand in einer Änderung der Transmission eines Probe-Lasers als Aufspaltung der elektromagnetisch induzierten Transparenz bemerkbar. Diese Aufspaltung ist direkt proportional zur Feld-Amplitude der eingetrahlten Mikrowelle. Durch Abbildung der Transmission des Probe-Strahls kann die räumliche Verteilung der Feldamplitude der Mikrowellen detektiert werden. Die Auflösung ist dabei nur durch das optische Abbildungssystem begrenzt und damit weit unterhalb der Wellenlänge der Mikrowelle (in unserem Fall 65 µm ensprechend zu $\lambda_{MW}/650$). Dieses Verfahren wurde an zwei Beispielen demonstriert, einer stehenden Welle zwischen einem Mikrowellen-Horn und einer Metallplatte und dem Nahfeld oberhalb einer Streifenleitung um eine Nahfeldmessung zu demonstrieren.

Diese Methode des anodischen Bondens zur Herstellung von Alkali-Dampfzellen kann nun genutzt werden um komplexere Strukturen in Dampfzellen zu integrieren. Möglichkeiten wären z.B. integrierte Schaltkreise, Implementierung von optischen Wellenleitern oder Mikrowellen-Leitern zur Nahfeldmessung und schließlich die Herstellung dünner Zellen für die Anwendung in der Quanteninformationsverarbeitung. Diese dünnen Zellen können außerdem zur grundlegenden Untersuchung von Wechselwirkungen zwischen Rydbergatomen und verschiedenen Oberflächen verwendet werden.

Introduction

Quantum information technology has experienced a continuing and increasing interest in the last years. It proposes the possibility to solve specific problems more efficiently than classical computations. One example of the advantage of quantum computation compared to classical calculation is the prime number factorization by Shor's algorithm [21]. Also a secure communication can be realized via quantum cryptography.

Systems needed for such applications are often based on single photon sources as information carrier and a system where entangled states can be created and read out. Promising realizations of quantum systems, like single photon sources or quantum gates are already realized with systems like quantum dots, nitrogen vacancy centers in diamond or trapped ions and atoms [1].

A different approach is the use of Rydberg atoms for quantum information processing [2, 3, 4]. The strong interaction between two Rydberg atoms induce a blockade of excitations surrounding the Rydberg atom. Within a certain blockade radius, only one of the atoms can be excited to the Rydberg state. This blockade radius can be on the order of several micrometer. This effect can for example be used for the deterministic creation or detection of single photons [5]. The demonstration of quantum logic gates [6, 7] and single photon sources [8] with Rydberg atoms has already been shown in ultracold experiments.

For scalability and applicability it would be much more convenient, if the quantum information technology with (Rydberg) atoms can be done in room-temperature vapor cells instead of ultracold experiments. A versatile realization of such vapor cells has been proposed in [9, 10]. It consists of an array of addressable microcells. Each microcell, which must be smaller than the Rydberg blockade radius corresponds to a qubit. The possibility to coherently excite Rydberg atoms in thin vapor cells and a possibility to avoid surface

interaction with the Rydberg atoms have already been shown [10]. To reach the frozen gas limit in a thermal vapor the whole excitation process has to be limited to short timescales [11]. Demonstration of single photon detection from Rydberg atoms in vapor cells still needs to be done. The addressability using the DC Stark shift and the ability to switch the transmission by an electric field has been shown in [12] and is also a topic of this thesis.

A slightly different application of atomic systems can be found in the definition of fundamental units. The reproducibility and accuracy of atoms make them perfect candidates for using atomic properties, like atomic transition frequencies, as standard definitions for length and time [13]. This has been realized also in miniaturized chip-scale atomic clocks [14], which are based on vapor cells, operated above room-temperature.

Alkali vapor cells at and above room-temperature are currently also used for magnetometry and electric and magnetic field sensors [15, 16]. They use atomic properties, like the sensitivity of atoms to magnetic or electric fields to detect such fields, with the advantage that such devices do not need a calibration because the atomic constants, like the polarizability of the atoms or transition dipole moments can be calculated and do not change for different samples. For some of these applications vapor cell production has reached an industrial level. They can be fabricated "on-chip", with processes similar to the ones in the semiconductor industry. All of them have in common, that they use alkali atoms in low excited state.

In contrary to that, and in the perspective for the use of microscopic vapor cells for quantum devices, the requirements for Rydberg spectroscopy are more strict. In particular, the vacuum level inside the vapor cells has to be much lower for Rydberg spectroscopy. In thin cells the surface interaction starts to play a role, which can lead to a significant decrease of the lifetime of the Rydberg atoms. For an array of addressable microcells, the single cells can either be structured inside the bulk glass, or addressability can be achieved by including an array of thin film electrodes similar to the pixels of a liquid crystal display. Then the transmission of each pixel can be switched by applying electric fields to them. Thin film structures, with the possibility to scale them down to µm-size cannot be implemented in common glass-blown vapor cells. For that reason a new fabrication method had to be found.

In the scope of this thesis, fabrication methods for room temperature vapor cells are developed, characterized and compared. One method for implementing integrated thin-film electrodes is glueing of structured substrates together to a cell [12]. A glue with a low outgassing rate has to be used to fulfill the requirement of low background pressure, which is needed for Rydberg spectroscopy. Gluing of glass cells for alkali vapor spectroscopy is a widely used technique. In experiments, where the cell is constantly pumped or buffer gases are used, outgassing of the glue is not such an important issue as in our case. We want to have a spectroscopy cell, that is sealed and detached from the vacuum pump after filling it with alkali atoms under high vacuum $(10^{-7} \,\mathrm{mbar})$. No buffer gases can be used, as they decrease the lifetime of the Rydberg atoms. As the finite outgassing rate of every glue lead to a limited lifetime of glued vapor cells, a sealing technique without glue would be preferable, that still allows for thin film electrical feedthroughs. A technique that is widely used in the fabrication of chip-scale atomic clocks and magnetometer is anodic bonding [22]. With this method silicon can be bonded to glass by heating it to elevated temperatures and applying such a high voltage between the two samples, that ions inside the glass become mobile. Then bonds on a molecular level are formed, that hermetically seal the cell. With such a method thin-film electrodes have been implemented in alkali vapor cells [18].

For the realization of transparent electrodes graphene layers were implemented in our vapor cells because conductive metal-oxides like indium tin oxide (ITO) react with alkali atoms and cannot be used. Boron doped diamond, which is also a transparent and conductive material is much harder to integrate on different substrate materials and structures because it can only be grown on specific surface materials. The large scale production of graphene, that has been recently realized [23], offers the possibility to implement large area graphene electrodes, that can be lithographically structured. The homogeneity of the electric fields produced by different electrode materials is described and possible sources for inhomogeneity discussed.

With the implementation of electrodes inside a vapor cell a new detection method of the Rydberg population [19] has been realized. Charges that are produced by ionization of the Rydberg state can be detected by measuring the current through the atomic vapor. The ionization current is on the order of nanoampere and can be detected via a current amplifier. Apart from the future realization of quantum systems with such vapor cells, already now there are plenty of applications of vapor cells with integrated electrodes as a field sensor or a detector of Rydberg atoms.

The same technique of vapor cell fabrication could be used to implement waveguides for optical or microwave frequencies inside the cell. Microwave frequencies, that are resonant to a transition between two different Rydberg states can be used to detect microwave electric fields without disturbing the field itself. A a proof of principle the spatial microwave field distribution of two different structures has been imaged by measuring the transmission of resonant light through a medium of Rydberg atoms [20].

Outline

During this thesis, the fabrication of vapor cells with thin film electrodes, that are suited for Rydberg spectroscopy has been realized. The properties of the vapor cells and the produced electric fields has been characterized.

In chapter 1 general properties of Rydberg atoms are described, especially the behavior in electric fields and ionization of Rydberg atoms by several processes. Furthermore, details about anodic bonding, an introduction to the material graphene and a short reminder of the properties of the photoelectric effect are given to understand the results described in the experimental sections.

All steps of the fabrication process of glued and anodically bonded vapor cells with thin-film electrodes are summarized in chapter 2. Also the fabrication of special cells is described, like a cell with a thin atomic vapor thickness and a graphene coated cell. A short description of the three-level-system and electromagnetically induced transparency is given in chapter 3.

The vapor cells are characterized in chapter 4, by testing the background pressure and the temperature stability of the cells, using Rydberg atoms as a sensitive probe. Detection of the Rydberg population in vapor cells by measuring the ionization current is shown in chapter 5. Electric field measurements and the determination of the homogeneity of them is described in chapter 6.

In chapter 7 vapor cells with a graphene layer on top of the chromium electrodes are characterized by detection of the photoelectric current, Raman spectroscopy and Rydberg spectroscopy.

The spatial detection of microwaves with Rydberg atoms with a resolution below the microwave wavelength is described in chapter 8.

At last a brief summary of the experimental results and an outlook for future possible applications and projects is given.

CHAPTER 1

Theory

For all experiments presented in this thesis, alkali Rydberg atoms in room temperature vapor cells are used. As the properties of Rydberg atoms are already very well understood and discussed elsewhere [24, 25, 26], only the main topics relevant for this work will be presented in section 1.1. This especially applies for the high polarizability, and thus the characteristics of Rydberg atoms in electric fields. Also the most important ionization processes of Rydberg atoms, that are relevant for our conditions, are described. New vapor cell fabrication methods have been developed, to fulfill all conditions required for Rydberg spectroscopy. A short overview over different vapor cell fabrication techniques is given in section 1.2. The process and properties of anodic bonding is discussed in detail in section 1.3. At last, some basic properties of graphene, section 1.4, and a quick reminder of the behavior of the photoelectric effect (section 1.5) are shown.

1.1 Rydberg atoms

1.1.1 General properties of Rydberg atoms

Rydberg atoms are atoms, where at least one electron is in a state with a high principal quantum number. In our experiments it is usually between n = 20 and n = 50. If we limit our considerations to atoms with one valence electron, as it is the case for alkali atoms, we can treat the atom and the

electron as a hydrogen-like system. The binding energy of such a system is defined by

$$W = -\frac{R_y}{n^2},\tag{1.1}$$

where R_y is the Rydberg constant. In a simple picture, one electron is orbiting around the core and the inner electrons. The core charge is screened by the inner electrons which are assumed to have spherical symmetry and cannot be polarized by the outer electron. Under these assumptions the system can be treated as a hydrogen-like atom. For Rydberg electrons which have a high probability density at the core, the screening is decreased and they see a potential which is deeper than the pure Coulomb potential. This is the case for valence electrons in a state with low angular momentum. Due to the deeper potential the binding energy for these electrons is larger compared to the hydrogenic states. It can still be calculated with the Rydberg formula, replacing the main quantum number with an effective main quantum number, which includes the so called quantum defects δ_{nlj} [27]

$$W = -\frac{R_y}{n^{*2}} = -\frac{R_y}{(n - \delta_{nlj})^2}.$$
(1.2)

The quantum defects δ_{nlj} can be calculated by the Rydberg-Ritz formula

$$\delta_{nlj} = \sum_{i=0,2,4,\dots} \frac{\delta_i}{(n-\delta_0)^i} = \delta_0 + \frac{\delta_2}{(n-\delta_0)^2} + \frac{\delta_4}{(n-\delta_0)^4} + \cdots$$
(1.3)

Values for experimentally determined quantum defects can be found in [28, 29, 30].

The scaling of some important properties of Rydberg atoms with the main quantum number is shown in Table 1.1.

The extreme electric field sensitivity, given by the scaling of the polarizability with n^{*7} , is important for the experiments described in this thesis. Already small electric fields are modifying the properties of the atomic medium, like the optical transmission for resonant light. Also the cross-section is important when we have a closer look at ionization properties of Rydberg atoms. The large geometrical cross-section is leading to high collision and ionization rates of Rydberg atoms.

Binding energy	$W = -R_y/n^{*2}$
Orbit radius	$< r > = \frac{1}{2}(3n^{*2} - l(l+1))$
Geometric cross-section	$\sigma = \pi < r >^2$
Polarizability	$\alpha \propto n^{*7}$

Table 1.1: Scaling of some important properties of Rydberg atoms with the effective main quantum number n^* [24].

1.1.2 Rydberg atoms in electric fields

When an electric field is applied, the electronic states of an atom are shifted. The new Hamiltonian describing this effect is

$$H_{Stark} = H_{Atom} + H_{Field}.$$
 (1.4)

 H_{Atom} is describing the atomic potential and H_{Field} includes the potential of the applied electric field. For atoms in ground states or in a state with low main quantum number, the Stark effect is very small. Due to the large size of Rydberg atoms the electron is on a large orbit and only weakly bound. The resultant very large polarizability is leading to a high electric field sensitivity. The perturbation due to the electric field is described by the potential

$$V_{el}(r) = -D \cdot E = e_0 r \cdot E \tag{1.5}$$

where D is the dipole moment of the atom, E the electric field and r the orbit radius. The energy and the wave function are calculated using perturbation theory [31]:

$$W_{a} = W_{a}^{0} + \langle a | V_{el} | a \rangle + \sum_{b \neq a} \frac{\langle a | V_{el} | b \rangle^{2}}{W_{a}^{0} - W_{b}^{0}}, \qquad (1.6)$$

$$\psi_a = \psi_a^{(0)} + \sum_{b \neq a} \frac{\langle a | V_{el} | b \rangle}{W_a^0 - W_b^0} \psi_b^{(0)}.$$
 (1.7)

For high l states (l > 3), the different sublevels remain degenerate without electric field, because due to the low probability density at the core, the energy levels are not perturbed by inner electrons. In that case one can observe a linear Stark effect. The electric field lifts the degeneracy.

At low-l states $(l \leq 3)$, the different l-states are already non-degenerate. Due to the symmetry of the perturbation potential all diagonal matrix elements in Eq. 1.6 vanish and only the quadratic Stark shift can be observed. Together with Eq. 1.5 one can see, that the energy change of the state is then proportional to the square of the electric field strength

$$\Delta W = -\frac{1}{2}\alpha_0 E^2,\tag{1.8}$$

where α_0 is the polarizability of the atom. In this case always a red shift is observed.

A Stark map of rubidium for states around the 32S state is plotted in Fig. 1.1a. The quadratic shift for S and D states and a linear shift for l > 3 can be seen. Due to the coupling between different sublevels, intersections between different states show avoided crossings.

Within the limits of low electric fields and for S-states, empirically determined values for α_0 can be used in our experiment. For the polarizability

$$\alpha_0 = 2.02 \cdot 10^{-9} \cdot n^{*6} + 5.53 \cdot 10^{-11} \cdot n^{*7} \left[\frac{\text{MHz}}{(\text{V/cm})^2} \right]$$
(1.9)

was used [33]. Fig. 1.1b shows a comparison between the calculation of the Stark shift of the 32S state by perturbation theory from Eq. 1.6, together with the quadratic approximation with the empirically determined value for α_0 from reference [33]. The approximation only deviates for high electric fields from the calculation using perturbation theory. For all our applications the approximation is sufficient.

The electric field of the first avoided crossing for all used states, calculated by

$$E_{AC} = \frac{4.638 \cdot 10^8}{n^{*5}} + \frac{1.528 \cdot 10^{10}}{n^{*7}} \left[\frac{\mathrm{V}}{\mathrm{cm}}\right]$$
(1.10)

[33] is at higher electric fields than we used in the measurements, which means we do not have to take into account couplings due to other atomic levels. We limit all our considerations to a single S-state for small enough electric fields.

In Table 1.2 the polarizability, electric field of first avoided crossing and electric field range used in our measurements is shown for the different Rydberg states that were used in the course of the work presented here.



(a) Stark map of the 32S state of rubidium. S and D states show a quadratic Stark shift, whereas the F manifold shows a linear Stark shift (calculated as in [25, 32]).



(b) Quadratic Stark shift of the 32S state of rubidium. Comparison between a calculation of the polarizability by perturbation theory (Eq. 1.6, blue curve) and an empirical formula (Eq. 1.9, red curve).

Figure 1.1: Stark effect of rubidium Rydberg states.

Rydberg state nS	Polarizability α_0	E_{AC}	Electric field range ΔE
22S	$0.1465 \frac{\mathrm{MHz}}{(\mathrm{V/cm})^2}$	$211.87\mathrm{V/cm}$	$0-60\mathrm{V/cm}$
30S	$1.3875 \frac{MHz}{(V/cm)^2}$	$34.63\mathrm{V/cm}$	$0-30\mathrm{V/cm}$
32S	$2.1987 \frac{MHz}{(V/cm)^2}$	$24.05\mathrm{V/cm}$	$0-20\mathrm{V/cm}$



1.1.3 Ionization processes of Rydberg atoms

The large size of Rydberg atoms results in a large geometric cross-section. Due to this large cross-section, Rydberg atoms can easily be ionized by different processes. Ionization processes of Rydberg atoms are discussed for two different reasons. First, due to the effect that ionization can effectively be treated as a decay from the Rydberg state, every Rydberg ionization process induces a decay, which can be observed as a broadening of the Rydberg signal. Second, all ionization processes, independent of what state has been ionized, produce free charges. When the number of these charges is large enough, they can considerably deteriorate the electric field, that has been applied externally. For that reason not only ionization of Rydberg atoms, but also other charge producing processes are discussed here.

The most important parameters for all processes are the density n_P of the perturber particles (atoms, electrons or photons), the relative velocity vbetween the two particles and the cross-section σ of their collision or process. The collision rate can then be calculated by

$$\gamma = n_P \cdot v \cdot \sigma. \tag{1.11}$$

This collision rate effectively acts as a decay of our atomic state and contributes to the line broadening of the atomic state. It can be observed as an additional increase in the line broadening if the collision rate is on the same order of magnitude than the linewidth of the atomic signal. Additionally, ionizing collisions produce free charges, that can be detected as a current through the atomic medium. The magnitude of the maximum ionization current can be estimated by

$$I = n_A \cdot V \cdot \Gamma \cdot e. \tag{1.12}$$

Here n_A is the density of the atoms in the considered state (ground, lower excited state or Rydberg state), Γ the ionization rate of the specific process and e the elementary charge.

As the detection efficiency of the ions will always be less than 100%, this is an upper limit for the current, that can be produced by a specific process.

Photoionization

Photoionization is the process when atoms are illuminated by light followed by ionization of the atom. The energy of one photon is then transferred to the valence electron. The atoms can be ionized when one photon has enough energy to overcome the binding energy of the electron.

The ionization energies from the ground, first excited, and Rydberg state of rubidium are shown in Table 1.3. For the excitation of rubidium into the Rydberg state via the D1 line we use a blue laser, which is for the 22S state at a wavelength of approximately 480 nm. This corresponds to a photon energy of 2.58 eV. This means that the Rydberg state with a ionization energy of 0.03 eV and the first excited state (5P), with an ionization energy of 2.44 eV can be ionized by this laser.

Atomic state	Ionization energy	Cross-section
$5S_{1/2}$	$4.18\mathrm{eV}$	_
$5P_{1/2}$	$2.44\mathrm{eV}$	$\approx 1.3 \times 10^{-21} \mathrm{m}^2[34]$
$22S_{1/2}$	$0.03\mathrm{eV}$	$5 - 10 \times 10^{-21} \mathrm{m}^2 [35]$

Table 1.3: Ionization energies of ground, first excited and Rydberg state of rubidium and measured photoionization cross-sections.

For a blue laser power of $50\,\mathrm{mW}$ the ionization rate of the Rydberg state can be estimated to

$$\Gamma = \rho \cdot c \cdot \sigma = 17 \,\text{kHz.} \tag{1.13}$$

Here, ρ is the number of photons, σ the cross-section and c the speed of light. The number of photons in the excitation volume can be calculated by the laser power P = 50 mW, the photon energy $E = hc/\lambda$, the time needed for the photons to pass the volume t = 5 mm/c and the excitation volume $V = \pi \cdot (300 \text{ µm})^2 \cdot 5 \text{ mm}$.

Ionization of atoms can usually be observed in the experiment as a broadening of the atomic lines. However, the expected ionization rate of 17 kHz is much smaller than any linewidth in our measurements in vapor cells at room temperature, which usually is several MHz. This means that it cannot be observed as a broadening, as the change in linewidth cannot be resolved.

But ionization of atoms is also inducing a current, that can be measured in our vapor cells using the ionization current detection method described later in Chapter 5. The expected charge production rate, that can be detected as an ionization current is

$$I = n_A \cdot V \cdot \Gamma \cdot e = 0.97 \times 10^{-9} \,\mathrm{A}.$$
 (1.14)

with the density of atoms in the (Rydberg) state n_A , the elementary charge e and the volume V. A typical measured ionization current signal is on the order of at least 10 nA which shows, that photoionization cannot be the leading ionization effect and probably is even negligible. This is proved experimentally, as an increase in laser intensity did not increase the atomic current signal. The current observed in the experiment is probably due to a different ionization process.

Ionization by black-body radiation

Black-body radiation is always present due to the temperature of the surroundings. As the energy difference between neighboring Rydberg states is small, a possible ionization path is the direct or stepwise ionization by absorption of black-body radiation. As estimated from [36] the ionization rate due to black-body radiation should only be around 1 kHz. This is expected to be negligible in our case as our linewidth is several MHz.

Collisions with electrons

Electrons can be produced through different processes in the cell. One possibility is the photoelectric effect in which electrons are ejected out of a metallic surface. Another effect might be ionization of the atoms, that will always produce positively charged ions together with electrons.

To estimate an ionization rate for collisions between Rydberg atoms and electrons, the electron density inside the vapor cell needs to be known. The electron density can be estimated for electrons produced by the photoelectric effect. This is the main source for electrons in our cells as explained later in Chapter 7.1. A typical photoelectric current in our vapor cells is about I = 10 nA. The number of electrons can be determined by $n_e = I \cdot t/e$ (t: traveling time of the electrons through the cell, e: elementary charge). The electron density is then

$$\rho_e = \frac{n_e}{V} = 2.3 \times 10^{12} \,\mathrm{1/m^3} \tag{1.15}$$

The electrons are emitted from the surface with a maximum velocity v, depending on the wavelength of the laser. For a work function of 2.16 eV for rubidium and a laser wavelength of 480 nm, corresponding to 2.58 eV, the electron velocity is 3.84×10^5 m/s. The maximum cross-section for ionization of Rydberg atoms by collision with electrons can be found in [37] for different main quantum numbers. From the cross-sections, the ionization rates $\Gamma_{ion} = n_e \cdot v \cdot \sigma$ can be calculated using the electron density and the electron velocity. Values for cross-sections of several rubidium Rydberg states and their ionization rates are given in Table 1.4.

Rydberg state	Cross-section σ [37]	Ionization rate Γ_{ion}
22	$2.1 \times 10^{-15} \mathrm{m}^2$	1.8 kHz
32	$9.2 \times 10^{-15} \mathrm{m}^2$	$8.1\mathrm{kHz}$
42	$2.7 \times 10^{-14} \mathrm{m}^2$	$24\mathrm{kHz}$

Table 1.4: Cross-sections of rubidium Rydberg states for electron collisions [37] and calculated ionization rates. For the calculation of the ionization rate the electron density was estimated from measurements of the photoelectric current and the velocity of the electrons from the difference of the work function and the photoe nergy as mentioned in the main text.

The ionization rates of the Rydberg states by electrons are also smaller than the linewidth of the atomic signal in our experiments and will not induce a broadening. The additional current due to collisions of electrons with Rydberg atoms, calculated by $I = n_A \cdot V \cdot \Gamma_{ion} \cdot e$ can also be neglected, as it is expected to be below 1 nA.

Rydberg-ground state collisions and other collision effects

Collisions between Rydberg atoms and different ground state atoms are investigated in detail in Chapter 4. Collisions with ground state rubidium atoms and with other perturber atoms are major contributions when a broadening of the linewidth is observed in vapor cells.

Self-broadening due to collisions of Rydberg atoms with rubidium ground state atoms has been observed in [38]. For rubidium nS states and main quantum numbers between n = 20 and n = 30 a broadening rate of $1.7476 \frac{\text{MHz}}{(10^{-3} \text{ mbar})}$ has been observed. Especially at temperatures above $100 \,^{\circ}\text{C}$ where the vapor pressure of rubidium can reach more than 10^{-3} mbar, this has an observable effect on the Rydberg linewidth.

The ionization current, expected from this self-broadening rate is for example estimated to 33 nA at $100 \,^{\circ}\text{C}$ for a Rydberg population of 10^{-3} , rising linearly with the density of the atoms.

The self-broadening can only lead to a significant broadening of the atomic signal at temperatures above 100 °C. Below that, only collisions with other perturber atoms can lead to a significant broadening, when the background pressure inside the vapor cell is too high. Some examples are presented together with experimental results in Chapter 4.

Other collision rates between Rydberg atoms and particles are expected to be small. For example Rydberg-Rydberg collisions [39] can be neglected due to the small Rydberg population of $10^{-3} - 10^{-6}$ in our experiments. However for different experimental parameters, like for example in pulsed experiments, where a high Rydberg excitation efficiency can be achieved, this effect has to be taken into account.

1.2 Common vapor cell fabrication methods

Nowadays atomic systems are usually investigated in ultracold experiments. These experiments in general need a large setup and vacuum chambers at ultra-high vacuum (UHV). In the last years more and more experiments are performed in vapor cells instead of vacuum chambers, as it turned out to be much easier for a lot of applications, for example atomic clocks or magnetometer [40, 41]. It has been a revival of the vapor cell fabrication technology. Common alkali vapor cells are fabricated by glass-blowing. Such a cell can then be filled via a connection tube with alkali atoms. For glassblowing temperatures above the melting point of glass are necessary. For the widely used borosilicate glasses, like Schott Duran or Corning Pyrex the melting temperature is 821 - 860 °C. When we want to include integrated thin-film electrodes inside vapor cells, they cannot be fabricated by melting and glass-blowing as the thin film metals would immediately vaporize during the melting of the glass. New fabrication methods had to be found that fulfill all requirements for high vacuum vapor cells under alkali atmosphere and can integrate thin-film structures.

An overview over different wafer bonding methods can be found in [42]. Typical vapor cell fabrication methods are for example

- Optical direct bonding
- Gluing
- Glass frit bonding
- Anodic bonding

Low-temperature bonding techniques like indium bonding are not considered here, because for thin vapor cells temperatures above $150 \,^{\circ}$ C are necessary to achieve a sufficiently high vapor pressure.

Optical direct bonding requires a high quality optically polished surface and typically high temperatures. Usually quartz glass with a melting temperature of 1600 - 1700 °C is used. Then a temperature of around 1270 °C is needed for optical direct bonding to induce diffusion between the two substrates. Here, as well as in the melting and glass-blowing processes the required temperatures are too high to include thin film electrodes inside the cell. Gluing with a low-outgassing glue has been used to fabricate some of our cells, but outgassing of the glue is still too high for long-term pressure stability, as found in measurements shown later in section 4. It could be used for ground-state spectroscopy or when buffer gases are included in the vapor cell, but not for long-term Rydberg spectroscopy.

Another possibility would be glass frit bonding. Liquid glass frit material is usually printed by screen printing with special machines on top of the substrate in the desired structure. Then solvents inside the glass frit material are evaporated by heating it in defined temperature steps and finally cured at around 500 °C. It could be useful for including thick electrode structures, as the glass-frit material can fill gaps at edges of steps. It could also be used for our vapor cells, but requires several sensitive technological methods, that were not available to us.

Anodic bonding has been used in our experiment for the fabrication of long-term pressure stable spectroscopy cells. This technique is free of any solvents, ensuring, that no outgassing or reaction products are produced, which would lead to a background pressure in the cell. This technique is explained in detail in the next section. The thickness of thin-film structures that can be integrated with the anodic bonding technique is limited. Only steps of around 50 nm are tolerated.

1.3 Theory of anodic bonding

Anodic bonding is the process of permanently joining two substrates utilizing a diffusion process, induced by a high voltage. Usually a silicon wafer is bonded to a glass wafer. When cavities are enclosed inside these two wafers and filled with atoms, it can be used for hermetic sealing of vapor cells. It can be used for miniaturization of vapor cells and with defined vacuum or buffer gases.

The process of anodic bonding was first described and patented by Wallis and Pomerantz in 1968/1969 [43, 44]. In their work they describe the bonding of several metals and semiconductors to glass. To date there has been extensive studies with different material combinations and for different applications. It turned out to be a convenient way, especially for the semiconductor industry to create any kind of wafer based silicon-glass devices for example pressure sensors [45], accelerometers [46, 47, 48] and other Microelectromechanical systems (MEMS, see [49, 22] and references therein). In the last years it also became more and more important for the fabrication of alkali vapor cells [14, 50, 51]. The most prominent application in that case is the use for fabricating chip-scale atomic clocks which are now a commercial product [52].

In our work anodic bonding is used for the fabrication of alkali vapor cells for Rydberg spectroscopy. In the following sections the details of the anodic bonding process are explained to demonstrate how a vapor cell for our requirements can be built with this technique.

1.3.1 The principle of anodic bonding

The mostly used material combination for bonding is silicon wafer and a glass wafer. It is necessary for the glass to contain mobile charges if heated to moderate temperatures of around 300 - 500 °C. For that reason borosilicate glasses are mostly used e.g. Schott Duran or Corning Pyrex. These glasses consist of 81 % SiO₂, 13 % B₂O₃, 4 % Na₂O and K₂O and 2 % Al₂O₃ [53]. It is reported, that a root mean square surface roughness of up to 50 nm can be tolerated [54]. Also the flatness of the surface is important and should be at most around 5 µm [55].

For bonding, the two wafers are placed on top of each other on a hotplate (see Fig. 1.2). If the surface roughness and flatness are good enough, Newton interference fringes can be observed if the air gap between the two substrates is around $0.5 - 30 \,\mu\text{m}$. Then the wafer stack is homogeneously heated to $300-500\,^{\circ}\text{C}$. In principle higher temperatures increase the conductivity of the glass and thus the bond strength, but the temperature should be kept below the glass transition temperature of $525\,^{\circ}\text{C}$ to avoid macroscopic deformations. Low temperatures up to $300\,^{\circ}\text{C}$ can be used for sensitive devices or coatings to avoid degradation or destruction of the structures.

A plate or a point electrode is put on top of the stack, and a high voltage, usually between 100-3000 V is applied in such a way, that the semiconductor or metal is the anode and the glass is on the cathode side. At temperatures of 300-500 °C, the sodium ions inside the glass become mobile. By applying an electric field, they diffuse through the glass in the direction of the cathode. As the oxygen ions are less mobile and still bonded to the silicon-oxide structure of the glass, a negatively charged depletion region is left behind at the glass



Figure 1.2: Silicon-glass anodic bonding. Silicon is bonded to glass by applying a high voltage between them which leads to diffusion of mobile sodium ions inside the glass. The remaining oxygen ions form bonds with the silicon from the silicon wafer.

surface facing to the silicon wafer (see Fig. 1.2). These charges create a high electric field directly at the interface of the two wafers, which pulls them together into intimate contact. At the point of intimate contact silicon atoms can diffuse into the glass wafer and bond to the oxygen atoms, left behind from the sodium ions. Now molecular bonds between the two wafers have been formed and created a strong and hermetic sealing.

1.3.2 Bonding conditions and materials

Materials

The most widely used material combination for anodic bonding in industrial applications is bonding of silicon to borosilicate glass. In principle several other metals and semiconductors can be used as anode materials (Al, Fe, Mo, Ni, Ta, Ti, GaAs, Ge) [22]. The main necessary properties of the anode material are [22]:

- 1. It prevents ion movement into or from the cathode.
- 2. The ability to form a high quality bond at the interface, such as through the formation of a thin adherent oxide layer of the anode material.
- 3. The coefficient of thermal expansion of the cathode material should match to the anode material to prevent breaking of the bond during the cooling after bonding.

Interestingly chromium can not be used as anode material, maybe because it forms conductive oxides [56]. It can even be used to avoid bonding at specific positions.

For the substrate at the cathode side only glasses or glass-ceramics are possible. A high sodium content of several percent is necessary to allow an ion current flowing through the material.

Glass-to-glass anodic bonding with intermediate layers

As in our application we need a completely transparent cell to access the atomic vapor with laser beams, we need glass on top and bottom of the cell. Glass-to-glass anodic bonding (or silicon-silicon) can be achieved by using intermediate layers. In Fig. 1.3 a schematic setup of glass-to-glass bonding with an intermediate layer is shown. Several materials are reported to be suitable for the use as intermediate layers in glass-to-glass bonding. Some examples are polysilicon, α -silicon, silicon nitride, silicon carbide, aluminum, or specific combinations of them [57].



Figure 1.3: Glass-to-glass anodic bonding with an intermediate layer. The intermediate layer acts as a diffusion barrier for the sodium ions. Furthermore, the silicon atoms from the intermediate layer are needed to bond to the upper glass wafer.

The purpose of an intermediate layer is, to act as a diffusion barrier for sodium ions from the lower glass substrate, see Fig. 1.3. The diffusion barrier prevents the sodium to migrate through the interface of the two glass substrate. This is necessary, because otherwise no electric field can be accumulated at the interface. As we want to include additional thin film electrodes on the substrate we are limited to non-conductive bonding-intermediate layers. Due to that, all further explanation is focused on non-conductive intermediate layers. Instead of an insulating bonding layer, it would also be possible to use an insulating layer above these electrodes for electrical insulation, then also conductive materials could be used as bonding layers. In our experiments 200 nm of silicon nitride were not enough to insulate the electrode layer from an additional metallic bonding layer. When conductive intermediate layers are used, the bonding voltage can be applied directly to the conductive bonding layer. Then the bonding process is independent of the anode substrate material and also substrates with high resistivity, like sodium-free glasses, can be used.

In Fig. 1.3 the schematic process of glass-to-glass anodic bonding with an insulating intermediate layer is shown. The process itself is similar to silicon-glass bonding. The only difference is, that in both substrates mobile sodium ions are present and migrate from both sides towards the cathode. Due to that, the sodium ions from one side must be prevented from reaching the second substrate. The intermediate layer acts as a diffusion barrier for these ions. The diffusion of sodium ions through silicon nitride is much slower than the diffusion of sodium through glass, which leads to an accumulation of charges at the interface. These charges at the interface create a high electric field in the gap between the substrates which pulls the two substrates together into intimate contact. Then the oxygen with open bonds can react with the silicon of the silicon nitride layer, which results in a strong molecular bond. Of course it is necessary for that process to have a good adhesion of the bonding layer to the anode substrate.

Current characteristics during anodic bonding

During anodic bonding, while the high voltage is applied, an external current can be measured. The time dependency of this current can be related to the microscopic processes, happening during bonding inside the glass [22]. The typical current-time characteristics consists of a sharp peak at the beginning of the bonding process and a slow exponential decay afterwards. An example is shown in Fig. 1.4.

Two competing effects are leading to this behavior:

Initially the two substrates are only at a few points in contact (see inset of Fig. 1.4), because the substrates are not perfectly flat. These are the points where current can flow through the glass. Due to the building up of an electrostatic force between the two substrates, they are pulled closer



Figure 1.4: Typical bonding current versus time. A sharp peak at the beginning indicates a fast rise in the intimate contact region. The building of a cation depletion layer is increasing the resistance, seen by an exponential decay of the current. For longer times, the bonding current stays almost constant. Then the bonding process is finished. Longer bonding times do not increase the bond strength anymore.

together, leading to an increase of the contacted area and by that to a fast increasing current during the first seconds.

At the same time a cation-depletion layer is forming inside the top substrate as sodium ions in the glass move outwards to the cathode. This slow diffusion process is leading to an increase of the resistivity in the depletion layer and thus to a slow decrease of the electrical current.

The current-time dependency can be modeled, for example by a variable capacitor, representing the cation depletion layer, in series with a constant resistance, representing the bulk glass [58]. Already such a simple model gives a qualitative, although not quantitative, description of the current dependency.

Due to the thick substrates in our experiments and the relatively low bonding temperatures (300 °C), the initial increase in contact area happens during the first seconds. The diffusion process for formation of a depletion layer and finally building of molecular bonds usually takes 10 - 100 min in our case, depending on the conditions and geometries.

Figure 1.5a shows the bonding current for different bonding voltages. The peak current is increasing roughly linearly with the applied bonding voltage. The maximum voltage that can be used for bonding is limited by the break-down voltage of air or glass. Depending on the thickness of the glass layer, the voltage cannot be increased to more than the shown 2.5 kV.

Figure 1.5b shows the high temperature sensitivity of the bonding current. For the red curve, the bonding was started immediately after the hot plate had the maximum temperature of 300 °C. It shows a slow increase in bonding current for 1 h. This already indicates, that the substrates have not been in thermal equilibrium because all diffusion processes should lead to a decrease of the bonding current over time. The blue curve shows a bonding process, when the substrates has been preheated for one hour at 300 °C to make sure, that the complete materials are at an equilibrium temperature of 300 °C. Then the peak current was higher and the fast decrease of the current indicates a good bond formation. Details about the temperature dependency of anodic bonding can be found for example in [59].

In principle, a higher voltage, and especially a higher temperature is increasing the bond strength. But the voltage is limited by the breakdown voltage, and the temperature must be limited to avoid degradation of any structures on the substrates. A longer bonding time usually does not increase the bond strength because the number of mobile sodium ions is limited at a specific temperature. As soon as the bonding current decreased to an almost constant value, no further molecular bonds are formed. The constant current arises only due to diffusion through the bonding layer or other leak currents through the material.


Figure 1.5: (a) Bonding current vs. time for different applied voltages. The bonding current increases proportional to the applied voltage.(b) Bonding current with (blue) and without (red) preheating.

Double-side anodic bonding

For the fabrication of a macroscopic cell, a third substrate with a drilled hole is used between the two outer substrates to define the vapor cell thickness. Then the upper and lower substrate have to be bonded from both sides to the middle substrate, hence double-side anodic bonding is necessary. Consecutive double-side anodic bonding was observed to be unstable [60] because a reversal of the bonding voltage destroys the previously formed bonds. Due to that, during bonding of the second side, debonding or at least weakening of the first bond is observed. Although in some cases it was possible to bond several sides one after the other, the bond strength was lower for the second side and weakened for the first side after bonding the second one [50]. Also an accumulation of metallic sodium was observed to occur at the first bonding interface while bonding the second one, which also weakens the first bonded side.

As in the case of glass-to-glass bonding the bond strength is anyway weaker compared to silicon-glass bonds, simultaneous double-side anodic bonding is preferred. Double-side anodic bonding is achieved by using for example a symmetric arrangement of the substrates as shown in Fig. 1.6.



Figure 1.6: Simultaneous double-side glass-to-glass anodic bonding. The bottom and the top electrode are on the same positive potential. The middle substrate is on a negative potential. Simultaneous bonding with equal bond strength on both sides can be achieved.

Here the upper and the lower electrode are kept at the same potential (GND) while the middle substrate is on a negative potential in respect to GND. In this case the outer substrates are coated with the bonding layer

 (Si_3N_4) . Sodium ions then migrate from both sides to the middle electrode. Here a wire around the middle substrate is used as middle electrode.

Pressure inside bonded cells

For the use of anodic bonding for vapor cell construction, the quality of the vacuum that can be achieved inside such cells is important. Spectroscopy of atomic vapors, and especially of Rydberg atoms is done in high vacuum $(10^{-3} - 10^{-7} \text{ mbar})$. In the usual fabrication technique of MEMS devices the cells are bonded for example with anodic bonding or with glass-fritbonding under vacuum. The disadvantage of this technique is, that every gas produced during the bonding stays inside the cell. Getter materials are usually implemented to further reduce the pressure inside the cavities. The simplest getter materials are metal layers which are deposited inside the cavities. The most commonly used getter material is titanium, as used in titanium getter pumps. But also aluminum, chromium and commercial non-evaporable getter are widely used [61, 62].

The pressure which can be achieved in such cavities is reported to be 1.3 - 2.6 mbar for cavities without any getter material, with Al getter 560×10^{-3} mbar, Cr getter 93×10^{-3} mbar, Ti getter 8×10^{-3} mbar and with commercial non-evaporable getter (NanoGetter) 1×10^{-3} mbar [63, 61]. It was observed, that during anodic bonding of cavities in vacuum, they filled with residual gas, probably oxygen, so that the gas pressure within the cavities is significantly higher than the gas pressure of the vacuum chamber [58, 64, 65].

For comparison, the vapor pressure of rubidium at $100 \,^{\circ}$ C is about 0.3×10^{-3} mbar [66]. The achievable pressures inside the cells mentioned above are too high for our applications. For Rydberg excitation the background pressure has to be low enough, that no broadening is visible. Therefore we have to evacuate and fill the cells after the anodic bonding is finished to avoid all gases produced during anodic bonding. An additional improvement of the background pressure is given by the metal layers, as we anyway use them as electrodes inside the cell. Typical getter materials are used as electrodes in our cells (Ni, Al and Cr). As a side effect, they show gettering of the background gases and further reduce the pressure inside the cells after filling and sealing them.

1.4 Introduction to graphene

For future applications of thin vapor cells with an array of electrically addressable pixels, it would be advantageous to have transparent and conductive electrodes, like in liquid-crystal displays. Unfortunately the typical electrode material, indium tin oxide (ITO) cannot be used in alkali vapor atmosphere, because the oxide reacts with alkali atoms. A different approach, but even more complicated is boron doped diamond. However it can only be fabricated on specific substrates, like silicon or quartz glass, is expensive in fabrication and for sufficient conductivity the transparency is in most cases less than 60 % [67]. An alternative is the novel material graphene which is used in this work and for that reason described here in more detail.

Graphene is a relatively new and exceptional material. Properties and applications are reported in plenty of publications, for example [68, 69, 70]. The high electrical conductivity in combination with a high optical transmittance for white light of 97.7%, but also other properties, such as chemical inertness and high thermal conductivity offer a great possibility for potential applications. Many of them are already realized and on the way to be used in industrial processes, for example transparent conducting electrodes for touch-screens, liquid-crystal displays, organic photovoltaic cells or organic light-emitting diodes. It can also be used as a sensor by detecting adsorbed molecules like CO, H_2O , NH_3 or NO_2 or in electronic circuits as ballistic transistor or field emitter.

Graphene consists of hybridized sp^2 -bonded carbon atoms in a honeycomb crystal lattice, see Fig. 1.7a. Strong σ -bonds stabilize the hexagonal structure, while the weak π -bonds define the interaction between the different layers.

Graphene can be characterized by Raman spectroscopy. Details about the Raman spectrum of graphene can be found in [71]. A typical Raman spectrum of single layer graphene is plotted in Fig. 1.7b. Several Raman peaks are visible. The G band at around $1585 \,\mathrm{cm}^{-1}$ is due to a doubly degenerate phonon mode of a TO and LO phonon at the center of the Brillouin zone. The 2D band at $2700 \,\mathrm{cm}^{-1}$ is a second-order two-phonon mode from two TO phonons from the edge of the Brillouin zone at the K point. The D band at around $1350 \,\mathrm{cm}^{-1}$ is not Raman active, but can be observed when there are defects in the graphene [68]. It is originating from one TO phonon and one



Figure 1.7: (a) Graphene consists of a monolayer of carbon atoms in a hexagonal structure. (b) Raman spectrum of pristine CVD grown graphene. From the Raman spectrum properties of the graphene layer can be determined.

defect at the K point. The G and the 2D peaks show characteristic shifts and broadening depending on the number of graphene layers. The D peak in Raman spectroscopy is only visible for few-layer graphene or due to grain size in single layer graphene. The 2D peak decreases with the number of graphene layers, while the G-peak is increasing for thicker graphene sheets. From the Raman spectrum shown in Fig. 1.7b we can infer, that our sample consists of single layer graphene, as the D peak is very small and the 2D peak consist only of a single peak [72].

Graphene was fabricated at first by mechanical cleavage of graphite. Nowadays there are several methods how single- or few-layer graphene can be produced. For example it can be fabricated by chemical vapor deposition onto a copper foil. Then the graphene is covered with poly-methyl-methacrylate (PMMA) as a support layer. The copper can be etched and the graphene can then be transferred onto any substrate. This has already been implemented into a large scale production of graphene sheets with 30 inches diagonal size [23]. The graphene samples for our experiments have also been produced by that method.

The charge carriers in graphene are massless Dirac fermions. They can be alternated between holes and electrons (called ambipolar) by changing the Fermi energy. It can be described as a semi-metal or a zero-gap semiconductor. However by doping the Fermi level can be shifted. The work function of intrinsic graphene is around $4.57 \,\mathrm{eV}$ and can be changed in the range of $4.5-4.8 \,\mathrm{eV}$ by different methods like doping with adsorbed molecules, metal contacts, electric fields or dipolar layers on the graphene surface. Then the Fermi level is either shifted up or down resulting in a lower sheet resistance while keeping over around 90% transmittance. Use of metal contacts or adsorbants with a lower work function than graphene, like chromium contacts, or rubidium adsorbants are reducing the work function of the graphene sheet.

In contrary to ITO graphene, can also be used for flexible devices, while ITO electrodes are too brittle. Carbon nanotubes (CNT) are also an upcoming alternative for ITO, as it has similar properties than graphene and might be implemented easier in industrial processes. One disadvantage could be the rougher surface.

1.5 Photoelectric effect

A short reminder of the photoelectric effect is given here to explain some effects, that have been observed in our experiments. The photoelectric effect has been a long-known effect, since Becquerel observed it in 1839 and Einstein received his Nobel prize for the explanation by introducing photons as discrete light particles. This effect can be used to determine some characteristic properties of the surface materials used in our experiments. In fact, as soon as we use an excitation laser with short enough wavelength, which is shining on a surface, we can not avoid the photoelectric effect, but have to include it in our discussion.

The principle of it is, that a (usually metallic) surface is illuminated by light with a specific wavelength λ . Part of the photon energy is used to overcome the binding energy of the electron, which is called the work function. As the photon energy can only be transferred completely to one electron, the remaining energy is transferred as kinetic energy to the electron and the electron is ejected out of the surface (Fig. 1.8a).

When a negative potential is applied between this metal surface and a second electrode, the electrons only reach it, when their kinetic energy is larger than the potential energy (Fig. 1.8b). When a positive voltage is applied to the electrode, the electrons can be detected as a photoelectric current (see Fig. 1.8c).





(a) Photoelectric effect for positive voltage.

(b) Photoelectric effect for negative voltage.



(c) Current characteristic of (d) Photoelectric effect for (e) Photoelectric effect for photoelectric effect. different intensities. different wavelengths.

Figure 1.8: Photoelectric effect

By determining the potential required to prevent the electrons from reaching the electrode for different wavelengths, the work function can be determined. This work function is a characteristic property for each material. By a determination of the work function, the material, that covers the surface can be determined.

When a positive voltage is applied, the emitted electrons are accelerated and collected by the electrode. The photocurrent increases with increasing applied potential difference, as at higher voltage, more electrons are collected. When the potential is high enough, the photocurrent gets saturated (see Fig. 1.8c). The amplitude of the saturation current is proportional to the number of ejected electrons, and thus to the power of the incident light (Fig. 1.8d). Due to different quantum efficiencies for different wavelengths and according to the Fowler law [73], the emission rate and thus the saturation current I changes with the light frequency as an approximation by

$$I = c \cdot (\omega - \omega_0)^n \tag{1.16}$$

where ω is the light frequency, ω_0 the threshold frequency and c a constant. The exponent is usually for metals n = 2 at a temperature T = 0 K, however it can be different for alkali metals, depending on the light polarization and metal film thickness.

With a repulsive potential the current decreases until no electrons reach the surface and the current is zero. This stopping potential is independent of the light intensity. It can be seen as a crossing between the curves at different intensities in Fig. 1.8d.

The velocity of the ejected electrons depends on the wavelength of the incident light. The negative stopping potential thus increases with shorter wavelength, as it linearly depends on the light energy (see Fig. 1.8e) but the saturation current should stay the same.

When electrons are emitted from two opposing surfaces (Fig. 1.9), a current can be measured for both electric field directions, leading to an antisymmetric current characteristic with applied positive and negative voltage. Then the work function can no longer be determined by a stopping potential. It can only be determined by changing the wavelength of the incident light and determining at which photon energy no photoelectric current can be detected anymore.

The electrons ejected from the anode side do not contribute to the measured current as long as all of the emitted electrons fly back to the same electrode from which they were emitted. The saturation current for high positive or negative potential thus only measures the number of electrons emitted from the cathode. If the number of emitted electrons is the same on both surfaces, then the flowing current should vanish when no voltage is applied and the saturation current for both field directions should have the same amplitude as in Fig. 1.9. When the number of electrons is different, then a small voltage is needed to compensate the current. From the asymmetry of the saturation intensities the difference in the number of emitted charges can be determined. This is the behavior of the photoelectric current that is observed in our cells.



Figure 1.9: Photoelectric effect when electrons are emitted from both surfaces. Schematic picture of electron behavior for both field directions. (b) Depending on the direction of the electric field a positive or negative photoelectric current can be measured. Only the electrons emitted from the cathode are measured as a current.

CHAPTER 2

Vapor cell construction

Rydberg spectroscopy in vapor cells already requires special conditions for the vapor cells. For example a low background pressure needs to be achieved. Also it should be fabricated out of borosilicate glass or quartz glass to obtain a high transparency for the blue spectral range and to have a high mechanical stability under temperature changes or gradients. When we additionally want to include thin film electrical feedthroughs, the requirements are even more strict. Then also the fabrication process needs to be at low temperatures of only up to 300 °C to avoid degradation of these structures. For these specific requirements there are no commercially available cells and we had to find our own fabrication method. We developed a method for self-made vapor cells based on anodic bonding which is compatible with rubidium, where Rydberg spectroscopy is possible and thin-film structures can be integrated. The principle description of anodic bonding is given in Section 1.3. In this chapter it is described how a vapor cell can be fabricated by this method. Also the different kinds of structures that have been realized are described here.

2.1 Geometry

The cell consists of a measurement part and a reservoir for the rubidium to be able to control the vapor pressure of rubidium in the measurement part. For the fabrication of the cells a 5 mm thick glass frame was used (Fig. 2.1a). This glass frame has a rectangular hole made by ultrasonic drilling. The thickness of this frame will later define the thickness of the cell. A minimum thickness of 5 mm is needed to attach a glass tube from the side to this frame. This tube will later be used to fill the cell with rubidium and acts as a reservoir for the rubidium. For thinner cells a slightly modified design, but the same technique can be used. For example, an additional glass block can be used as inlay inside the cell to reduce the inner thickness of the cell. This is described later in Section 2.6. Other designs, like etched structures in glass are of course also supported by this technique.



Figure 2.1: Design of the vapor cells. (a) Schematic picture of the cell. Two glass plates, structured with different electrode materials and shapes are bonded or glued to a glass frame. Via a glass tube, which is connected to the frame, the cell can be filled with alkali atoms. (b) The glass plates are coated with a metal structured to stripes, which are used as electrodes. On top of the electrodes 200 nm of silicon nitride is sputtered.

Electrodes inside a vapor cell are usually realized by melting of metal wires into the glass-blown vapor cell, but then no specific structure can be made. For that reason we decided to use thin film electrodes, as they also offer the possibility to reduce the structure size down to the µm-regime. For this purpose the glass plates are coated with different conductive materials, e.g. chromium. These conducting materials can be structured in any arbitrary shape to get the desired electrode design inside the cell.

For some cells these structured glass plates were then glued with a lowoutgassing epoxy onto both sides of the frame [74, 12]. This is an easy-to-use technique, as it only requires to put glue on both sides of the frame, attach the structured glass plates from both sides to it and cure the glue in an oven. The disadvantage of this method is, that the outgassing rate of the glue was still too high for our application.

The challenge in this work was to find a sealing method which is compatible with the desired electrical feedthroughs without the use of glue or any other material that would give rise to any pressure broadening. Anodic bonding, as described in Section 1.3, is a perfect choice for that, as the required temperatures can be decreased to 300 °C. Furthermore electrodes can be included if they are thin enough. In contrast to the usual anodic bonding applications based on silicon wafer, we need transparent substrates on top and bottom, as we want to address the atoms inside with lasers in a counterpropagating geometry. The thick plate in the middle also needs to be glass to match the coefficient of thermal expansion. Additionally a glass filling tube can then easily be attached to it. Successive anodic bonding of several wafers on one device is reported by several groups [50, 60, 75] although they also observe, that by bonding a second side, the reversal of the voltage leads to a decrease of the bond strength at the first side. In our case it turned out to be infeasible to bond one side after the other. For that reason simultaneous double-side anodic bonding, as described in Section 1.3, was used.

In the next sections the whole fabrication process is described in detail. It consists of structuring the glass plates with different materials, building the cell by either gluing or anodic bonding and filling of the cells with alkali metals. Then special cells, like a cell with an inner thickness of 30 to 80 μ m and a cell with graphene electrodes are described.

2.2 Structuring of electrode materials

Different conductive materials have been tested as electrode materials. Also for the different fabrication methods different additional layers are necessary. One important aspect was to find out which materials are compatible with the rubidium atmosphere. One other issue are the conditions during the bonding process, especially the temperature and the ion current through the glass, that can lead for example to oxidation of thin metal layers. All coatings and structuring has been done in the cleanroom facilities of the Institut für Großflächige Mikroelektronik of the Universität Stuttgart.

Two different types of glass substrates were used. For the glued cells a standard alkali free display glass was used (Corning Eagle XG) but this

technique is independent of the type of glass and could also be done with every other glass type.

For the anodically bonded cells we were limited to borosilicate or other sodium-containing glasses as a high sodium content is needed to get a reasonable ion conductivity at the bonding temperature of 300 °C. We used Schott Duran (Borofloat 3.3). Due to this limitation we were also limited to some coating and etching methods in the cleanroom, as in some processes the sodium would diffuse out of the glass, which would make it useless for anodic bonding.

The glass plates are first cleaned with a standard cleaning procedure using successive ultrasonic cleaning in deionized water and Mucasol (Merz) solution. Then the conductive electrode materials are sputtered onto the substrates with a DC and HF sputter machine (Leybold ZV6000) with the sputter parameters given in Table 2.1. Except for the chromium/gold combination only single layers were used. For gold an adhesive layer of chromium is needed. The velocity and the number of oscillations define the thickness of the layer. The surface resistivity is measured by a four-point probe. The transparency refers to white light.

Material	Thickness	Transparency	Oscill.	Velocity	Resistivity
ITO	$100\mathrm{nm}$	> 0.8	3	$0.25\mathrm{m/min}$	$20.7\Omega/\Box$
Al	$7\mathrm{nm}$	> 0.65	1	$3\mathrm{m/min}$	$117\Omega/\Box$
Ni	$5\mathrm{nm}$	0.74	1	$3\mathrm{m/min}$	$285\Omega/\Box$
Cr/Au	$7\mathrm{nm}$	0.82	1/1	$6/6\mathrm{m/min}$	$53\Omega/\Box$
Cr	$20\mathrm{nm}$	not transp.	1	$0.76\mathrm{m/min}$	$25\Omega/\Box$

Table 2.1: Sputter parameters for all coatings. Velocity and number of oscillations define the thickness of each layer. The surface resistivity is measured by a four-point probe.

Then these layers are photolithographically structured. Therefore the substrates are spin-coated with a photoresist (either AZ1514 or AR-P 10A), which is then dried on a hot plate. For the exposition with UV light a foil mask is used, as the structure size is only in the order of millimeters. For much smaller structures of the size of micrometers, chromium masks on glass substrates can be used. The photoresist is exposed to UV light and then developed in AZ Developer for AZ1514 resist or in TMA238WA for AR-P 10A. Then all conductive layers (ITO, Al, Ni, Cr/Au, and Cr) are wet etched with standard commercial etch mixtures for each material. Afterwards the photoresist is removed in three successive ultrasonic baths of two times acetone and one time propanol and the substrates are dried using pure nitrogen. In Fig. 2.2 an overview of the fabrication processes of the different structures is given.

For ITO instead of cleaning with acetone and propanol, photoresist stripper (PRS) was used, which leads to a cleaner surface, but is more poisonous. The ITO has to be covered with a protection layer of Si_3N_4 or SiO_2 because rubidium reacts with ITO. These materials were deposited by plasmaenhanced chemical vapor deposition (PECVD), which is much faster than sputtering non-conductive materials. The protection layer is then again photolithographically structured and plasma-etched.

The substrates with a 20 nm chromium layer are used for anodic bonding. Only chromium is stable enough for the anodic bonding process temperatures of 300 °C, all other available metals would oxidize during the bonding process. Even for chromium a minimum layer thickness of 20 nm was necessary to avoid complete oxidation. Here also a second layer of Si_3N_4 is needed as a bonding layer. But as for anodic bonding borosilicate glasses are needed, it is not possible to use the PECVD machine for deposition and structuring of the Si_3N_4 layer, as the sodium would diffuse out of the glass during the process. Si_3N_4 can also be sputtered. For structuring of the coarse structures, tape was used as lift-off mask to cover the parts where no $\mathrm{Si}_3\mathrm{N}_4$ should Si_3N_4 was sputtered with 20 oscillations and a velocity of be deposited. 0.1 m/min to get a thickness of roughly 200 nm. A pure argon plasma was used during sputtering. This increases the silicon content of the silicon nitride resulting in a non-stoichiometric silicon nitride layer. This is advantageous for the anodic bonding, because only the silicon atoms form bonds with the silicon oxide of the glass. The slightly reduced resistivity and transparency do not disturb the characteristics of the vapor cell. After the sputter process the tapes are removed and the structured substrates are cleaned again to remove potential residues of the tape. Afterwards the substrates are cut to the final dimensions.



Figure 2.2: Structuring of the electrodes and the bonding layer for three different kind of fabricated cells. For the glued cells with metal electrodes only steps 1 and 2 are used. For the glued cells with ITO, the electrodes are completely covered with Si_3N_4 on the inside of the cell (middle column). In the anodically bonded cell, the Si_3N_4 acts as a bonding layer, structured as a frame (right column).

2.3 Fabrication of glued cells

The substrates with ITO, Al, Ni and Cr/Au structures were used to build glued cells. The low-outgassing glue Epo-Tek 377 was used. A thin line of the glue was applied on both sides of the frame and two of the structured substrates were attached with the conductive structures on the inside of the cell. Care must be taken to use as little glue as possible in order to avoid macroscopic amounts of glue inside the cell. Although this is a low-outgassing glue, the outgassing rate is still too high for long-term Rydberg spectroscopy. The glue was cured in an oven at 150 °C for 75 minutes. Then the cell can be filled with rubidium. More details about the fabrication and the properties of these cells can be found in [12, 74]. A picture of the glued and already filled cell is shown in Fig. 2.3. There is only a thin film of glue between the glass plates which is not visible in the picture. Cables are attached to two opposing electrodes to apply electric fields inside the cell.



Figure 2.3: Picture of a glued cell filled with rubidium. Two of the electrodes are connected to wires to apply electric fields inside the cell.

2.4 Fabrication of double-side anodic bonded cells

The principle of anodic bonding is described in Chapter 1.3. For fabrication of our vapor cells simultaneous double-side anodic bonding is used [18]. To achieve simultaneous double-side anodic bonding, conductive silver is pasted around the 5 mm thick glass frame and a wire is wrapped on top of this paste to have the possibility to apply a voltage to the middle of the frame (see Fig. 2.4 and Fig. 2.1a).



Figure 2.4: Setup for simultaneous double-side anodic bonding. The electrode layer (for example 20 nm Cr) is located below the bonding layer of Si_3N_4 . A wire is wrapped around the middle glass plate to apply the high voltage there (see also Fig. 2.1a).

The frame and two coated substrates are then carefully cleaned with acetone and ethanol and afterwards dried with canned air. Then the three glass substrates are stacked on a hot plate and aligned to make sure, that the electrodes on both sides are on top of each other. An additional heater is put on top of the upper electrode to heat symmetrically from top and bottom.

The upper and the lower temperature as well as the total bonding current and the current through the upper plate is plotted in Fig. 2.5 versus time for the complete heating, bonding and cooling process. The whole stack is heated with a heating rate of 5 °C/min from room temperature to 300 °C. This temperature was kept for about 60 min to ensure a homogeneous and constant temperature distribution over the whole assembly. Then a high voltage was applied between the two outer electrodes as ground and the wire in the middle of the glass frame. Usually a voltage between 600 V and 2000 V was used. The applied high voltage is negative in respect to ground. During approximately 40 min of bonding time the currents through the lower and through the upper glass plate were observed separately. Both currents first show a sharp peak when the high voltage is turned on. Then an exponential decrease is observed until the current stays almost constant. The origin of these constant currents are leak currents through the glass plates. Thev do not contribute to the bonding process, therefore further increase of the bonding time would not increase the bond strength.



Figure 2.5: Temperature of the hot plate (red) and the upper glass plate (blue) and bonding current (magenta and cyan) measured during anodic bonding. After preheating to 300 °C, a waiting time of 60 min was used to ensure a homogeneous temperature distribution before the bonding was started.

After the bonding has finished, the high voltage can be turned off again and the cell is cooled down slowly with $2 \,^{\circ}C/min$ to avoid temperature gradients over the bonded interface as they could result in a breaking of the bond.

A closer look at the bonding currents together with fits of the time constants is given in Fig. 2.6a. As soon as the high voltage is applied, the currents rise to their maximum during the first seconds. This indicates, that immediately after applying the voltage the contact area between the plates is at a maximum. This effect is also described in [22]. Then an exponential decay of the currents is observed as the polarization current decreases due to the formation of a depletion layer at the interface. After 8 min the voltage was increased from 800 V to 900 V because the current decreased so fast that there would not have been enough charges to build up a sufficiently strong bond. The measured current was scaled to be able to fit an exponential decay to the whole data. The 1/e time constants for the two sides were 8.6 min and 6.0 min for the upper and lower current, respectively. In Fig. 2.6c a picture of both sides of the cell after the first bonding step is shown. In the lower picture Newton interference fringes can be seen at the side close to the filling tube.

The Newton interference fringes seen after this first bonding step, visible in Fig. 2.6c indicate, that the glasses are not bonded at that position. A second bonding step has been performed to complete the bonding. For that, the cell was turned around, so that the interference fringes from the lower glass plate are now on top. A voltage of 900 V has been used. The bonding current of the second bonding step is shown in Fig. 2.6b. Now the main current contributing to the bonding process flows through the upper glass plate. The current through the lower glass plate is almost constant because the temperature was kept a few degrees lower, as this side is already completely bonded. In Fig. 2.6d the same cell is shown after the second bonding step. Now the cell is completely bonded and the interference fringes have vanished completely.

Integrating over the whole bonding time a charge of 0.380 mC/cm^2 for the upper bond and 0.301 mC/cm^2 for the lower bond can be derived for the first bonding step. For the second bonding step the total charge through the upper plate was 0.223 mC/cm^2 and through the lower plate 0.203 mC/cm^2 . The total charge for both bonding steps was 0.583 mC/cm^2 for the upper and 0.524 mC/cm^2 for the lower plate. According to [76] the required charge for successful bonding is between 3 and 5 mC/cm^2 which corresponds to an oxide layer of $\sim 1.4 \text{ nm}$. Leak currents are still included in these numbers, the offset has not been subtracted, as it depends on the applied voltage. The measured charge during our bonding process is much lower than the desired charge, but enough to build a hermetically sealed cell which stays vacuum tight over several month. This long-term stability will be further investigated in Chapter 4.



(a) Current on both sides during anodic (b) Current on both sides during anodic bonding for the first bonding step.

bonding for the second bonding step.



(c) Picture of the cell after the first bonding (d) Picture of the cell after the second bondstep. ing step.

Figure 2.6: Bonding current and pictures from both sides of the cell for the first and the second bonding step. After the first bonding step on one side of the cell there were still Newton interference fringes visible ((c) Side 2). For that reason a second bonding step has been performed while the cell was turned around (see inset of (a) and (b)). After that the whole coated area was bonded to the glass frame and the cell was hermetically sealed and was ready to be filled with rubidium.

2.5 Filling of cells with rubidium

All cells were filled with rubidium using the same method. The glass tube, which is attached to the glass frame is connected to a glass manifold with a breakseal ampoule of rubidium. A steel sphere was put inside the manifold to break the seal afterwards while the whole manifold is attached to a vacuum pump. The cell and the manifold are evacuated with a turbo pump to a



Figure 2.7: Schematic of the glass manifold for filling the cells with rubidium. It is connected to a vacuum pump and evacuated to 10^{-6} mbar. A magnet and a steel sphere is used to open the breakseal ampoule. Liquid rubidium can then be transferred to the vapor cell. After filling, the connection tube to the vapor cell is sealed with a flame.

pressure of less than 10^{-6} mbar for two days. During that time the cell is heated to $120 \,^{\circ}$ C. Then the seal of the ampoule is broken with the steel sphere and a droplet of rubidium is transferred into the cell. As there might be some chemical reactions, for example between the epoxy glue and rubidium, or even between chromium or chromium oxides and rubidium [77], we made sure, that the rubidium droplet did not block the tube connected to the pump, so that every gaseous reaction product can be pumped out. If the rubidium droplet blocks the filling tube, a reaction with gaseous products can be seen as an increased pressure broadening of the Rydberg signal. The cells are then further pumped and heated for several days. Then the cell is sealed by melting off the connection tube with a flame.

2.6 Fabrication of thin cells

To fabricate a thin cell with an atomic layer thickness on the order of 20-500 µm the same method for cell fabrication can be used. A cell with an inner thickness of 40 - 70 µm with chromium electrodes on one side has been realized by anodic bonding. Gluing is not an option for thin cells, as higher temperatures are needed to reach an optically dense atomic vapor and an increased temperature increases the outgassing of the glue.

For the fabrication of such a cell a 5 mm glass block was polished down to a thickness of 4.85 mm. The glass frame was also polished and had a final thickness of around 4.9 mm. The glass block was then anodically bonded to one of the structured glass plates (see Fig. 2.8a). An aluminum coated glass plate was used, as aluminum can also serve as a bonding layer. During anodic bonding all aluminum is completely oxidized which results in an almost transparent layer. After that, this plate and a second structured glass plate are bonded from both sides to a glass frame, as explained in Section 2.3. The second plate was coated with chromium electrodes.



(a) Schematic of a thin cell

(b) Picture of a thin cell

Figure 2.8: Schematic drawing and picture of a thin cell. A substrate with a glass block is bonded on one side and a structured substrate with electrodes to the other side of the frame.

In Fig. 2.8 a schematic and pictures of the finished cell with the glass block inside are shown. In the photograph the upper picture shows the side with the aluminum coating where the glass block was bonded to. The lower picture shows the side with the chromium electrodes. From measurements with a microscope the final thickness was determined to be around 40 - 70 µm. In this configuration the electrodes are only on one side and even with an AC frequency applied on the electrodes, no Stark shift could be measured inside that cell. This cell was therefore mainly used to test the temperature stability of the anodic bonding technique. With slight changes in the cell design, a thin vapor cell with electrodes on both sides can in principle be realized with the same fabrication method.

2.7 Fabrication of cells with transparent graphene electrodes

For our goal of a device consisting of a thin vapor cell with a large array of electrodes for electrical control, it is highly desirable to have transparent electrodes at the inside of such a cell. The thin metal film electrodes used for the glued cells were a step in this direction, as they are semi-transparent, but those were unfortunately not compatible with the anodic bonding technique. The high temperatures of 300 °C as well as the high polarization of the ions inside the glass while the high voltage for bonding is applied, lead to an oxidation of the complete metal layers.

Widely used transparent and conductive materials are in the most cases also oxides. One of the most famous materials is indium tin oxide (ITO) as it is used industrially for liquid-crystal displays and solar cells. Others are for example aluminum doped zinc oxide (AZO) or doped titanium oxide. All of these metal oxides are highly reacting with alkali atoms and therefore loose their transparency in an alkali atmosphere.

Although graphene is a quite new material, it can be fabricated nowadays already on a large almost industrial scale. It has already been successfully used for building solar cells. Carbon-nanotubes (CNT), with similar properties as graphene have also been used for building liquid crystal displays. Both graphene and CNTs are highly transparent as they are consisting of only a few molecular layers and also have a high electrical conductivity. Due to its enormous temperature stability and the lack of any material that could react with alkali atoms, graphene is the perfect choice as conducting and transparent electrode material in combination with alkali atoms.

The graphene used in this work was produced and transferred to our cells in a collaboration with the group of L. Bogani from the 1. Physikalisches Institut of the Universität of Stuttgart. The graphene was grown on a copper plate. Then it was covered by PMMA and the copper could be etched. The graphene on top of the PMMA foil can then be cut into the desired size and format. Then the PMMA is solved in water and the graphene can be transferred from the water to our structured glass plates. As shown in the schematic picture of Fig. 2.9a, one large graphene flake is covering all of the chromium electrodes. For future applications, the graphene can also be structured to arbitrary electrode configurations, either by optical photolithography or with an electron beam, for structures down to 100 nm in size.

The chromium electrodes are still needed to connect the graphene flake at the inside of the cell to the outside. Cables can be attached to the chromium



Figure 2.9: (a) Schematic picture of the coated glass plate with graphene flake. The glass plates are coated with 20 nm of chromium structured to stripes, which are used as feedthroughs. On top of the chromium 200 nm of silicon nitride is sputtered in the shape of a frame as a bonding layer. A large graphene flake $(8 \times 15 \text{ mm})$ is put on top of the chromium electrodes to obtain a highly transparent and conductive electrode. (b) Picture of a cell with graphene on top of the chromium electrodes. Slight damage of some electrodes due to overheating can be seen. Due to the high transparency of graphene, this layer cannot be seen in the picture. electrodes on the outside to apply a voltage to the graphene. Two of such glass plates are then again used to build a vapor cell by anodic bonding. It can be filled by the usual filling process, described in Section 2.5. In Fig. 2.9b a picture of the final cell is shown. As can be seen in this figure, part of the chromium electrodes and maybe also the graphene layer were partially damaged during the anodic bonding process. The reason for that is, that the temperature stability of graphene under vacuum or inert gas atmosphere is $800 \,^{\circ}$ C, but our anodic bonding temperature of $300 \,^{\circ}$ C is probably too close to the oxidizing temperature. This could be avoided by either reducing the bonding temperature, which would result in a decrease of bond strength, or by bonding under an inert gas atmosphere. Still the conductivity of these chromium and graphene electrodes is sufficient for our purpose.

After transferring the graphene onto the structured glass plates, the resistivity has been measured between all adjacent electrodes with a 2-point and with a 4-point measurement before anodic bonding. Both measurements are shown in Fig. 2.10a.

As both measurements give similar results, we can assume, that for the complete cell, where we can do only 2-point measurements, it should give a reasonable result. The resistance between each of the electrodes is around 1000Ω .

After anodic bonding, the resistance between all electrodes has been measured again with a 2-point measurement (Fig. 2.10b). On one side of the cell, the resistance is similar, while on the other side the resistance is increased. The reason for that may be that the chromium or the graphene was overheated during anodic bonding. The numbers in the two plots correspond to the numbers given in Fig. 2.11. For all measurements of the atomic signals, the voltages were applied to the electrodes number 2 and number 3.



Figure 2.10: Resistance between neighboring electrodes before (a) and after (b) anodic bonding. Before bonding the resistance between all electrodes is around $1 k\Omega$, after anodic bonding the resistances on side 2 increased probably due to overheating, but are still measurable. The electrode numbers are defined in Fig. 2.11. The electrodes mostly used in our experiments are the electrodes number 2 and 3.



Figure 2.11: Positioning of the large graphene flake on top of the chromium electrodes. Electrode numbers refer to the resistance measurements shown in Fig. 2.10.

Chapter 3

Rydberg EIT spectroscopy and detection setup

Electromagnetically induced transparency on Rydberg states in rubidium is used as an optical characterization method of our vapor cells. A short description of the calculation of the three-level-system is shown in Section 3.1. In Section 3.2 the laser setup together with the laser locking scheme and a reference signal is shown.

3.1 Three-level system and electromagnetically induced transparency

For optical detection of a Rydberg signal electromagnetically induced transparency (EIT) in the ladder scheme was used (see Fig. 3.1). The theory of atom-light interaction is described in detail in standard atomic physics textbooks. Also electromagnetically induced transparency is discussed in several other publications, for example [79]. Here only the basics of a three-level calculation are reviewed.

In almost all our experiments rubidium is used. The ground state of rubidium, $|g\rangle = 5S_{1/2}$, is coupled via a weak resonant probe laser with a wavelength of 795 nm to the excited state $|e\rangle = 5P_{1/2}$ (D1-line). Via a reference spectroscopy and a DAVLL lock [13], this laser is locked on resonance to the ⁸⁵Rb $5S_{1/2}F = 3 \rightarrow 5P_{1/2}F = 2$ transition. A complete level scheme of the 5S to 5P transition of rubidium for ⁸⁵Rb and ⁸⁷Rb can be found in the appendix. The $5P_{1/2}$ state is coupled with an intense coupling laser with a wavelength of 474 nm to a Rydberg state $|r\rangle = nS$. Rydberg states between n = 20 and $n \approx 60$ can be chosen with our current laser system. The Rabi



Figure 3.1: Three-level-system in ladder scheme with ground $|g\rangle$, excited $|e\rangle$ and Rydberg state $|r\rangle$ and the atomic states and wavelengths λ_P , λ_C for rubidium used in our experiment. Δ_P , Δ_C , Ω_P and Ω_C denote the detunings between the probe and coupling laser from the atomic transition and the respective Rabi frequencies of the two lasers.

frequency is defined by $\Omega_R = d/\hbar \cdot E_0$, with the transition dipole matrix element d and the light field $E_0 = \sqrt{2I/(\epsilon_0 c)}$. It describes the coupling of the atomic levels by the light field. For a constant laser output power of $P_C = 60 \text{ mW}$ the Rabi frequency is decreasing for increasing main quantum number proportional to the dipole matrix element.

The calculation of the three-level system is based on a numerical solution of the Liouville-von Neumann equation

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[\hat{H},\rho] + L(\rho), \qquad (3.1)$$

where the Hamiltonian in the rotating-wave approximation, given by

$$\hat{H} = \begin{pmatrix} 0 & \frac{1}{2}\Omega_P & 0\\ \frac{1}{2}\Omega_P^* & -\Delta_P & \frac{1}{2}\Omega_C\\ 0 & \frac{1}{2}\Omega_C^* & -(\Delta_P + \Delta_C) \end{pmatrix}$$
(3.2)

describes the interaction between the atom and the light field. Δ_P and Δ_C are the detunings of the probe and the coupling lasers from the atomic

resonance and Ω_P and Ω_C are the Rabi frequencies of the two lasers. The density matrix

$$\rho = \begin{pmatrix}
\rho_{gg} & \rho_{ge} & \rho_{gr} \\
\rho_{eg} & \rho_{ee} & \rho_{er} \\
\rho_{rg} & \rho_{re} & \rho_{rr}
\end{pmatrix}$$
(3.3)

contains the populations ρ_{ii} and the coherences ρ_{ij} $(i \neq j)$, with $\rho_{ij} = |i\rangle\langle j|$. The Lindblad operator defined by

$$L(\rho) = \begin{pmatrix} \Gamma_{rg}\rho_{rr} + \Gamma_{eg}\rho_{ee} & -\frac{1}{2}\Gamma_{eg}\rho_{ge} & -\frac{1}{2}\rho_{gr}(\Gamma_{re} + \Gamma_{rg}) \\ -\frac{1}{2}\Gamma_{eg}\rho_{eg} & \Gamma_{re}\rho_{rr} - \Gamma_{eg}\rho_{ee} & -\frac{1}{2}\rho_{er}(\Gamma_{re} + \Gamma_{rg}) \\ -\frac{1}{2}\rho_{rg}(\Gamma_{re} + \Gamma_{rg}) & -\frac{1}{2}\rho_{re}(\Gamma_{re} + \Gamma_{rg} + \Gamma_{eg}) & -\rho_{rr}(\Gamma_{re} + \Gamma_{rg}) \end{pmatrix}$$
(3.4)

includes the decay rates from the Rydberg to the ground state Γ_{rg} , from the Rydberg to the excited state Γ_{re} and from the excited to the ground state Γ_{eg} . The solution of the Liouville-von-Neumann equation is determined for the stationary case $d\rho_{ij}/dt = 0$ with the boundary condition $\rho_{gg} + \rho_{ee} + \rho_{rr} = 1$. The density matrix elements are derived by a numerical solution.

The absorption and dispersion of light in a medium can in general be described by the polarization of the medium

$$P = \epsilon_0 \chi E \tag{3.5}$$

with the susceptibility χ [80]. For atoms with a density n it can be described by

$$P = n\langle er \rangle = nTr(\hat{\mu}\hat{\rho}). \tag{3.6}$$

The imaginary part of the linear susceptibility describes the absorptive properties and the real part describes the dispersive properties of the atomic medium and has the meaning of a response of the atomic medium to an oscillating electric field. For optically dense media one has to include Lambert-Beers law which describes the exponential decrease of the light field, traveling through the medium. Then the transmitted electric light field is given by

$$E_{out} = E_{in} \exp\left(ikl\chi_{eg}/2\right) \tag{3.7}$$

for $d\chi_{eg}/dE \approx 0$.

The effect of electromagnetically induced transparency is due to the fact that the unperturbed states are no longer eigenstates of the perturbed atom. By coupling the excited state with a coupling laser to a third state, in our case a Rydberg state, the excited state effectively splits into two new states, symmetrically detuned around the excited state level. On the excited state resonance a transparency window opens leading to a higher transparency here. In Fig. 3.2 the normalized $\text{Im}(\rho_{ge})$, corresponding to the transmitted signal and the normalized Rydberg population ρ_{rr} is plotted versus the coupling detuning Δ_C . As two of the new eigenstates of the three-level system are symmetrically detuned around the intermediate level, a transparency window opens at the two-photon resonance. The coherence consists of a Lorentzian peak with enhanced absorption dips on the side wings. The origin of the enhanced absorption is the summation over different velocity classes [10]. These are the two signals that are usually observed in our experiments.



Figure 3.2: Normalized coherence $\text{Im}(\rho_{ge})$ (blue) and Rydberg population ρ_{rr} (red) vs. coupling detuning for $\Omega_P = 5 \cdot 2\pi \text{ MHz}$, $\Omega_C = 5 \cdot 2\pi \text{ MHz}$ and $\Gamma_{rg} = \Gamma_{tt} = 0.7 \cdot 2\pi \text{ MHz}$ (Γ_{tt} : transit-time broadening.

3.2 Spectroscopy setup

A scheme of the spectroscopy setup is plotted in Fig. 3.3a. Amplitudemodulation spectroscopy is used, to increase the signal-to-noise of the Rydberg signal. The blue laser is amplitude-modulated via an AOM with a modulation frequency of 50 kHz. The zeroth order of the AOM was used for spectroscopy to maximize the usable intensity. The two laser beams are aligned in counterpropagating geometry, both focused into the cell. The waist at the focus for the blue beam $(1/e^2 \text{ diameter})$ is 530 µm and for the red beam 275 µm. The waist of the blue laser is larger than the one of the red beam to ensure an almost constant Rabi frequency in the whole probed volume, defined by the waist of the red beam. The transmission of the probe laser is detected with a pre-amplified photodiode (Thorlabs PDA36A) and the photodiode signal is demodulated with a Lock-in amplifier.

The vapor cell is put in an oven. The temperature of the rubidium reservoir and of the cell oven can be set independently. The reservoir temperature determines the vapor pressure of rubidium inside the cell. The temperature of the cell is always kept higher than the reservoir to avoid condensation of rubidium in the cell. A definition of the direction of the electric field, used in the Stark shift measurements of Chapter 6, is given in Fig. 3.3b.

The probe laser is locked to the $5P_{1/2}F = 2$ state while the coupling laser is scanned over the Rydberg state. Simultaneously, a Rydberg signal of the $5P_{1/2}F = 3$ state can be observed because the hyperfine splitting of these intermediate levels is only 361.58 MHz. Part of the $5S \rightarrow 5P$ absorption spectrum is shown in Fig. 3.4.

Due to the counterpropagating geometry and the different k-vectors of the two lasers, the second hyperfine level is seen in the transmission signal at a different detuning (see Fig. 3.5a). In the resonant case, atoms with velocity v = 0 are addressed. For a detuning of $\Delta_P = 361 \text{ MHz}$ the atoms need to compensate the detuning by the Doppler effect, hence a specific velocity class, defined by

$$\Delta_P = k_P \cdot v_1 \tag{3.8}$$

is addressed that see the red laser resonant to the atomic transition. The same atoms see the blue laser detuned by

$$\Delta_C = -k_C \cdot v_1. \tag{3.9}$$



Figure 3.3: (a) EIT spectroscopy setup. Probe and coupling laser are in counterpropagating geometry. The coupling laser is amplitudemodulated by an AOM for lock-in detection. The transmission of the probe laser is observed while the coupling laser is scanned over the Rydberg resonance. Electric fields inside the vapor cell are applied along the laser direction. The polarity, named pol(+) and pol(-) of the electric field direction is defined in (b).



Figure 3.4: Part of the saturation absorption spectrum for the rubidium D1 transition from $5S_{1/2}$ to $5P_{1/2}$. For all Rydberg EIT measurements, the red laser is locked to the transition ⁸⁵Rb $5S_{1/2}$ F=3 to $5P_{1/2}$ F=2. The transition to $5P_{1/2}$ F=3 at a detuning of $\Delta = 361.58$ MHz can also be seen in our measurements and is used as a frequency reference.

Thus the resulting detuning from the resonant intermediate level is

$$\delta = \Delta_C + \Delta_P = -k_C \frac{\Delta_P}{k_P} + k_P \frac{\Delta_P}{k_P} = -236.4 \text{ to } -243.2 \text{ MHz}$$
 (3.10)

depending on the exact blue wavelength between 480.7 - 475.3 nm, which depends on the chosen Rydberg state. When the coupling laser is scanned, the F = 3 is observed at a larger detuning (positive in Fig. 3.5b) relative to the F = 2 resonance. As the difference between those two levels is defined by the two wavelengths and independent of the coupling laser detuning and the Stark shift of the Rydberg state, they are used to calibrate the frequency axis in all our measurements. Additionally for the absolute position of the Rydberg signal a second Rydberg EIT signal from a reference cell was taken simultaneously.



(b) EIT spectrum with both intermediate F-states.

Figure 3.5: Rydberg EIT signals from both intermediate states $5P_{1/2}$ F=2 and $5P_{1/2}$ F=3 can be seen and the known frequency difference between them is used for calibration of the frequency axis. Due to the counterpropagating geometry and the two different wave vectors of the excitation lasers, the state F=3 is seen at a different detuning $\Delta = 236.4$ to 243.2 MHz, depending on the exact wavelengths of the lasers.
CHAPTER 4

Lifetime and background pressure of cells

For industrial applications like atomic clocks or sensors based on vapor cells, a long-term stability concerning the cell vacuum and the temperature stability are required. Almost all of the devices, that are up to now commercially available operate with a buffer gas background pressure of typically several millibar. Therefore the achievement of a high vacuum in such cells is not an issue. For Rydberg spectroscopy the requirements are more strict. The linewidth of the Rydberg signal is much more sensitive to background gases because of the high polarizability and large cross-section of Rydberg states. Because of the high sensitivity of Rydberg atoms collisions with background gases induce a decay of the Rydberg state and a high vacuum is necessary to prevent that. For applications that require thin cells high operating temperatures are needed to achieve sufficiently high optical depths.

With our anodic bonding technique vapor cells can be fabricated, that keep their high vacuum for several months and can be used for operating temperatures of at least up to 230 °C. The vapor cells, that have been fabricated in an earlier stage utilizing gluing [12] and recently anodic bonding techniques [18], as described in Chapter 2, have been used for the spectroscopy of rubidium atoms. The Lamb dips of saturated absorption spectroscopy give a first indication of the background pressure inside the cell. Rydberg EIT spectroscopy is used to determine the long-term stability and the temperature stability of the bonded cells.

4.1 Saturated absorption spectroscopy

If the vacuum level inside the cells is low enough saturated absorption spectroscopy can be used to give a first estimate of the background pressure. For saturated absorption spectroscopy two laser beams of the same wavelength are aligned in a counterpropagating geometry. Because of the Doppler effect only the atoms with a velocity of v = 0 are resonant to both laser beams. One weak probe and one strong pump laser beam with a wavelength of $\lambda = 795 \,\mathrm{nm}$ couple the $5S_{1/2}$ state of rubidium to the $5P_{1/2}$ state. The strong pump beam pumps the atoms from the ground state into the excited state. The weak probe beam then detects the atoms in the ground state, and a smaller absorption at each resonance is observed. The signal then consists of a Doppler-broadened absorption spectrum of the D1-line of rubidium together with narrow Lamb dips. Due to the counterpropagating geometry these Lamb dips have a narrow linewidth, that depends on the natural linewidth and the Rabi frequencies, collisional broadening with background atoms and at high vapor densities self-broadening by collisions with other rubidium atoms.

One example of such a saturated absorption spectrum of the D1 line of rubidium is shown in Fig. 4.1. It was taken in an anodically bonded cell one day after filling it. It shows a Doppler-broadened absorption spectrum with narrow Lamb-dips. The spectrum was taken at a reservoir temperature of $T_R = 46 \,^{\circ}\text{C}$ and a cell temperature of $T_C = 94 \,^{\circ}\text{C}$. The probe Rabi frequency was $\Omega_{probe} = 10.3 \cdot 2\pi \,\text{MHz}$ (corresponding to a power of $P_{probe} = 31 \,\mu\text{W}$) and the pump Rabi frequency $\Omega_{pump} = 23 \cdot 2\pi \,\text{MHz}$ (corresponding to $P_{pump} =$ $150 \,\mu\text{W}$). The observed width of the Lamb dips is $31.3 \pm 4.1 \cdot 2\pi \,\text{MHz}$. The natural linewidth of the $5P_{1/2}$ state is $5.75 \cdot 2\pi \,\text{MHz}$. The broadening of the observed linewidth is dominated by power broadening due to the pump beam, which is expected to be $32.0 \cdot 2\pi \,\text{MHz}$.

Anodic bonding is mainly used for vapor cells, that are additionally filled with a buffer gas to reduce the velocity of the atoms. In that case even a broadening of the Doppler-broadened absorption spectrum can be seen. Any additional broadening due to outgassing of gases like oxygen during bonding can be neglected in their case. In our case, especially for Rydberg spectroscopy, we want to resolve a linewidth of only several megahertz. The fact, that Lamb dips can be observed in our vapor cells is a sign, that the back-



Figure 4.1: D1 saturation absorption spectroscopy in rubidium in an anodically bonded cell. The narrow linewidth of the Lamb dips indicate a low background pressure.

ground pressure in our cells is already very low. However an exact evaluation can only be done with Rydberg spectroscopy as in that case additional other broadening mechanisms play a role. For that reason a detailed evaluation of the linewidth and the background pressure together with an overview over different broadening mechanisms is given in the next sections, where Rydberg spectroscopy has been used.

4.2 Rydberg EIT spectroscopy

Electromagnetically induced transparency (EIT) of a Rydberg state was used to determine the background gas as pressure broadening inside the cell, as the natural linewidths of Rydberg states is on the order of kilohertz and Rydberg states are much more sensitive to broadening mechanisms. The minimum achievable linewidth of the Rydberg EIT signal is determined by several effects. The Rabi frequencies of the two excitation lasers lead to power



Figure 4.2: Linewidth of the EIT signal in glued and bonded cells with different electrode materials versus time during the first 50 days after filling the cells.

broadening. Transit-time broadening due to the focused laser beams plays a minor role in our current configuration as discussed in the next section. Collisional broadening due to the presence of a background gas dominates in most of our vapor cells. The different broadening mechanisms are further investigated and compared in the next section.

In Fig. 4.2 the measured full linewidth of the EIT signal (FWHM) for different glued cells and the bonded cell is plotted. Glued vapor cells have been built with different electrode materials, nickel, aluminum and indium tin oxide with a protective layer of either silicon nitride or silicon oxide. In the anodically bonded cell chromium was used as electrode material, as all other materials degraded during bonding. In the glued cells the 32S state was used and in the bonded cell the 22S state. This should not make a difference in the linewidth, as the broadening rates for all Rydberg states within this range are very similar (22S: 1.75 MHz/(10^{-3} mbar), 32S: 1.82 MHz/(10^{-3} mbar) [38]).



Figure 4.3: Zoom into Fig. 4.2 for linewidths below 50 MHz for a glued cell with nickel electrodes (red) and a bonded cell with chromium electrodes (blue) versus time.

In Fig. 4.2 the glued cells without any metal layer (ITO+SiN and ITO+SiOx) show a width of up to $800 \cdot 2\pi$ MHz. The linewidth of the cell with ITO and Si₃N₄ coating is even increasing during the first 20 days from $50 \cdot 2\pi$ MHz to $600 \cdot 2\pi$ MHz. All metal coated cells (Ni, Al, Cr) have a linewidth below $200 \cdot 2\pi$ MHz. The fact, that metal coated cells have a lower background pressure than those without metallic layer indicates, that there is some getter effect which can help to achieve a low background pressure. These metals are known as typical getter materials. Some example values for pressures inside cells with these materials have been given in Section 1.3.2.

Figure 4.3 shows a zoom into the linewidth region below 50 MHz, which was only reached with the glued cell with nickel electrodes and the anodically bonded cell with chromium electrodes. In the nickel coated cell the linewidth increased from $17 \cdot 2\pi$ MHz to $40 \cdot 2\pi$ MHz during one month. After 40 days the glued cell was no longer usable for Rydberg spectroscopy, as with increasing broadening the signal amplitude decreases. In the bonded cell, which has a relatively thick chromium layer (20 nm) in it, the Rydberg signal has a linewidth of only $(7.65 \pm 1.07) \cdot 2\pi$ MHz and it did not change over 270 days of measurement. The minimum observed linewidth was $6.1 \cdot 2\pi$ MHz at $52 \degree \text{C}$ with Rabi frequencies of $\Omega_{probe} = 4.9 \cdot 2\pi$ MHz and $\Omega_{coupling} = 3.1 \cdot 2\pi$ MHz in the bonded cell, resulting in an expected linewidth due to power broadening of

$$\Gamma_{pb} = 2 \cdot \sqrt{\frac{(\Omega_P^2 + \Omega_C^2)^2}{4\Gamma_{12}^2 + 8\Omega_P^2}} = 3.7 \cdot 2\pi \,\text{MHz}.$$
(4.1)

In some of the glued cells an increase in linewidth with time was observed, for example in the glued cells with nickel or ITO and Si_3N_4 coatings. As the increased linewidth can mainly be attributed to collisional broadening due to a background gas, an increase of the background gas with time is assumed. This indicates, that the glue is the origin of the background gas and is still outgassing over several weeks. The gettering effect of the metals can for some time compensate the increase in background gas, but on longer timescales the background pressure will always rise in the glued cell, leading to a broadening of the atomic lines. A long-term stable vapor cell can only be achieved by avoiding glue completely.

The anodically bonded cell, where no glue is needed for the fabrication, shows a stability of several months without any increase in background pressure. Cells without a metallic layer have also been assembled by anodic bonding and no increase in linewidth could be observed. This also indicates, that the getter effect of the metallic layers is no longer needed in the anodically bonded cells.

4.3 Broadening mechanisms

Different broadening mechanisms can influence the width of the EIT signal. The leading effects are power broadening, transit-time broadening, collisional broadening and residual Doppler broadening.

Due to the different wavelengths of the two-photon-excitation of $\lambda_P =$ 795 nm and $\lambda_C \approx 480$ nm for the 22*S* Rydberg state we always get a residual Doppler broadening of

$$\Gamma_{rD} = \Gamma_{eg} \cdot \left(1 - \frac{k_C}{k_P}\right) = 3.8 \,\mathrm{MHz}.$$
(4.2)

As this is defined by our excitation scheme, we cannot avoid it. Both lasers are focused into the vapor cell. The red laser beam has a waist of $w = 275 \,\mu\text{m}$. The blue laser beam has a waist of $w = 530 \,\mu\text{m}$ to ensure an almost constant laser power over the whole excited area. The transit-time broadening is determined by the size of the smaller laser beam (in our case the red laser), and is given by

$$\Gamma_{tt} = \frac{4v}{w} \sqrt{2 \cdot ln(2)} = 0.7 \cdot 2\pi \,\mathrm{MHz} \tag{4.3}$$

[81], with the mean velocity v of the atoms. The transit-time broadening is much smaller than the observed linewidth in the bonded cell and has only a minor contribution to the total linewidth.

A power broadening of $\Gamma_P = (3.5 - 9.5) \cdot 2\pi$ MHz occurs due to the relatively high Rabi frequencies of up to $\Omega_P = 15 \cdot 2\pi$ MHz. Such high Rabi frequencies were needed especially in the glued cells, otherwise the Rydberg signal would have been too small to observe. In the anodically bonded cell, the power broadening together with the residual Doppler broadening can already explain the observed linewidth.

Several decay channels of the Rydberg state have been discussed already in Section 1.1.3. Photoionization, ionization by black-body radiation and collisions with electrons may contribute to an ionization current, as described in Chapter 5, but the decay rates from all these processes are too small to be observed as a broadening of the Rydberg EIT signal under our conditions. Also collisions between Rydberg atoms and ground state rubidium atoms, as will be described in Section 4.4, have only an observable effect for higher ground state vapor densities.

The largest effect especially, in the glued cells, is due to collisional broadening. All these long-term linewidth measurements have been done at temperatures below 80 °C. Therefore the ground state rubidium density is too low for collisions between Rydberg atoms and rubidium ground state atoms. It is assumed, that the main broadening effect is due to collisions of rubidium atoms with the atoms or molecules of a background gas. As we expect that the origin of the background gas is outgassing from the glue, the type of perturber gas is not known. As an estimation the cross-sections for rubidium Rydberg states by collision with several perturber gases together with an estimated broadening rate are shown in table 4.1.

perturber gas	collisional broad MHz/ (10^{-3}m)	dening bar)
He, Ne, Ar, Kr, Xe	0.0025 to 0.49	4 [82]
H_2	0.055	[83]
N_2	0.033	[84]
CO	0.223	[85]
NH_3	15	[86]
$Rb\left(5S_{1/2} ight)$	1.75	[38]

Table 4.1: Collisional broadening rates for rubidium Rydberg states for dif-
ferent perturber gases.

Some of these gases are usually used as buffer gases in alkali vapor cells. The cross-sections in these references were measured in the same range of main quantum numbers as our experiments (n = 20 - 35). From the cross-sections noted in the referenced publications, the broadening rates [87] were calculated by

$$\gamma = 2 \cdot n_P \cdot v \cdot \sigma, \tag{4.4}$$

were n_P is the perturber density, v the relative velocity between the rubidium and the perturber atoms or molecules and σ the effective cross-section for the impact broadening. For the perturber density the corresponding particle number was calculated for 1 mbar by the ideal gas law and the average relative velocity was assumed to be 300 m/s (mean thermal velocity of rubidium atoms). For comparison, the vapor pressure of rubidium is 1.1×10^{-3} mbar at 120 °C. This means that for almost all the above mentioned gases, the broadening should be far below 1 MHz at 120 °C. But it also indicates, that larger molecules have a higher cross-section, and thus a larger broadening rate. The molecules outgassing from the epoxy glue, which is used to seal the cell, might contain large molecules which could then have a much higher cross-section and broadening rate than the gases mentioned above.

As the type of perturber gas is not known, no absolute pressure of the cell can be given. In the glued cell, the line broadening is dominated by the background pressure. In the anodically bonded cell however, no additional broadening with time can be observed. The residual broadening in this cell could either be the result of power broadening, or background gases that have been produced from a reaction between rubidium and chromium.

As a rough estimation of the leakage rate we could assume that we have N_2 as perturber gas which would also be the case if there is a leak. Although the collisional broadening with larger molecules originating mainly from the glue is expected to be larger. In the case of N_2 the known broadening rate given in table 4.1 can be used to determine the pressure in the glued cell with nickel electrodes and in the bonded cell to

$$p(t = 40 \text{ days}) = 1.2 \text{ mbar}$$
 for the glued cell and (4.5)

$$p(t = 270 \text{ days}) = 0.182 \text{ mbar}$$
 for the anodically bonded cell. (4.6)

which results for a cell volume of $V = 1.5 \times 10^{-3}$ l in a leakage rate of

$$Q = 5.2 \times 10^{-10} \,\frac{\text{mbar} \cdot \text{l}}{\text{s}} \qquad (\text{glued cell}) \qquad (4.7)$$

$$Q = 0.1 \times 10^{-10} \,\frac{\text{mbar} \cdot \text{l}}{\text{s}} \qquad \text{(bonded cell)}. \tag{4.8}$$

The exact leakage rate can of course only be determined when the type of perturber gas and the cross-section of the process is known.

4.4 Temperature dependency

The linewidth of the EIT signal in the anodically bonded cell was also measured depending on the density of the rubidium. This measurement was performed in a thin cell (thickness of the atomic vapor layer roughly 30 - 70 µm) to reduce the optical depth.

In Fig. 4.4 the linewidth of the Rydberg EIT signal at a cell thickness of around 50 µm in the thin cell is plotted versus the temperature (Fig. 4.4a) and versus the ground state density (Fig. 4.4b). From absorption measurements the optical density is determined. From that, the corresponding atomic density and the actual temperature was calculated. An exponential increase in the linewidth of the EIT signal with increasing temperature is observed, which corresponds to a linear increase with the rubidium ground state density. The fluctuations of the data points might be due to slightly different Rabi frequencies in the different measurements.



Figure 4.4: Linewidth of the Rydberg EIT signal depending on (a) the temperature and (b) the ground state density of rubidium.

The temperature dependent broadening can be explained by collisions between Rydberg atoms and ground state rubidium atoms. This so called self-broadening rate has been measured in [38] to

$$\gamma_{sb} = 1.7476 \,\mathrm{MHz}/(10^{-3} \mathrm{mbar})$$
(4.9)

for the 22S Rydberg state of rubidium. The self-broadening Γ_{sb} of the Rydberg signal is then the vapor pressure p of rubidium times the self-broadening rate γ_{sb}

$$\Gamma_{sb} = p \cdot \gamma_{sb}.\tag{4.10}$$

The vapor pressure of 85 Rb is taken from [66]

$$p = 10^{2.881 + 4.312 - \frac{4040}{273 + T}} / 0.75006 \,\mathrm{mbar.} \tag{4.11}$$

The self-broadening Γ_{sb} is plotted in Fig. 4.4 as a dashed line. This theoretical self-broadening curve contains no free parameters except a constant offset of 15 MHz, which was introduced to take into account the linewidth at low temperatures. Part of this offset might again be the transit-time broadening of $\Gamma_{tt} = 0.95 \cdot 2\pi$ MHz in the 50 µm thick cell. The larger part of it is probably a constant amount of a residual gas that could not be avoided during filling of the cell. This can lead to collisional broadening, as described in the last section.

In addition to the theoretical broadening curve, a least-square fit of our data points is shown in Fig. 4.4. From that fit curve, the actual broadening rate of

$$\gamma_{act} = 2.7505 \,\mathrm{MHz}/(10^{-3} \,\mathrm{mbar})$$
 (4.12)

was determined. As this value is larger than the previously measured one in [38], we expect that still a small amount of an additional background gas might be inside our cell. This would also explain the linewidth of 15 MHz at temperatures below 100 °C.

A shift of the Rydberg state could not be observed in our measurements. For temperatures below 150 °C the expected shift rate of $0.8 \text{ MHz}/(10^{-3} \text{mbar})$ [38] was too small to be observed. For the high temperature measurements an offresonant laser lock was used to reduce absorption and no reference was available in this case.

From the measured broadening in Fig. 4.4b the cross-section σ_{exp} of the broadening mechanism can be determined by $\sigma = \Gamma/(n \cdot v)$. For a broadening

rate of, for example $\Gamma = 20 \cdot 2\pi$ MHz, a ground-state density of $3.5 \times 10^{19} \, 1/m^3$ (at 130 °C) and a relative velocity of around 300 m/s, the collisional cross-section would be

$$\sigma_{exp} = 1.2 \times 10^{-14} \,\mathrm{m}^2. \tag{4.13}$$

The collisional cross-section, that describes the interaction area of the Rydberg atom is of course much larger than the geometrical cross-section of the 22S Rydberg state of 2.5×10^{-15} m² which corresponds to an electron radius of the atomic state.

The linewidth in this vapor cell is mainly limited by the self-broadening of collisions between the Rydberg and ground state atoms. The constant offset in the linewidth might in part be due to a background gas. This background pressure is also the reason for the slightly increased broadening compared to the expected self-broadening rate.

4.5 High temperature compatibility

For the future application of addressable cells, thin cells with a thickness of $1-100\mu m$ are necessary. In such thin cells, heating the rubidium reservoir to temperatures of $150-250\,^{\circ}C$ is needed to achieve a high optical depth. For that reason the anodically bonded cells were tested about their high temperature compatibility. All glued cells could not be heated to more than $100\,^{\circ}C$, as otherwise the outgassing of the glue is irreversibly increased too much.

The anodically bonded cell can be used at least up to a cell temperature of $230 \,^{\circ}\text{C}$ without any degradation or additional pressure broadening except the self-broadening of rubidium. Measurements at high cell oven temperatures are shown in Fig. 4.5. The reservoir temperature, that controls the optical depth was kept below $135 \,^{\circ}\text{C}$.

The measurements were done with high red Rabi frequencies ($\Omega_{probe} = (9-45) \cdot 2\pi \text{ MHz}$) to be able to detect optical transmission also at high optical depths. This induces $(6-32) \cdot 2\pi \text{ MHz}$ of power broadening. Additionally the red laser was locked off-resonant to the ⁸⁵Rb $5S_{1/2} F = 3$ to $5P_{1/2} F = 3$ transition to further decrease the optical depth at the transition to $5P_{1/2} F = 2$. Self-broadening is expected to be $4.86 \cdot 2\pi \text{ MHz}$ at the highest temperature. The observed signal has a width of $(22-184) \cdot 2\pi \text{ MHz}$



Figure 4.5: Measurements at high oven temperatures. At oven temperatures of up to $T_O = 220$ °C narrow EIT linewidths can be observed. The only broadening arises mainly due to the increased laser power. The highest reservoir temperature was $T_R = 135$ °C.

which was dominated by power broadening. Relatively high laser powers were needed to compensate the high optical depth at these temperatures. When the cell is cooled down to $50 \,^{\circ}$ C a narrow EIT signal can be achieved again. This shows directly that no irreversible processes are happening and the cell can be used at operating temperatures of at least $230 \,^{\circ}$ C for several days without any degrading.

CHAPTER 5

Rydberg ionization current measurements

Additionally to Rydberg EIT measurements a new method was developed for the detection of the Rydberg population in vapor cells at and above room temperature [19]. Detection of the number of Rydberg atoms by field ionization and subsequent counting of the number of ions with a Multi-Channel-Plate (MCP) is a well-known technique in ultra-cold atom experiments. The detection method presented here is quite similar, but can be used in vapor cells at and above room temperature at pressures, that are incompatible with MCPs and Channeltrons.

Similar to the detection with an MCP the atoms are ionized and collected by electrodes. The difference is, that in vapor cells, especially at high vapor densities or with a large background pressure, the ionization process is an inherent process due to collisions of Rydberg atoms with other atoms or molecules present inside the cell. Therefore no electric field for ionization is necessary. Charges due to collisional ionization are produced continuously and can also be detected continuously by measuring the ion current through the atomic medium. However due to this continuous ion production there is no state-selectivity. Usually this is done by selecting the electric field pulse amplitude or using an electric field ramp. In our case we have to take into account all ionization mechanisms and other atomic states, like the ground and first excited state of rubidium.

The tremendous improvement for vapor cell physics due to this detection method is first, that instead of the optical coherence ρ_{12} , which is usually observed in vapor cell experiments, a second parameter, namely the Rydberg population ρ_{33} can be observed with this current detection method. Second, this method offers the great possibility to integrate a spatially resolved detection of Rydberg atoms directly "on-chip" into a vapor cell. It can presumably be combined with standard integrated electronics already used for example in liquid-crystal display technology or in the semiconductor industry.

In this chapter the principles of this new detection method are described. The observed Stark map signals for different conditions are shown and compared to the standard optical detection method. The different observed signal amplitudes for different parameters can be explained using a four-level calculation. Last, the dependency of the ionization current on the two Rabi frequencies is shown and the conditions for which this detection method can be used are given.

5.1 Ionization current detection

Detection principle

Different ionization mechanisms of Rydberg atoms are described in the theory Section 1.1.3. In our experiment we expect collisions between Rydberg atoms and perturber atoms and molecules to be the main ionization source. Perturber gases can either be the ground state atoms of rubidium itself, which is mostly important for high rubidium densities, as described in Section 4.4. Or there can be other perturber gases present in the vapor cell, either intentionally included as buffer gases, or unintentionally due to outgassing of the glue that is used for sealing of the vapor cell. This is the case for our glued vapor cells, as observed in Section 4.2. In our anodically bonded vapor cells, collisional ionization probably also occurs due to a small amount of perturber gas. Perturber gas can also occur if there are reactions between the glue and rubidium or the electrode materials and rubidium during or after filling the cell.

The system can be considered as atoms between two capacitor plates where a voltage is applied, see Fig. 5.1a. When some of the atoms are ionized, the resulting charges are accelerated towards the electrodes driven by the electric field. There, the electrons are detected, while the ions can recombine. These charges can then be detected as a small current. The expected ionization current amplitude is in the nanoampere regime, as estimated from ionization processes, described in Section 1.1.3. Nanoampere can easily be measured experimentally, using a current amplifier or an electrometer, although the detection with an electrometer can only be done with a small bandwidth leading to an increased measurement time.





(a) Ionized atoms and electrons are accelerated to the electrodes by a small electric field and are detected as a current.

(b) Schematic electronic circuit for current detection. A voltage is applied to the cell, the current through the cell is detected by a current amplifier.

Figure 5.1: Ionization current detection method

Ionization current signal

The ionization current detection cannot distinguish between different ionization processes, it only detects the total number of charges. However, the Rydberg electron has a low binding energy and Rydberg atoms have a large geometrical size. This leads to a large cross-section and a large ionization rate of Rydberg atoms which is much higher than the ionization rate of atoms in ground or low excited states. Also the ionization energy from the Rydberg state is much smaller, than from the 5S and 5P state.

All excitation lasers are continuous wave lasers in all our experiments. The Rydberg laser is scanned over the resonance (see laser setup in Chapter 3). The detected current consists of a continuous background current and a resonant Rydberg signal. The resonant Rydberg signal depends on the detuning of the Rydberg laser and is proportional to the Rydberg population. An example calculation of the optically observed transmission, which is proportional to $\text{Im}(\rho_{12})$ and the electrically detected signal, which is proportional to the population ρ_{33} is given in Section 3.1 in Fig. 3.2. The constant background current includes all ionization processes, that do not involve Rydberg atoms, such as photoelectric effect on the cell surface, ionization of ground

and excited state rubidium atoms or leak currents through the glass. It depends for example, on the incident laser power and has an amplitude on the order of $10^{-6} - 10^{-8}$ A. This offset current and the photoelectric effect are further investigated inChapter 7.1.

Only the resonant signal, that is observed by scanning the Rydberg laser is described here. It has an amplitude of $10^{-9} - 10^{-10}$ A. The constant offset due to other ionization effects is subtracted by the current amplifier for all measurements in this chapter.

Detection of the ionization current

For the detection of the Rydberg ionization current, electrodes are included inside the vapor cell. Positive or negative voltages can be applied to the individual electrodes, see Fig. 5.1b. The electrical current arising from the ionization processes can then be measured using a current amplifier (DL instruments preamplifier model 1211 or Keithley electrometer 610 C). A current can already be measured without any external applied voltage, because charges inside the cell can induce a potential difference between the two capacitor plates, leading to a movement of the atoms. Asymmetric charge production inside the cell defines the direction of the current. However at least a small voltage is recommended to accelerate the charges to the electrodes. Then more charges can be collected, which increases the signal amplitude. The reason for the asymmetric charge production is further investigated in Chapter 7.1.

5.2 Stark map of the optical and electrical signal

The ionization current detection method was used to measure Rydberg signals in several of the previously described vapor cells and compared to the optical signal, measured by electromagnetically induced transparency (EIT). Stark maps were recorded with both detection methods in a glued and in an anodically bonded cell. As in all measurements S-states were used, a quadratic Stark shift can be observed with increasing electric field.

In Fig. 5.2 Stark maps from measurements of the 42S Rydberg state in the glued vapor cell with nickel electrodes and of the 22S state in the anodically bonded vapor cell with chromium electrodes are shown. In each cell the EIT (left pictures) and the current signal (right pictures) are taken for the same parameter set. Although due to the different background pressure conditions in the two cells (described in Section 4) different parameters were used for the measurements in the glued and in the bonded cell.

In all cases a quadratic Stark shift could be observed. The only differences were the linewidths and the signal-to-noise ratios. The reason for this are the different parameter sets used for each measurement. The amplitudes and the signal-to-noise ratios of all signals are investigated in more detail in the next sections.

As can be seen in Fig. 5.2, for the glued cell the signal-to-noise ratio of the EIT signal is much worse than the ionization current signal. In the bonded cell instead the signals are almost the same, the EIT signal is even slightly larger. One other striking difference is, that both signals in the bonded cell are, at least for small voltages, much narrower than in the glued cell, which is partly due to power broadening and pressure broadening in the glued cell. However in both cells the line seems to split for higher voltages. Possible reasons for that are discussed later in Chapter 6.

Parameter sets for the measurements

Different parameters for the Rabi frequencies, the Rydberg state and the Rydberg ionization rate have been used in the two cells. They explain some of the features observed in Fig. 5.2. In the glued cell a high probe Rabi frequency was used ($\Omega_P \approx 50 \cdot 2\pi \text{ MHz}$), because due to the large pressure broadening from the background gas, high intensities of the probe laser were



Figure 5.2: Stark maps from glued (upper) and anodically bonded (lower) cell. Optical (left) and electrical (right) signal. (5.2a and 5.2b taken from [19]). In all cases a quadratic Stark shift can be observed. The signal-to-noise ratio in the anodically bonded cell is better, especially for the optical signal.

needed to observe an optical signal at all, which then additionally introduces power broadening. As a high Rydberg state was used in this measurements, the coupling Rabi frequency was comparably small ($\Omega_C \approx 0.5 \cdot 2\pi$ MHz) due to the limited coupling laser power. In the glued cell only low temperatures, and therefore low rubidium densities were used to avoid outgassing from the glue as much as possible. The ionization rate due to collisions is estimated from the EIT linewidth to be around $\Gamma_{ion} = 50 \cdot 2\pi$ MHz. In the anodically bonded cell, the probe Rabi frequency could be reduced without loosing the signal as the linewidth was much narrower due to much less background gas. As a low Rydberg state was used (22S), the coupling Rabi frequency was comparably high, leading to a strong optical and electrical signal. Because of the low background pressure, the ionization rate was low ($\Gamma_{ion} \approx 2 \cdot 2\pi$ MHz), leading to a narrow signal, but also to a decrease of the electrical signal as the measured current is directly proportional to the ionization rate.

The influence of this parameters on the observed signals is described by the four-level calculations in the next sections. Values for the two parameter sets are given in table 5.1.

	glued (Ni)	bonded (Cr)
Rydberg state	42S	22S
Ω_p	$5-180\cdot 2\pi\mathrm{MHz}$	$< 5 \cdot 2\pi \mathrm{MHz}$
Ω_c	$0.2 - 0.5 \cdot 2\pi \mathrm{MHz}$	$\approx 5 \cdot 2\pi \mathrm{MHz}$
Γ_{ion}	$50 \cdot 2\pi \mathrm{MHz}$	$2 \cdot 2\pi \mathrm{MHz}$

Table 5.1: Parameter sets for measurements in the glued and the bonded cell. The ionization rate Γ_{ion} was determined by the width of the EIT signal in each case. Ω_P and Ω_C denote the Rabi frequency ranges accessible in the experiments.

5.3 Signal amplitude of optical and electrical signal

To compare the two signals of the electrical and optical detection method in more detail cuts through the 2D plots of Fig. 5.2 are investigated. In Fig. 5.3 cuts through the Stark maps of the EIT and current signals for 0V are plotted for both cells (blue curves).



(c) EIT in bonded cell for low electric (d) Current in bonded cell for low elecfields tric fields

Figure 5.3: EIT ((a)+(c)) and current ((b)+(d)) measurements in the glued ((a)+(b)) and in the anodically bonded cell ((c)+(d)). In the glued cell, the current signal is much larger than the optical signal, because the high collision rate with the background gas increases the Rydberg ionization. In the anodically bonded cell due to a low background pressure the linewidth is more narrow and thus the optical signal is larger. Still a large current can be detected. The second peak at $\Delta_C \approx 240 \cdot 2\pi$ MHz detuning corresponds to a nearby hyperfine level of the intermediate state as mentioned in Chapter 3.1. A background current, which occurs mainly because of photoelectrons produced by the blue light, has already been subtracted from all current measurements. This effect will be discussed in more detail inChapter 7.1.

In the anodically bonded cell (Fig. 5.3c and Fig. 5.3d), without an applied voltage, the signal-to-noise ratio of the EIT signal was even better than the current signal. The reason for this is the much narrower linewidth due to the low background pressure, leading to a higher amplitude with the same number of atoms. The signal-to-noise ratio of the current signal is roughly the same in the glued and in the anodically bonded cell (Fig. 5.3b and Fig. 5.3d). When there is no voltage applied (blue curves), the direction of the current is determined by the production processes of the ions. In that case the potential difference in the cell is not high enough to collect all the produced charges. It can even happen, that the direction of the current changes during one scan, because the number of charges is changing on resonance and therefore also the potential created by these ions. One example of this effect is shown in Fig. 5.4. For a positive (green curve) or negative (red curve) voltage, the direction of the ionization current is defined by the externally applied voltage. Without externally applied voltage (blue curve) the current is almost zero. On resonance, when a high number of Rydberg atoms is produced and ionized, the direction of the ionization current changes from negative to positive.

The maximum current signal was achieved for an electric field of 2 V/cm in the anodically bonded cell (see red curves in Fig. 5.3c and Fig. 5.3d). Below that value not all charges are collected and above that value the amplitude is decreasing due to an inhomogeneous broadening of the signal. With a field of 2 V/cm both detection methods (optical and electrical) are equivalent in the signal-to-noise ratio in the bonded cell. In the glued cell, the current signal is always much larger than the optical signal, as seen inFig. 5.3a and 5.3b. This behavior can be explained by looking at theoretical calculations of a four-level system described in the following section.



Figure 5.4: Change in the direction of the ionization current due to the potential created by the charges inside the cell. At 0 V the direction of the Rydberg current changes during one scan, because the number of charges inside the cell, changes on resonance.

5.4 Calculated transmission and population

The effect, that the current signals in the cells with a higher background pressure were much higher than the optical signals can be reproduced by calculating the transmission and population of a three-level-system, as shown in the following. Additionally to the three-level system described in Section 3.1, a fourth level has been included to describe the ionization continuum, see Fig. 5.5. The process of EIT is based on the effect, that two different pathways of possible excitations to the 5P state lead to destructive interference of the two-photon resonance. The coherence of process (2) in Fig. 5.5a is necessarily required for the interference. The ionization of the Rydberg state can be implemented in this model as a decay from the Rydberg state into a fourth level (Fig. 5.5b). This decay reduces the coherence of the two-photon process, which can be observed as a decrease of the optical transmission peak.

In Fig. 5.6a and 5.6b the coherence ρ_{12} and the population ρ_{33} are calculated for such a four-level-system for different red Rabi frequencies (increasing from bottom to top) for a low ionization rate $\Gamma_{ion} = 2 \cdot 2\pi$ MHz. This corresponds to the case of the anodically bonded cell.



Figure 5.5: (a) Excitation scheme for EIT with low Rydberg decay rate. The interference between two excitation pathways leads to electromagnetically induced transparency. When the Rydberg atom is ionized (b), this coherence is destroyed. This induces a decreased Rydberg population and an increased linewidth of the Rydberg signal.

The optical signal (Fig. 5.6a) first increases with a higher probe Rabi frequency and then decreases again, as the linewidth gets broadened due to power broadening. The population (Fig. 5.6b) instead is always increasing for higher Rabi frequencies. For a high ionization rate $\Gamma_{ion} = 50 \cdot 2\pi$ MHz the transmission signal Im(ρ_{12}) is already broadened because of the high decay rate. This case, corresponding to the conditions in the glued vapor cell, is shown in Fig. 5.6c and 5.6d. It shows the same behavior for increasing probe Rabi frequencies, but the absolute amplitude is already much lower due to the increased linewidth.

While the measured optical signal is proportional to the calculated coherence Im(ρ_{12}), the measured ionization current is proportional to the Rydberg population times the ionization rate $\rho_{33} \cdot \Gamma_{ion}$. The calculated signal amplitude at resonance ($\Delta_C = 0$) is plotted in Fig. 5.7 versus the probe (5.7a and 5.7b) and the coupling Rabi frequency (5.7c and 5.7d), for the two parameter sets given in Table 5.1, that were also used for the measurements. For the blue curves the parameters in the anodically bonded cell were used and for the red curve the parameters for the glued cell. As the signals broaden with higher probe Rabi frequency the amplitude of the optical signals decreases, as can be seen in Fig. 5.7a. The optical signal at a high ionization rate is much smaller compared to the one for a low ionization rate. The electrical signal is on the same order of magnitude, as it is also directly proportional to the ionization rate. The absolute values of the electrical signals depend on the exact ionization rates. For that reason the relative amplitude between the two cases in the electrical signal could deviate by up to a factor of 3, as the decay rates are only an estimation determined from the width of the Rydberg signals. With increasing coupling Rabi frequency (Fig. 5.7c and 5.7d), the optical and the electrical signals are increasing for a low as well as for a high Rydberg decay rate.

Typical measurement parameters are indicated by arrows. For a high ionization rate and low coupling Rabi frequency a very small optical signal is expected. Also the electrical signal is roughly by a factor of 10 smaller compared to the one for a low ionization rate and high coupling Rabi frequency. This is exactly what has been observed in the measurements of the Stark maps shown in the beginning of this chapter (Fig. 5.2). The main reason is, that the optical signal is depending almost linearly on the coupling Rabi frequency. In the glued cell only low coupling Rabi frequencies have been used. In this case the electrical signal can still have a large amplitude, as ionization processes are enhanced in the glued cell.



Figure 5.6: Calculated coherence $\text{Im}(\rho_{12})$ (optical signal) and population ρ_{33} (electrical signal) for a three-level system with increasing probe Rabi frequency (bottom to top $\Omega_{12} = (1-10) \cdot 2\pi \text{ MHz}$).



(a) Transmission with $\Gamma_{ion} = 2 \cdot 2\pi \text{ MHz}$ and $\Omega_C = 5 \text{ MHz}$ (blue) and Γ_{ion} $50 \cdot 2\pi$ MHz and $\Omega_C = 0.5$ MHz (red, 10) times magnified).



(b) Population times ionization rate with $\Gamma_{ion} = 2 \cdot 2\pi \,\mathrm{MHz}$ and $\Omega_C = 5 \,\mathrm{MHz}$ (blue) and $\Gamma_{ion} = 50 \cdot 2\pi \text{ MHz}$ and $\Omega_C = 0.5 \,\mathrm{MHz}$ (red, 10 times magnified).



(c) Transmission with $\Gamma_{ion} = 2 \cdot 2\pi$ MHz and (d) Population times ionization rate with $\Omega_P = 5 \,\mathrm{MHz}$ (blue) and $\Gamma_{ion} = 50 \,\cdot$ 2π MHz and $\Omega_P = 14$ MHz (red).

 $\Gamma_{ion} = 2 \cdot 2\pi \text{ MHz} \text{ (blue)} \text{ and } \Gamma_{ion} = 50 \cdot$ 2π MHz (red).

Figure 5.7: Calculated amplitude of coherence $Im(\rho_{12})$ (left), corresponding to optical signal in the experiment, and population $I = \rho_{33} \cdot \Gamma_{ion} \cdot n \cdot e \cdot V$ (right), corresponding to the electrical signal in the experiment calculated from a three-level-system for the parameter sets used in the glued cell (red) and the bonded cell (blue) versus the probe (upper) and coupling (lower) Rabi frequencies (n: rubidium density, e: elementary charge and V: excitation volume). Arrows indicate the Rabi frequencies used in the experiments.

5.5 Measurement of the ionization current for different Rabi frequencies

The behavior of the electrical signal with increasing probe and coupling Rabi frequencies has been measured in the glued cell. This is depicted in Fig. 5.8.

For the probe, as well as for the coupling Rabi frequency the ionization current follows the expected behavior for high Rydberg decay rates (red curves in Fig. 5.7b and 5.7d). The only fitting factor was a constant prefactor to the red curves, shown in Fig. 5.7b and 5.7d which describes the detection efficiency. The expected ionization current can be estimated by using the number of Rydberg atoms (defined by the excitation volume V, the atom density n and the Rydberg population ρ_{33}), the ionization decay rate Γ_{ion} and the elementary charge e

$$I = e \cdot V \cdot n \cdot \rho_{33} \cdot \Gamma_{ion}. \tag{5.1}$$

Under the assumption, that all observed broadening originates from the ionization process, the ionization rate Γ_{ion} can be estimated from the widths of the optical signal or the current signal. This will definitely overestimate the ionization rate. For the parameters of the measurements in the glued cell a current of I = 7.6 nA can be derived. For the measurements in the bonded cell higher temperatures and thus higher densities could be used while the decay rate is only $\Gamma_{ion} = 2 \cdot 2\pi$ MHz. Then the ionization current would be around 80 nA. The measured ionization current is on the order of 10^{-10} A in the glued cell and around 10^{-9} A in the bonded cell. From that we estimate a detection efficiency of the ionization current detection method of 10 %.



Figure 5.8: Measurement of the ionization current depending on the Rabi frequencies. The theoretical curve, shown as red curve in Fig. 5.7b and Fig. 5.7d was fitted to the measurements. The only free parameter is a proportionality factor, which describes the detection efficiency. It is determined to be in average 10%.

5.6 Applications and conditions for the ionization current detection method

This ionization current detection can be used in the case of high background pressure, which is either due to outgassing materials inside the cell, or due to an included buffer gas. Also this method can be used when the atom density is so large, that no optical signal can be detected. In all these cases there is an increased collision probability. These collisions increase the number of detected charges and thus the signal-to-noise ratio of the ionization current also increases. This method also gives additional information when not only the optically observed coherence ρ_{12} , but also the Rydberg population ρ_{33} is of interest. It could also be implemented inside the cells so that no other external detection would be needed. Standard technologies used in liquid crystal displays or by the semiconductor industry could be used to further improve the detected Rydberg signals.

CHAPTER 6

Measurements of electric fields inside vapor cells

Implemented electrodes inside vapor cells open plenty of applications that cannot be done by addressing the atoms from outside the cell. Some examples are the spatial dependent addressing of atoms, tuning of the vapor transmission by shifting the atomic states with electric fields or detecting the Rydberg population as described in the previous Chapter 5. Using optical and electrical read-out the properties of the electric fields inside the cell, like attenuation of the field by shielding or additional space charges can be determined. Such an evaluation is not possible with electrodes on the outside of the cell because charges that are produced inside the cell would shield every DC field.

The implemented electrodes have been used to apply electric fields and address the atoms. Several effects are observed inside the cells. These effects are described and investigated in this chapter. It was observed, that space charges are present inside the vapor cell originating from the photoelectric effect taking place at the inner surface of the vapor cell. They lead to an inhomogeneous electric field distribution inside the cell. The determination of the electric field distribution and the dependencies on some parameters are shown in this chapter.

6.1 Measurement with DC electric field

The DC Stark effect can be used to investigate the electric fields inside the cells. We have applied a DC electric field and observed the Stark shifts of the Rydberg level. As described in Section 1.1.2 in approximation for low electric

field amplitudes the theoretical Stark shift for an S state can be calculated by

$$S = \frac{1}{2}\alpha_0 E^2 \tag{6.1}$$

where the polarizability α_0 can be calculated from an empirical formula by [33]. Another possibility would be to determine α_0 for the observed electric field region by a fit to the full calculation. In Fig. 6.1 the Stark shift of the 22S Rydberg state in a 5 mm bonded cell with chromium electrodes for both electric field directions (blue and red curve) is plotted, and in Fig. 6.2 the Stark shift of the 32S state measured in a glued cell with Ni electrodes is plotted. For each electric field (0 - 60 V/cm) the Rydberg EIT signal is observed by measuring the transmission of the probe laser while the coupling laser was scanned over the Rydberg resonance. If a homogeneous electric field would be present inside the cell, the single EIT peak should shift quadratically along the green line. In contrary to that, we observed that our EIT signal splits into two peaks. The measurements were done at a reservoir temperature of $T_R = 70 \,^{\circ}\text{C}$ and a cell temperature of $T_C = 80 \,^{\circ}\text{C}$ in the anodically bonded cell. The measurements in the glued, Ni coated cell have been done at $T_R = 40 \,^{\circ}\text{C}$ and $T_C = 70 \,^{\circ}\text{C}$.

There are several effects that need to be explained. The given conclusions in the following overview are derived in the sections mentioned, along with further investigations.

• Instead of a single shifted line (theoretical shift is plotted as green line), we see a splitting, which increases with higher electric fields. This splitting is not due to other Rydberg levels, as the first avoided crossing is at much higher electric fields.

 \rightarrow The reason for the splitting are inhomogeneous electric fields produced by charges. They occur due to ionization of the (Rydberg) atoms and the photoelectric effect on the inner glass surface of the cell (see Section 7.1).

• The direction of the electric field does have an influence on the shift and splitting of the Rydberg level, which should not be the case as the cell is symmetric and the Stark effect is quadratic.

 \rightarrow Due to asymmetric or inhomogeneous charge production inside the cell, an inhomogeneous electric field is created (see Section 6.4).

• The lineshape in the Ni coated and in the Cr coated cell are slightly different. In the Ni coated cell one broad line can be observed, while in the Cr coated cell it has a double-peak structure.

 \rightarrow The reason is the increased pressure broadening due to background gases in the glued cells (see Section 4).

The reasons for these effects are further investigated in the next sections.



Figure 6.1: Stark shift measurements of 22S state in a 5 mm cell for both electric field directions (blue and red) in a anodically bonded cell with chromium electrodes. The electric field directions are defined in Fig. 3.3b in Section 3.1. The green line shows the expected quadratic shift of this state. Additionally to the quadratic Stark shift a splitting of the Rydberg EIT signal is observed. The origin of this splitting is investigated in the next sections.


Figure 6.2: Stark shift measurements of the 32S state in a 5 mm cell in a glued cell. The green line shows the expected quadratic shift of this state. Additionally to the quadratic Stark shift a splitting of the Rydberg EIT signal is observed. The origin of this splitting is investigated in the next sections.

6.2 Electric field distribution due to the electrode configuration

In the bonded cell, the chromium electrodes are not transparent. The two excitation lasers have to be aligned between two neighboring electrodes, which are on the same potential (see Fig. 6.3 and Section 2). This electrode configuration is not a perfect plate capacitor. Therefore the electric field inside is not completely homogeneous. The electric field in such an electrode configuration was simulated with a finite element simulation in Comsol 4.4 to determine the inhomogeneity of the electric field created by this specific electrode configuration.



Figure 6.3: Electrode configuration that has been used for the simulation of edge fields inside the vapor cell. Two glass plates with 1 mm thickness and a distance of 5 mm have been used. On top of each glass plate are two 2 mm wide thin metallic electrodes, with a spacing of 1 mm. The two electrodes on the same glass plate are kept at the same potential.

In the 2D simulation we used 4 metallic electrodes with glass plates on the backside to simulate the cell (schematic see Fig. 6.3). The whole assembly was put in a large box of air. The resulting electric field is plotted in Fig. 6.4a for an applied voltage of 10 V. As the vapor cell thickness is 5 mm, the homogeneous electric field in a plate capacitor would be 20 V/cm. In Fig. 6.4b a cut along the laser direction is shown. One can see, that the maximum field is below 20 V/cm. The total width of the electrodes is the same size as the distance between the capacitor plates. Therefore the electric field is not constant in the whole capacitor region. Between the neighboring electrodes on each side, the electric field is decreased. The laser beams are propagating through the cell along the indicated white line.



Figure 6.4: (a) Simulated electric field distribution inside a capacitor with two electrodes on each side and a potential difference of U =10 V. The indicated white line denotes the laser propagation axis. (b) Cut along the indicated white line. The electric field is reduced on each side, resulting in an electric field, that is not constant over the whole cell. (c) Simulated transmission $(\text{Im}(\rho_{ge}), \text{ blue})$ and Rydberg population $(\rho_{rr}, \text{ red})$ with the two electrodes configuration for a potential difference of 20 V. Due to the inhomogeneous field, seen in (a) and (b), the EIT signal is not symmetric anymore and the peak maximum is shifted by Δs less than expected from a homogeneous field of 40 V/cm. However the asymmetry observed in the experiment is much larger, than expected from that calculation. As the electric field is not completely homogeneous along this line, atoms at different positions feel different electric field amplitudes. The atomic signal that is probed by measuring either the transmission of the probe laser or detecting the ionization current, is a summation of all atomic signals along the laser beam (white line in Fig. 6.4a). Therefore the resulting atomic signal for a specific electric field distribution can be calculated. A calculated EIT signal from a 3-level-calculation is quadratically shifted for each position inside the cell. All signals are summed up to get the averaged signal.

In Fig. 6.4c the expected signal for an applied voltage of 20 V is calculated. The resulting peak position is by Δs less shifted than expected from the applied voltage on a homogeneous plate capacitor. This means that due to the electrode configuration the measured electric field in that cells will always be around 3% less than expected from a homogeneous capacitor. Due to averaging over different electric field amplitudes inside the cell, also a slight asymmetry of the EIT peak can be seen in the calculated lineshapes. The inhomogeneity due to the electrode configuration should be observable, but it cannot explain the lineshape observed in the measurement. This leads to the conclusion, that the splitting, observed in the measurements, cannot be due to the electrode configuration.

For comparison in Fig. 6.5 the calculated electric field for one large electrode is plotted. This is also the electrode configuration in the glued cells. As they have semi-transparent electrodes of nickel or aluminum the lasers can be aligned through the electrodes (again indicated as white line). The electric field is almost constant in the whole capacitor region.

The corresponding calculated signal is plotted in Fig. 6.5c. There is only a slight inhomogeneity due to the edge fields of the capacitor. This results in a slight broadening of the atomic signal but no additional shift or asymmetry.

From the simulations it can be concluded, that the splitting observed in the cell with Ni electrodes cannot arise due to the limited size of the electrodes. For both electrode configurations the simulated changes in the resulting line-shapes are too small to be observed in the experiment. Although for the configuration with two separate electrodes we have to take into account, that the maximum electric field will always be approximately 3% lower compared to an ideal plate capacitor which converts into a less shifted Rydberg signal. But the line should in both electrode configurations consist of a sin-



Figure 6.5: (a) Simulated electric field inside a capacitor with one large electrode on each side and a potential difference of U = 10 V. The indicated white line denotes the laser propagation axis. (b) Cut along the indicated white line. The electric field is almost constant along the whole laser propagation line. (c) Simulated signal with one electrode on each side for a potential difference of 20 V. Due to the almost completely homogeneous electric field a single and symmetric EIT peak should be observable.

gle peak. This indicates, that the origin of the inhomogeneity, seen in the measurements, is not due to the electrode configuration.

6.3 Measurement with AC electric field

To eliminate the dependence of the electric field direction the Stark shift was also investigated for AC electric fields. As a square wave was used for applying the AC voltage, the electric field should correspond to a fast switching between the two electric field directions. If no other effects occur inside the cell then an average between both field directions would be expected. The Stark shift for an AC electric field with 1 MHz frequency is plotted in Fig. 6.6a. For this data the anodically bonded cell was used, but the other cells show similar results.



Figure 6.6: (a) Stark shift of Rydberg EIT (22S state) with AC electric field at 1 MHz. In contrast to the measurements at DC electric fields, here only one single peak is observed, even for higher electric fields. The theoretical curve (green line) is taking into account, that the field in the cell with two separate electrodes is always 3% smaller than in a ideal plate capacitor. (b) Fit of the Stark shift data (red) and theoretical shift (green). The detected electric field shift is slightly smaller than expected.

The theoretical value, plotted in Fig. 6.6a and 6.6b as green line already takes into account that the observed field in this electrode configuration with two separate electrodes is always 3% less compared to a homogeneous plate capacitor as explained in Section 6.2.

With an AC instead of a DC voltage, no splitting of the EIT peak is observed which would not be expected if we would see only averaging over the two field directions. The measured Stark shift is only slightly smaller than the theoretical shift. A fit of the polarizability (plotted in Fig. 6.6b), results in a polarizability of $\alpha_0 = 0.1295 \text{ MHz}/(\text{V/cm})^2$. The theoretical value calculated by the empirical formula from reference [33] is $\alpha_0 = 0.1465 \text{ MHz}/(\text{V/cm})^2$. Additional charges, that are present inside the cell can shield the applied voltage. This can be the reason for the smaller Stark shift.

These charges can also be the reason for the splitting, that was observed with DC electric fields. The difference between DC and AC fields is, that in the DC case all charges are continuously accelerated in one direction, leading to an inhomogeneous charge distribution. For AC fields, the charges are only accelerated back and forth if the AC frequency is large enough. Then these charges are in average fixed in space and this is a different situation than averaging over two field directions. The frequency has to be high enough, that these charges do not reach the surface. For our configuration the necessary frequency for electrons would be 93 MHz and for rubidium ions due to their larger mass 238 kHz. The AC frequency during the measurements was 1 MHz. For that reason only the rubidium ions are affected by it.

One possible explanation for our observed effects could be, that electrons, created by the photoelectric effect on the glass surface create a negative background charge density. Any positive rubidium ion that is produced might reduce this negative charge density. The number of electrons is expected to be about 10 times higher than the number of rubidium ions, as concluded from the measurements of the Rydberg ionization current in Section 5, and from measurements of the photoelectric current in Section 7.1. However for AC voltages the duration of stay of the ions inside the cell volume might be increased, which then could compensate the negative charge density of the continuously produced electrons.

Although there is no splitting of the EIT signal when an AC electric field is applied, an increasing inhomogeneity can be seen in the increasing linewidth (Fig. 6.7). The signal starts to broaden starting from a certain electric field.



Figure 6.7: Linewidth of the EIT signal versus the applied voltage. For increasing voltage, the remaining inhomogeneities, for example due to the electrode configuration, described in Section 6.2, linearly increase the linewidth of the EIT signal.

Above this threshold the width increases linearly. Any inhomogeneity in the electric field, for example due to the electrode configuration also increases linearly with the electric field itself. The threshold behavior is probably simply because the minimum linewidth of 8 MHz is limited by pressure broadening due to a residual background gas and power broadening of 5.3 MHz.

6.4 Determination of the electric field distribution

We can determine which electric field distribution would cause such a doublepeak lineshape that was measured for DC electric fields. For that we used data from EIT and Rydberg ionization current measurements taken with the same parameters. This data is plotted in Fig. 6.8. For that measurement the anodically bonded cell with chromium electrodes and the 30S Rydberg state was used.

When we measure the optical transmission of the probe laser, we detect the coherence $\text{Im}(\rho_{12})$ of the system. To get a second independent measurement, we can also detect the ionization current. In this case instead of the coherence $\text{Im}(\rho_{12})$ the signal is proportional to the Rydberg population ρ_{33} as described in Chapter 5.

In Fig. 6.8 the optical signal (blue) looks like a double-peak line, as observed before. The electrical signal instead seems to be a continuous flat-top signal, which is almost constant from a minimum to a maximum shift. This could happen if there is a continuous distribution of different electric field strengths inside the cell. When atoms at different positions see a different electric field due to an inhomogeneous electric field, their Rydberg level is shifted by a different amount. A summation over all EIT signals of atoms at different positions then lead to a continuous distribution of the total transmission signal and the ionization current signal.

To determine the electric field distribution inside the cell, a three-levelsystem was used to calculate the coherence and the population with the same Rabi frequencies, used in the experiment. To get a high ionization current a high population is needed, which can be achieved by high intensities of the excitation lasers. The broad lines in the EIT as well as in the current signal can be explained by the probe Rabi frequency of $\Omega_P = 18.5$ MHz which results in a power broadening of 13 MHz. The broadening especially in the current signal makes it harder to distinguish between a continuous signal and two separate peaks.

One question is, whether the signal consists of two separate lines which would correspond to two specific fields in the cell, or if it is a continuous maybe linear electric field. Due to the enhanced absorption in the optical signal (see Section 3.1) a peak and enhanced absorption could be averaged to zero. For that reason a continuous electric field can result in an optical



Figure 6.8: Simultaneous measurement of optical signal (EIT, red curve) and ionization current (blue curve) of the 30S state. Both signals show a splitting or a broadening, respectively.

signal, that looks like two separate peaks. But the Rydberg population can only be positive. A summation over a continuous distribution of different electric fields will always result in a continuous signal.



Figure 6.9: Measurement of EIT (a) and current (b) fitted for an electric field with two specific values (c).

In Fig. 6.9 two specific fields (shown in Fig. 6.9c) are assumed and the data for an applied electric field of 28 V/cm is plotted for the EIT in Fig. 6.9a and the current in Fig. 6.9b. The theoretical lineshape of the coherence ρ_{12} and the population ρ_{33} , calculated from a three-level system, were shifted corresponding to the assumed electric field, and the amplitude and the offset of the resulting curve was fitted to the data. For the theoretical curve the same Rabi frequencies than in the measurements are used. Two single peaks can be seen in both theoretical curve of EIT and current. This is expected, when we assume two specific electric fields inside the cell. The data however show a more continuous distribution.



Figure 6.10: Measurement of EIT (a) and current (b) fitted for a linear electric field (c).

In first approximation we can assume, that the continuous electric field in the cell is linear (Fig. 6.10c). The expected theoretical lineshape we would get for such an electric field is again calculated as before. The resulting theoretical curves are plotted in Fig. 6.10a and 6.10b. Now the calculation shows a continuous distribution of the EIT and the current lineshape, similar to the experimental data.



Figure 6.11: Measurement of EIT (a) and current (b) fitted with electric field of the shape of an errorfunction to imitate an electric field that deviates slightly from a linear field (c).

If we finally allow slight deviations from the linear electric field, we can take into account, that there might be larger regions of the highest or lowest electric fields. To get a smooth transition between the linear region and regions with higher or lower electric field we used an error function to model such a distribution. The origin of such a distribution can be charges as will be described in Section 6.4.1. With that function we can fit the data perfectly (see Fig. 6.11). It seems that apart from slight deviations, the electric field is linear. The fitted electric fields, shown in Fig. 6.9c, 6.10c and 6.11c do not correspond to a spatial field distribution, but just mean how often which electric field strength needs to be present in the cell to result in such a signal, similar to a histogram. The spatial distribution can in principle look completely different.

The fit of the electric field distribution has also been done for the Stark measurements in the nickel-coated cell (Fig. 6.12). In that case the electrode



Figure 6.12: Measurement of EIT (a) and fitted electric field (b) in Nicoated cell. The lineshape can be reproduced by an almost linear electric field.

configuration should not play a role, as it was one large semi-transparent electrode on each side of the cell. Here only the optical signal has been observed. Also for that measurement the electric field is almost linear, with only slight deviations, although the lineshape of the measured EIT signal looks quite different compared to the one in the anodically bonded cell. The reason is, that already slight changes in the slope of the theoretical electric field change the lineshape of the resulting signals significantly.

Independent of the electrode configuration the electric field inside the cell seems to be almost linear. Slight deviations from this linearity can occur due to the specific conditions in each single cell due to different space charge distributions. This could arise because of a different surface coverage of rubidium, different vapor pressure or the surface materials.

6.4.1 Capacitor with homogeneous space charge

A similar electric field distribution as has been determined from the measurements, can be modeled by including a homogeneous space charge in the finite element simulations, shown in Section 6.1. In the configuration with two separate electrodes on each side of the cell, a homogeneous space charge was added in the whole region between the electrodes (Fig. 6.13b). This corresponds to fixed charges, homogeneously distributed in a plate capacitor which theoretically yields a linear electric field between the two capacitor plates. The physical meaning in our vapor cell would be an equilibrium between production and annihilation or extraction of charges, leading to a homogeneous distribution of all charges in the whole cell region.



Figure 6.13: Simulation of a plate capacitor consisting of two electrodes on each glass plate with a homogeneous space charge ρ between the two glass plates. The simulated electric field is almost linearly increasing from one side to the other. The indicated white line shows the position of the lasers.

An applied voltage of 11.5 V was used to match the actual shift, measured in the experiment (measured at 14 V). Then the simulated field distribution was used to calculate the corresponding theoretical optical and electrical lineshapes (see Fig. 6.14a and 6.14b). A constant space charge of $\rho = 1.2 \times 10^{-6} \text{ C/m}^3$ was used in the simulation to match the simulated lineshape to the actual measured data. Both the optical and the current signal show a good overlap between simulation and experiment.

For this calculation the Rabi frequencies from the experiment were also used in the calculation of the three-level-system. Additionally the decay rate from the Rydberg to the ground state was increased to $\Gamma_{31} = 1.3 \cdot 2\pi \text{ MHz}$ in the calculation to adapt the calculated to the measured lineshape. The reason for the increased decay is the transit-time broadening, as explained in Section 4.



(a) Transmission data and simulation with (b) Ionization current data and simulation with homogeneous space charge. homogeneous space charge.



(c) Determined electric field distribution (d) The determined electric field distribuwith a homogeneous space charge vs. spatial position inside the capacitor.

tion with a homogeneous space charge sorted in ascending order shows an almost linear behavior.

Figure 6.14: Measurements of EIT (a) and ionization current (b) and simulations of electric field distribution in a capacitor with a homogeneous space charge distribution. The simulated electric field distribution can almost exactly reproduce the measurements.

A cut through the simulated electric field along the indicated white line in Fig. 6.13b is plotted in Fig. 6.14c versus the actual position in the cell. This cut has been used for the calculation of the lineshape. When the electric field is sorted in ascending order, as plotted in Fig. 6.14d, it looks similar to the fitted electric field previously determined to match an arbitrary field distribution to the data, Fig. 6.11c. It is linear with slight deviations at the lowest and the highest electric field. As the actual charge production and the recombination processes are not completely homogeneous over the whole cell volume, deviations from this continuous space charge density can easily lead to deviations from the calculated electric field distribution.

The space charge of $\rho = 1.2 \times 10^{-6} \,\mathrm{C/m^3}$ that has been used for the simulation correspond to 7.5×10^6 charges/cm³. A homogeneous space charge can be explained by an equilibrium between production of charges by ionization processes or photoelectric effect and recombination of charges at the electrodes. The possible electron density due to the photoelectric effect has been estimated in Chapter 1.1.3 to be $\rho_e = 2.3 \times 10^6$ charges/cm³ (corresponding to a measured photoelectric current of 10 nA). Although there must also be positive and negative charges from ionization of the Rydberg state in equilibrium, the amount of Rydberg ions are expected to be 10 times smaller. For that reason the inhomogeneity is mainly related to the number of electrons produced by the photoelectric effect on the cell surface.

6.5 Dependency from surface coverage

One source for charges is due to the photoelectric effect at the surface. As the work function of chromium is 4.5 eV and the laser energy is only 2.58 eV (corresponding to the blue wavelength 474 nm) it cannot be a photoelectric effect on the chromium surface. But depending on the temperature difference between the cell oven and the reservoir (see schematic in Section 3.2), the inner surface of the cell is covered by a thin layer of rubidium. As the work function for solid rubidium is 2.16 eV the blue laser has enough energy to eject electrons from rubidium. To determine the effect of the surface coverage of rubidium on the splitting, the Stark shift was measured at two different cell oven temperatures. They correspond to two different surface coverages of rubidium. The reservoir temperature was kept constant to have the same rubidium density in both measurements. In Fig. 6.15 and Fig. 6.16 the measured Stark shift at a reservoir temperature of $T_R = 60 \,^{\circ}\text{C}$ and cell temperatures of $T_C = 110 \,^{\circ}\text{C}$ (blue curves) and $T_C = 65 \,^{\circ}\text{C}$ (red curves) is plotted. These two plots show the measurements for the two different electric field directions as defined in the inset of each figure.



Figure 6.15: Stark shift data for positive applied voltage for two temperature differences between cell reservoir and oven $\Delta T = 5 \,^{\circ}\text{C}$ (blue) and for $\Delta T = 50 \,^{\circ}\text{C}$ (red) for both electric field directions. Asymmetric charge production inside the vapor cell might break the symmetry, leading to a different electric field distribution for the two electric field directions.

One can see, that at a smaller temperature difference (blue curves), which means a higher surface coverage, the observed splitting increased. As the reservoir temperature of the vapor cell and the laser intensity was kept constant, the rubidium density and the Rydberg population did not change between these measurements. At a high temperature difference the surface



Figure 6.16: Stark shift data for negative applied voltage for two temperature differences between cell reservoir and oven $\Delta T = 5 \,^{\circ}\text{C}$ (blue) and for $\Delta T = 50 \,^{\circ}\text{C}$ (red) for both electric field directions. Asymmetric charge production inside the vapor cell might break the symmetry, leading to a different electric field distribution for the two electric field directions.

coverage with rubidium is expected to be low. In that case the splitting has almost vanished (red curves).

For a more quantitative analysis the two observed peaks were fitted with two Lorentzian functions to determine the absolute splitting. The peak position at each applied voltage is plotted in Fig. 6.17a for the case when a positive voltage is applied.

From the Stark shift the actual electric field present in the cell was calculated. The difference between the expected electric field for a homogeneous capacitor and the electric field detected by Rydberg EIT is plotted in



Figure 6.17: (a) Stark shift for positive applied voltages (Fig. 6.15) for both temperature differences. The splitted signal was fitted with two peaks. (b) Difference ΔE between the measured electric field and the field E expected from a homogeneous plate capacitor with E = U/d. It indicates the additional potential difference and thus additional charges, that are present inside the cell.

Fig. 6.17b for both peaks and both surface coverages. An additional charge needs to be present in the cell, that for low surface coverage ($\Delta T = 50 \,^{\circ}$ C, red curves) creates a field of up to $\Delta E_L = \pm 7.8 \,\text{V/cm}$ and for high surface coverage ($\Delta T = 5 \,^{\circ}$ C, blue curves) up to $\Delta E_H = \pm 16.8 \,\text{V/cm}$. From that electric field difference, the charge density, that creates such an additional electric field can be estimated by the Maxwell equation $\delta E / \delta x = \rho / \epsilon_0$ to

$$\rho_L = 8.6 \times 10^6 \,\mathrm{charges/cm^3} \tag{6.2}$$

for low surface coverage ($\Delta T = 50 \,^{\circ}$ C), and

$$\rho_H = 18.5 \times 10^6 \,\mathrm{charges/cm^3} \tag{6.3}$$

for high surface coverage ($\Delta T = 5 \,^{\circ}$ C). This rough estimation of the necessary space charge to create such a field distribution is on the same order of magnitude like the one determined in Section 6.4 by matching the exact lineshape of the EIT signal to a simulation. The change in the number of space charges by a factor of two is indicating, that also the surface coverage with rubidium is changing by that amount. The significant change in the field distribution for different surface coverages of rubidium clearly shows, that charges created by the photoelectric effect play an important role in our cells. The photoelectric effect in our vapor cells is further investigated in Section 7.1.

When the surface coverage of rubidium on the glass is different for the two conditions, then also the surface conductivity should be different because of the conductivity of rubidium itself. The surface conductivity can be estimated by applying a voltage between two neighboring electrodes and measuring the current between them. However, as the surface conductivity is very low, no difference in the surface conductivity between the two conditions were measurable, but only a minimum resistance of

$$R = 17 \,\mathrm{G}\Omega \tag{6.4}$$

for both cases could be estimated. A different method for the determination of the surface coverage need to be found. One approach could be to use the photoelectric effect, that is described later in Section 7.1 and determine the difference in the photoelectric current under these two conditions.

Change in field distribution

With the method described in Section 6.4 the actual measured electric field distributions are determined for both temperature differences and both polarities for an electric field of 58 V/cm (data from Fig. 6.15 and Fig. 6.16). The determined electric fields are plotted in Fig. 6.18. Here one can see again, that all electric fields are more or less linear, with slight deviations.

For a larger temperature difference ($\Delta T = 50$ °C), plotted as dashed line, the spread of the electric field is from E = 54 to 62 V/cm (red) and from E = 48 to 57 V/cm (blue) for the two field directions. At a temperature difference of $\Delta T = 5$ °C, the measured electric field reaches from E = 45 to 68 V/cm for negative (red) and from E = 42 to 61 V/cm for the positive (blue) field direction. This means, that at a low temperature difference, corresponding to a high surface coverage with rubidium, the inhomogeneity is much larger than with high temperature difference (low surface coverage). When a higher number of rubidium atoms is adsorbed on the glass surface, then more electrons can be ejected by the photoelectric effect. These electrons can then form a space charge distribution in the cell, which produces an inhomogeneous electric field.



Figure 6.18: Electric field distributions, resulting from the fit of the data, plotted in Fig. 6.15 and 6.16. Blue: positive voltage (+), red: negative voltage (-), continuous line: $\Delta T = 5 \,^{\circ}$ C, dashed line: $\Delta T = 50 \,^{\circ}$ C, green: expected field for a homogeneous capacitor without space charges. For a smaller temperature difference ($\Delta T = 5 \,^{\circ}$ C, continuous line), which means a high surface coverage, the spread of the electric field distribution is larger, which corresponds to a larger number of space charges.

The deviation from a linear field is larger in case of positive applied voltages (field direction as defined in Fig. 6.15). For negative applied voltages (as defined in Fig. 6.16) the electric field is also closer to the expected field, while for positive applied voltages the electric field seems shielded. One explanation could be, that a different amount of charges is produced on each side of the cell. Depending whether the larger number of charges is attracted or repelled from the closest electrode, this leads to a different charge distribution inside the cell.

6.6 Dependency on the Rydberg population

The double-peak Rydberg signal arising with increasing electric field has also been investigated for different Rydberg populations, which means different total numbers of Rydberg atoms. The absolute number of Rydberg atoms can be changed by changing the Rabi frequencies of the two excitation lasers, or by changing the vapor pressure of rubidium.

In Fig. 6.19a the Stark shift is plotted for three reservoir temperatures, which means three different densities of Rydberg atoms inside the excitation volume. The EIT signal has been fitted with two peaks denoting the smallest and highest electric field present in the cell. One example fit curve is shown in Fig. 6.19b. Calculated from the vapor pressure and the Rydberg population, the Rydberg atom density inside the cell should change for the different reservoir temperatures from

$$0.2 \times 10^9 \,\mathrm{Rydberg \ atoms/cm^3}$$
 (6.5)

for the lowest temperature (cyan in Fig. 6.19a), to

$$4.2 \times 10^9 \,\mathrm{Rydberg \ atoms/cm^3}$$
 (6.6)

for the highest temperature (red in Fig. 6.19a). The Rabi frequencies in all three measurements were $\Omega_P = 7.4 \cdot 2\pi \text{ MHz}$ and $\Omega_C = 1.5 \cdot 2\pi \text{ MHz}$.

Although the number of Rydberg atoms is changing by almost a factor of 20, only small changes in the splitting of the Rydberg line for different rubidium densities is observed. For higher densities, the splitting is slightly smaller. This could mean, that the inhomogeneous electric field is only slightly influenced by the Rydberg atoms inside the cell. The source for the inhomogeneous electric field and the charges are not the atoms itself, but an independent effect. This confirms the assumption, that the inhomogeneity is caused by the electrons, created by the photoelectric effect, which is described in Section 7.1. When the inhomogeneous electric field is produced by a negative charge density, then an increase of the Rydberg atoms, which should lead to an increase of positive ions, is partly compensating the negative space charge. The fact, that inhomogeneity is almost not changing supports the estimation, that the amount of positive ions from Rydberg atoms is much less than the number of electrons.

In Fig. 6.20a and 6.20b the change of the splitting of the EIT line is plotted for two different red and blue laser intensities, respectively. Again the Starkshifted signals for each electric field were fitted with two Lorentzian peaks to determine the minimum and maximum electric field present inside the cell. For different blue Rabi frequencies (Fig. 6.20a), there is almost no difference between the two curves, the splitting is roughly the same, only the absolute shift changes slightly, although the Rydberg population is doubled from 0.01 (blue curve) to 0.02 (red curve). The reason might again be, that not only the number of positive ions is increased, but also, due to the increased blue intensity, the photoelectric effect is increases the number of electrons. Then in total almost no change is visible.

For a higher probe Rabi frequency (Fig. 6.20b), the observed electric field splitting as well as the total Stark shift is smaller. With a higher Rabi frequency, which means a higher population, the number of positive charges is expected to increase, while the number of photoelectrons stay the same. The Rydberg population changes from 0.02 to 0.03 for increasing the red Rabi frequency from $\Omega_P = 7.4$ MHz to $\Omega_P = 18.0$ MHz. An indication for the higher number of positive charges can be the observed shielding of the electric field. Shielding can be seen in the measurement as the center of gravity of the Rydberg signal is shifting to smaller detunings for higher red Rabi frequencies. As an additional effect, more positive charges from the larger population could reduce the inhomogeneity that is created by the electrons of the photoelectric effect.



Figure 6.19: (a) Stark shift of the two fitted peaks versus applied voltage for three different rubidium densities, defined by the reservoir temperature T_R . The cell oven temperature was always kept 20 °C higher to avoid condensation of rubidium in the measurement part of the cell. There is almost no change for different rubidium densities, which shows the independence of the electric field distribution from the rubidium density and the Rydberg atoms. (b) Example fit of signal with two peaks. Each signal was fitted with two Gaussian peaks to determine the spread of the electric field distribution.



Figure 6.20: Change in electric field inhomogeneity is visible as a change in the splitting of the two peaks for two different coupling (a) and probe (b) Rabi frequencies. Only for a higher probe Rabi frequency a significant change in the splitting of the EIT peak is visible.

6.7 Conclusion

In summary the electric field inside our vapor cells is not homogeneous but rather linear. This is not due to the edge fields of our capacitor plates, but rather because of free space charges inside our vapor cell. The linear electric field can be explained by a constant space charge density in the whole cell which reproduces the observed double-peak signal shape of the EIT and the ionization current. The photoelectric effect can be identified as the main source for the space charges as further investigated in chapter 7.1. A change in the Rydberg atom density is almost not influencing the electric field distribution created by the electrons from the photoelectric effect because the number of ionized Rydberg atoms is much less then the number of electrons from the photoelectric effect. Only a slight reduction of the the inhomogeneity can be observed for increased positive charges, which also shows, that the inhomogeneity is created by negative space charges.

CHAPTER 7

Cells with graphene layers

Up to now only vapor cells with metallic electrodes have been considered. For the possibility to apply or detect spatial dependent electric fields inside a vapor cell, preferably with a high resolution in the micrometer regime, it would be convenient to have optically transparent electrodes. As indium tin oxide (ITO) cannot be used in combination with alkali atoms due to chemical reactions, we focused on graphene as electrode material.

Here we show, that graphene is inert to chemical reactions with rubidium and can be used inside alkali vapor cells as transparent electrodes. Although alkali atoms are generally highly reactive, the conductivity and transparency of graphene does not degrade under rubidium atmosphere. The only observed reaction is an adsorption of rubidium atoms onto the graphene surface, which does not disturb the transparency or conductivity of the graphene layer. With this not only Rydberg excitation is possible in graphene coated cells, the graphene can also be used for the ionization current detection method described in Chapter 5. We also observed that the photoelectric effect is largely increased on top of the graphene surface. The high number of charges emitted from the surface due to the photoelectric effect is the reason for the inhomogeneous electric fields, described in the previous chapter. In future experiments this source for inhomogeneity could be avoided using a threephoton excitation instead of a two-photon excitation, because then only red and infrared lasers are needed. Then it should be possible to increase the homogeneity of the electric fields inside the cells. By measuring the photoelectric current, the work function of the electron emitting surface could be determined and identified as rubidium. Rubidium as dopant for graphene could be a useful technique for tuning the properties of graphene for applications like field-effect transistors or other electronic devices based on graphene as electrode material. The Raman spectrum of graphene also changes, when it is exposed to rubidium. In this chapter first the photoelectric effect and the determination of the work function are described. Then the changes in the Raman spectrum are shown. At last Rydberg spectroscopy in graphene coated cells is shown.

7.1 Photoelectric effect on surfaces

When the cell is illuminated solely by blue laser light, which is not resonant to any rubidium transition, then there is no electronic excitation of the rubidium atoms present. Nevertheless, a current depending on the blue light intensity is observed. The origin for this current is the photoelectric effect, taking place at the surface inside the cell. This effect is greatly enhanced for cells with graphene coated surfaces compared to cells where the rubidium layer is adsorbed directly on the bare glass surface. During all ionization current measurements, described in Chapter 5, this photoelectric current is always present as a constant offset current and was subtracted for all Rydberg ionization current measurements. While this offset current can have an amplitude of up to 1 μ A, the ionization current signal of the Rydberg atoms was on the order of several nanoampere.

A schematic picture of the photoelectric effect for our geometry is shown in Fig. 7.1a. The whole cell, which means both inner surfaces are illuminated by laser light of a specific wavelength, for example 474 nm. Due to the photoelectric effect electrons are emitted from both surfaces. The electrons on the anode side directly fly back to the anode and do not contribute to a flowing current. The photoelectric current was measured versus an externally applied voltage. The magnitude of the photoelectric current for a graphene coated cell is plotted in Fig. 7.1b.

It shows the characteristic behavior of photoemission of electrons. As electrons are emitted from both inner surfaces, the current shows an antisymmetric behavior for positive and negative applied voltages. For low voltages the current is linear with the applied voltage, because without an electric field the emitted electrons are not drained to the electrodes. With increasing voltage, more electrons reach the electrodes. Starting from a certain voltage, depending on the geometry of the arrangement, all electrons reach the



Figure 7.1: Photoelectric effect in vapor cells. (a) Both electrodes are illuminated with light and electrons emitted from the surface. A voltage is applied between the two electrode plates. (b) Photoelectric current characteristic. Depending on the direction of the applied electric field, the electrons of the positive or negative plate are measured as a positive or negative photoelectric current. The photoelectric current gets saturated when the applied voltage is high enough to collect all electrons.

electrodes and the photoelectric current is saturated. Due to the symmetric arrangement of two surfaces, electrons are emitted from both surfaces. Depending on the electric field direction, a positive or negative current can be measured.

A different saturation current for positive and negative voltages is observed. The asymmetry for positive and negative electric fields, visible as different saturation current amplitudes, can be attributed to the emission of different number of electrons from the two surfaces. According to the direction of the electric field, for a positive applied voltage the electrons from the side with the partially damaged surface, which was described in Section 2.7, are measured. The absorption of the blue light by the graphene can be excluded, as all reflections on the glass surfaces are taking place before the light is entering the cell or after the light has left the cell. Both graphene samples are only separated by the atomic medium. Absorption of the blue light by the atomic medium can also be neglected, especially as the light is not resonant to any atomic transition frequency. A different light intensity on the two glass plates due to a different beam size would also directly cancel out and cannot be the reason for the asymmetry, because the number of emitted electrons depend only on the power.

The electron emission rate can be calculated from the measured saturation current I and the power of the incoming light P. For a regime where the absolute number of emitted electrons depend linearly on the illuminated area A (for constant light intensity) the emission rate depends only on the total power of the incoming light. For both surfaces the emission rate is calculated to

$$\gamma_{El} = \frac{I}{A \cdot P/A} = \frac{0.17 \times 10^{-6} \,\mathrm{A}}{20 \,\mathrm{mW}} = 5 \times 10^{10} \,\frac{\mathrm{Electrons}}{\mathrm{s \cdot mW}}$$
(7.1)

$$\gamma_{El} = \frac{I}{A \cdot P/A} = \frac{0.12 \times 10^{-6} \,\mathrm{A}}{20 \,\mathrm{mW}} = 3.7 \times 10^{10} \,\frac{\mathrm{Electrons}}{\mathrm{s \cdot mW}}.$$
 (7.2)

The different current amplitude means that either the number of adsorbed rubidium atoms is decreased on one side due to the different surface properties, or, more likely, the conductivity on the overheated side of the glass cell is reduced which leads to a slower refill of electrons into the surface and thus to a smaller current. The altered properties of the surface could also be the reason, that for positive voltages the photoelectric current is not constant in the saturation region. In the following sections the photoelectric current of a graphene coated cell is compared to a cell, where the photoelectric effect can take place only on the bare glass surface and the intensity dependence of the current is investigated.

Intensity dependency

Another characteristic of the photoelectric effect is the linear dependence between the photoelectric current and the number of incoming photons, which means the intensity of the illuminating light. It is another proof, that the measured current is due to the photoelectric effect. In Fig. 7.2 the photoelectric current in a cell without graphene (Fig. 7.2a) and in a graphene coated cell (Fig. 7.2b) is plotted for different intensities of blue light with a wavelength of 474 nm. The illuminated area was always 0.22 mm^2 .

For a higher light intensity more electrons are emitted from the surface. This leads to an increase of the current with increasing light intensity. The intersection between all curves of different intensity is usually when the applied voltage equals the work function of the surface material. In our case it is almost zero, because we have emission of electrons from two opposing surfaces. Depending of the direction of the electric field, only the emitted electrons from the cathode side are detected. The electrons from the anode are expected to be negligible because they should directly fly back to the surface, from which they are emitted.

In Fig. 7.3 the photoelectric current is plotted versus the blue laser intensity for 0 V (blue curve) and both electric field directions with ± 10 V (red and green curve). This measurements have been done in the cell with graphene electrode. The offset setting of the current amplifier was set such, that for zero light intensity and no applied voltage, zero current was flowing. All curves show a linear dependence with respect to the intensity of the blue light. Therefore the number of charges depend linearly on the number of incoming photons. Even for 0 V applied this dependency can be observed, although without electric field the charges should distribute homogeneously in the cell and should not be drained. Inside the cell charges are produced on both glass surfaces. When the charges would be produced with the same rate on both surfaces, they should always compensate at U = 0V. Different number of charges on each surface lead by itself to a potential difference between the two electrodes, which induces a compensation current without any externally applied field. A reason for the different photoemission rate can be, that part of the electrodes in the graphene coated cell were overheated during the anodic bonding process on one side (see Section 2.7) because the bonding temperature of 300 °C is close to the temperature when graphene

starts to oxidize on air (400 °C). This asymmetry in charge production also explains the different saturation currents for positive and negative applied voltages, seen in Fig. 7.2b. In the cell without graphene (Fig. 7.2a) no such asymmetry in the saturation current could be observed. This supports the assumption, that the rubidium, which is the origin of the photoelectric effect, is preferably adsorbed onto the graphene sheet. Comparing the amplitudes of the saturation currents with and without a graphene layer (Fig. 7.2) for $P = 50 \,\mathrm{mW}$ light power a saturation current of $I = 0.01 \,\mu\mathrm{A}$ can be measured without graphene layer. With graphene layer a saturation current of 1 µA is observed. It indicates, that the surface coverage of rubidium on top of graphene is expected to be 100 times higher than on the glass surface. Although the difference in surface conductivity can also play a role for the photoelectric effect, it can not explain the different currents here, because the resistance of graphene in our cell is around $1 \,\mathrm{k}\Omega$ and without graphene at least $1.7 \times 10^{10} \Omega$, as described in the sections 2.7 and 6.5. To investigate which material is the origin of the photoelectric current the work function of the electron emitting surface is determined.



Figure 7.2: Photoelectric current under illumination of blue light (474 nm) versus applied voltage for 7 mW (blue), 20 mW (red) and 50 mW (black) in a cell without graphene electrodes (a) and with graphene electrodes (b). With graphene, the photoelectric current is 100 times larger than without graphene.



Figure 7.3: Photoelectric current versus intensity of blue laser light (474 nm) for an applied voltage of 0 V (blue curve), +10 V (red curve) and -10 V (green curve). Due to the linear increase of incoming photons, also the number of ejected electrons increase linearly. The asymmetry indicate, that a different number of photoelectrons are produced on the two surfaces.
Wavelength dependency

To verify that the electrons originate from the photoelectric effect on rubidium and not from pure graphene or chromium, the wavelength dependency of the photoelectric current is investigated in more detail and the work function is determined. Theoretically for wavelengths below the work function, no photoelectric current is expected. As soon as the energy of the light equals the work function, the characteristic current versus applied field should be measurable. The amplitude of the saturation current is increasing quadratically for increasing light energy for metals and at a temperature $T = 0 \,\mathrm{K}$. However in real systems, due to the high ambient temperature, the step function is broadened. Also other effects like the different emission efficiency or a polarization dependency are leading to an increase of the photoelectric current with increasing light energy. Figure 7.4 shows the measured photo electric current vs. the applied voltage for different wavelengths of the incident laser light at 2 mW input light power which corresponds to an intensity of $28 \,\mathrm{W/cm^2}$. In the cell without graphene sheet (Fig. 7.4a) only two wavelength have been measured $(530 \,\mathrm{nm}, \mathrm{green} \mathrm{line} \mathrm{and} 474 \,\mathrm{nm}, \mathrm{blue} \mathrm{line})$ as the current amplitude was too small at that intensity and the fluctuations of the current too high to observe the characteristic current dependency. In the cell with graphene electrode (Fig. 7.4b) the current has been measured for four wavelengths, namely 795 nm (red curve), 530 nm (green curve), 474 nm (blue curve), 405 nm (purple curve). For the cell with graphene electrodes, the photoelectric current is up to $150 \,\mu\text{A}$ for $2 \,\text{mW}$ input power and a wavelength of 405 nm. However for red laser light (795 nm) almost no current can be measured. It was observed, that the current with the red laser is voltage independent. From that observation, it is assumed, that the resulting current in that measurement, with a mean value of 4.1 ± 2.0 nA is due to a different laser effect, for example heating. Starting from the green wavelength (530 nm) the saturation current increases for higher photon energy, which means shorter wavelength.



Figure 7.4: Voltage dependent photoelectric current for different wavelengths: 795nm (red), 530nm (green), 474nm (blue), 405nm (purple) in a cell without (a) and with (b) graphene electrode. For all measurements a power of 2 mW was used. Without graphene, the photoelectric current was too low to observe any voltage dependency, as the fluctuations were too high. With graphene an increase in the photoelectric current for shorter wavelength could be observed.

As for positive voltages the current in the saturation region is not constant (see Fig. 7.1b), probably due to the overheated surface described previously, only the current for negative voltages has been used for the determination of the work function. For all four wavelengths the current for every voltage in the saturation region is plotted in Fig. 7.5 versus the photon energy.



Figure 7.5: Determination of the work function. The photoelectric current values of the saturation region for different wavelength shown in Fig. 7.4 are plotted versus the photon energy. They give an estimation of the work function of the surface by determining the point, when the photoelectric current gets zero. The determined value of 570.7 ± 5.3 nm matches to the theoretical work function of bulk metallic rubidium of 574 nm.

From that figure the work function can be determined as below the value of the work function no photoelectric current should occur. The offset current measured without light is already subtracted from the other data to get the pure light induced photoelectric current. Then for each voltage the values for 405nm, 474nm and 530nm were fitted to

$$I = c \cdot (\hbar\omega - \hbar\omega_0)^n. \tag{7.3}$$

Here $\hbar\omega_0$ is the work function of the electron emitting surface, ω the light frequency and c a constant. The exponent is n = 2 for metals, but the exact behavior also depends on the light polarization and surface properties like the metal film thickness. For that reason the exponent was used as a fit parameter and by that determined to $n = 1.41 \pm 0.07$. The deviation to n = 2 might arise, because the rubidium layer is expected to be only a few atomic layer thick. All fits are plotted as gray lines in Fig. 7.5. The spread of all gray lines denote the error of the determination of the work function. The intersection of the average of all gray lines with zero current denotes the work function of the material. The intersection point with zero current was determined to be at 570.7 ± 5.3 nm. It is indicated with a horizontal black errorbar in Fig. 7.5. The corresponding photon energy of $2.17 \pm 0.02 \,\text{eV}$ is close to the work function of bulk metallic rubidium at $574 \,\mathrm{nm}$ (2.16 eV), indicated by a black dashed line in Fig. 7.5. As the work function of chromium $(4.5 \,\mathrm{eV}$ / 275 nm) as well as of graphene (4.57 eV / 271 nm) are both much higher than the observed work function, it is most likely, that the photoelectric current we are measuring is due to photoemission of electrons from metallic rubidium. According to [69] and the references therein the work function of graphene itself is usually only changing between 4.5 eV and 4.8 eV for common doping materials and doping levels. For that reason a change of the work function of graphene by more than 2 eV due to rubidium doping can be excluded.

As mentioned above, the photoelectric current without graphene is much lower. Due to the high current fluctuations and the limited power of the different lasers, the determination of the work function could not be done in a cell without graphene, as even for blue laser light (474 nm) the fluctuations of the current are to high (see Fig. 7.4a).

The observation, that the photoelectric effect is due to rubidium, and greatly enhanced in combination with graphene compared to rubidium on a glass surface indicates that a much higher amount of rubidium is covering the graphene than the bare glass. The change in surface coverage by a factor of 100, as determined from the measurements in Fig. 7.2 should also have an effect on the Raman spectrum of graphene as shown in the next section.

7.2 Raman spectroscopy on rubidium doped graphene

The reason why the photoemission with graphene is much higher than without is probably, that rubidium is preferably adsorbed on top of the graphene layer and electrons can only be emitted from rubidium, not from the bare glass or pure graphene. Rubidium atoms adsorbed on the graphene has an effect on the vibrational modes of graphene that can be observed by Raman spectroscopy. Raman spectroscopy was performed for different produced samples. One sample was covered with rubidium and inflated with air afterwards. The other one was kept under rubidium atmosphere during the Raman measurement. In Fig. 7.6 Raman spectra of the two different samples, that have been under rubidium atmosphere, are plotted. For comparison a Raman spectrum of pristine CVD grown graphene is shown. The Raman spectrum of pristine graphene is explained shortly in Section 1.4. More extensive descriptions can be found for example in [71]. In CVD graphene the G peak and the 2D peak are clearly visible. Also a small D peak can be seen.

To investigate the effect of rubidium onto the graphene, one graphene sample was put into a small glass tube, which then was attached to the vacuum pump, evacuated to 10^{-7} mbar and filled with rubidium. The sample was kept under alkali atmosphere for several days and heated to about $130 \,^{\circ}\text{C}$ to cover the graphene sample with rubidium vapor. Then it was opened again and by that inflated with air. As leftover rubidium was probably still on top of the graphene sample, it oxidized when the glass tube was opened. Then a Raman spectrum of the sample was measured. Around the G peak at around $1585 \, \text{cm}^{-1}$ additional peaks are observed, seen as a broadening of the G peak. The largest peak is marked in the plot as a red fit curve, but a second additional peak is assumed to be on the right hand side of the G peak. It is assumed, that the additional peak arises due to the doping of graphene with rubidium oxide. For future applications it would be advantageous to investigate systematically the behavior of graphene for defined alkali doping in vacuum or in an inert gas atmosphere.

A Raman spectrum was also taken of the graphene cell, which was used for all photoelectric current and Rydberg spectroscopy measurements. For that measurement the cell was still under vacuum and the rubidium did not oxidize. While the G peak and the D peaks were not changing their amplitude



Figure 7.6: Raman spectra for different samples with and without alkali atom doping. The Raman active peaks are fitted by lorentzian functions (D: light blue, G: magenta, 2D: green). In both samples with rubidium doping an additional peak (fitted as red curve) is seen. In the rubidium cell the 2D peak is vanished as also reported in [88].

or widths, the 2D peak completely vanished. Such an effect has been observed before in [88], where they reported a continuous decrease of the amplitude of the 2D peak with increasing rubidium doping level. In our cell, the rubidium doping is so high, that the 2D peak completely vanished which is confirming, that rubidium is adsorbed on top of the graphene layer. Also in that Raman spectrum an additional peak at 1485 cm^{-1} is observed which is not visible in pristine graphene and also not observed in the previous mentioned reference [88]. One difference compared to our other measurements is the substrate on which the graphene sample was prepared. For the vapor cell borosilicate glass is needed for the anodic bonding process. The other graphene samples

(pristine + Rb oxidized) has been prepared on standard microscope slides, which is usually soda-lime glass. Borosilicate glass can have a Raman peak close to that position, depending on the exact glass composition. However this peak is expected to be too small to observe. More likely the additional peak also comes from the adsorption of rubidium or some leftover rubidium oxide.

Conclusively, for all samples exposed to alkali vapor, a change in the Raman spectrum was observed, which supports the assumption, that the graphene samples are covered with a thin layer of alkali atoms. The high rubidium doping of graphene, seen especially by the vanishing 2D peak, explains, why such a large photoelectric effect, that has been described in the previous section, can be observed. Doping of graphene is a widely used technique for tuning the properties of graphene. The intentional doping of graphene layers with alkali atoms can maybe in future also be used for improving the designs of electronic devices based on graphene. How these charges due to the photoelectric effect change the electric field distribution inside the cell and how it affects the Rydberg spectroscopy is described in the next section.

7.3 Rydberg spectroscopy in graphene coated cells

Rydberg EIT measurements have been done in graphene coated cells to test whether graphene can be used as transparent electrodes for alkali vapor cells. As previously explained in detail in Chapter 6 the electric field in a cell with chromium or nickel electrodes was observed to be inhomogeneous probably due to space charges inside the cell. They lead to a Rydberg signal that looks like a split line, but actually correspond to a broad inhomogeneous electric field distribution. With the findings of the last chapter the dependence of that splitting on the electric field direction can be attributed to different charge production rates on each surface. In contrast to that with graphene electrodes the number of space charges should even be increased by a factor of 100. In Fig. 7.7 Stark shift measurements in graphene coated cells are compared with some of the previous measurements from the cells without graphene.

It is observed, that the splitting due to inhomogeneous electric fields is much smaller, or even not observable in the graphene cells. But the absolute



Figure 7.7: Stark shift measurements in a cell without graphene (a) compared to a graphene coated cell (b) for both electric field directions (blue and red). With a graphene electrode almost no splitting of the EIT signal has been observed which indicates a much more homogeneous electric field distribution. However the absolute shift is smaller, indicating a shielding of the applied field. A reason for the shielding can be the increased number of space charges.

electric field shift is also smaller than expected from the applied electric field. This behavior can be attributed to shielding. It was also observed for high red laser intensities (Chapter 6.6) where we assume, that the number of positive charges is increased due to a higher Rydberg population while the number of negative charges due to the photoelectric stays the same.

For the graphene coated cell we assume, that the number of negative charges is largely increased. The reason is, as showed in the previous section, the much higher background current, originating from the photoelectric effect on the glass surfaces. However, the exact processes, how this charges can possibly decrease the inhomogeneity are still unclear although the properties



Figure 7.8: Actual measured electric field in a graphene coated cell versus the applied voltage. For low voltages, the measured field follows the expected line. At higher voltages, the electric field seems shielded, probably due to the high number of space charges. Errorbars denote ± 5 MHz in frequency shift (half linewidth).

of the inhomogeneous electric field has been systematically investigated in Chapter 6. One possible reason might be, that the negative space charge distribution might not be constant over the whole cell volume, because the production of the negative charges happen at the surface of the cell. If there is a cloud of space charges close to the surface, this might effectively shield the applied voltage, and hence a smaller electric field is observed by the atoms.

The photoelectric effect could be avoided by using three-photon-excitation. Then no blue light is incident on the surface, and all infrared lasers have a photon energy too low to eject electrons from the rubidium surface.

If we compare the actual measured electric field, determined by the shift of the EIT peak measured in the graphene-coated cell (Fig. 7.8), we see, that for low voltages the measured field follows the applied voltage, while above $\approx 8 \text{ V}$ the measured field is reduced. An explanation might be, that the ionization energy of the rubidium ground state atoms is 4.2 eV. If we assume, that a

charge of q = e starts in the middle of the cell, and is accelerated to one electrode, an electric potential of minimum 8.4 V would be needed for the charge to achieve the ionization energy. Collisions of this charge with ground state rubidium atoms could then produce more charges, that finally shield the external electric field. Additionally the high amount of charges that are present in the graphene coated cells due to the photoelectric effect shield effectively the externally applied field.

7.4 Outlook

Graphene seems to be a qualified material, to be used as transparent electrodes in alkali vapor cells, as all other widely used transparent and conductive materials are usually metal oxides and the oxides react with the alkali metals. Although the observed background current is largely increased due to the photoelectric effect on the rubidium which is adsorbed on the graphene, this does not disturb the homogeneity of the electric field or the performance of the cell. However the exact process happening inside the cell are still unknown. For future applications graphene can also be structured by electron beam lithography or by optical photolithography to arbitrary structures. Another system for transparent electrodes which is inert against alkali metals could be boron doped diamond. However this is harder to integrate into a vapor cell and graphene is superior in transmission as well as in conductivity.

CHAPTER 8

Spatially resolved microwave detection using Rydberg atoms

Rydberg atoms are not only influenced by DC electric fields, they can also be used for the detection of microwave electric fields. Calibrated antennas, that are usually used for that purpose, are typically on the size of the wavelength of the microwave and consist of conductive materials, which are disturbing the microwave field. With such antennas no sub-wavelength distribution or nearfield can be measured without modifying the microwave field itself. When atoms are used as detectors for microwaves, the resolution is only limited by the optical detection system and the optical wavelength for probing the atoms. This resolution can easily be below 100 µm, which for microwaves in the gigahertz regime corresponds to $\lambda_{MW}/300$. Atoms also do not disturb the microwave field. Small distortions can however be expected from the cell containing the atoms. Atoms also have the advantage that no calibration of the detector is necessary because all atomic constants, like transition dipole moments and frequencies can be calculated. In contrast to that, standard dipole antennas need to be calibrated on a regular basis to compensate aging of the materials.

There are already experiments, that are able to visualize the magnetic contribution of a microwave field using the ground-state transitions of atoms [89]. With our method, instead of the magnetic field, the electric part of microwaves can be determined. This is important to retrieve the full information of microwave fields, especially in the near field.

In our experiments we have used Rydberg atoms to detect spatial dependent microwave electric fields. The principle method for using Rydberg atoms to sense microwave fields with a high sensitivity was described in [15]. During this thesis we extended this method to image spatial dependent microwave fields with a spatial resolution far below the microwave wavelength [20]. Here the principle method of detecting resonant microwaves with Rydberg atoms is described. We show that the spatial detection of a standing wave in front of a horn antenna is measurable with a resolution of 66 µm. To visualize the applicability of that method we describe how it can be used to image the near field above a printed-circuit board.

8.1 Four-level-system



Figure 8.1: Level scheme for microwave measurements. Cesium atoms are excited via a two-photon EIT scheme to a Rydberg state. This Rydberg state is coupled via a microwave to the next neighboring Rydberg state.

A four-level-system was used for the detection of a microwave (see Fig. 8.1). Cesium atoms are excited via a two-photon process to a Rydberg state, for example $47D_{5/2}$ by the same EIT scheme that is described previously in Section 3.1 for rubidium. The transition to the next neighboring Rydberg state is then a microwave frequency, in that case 6.9 GHz. This scheme can thus be used to detect specific microwave frequencies. By choosing the main quantum number of the Rydberg state, the MW frequency to the next neighboring Rydberg state is defined. For cesium Rydberg D states with a main quantum number in the range of 30 to 60, the transition to the next



Figure 8.2: Transmission signals of the probe laser for (a) Two-level (absorption), (b) Three-level (EIT) and (c) Four-level systems (Autler-Townes splitting of EIT) while scanning it over the resonance of the first transition (probe laser).

neighboring P states are MW frequencies ranging from 3.2 (n = 60) - 39.9 (n = 30) GHz.

The observed lineshape of a four-level-system can be understood qualitatively as follows:

For a simple two-level-system when a laser is resonant to the two levels absorption is observed (Fig. 8.2a). When a second laser couples the exited state to a third level, then electromagnetically induced transparency (EIT) can be observed, as described in Chapter 3.1. In Fig. 8.2b the transmission of the probe laser is shown when the probe laser is scanned. In our case the third level is, as well as in the previous experiments, a Rydberg state. This Rydberg state can be coupled via a microwave frequency to a second Rydberg state. The observed EIT transmission of the probe laser is then reduced on resonance, which for high microwave Rabi frequencies looks like a splitting of the EIT peak (Fig. 8.2c). Determination of the EIT splitting is a direct measure of the microwave electric field amplitude.

In our experiment usually the probe laser frequency is locked resonant to the first two levels, and the frequency of the coupling laser is scanned over the resonance of the Rydberg state. Then without microwave field a single EIT peak is visible, as seen in Fig. 8.3a (blue curve). For low microwave Rabi frequencies a dip in the EIT peak is observed. For higher Rabi frequencies the EIT peak is split into two clear peaks (Fig. 8.3a). The splitting is proportional to the microwave Rabi frequency, and thus proportional to the square root of the microwave power (Fig. 8.3b).

Setup

The laser setup for the spatial microwave detection is shown in Fig. 8.4. The two excitation lasers are aligned in counterpropagating geometry, with a large beam waist of w = 2.78 mm (2.47 mm) of the probe (coupling) laser to image a relatively large part of the microwave field at once. For all the microwave measurements a large standard commercial glass cell with a length of 3 cm and a side length of 1 cm is used. The large cross-section of $1 \text{ cm} \times 1 \text{ cm}$ of the cell is needed to be able to align the lasers in the middle, to get only minimal distortions of the microwave field from the edges and sidewalls of the cell. No electrodes, graphene or other layers have been used in that cell. The middle of the cell is imaged with a 4f-imaging system onto a CCD camera (Pco Pixelfly) with a single lens ($f = 400 \,\mathrm{mm}$). The depth of focus is then about 9 mm and the diameter of the Airy disk is 65 µm. An averaging of the image over $66 \times 66 \,\mu\text{m}$ has been done to improve the signal-to-noise ratio. This size determines the optical resolution of the imaging. A microwave horn antenna is put next to cell, an aluminum plate on the other side. Then a standing wave is built up at the position of the cell and can be imaged. Alternatively instead of the horn antenna, a printed-circuit board can be set close to the vapor cell and the near-field above the board can be imaged.



quency $\Omega_{MW} \propto \sqrt{P_{MW}}$.

Figure 8.3: Power dependency of microwave signal. With increasing microwave power, the Autler-Townes splitting of the EIT is increasing linearly. (a) Signal for microwave Rabi frequencies of $\Omega_{MW} = 0$; 10; 30; 50 MHz. (b) EIT splitting versus microwave Rabi frequency.



Figure 8.4: Setup for microwave measurements. The two excitation lasers are in counterpropagating geometry. Both have a large diameter of 2.78 mm (probe) and 2.47 mm (coupling) to image a large area of the cell at once. The middle of the vapor cell is imaged by a 4f-imaging-configuration onto a CCD camera.

8.2 Spatial dependent measurements

For a spatial dependent measurement of the microwave electric field the coupling detuning Δ_C was changed in discrete steps. For each detuning a picture of the transmission of the probe laser was taken with the CCD camera (Fig. 8.5a). As the whole beam was imaged onto the camera, each picture shows the beam profile of the probe laser.



Figure 8.5: Scheme of measurement: (a) A picture of the probe laser transmission is taken for every coupling laser detuning Δ_C . (b) For each pixel a spectrum can be assembled and the splitting s of the EIT due to the microwave field is fitted. (c) The splitting s of each pixel corresponds to the microwave Rabi frequency Ω_{MW} at a specific position. By that method a picture of the spatially varying microwave field is derived. That measurement shows for example the far-field radiation of a microave stripline.

From all pictures for each pixel a spectrum can be assembled. This then has the lineshape of the previously described four-level signal, consisting of two transmission peaks, that are split by the microwave Rabi frequency (Fig. 8.5b). Each of this spectra is fitted with two Lorentzian peaks to determine the microwave splitting. As this splitting s is proportional to the microwave Rabi frequency, the microwave field amplitude at that pixel can be calculated with the well-known dipole matrix element for the specific atomic transition. This splitting is then plotted for each pixel in a 2D image which then represents the spatial distribution of the microwave electric field amplitude (Fig. 8.5c). With this method a picture of arbitrary microwave fields can be obtained. As a proof of principle it has been applied to two different geometries. The first one is the detection of a standing wave between a microwave horn antenna and an aluminum plate, the second one is the sensing of the field above a printed-circuit board with a microwave stripline.

8.2.1 Reflection of a microwave on an aluminum plate

As a proof of principle spatial dependent measurements were done with a microwave horn antenna. An aluminum plate was placed $3\lambda_{MW}$ away from the horn antenna to reflect back the microwave (see setup Fig. 8.4). A standing wave with a period of $\lambda_{MW}/2$ is created between the horn antenna and the aluminum plate. The horn antenna and the aluminum plate can be moved simultaneously via a translation stage to increase the imaged area, while the position of the vapor cell stays fixed. A finite element calculation has been used to simulate the microwave field distribution. The complete simulation including the horn antenna and the reflecting aluminum plate is shown in Fig. 8.6a. A picture of the measured field distribution of a small region from 73 – 100 mm distance from the horn antenna is shown in Fig. 8.6c. The imaged area is marked in Fig. 8.6a. A cut along the horizontal axis of the imaged field is plotted in Fig. 8.6b and compared to the simulation.

The expected standing wave can be observed and fits to the simulation. The optical resolution is 65 µm, which corresponds to $\lambda_{MW}/650$ for a frequency of 6.9 GHz. This is determined by the size of the Airy disk of the optical imaging setup, which is calculated by the beam size and the imaging lens and distances. As the Rayleigh length is about 9 mm, spatial averaging due to the long cell (3 cm) is expected to be small.

The imaging data is also compared to an additional measurement, where the spectrum versus coupling detuning is directly recorded by a photodiode. The position of the photodiode was scanned along the horizontal axis for spatial detection. A 300 μ m pinhole was used before the photodiode to cut out spatially a small area that is observed with the photodiode. This measurement also agrees with the results of the imaging method and the simulation, although the spatial resolution is here limited by the size of the pinhole.



Figure 8.6: Measurement and simulation of the reflection of a microwave at an aluminum plate. (a) 2D simulation of the microwave horn antenna and reflection at an aluminum plate. (b) Measurement and simulation of microwave field vs. distance from the horn antenna. (c) Imaging measurement of microwave electric field of a horn antenna.

8.2.2 Microwave electric field above a microstrip waveguide

This spatial detection method offers the possibility to detect near-field microwave electric field distributions above arbitrary structures with a resolution far below the microwave wavelength without distorting the measured field. Examples are field distributions above microwave electronic circuits or metamaterials. To demonstrate this possibility, a stripline waveguide printed circuit board (PCB) was designed to produce a predefined microwave field above the board. This theoretical microwave field distribution can then again be compared to the measured microwave field.

A stripline can be used instead of a conventional hollow conductive metal waveguide to guide a microwave signal which is a common technique in highfrequency technology. In our case we used a coplanar waveguide. It consists of a flat metallic strip on top of a dielectric substrate together with ground planes on each side (coplanar) on the same layer. No back-gated substrate was used to suppress radiation of the waveguide.

The performance of the waveguide can be estimated by the scattering parameters (S-parameters). The S-parameters denote the transmission and reflection of a wave through a system. Then the entries of the S-matrix describes the part of the wave that is reflected or transmitted. In general for one input and one output port it is

$$\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} = \begin{pmatrix} s_{11} & s_{12} \\ s_{21} & s_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$
(8.1)

where a describes the incoming wave, b the outgoing wave, s the S-matrix and 1 and 2 the two ports of the system. For example s_{11} describes, how much of an incoming wave at port 1 is reflected back from the system to the incoming port, and s_{12} describes the transmitted part. Of course the S-parameters are frequency dependent $s = s(\omega)$. In the following, the frequency dependence of the reflectance and transmittance is simulated and measured.

For the design of the waveguides and the simulation of the impedance matching, the S-parameters were simulated in Advanced Design System (ADS). All parameters of the coplanar waveguide (width, distance to ground planes, length) are adapted to minimize reflection and radiation of the waveguide. A simulation of the scattering parameters is shown in Fig. 8.7. The reflection of the microwave at the input port is $-40 \,\mathrm{dB}$ in the optimized simulation, while the transmission is simulated to more than $-0.6 \,\mathrm{dB}$.

After the fabrication of the board, the scattering parameters have been measured with a network analyzer. The measurements of one board, designed for a microwave frequency of $f \approx 14 \,\text{GHz}$ is shown in Fig. 8.7. Several resonances can be seen with a spacing of $\Delta f \approx 0.7 \,\text{GHz}$, as also expected from the simulations. The overall measured reflectivity is around -10 to $-30 \,\text{dB}$. The transmission through the stripline decreases for higher frequencies from $-1 \,\text{dB}$ to $-4 \,\text{dB}$.



Figure 8.7: Simulation and measurement of scattering parameter of one of the microwave boards. S_{11} correspond to the reflection of the waveguide (blue and cyan) and S_{12} to the transmission through the waveguide (red and magenta). As the microwave board is symmetric, reflection and transmission on the second port is the same. The measured transmission through the waveguide is slightly smaller than simulated, which means that there are additional losses, that are not included in the simulation. The resonances are similar to the ones in the simulation.

The microwave electric field above this microwave stripline has been simulated with CST Studio. As a substrate Rogers without backplane was used. A three-dimensional model was used with one input and one output port.



Figure 8.8: Measurement and simulation of the microwave field above a printed-circuit board with a microwave stripline. (a) 2dimensional simulation and (b) measurement. (c) Cut along a line versus the distance from the waveguide. The inset shows the geometry of the setup with cell position above the coplanar waveguide.

Like in the measurements of the standing wave between the microwave horn antenna and the aluminum plate, the microwave field above the microstrip line has been measured by imaging the probe light onto a CCD camera. For each coupling laser detuning, an image was taken and the transmitted signal on the camera calculated back into a field amplitude of the microwave. Simulation and measurement of the microwave field above such a board are shown in Fig. 8.8. The minimum distance of 2.7 mm from the board is due to the cell walls of the glass cell and the Gaussian profile of the imaging beam. The measured decrease of the microwave electric field amplitude with increasing distance from the board is in good agreement with the simulation. This means, that field distortions from the glass cell can be neglected when the cell is much larger than the imaging laser beam. The glass cell can lead to slight distortions of the microwave field close to the glass walls and especially when the surface conductivity of the glass is increased, for example due to a thin atomic layer of rubidium atoms. This measurement scheme is also working in the near field regime, and as there $k \perp E \perp B$ is not always valid, a measurement of the magnetic part is not sufficient in the near field.

For future experiments, the anodic bonding technique, described in the previous chapters, allows to have a MW circuit based on silicon-on-insulator (SOI) technique inside the glass cell. Possible applications are for example the characterization of metamaterials and small microwave circuits. Further improvement of the sensitivity of the microwave detection method could be achieved if we make use of the refractive index change of the atomic medium.

CHAPTER 9

Summary and outlook

During this thesis methods were developed for the hermetical sealing of alkali vapor cells, that offer the possibility to include thin film structures. These vapor cells have such a low background pressure, that they can be used for Rydberg spectroscopy. Such thin-film structures can for example be conductive materials that can be used as electrodes to apply electric fields inside vapor cells or used as ion detector for ionized atoms.

The combination of anodic bonding, together with filling of the cells after the bonding process, leads to an outstanding low background pressure, similar to glass-blown vapor cells. While in glued vapor cells, the background pressure increases during several weeks to a level which is too high for Rydberg spectroscopy, anodically bonded cells keep their low background pressure at least over several months. This cells can also be used at temperatures of at least 230 °C without any irreversible broadening. Such high temperatures are necessary when the cells are used to observe single photon signals in the blockaded regime, or when surface interactions of the Rydberg atoms are investigated. In contrast to glass-blown vapor cells, thin film structures can be implemented here. During this work, metal structures have been implemented, inside the cell, and used as electrodes to create a spatial dependent electric field. For future applications also other structures can be implemented,for example integrated circuits for improved detection of currents inside the cell or optical or microwave waveguides.

Detection of Rydberg population in vapor cells

Such cells with electrodes at the inside of vapor cells, have been used to directly detect the Rydberg population. Direct detection of the population in vapor cells is up to now only possible with thermionic diodes. In our method, the required setup is much simpler, as one only need to include electrodes inside the cells and preferably a small additional decay of the Rydberg state to increase the signal. The Rydberg state is very sensitive to collisional effects due to its large cross-section. A small amount of background gas can already increase the decay rate of the Rydberg state to several megahertz. Charges, that are produced by ionization processes due to such collisional processes can be detected with the implemented electrodes and a resonant signal proportional to the Rydberg population is seen. Other charge production processes can be eliminated in the signal by a proper offset subtraction. Depending on the parameters for measurement, the ionization current detection method can have a much larger signal-to-noise ratio than the widely used optical detection. For example at slightly higher background pressures, which can intentionally be included by buffer gases, the current detection method still gives a reasonable large signal amplitude, while no optical signal can be observed. Another application could be, if very high, or very low probe Rabi frequencies are desired. Even if there is no transmission of the probe laser through the atomic medium, the excitation of Rydberg atoms can be detected via the ionization current. As this method is detecting directly the Rydberg population instead of the optically observed coherence, additional information about the atomic system is obtained using both electrical and optical read-out. In future this method can be used for implementing electronic circuits inside vapor cells, that can give for example spatial dependent information of the Rydberg population.

Electric field distribution inside alkali vapor cells

With integrated thin film electrodes inside vapor cells, DC electric fields can be used to create arbitrary electric field distributions or to control electric fields in vapor cells. A continuous inhomogeneous electric field distribution of an almost linear shape has been observed in all cells and a constant distribution of space charges has been identified as the most probable origin of this distribution. The source for the inhomogeneity are the large number of charges, that are continuously produced by the photoelectric effect on the surface of the cells. The photon energy of the blue laser, that is used for Rydberg excitation, is large enough to overcome the work function of rubidium. Depending on the temperature of the cell and the rubidium reservoir a thin metallic layer of rubidium is always covering the glass surface. The photoelectric current can be distinguished from the Rydberg ionization current, as a continuous background current, which is independent of the atomic resonance. The photoelectric current has been measured for several wavelengths, and by that the work function of the process could be determined to be close to the theoretical value of the bulk rubidium work function. To avoid the charges from the photoelectric effect three-photon excitation instead of twophoton excitation could be used for Rydberg excitation. Then all necessary wavelengths are in the red and infrared regime which have a too small photon energy to emit electrons from rubidium by the photoelectric effect.

Graphene and other transparent electrodes

We showed in this thesis, that graphene can be used as transparent and conductive electrodes inside alkali vapor cells. No molecular reaction or additional pressure broadening has been observed in such cells. In contrast to the usual transparent and conductive material, indium tin oxide and aluminum zinc oxide, which react with rubidium, graphene keeps its conductivity, as well as its high optical transparency under alkali atmosphere. The photoelectric current due to rubidium which is covering the inner cell surface was observed to be greatly enhanced on top of the graphene compared to a bare glass surface. We assume, that a large amount of rubidium adsorbed on the graphene surface. Compared to the glass surface we estimate a 100 times higher surface coverage on top of graphene. The field inhomogeneity changed in the graphene coated cells, probably due to the different amount of space charges, which led to an improvement of the homogeneity of the electric field. The Raman spectrum of the graphene coated cell shows, as has been observed before [88], that one of the Raman active peaks is completely vanishing when it is exposed to rubidium. This already shows, that a large amount of rubidium is covering the graphene. We observe an additional peak in the Raman spectrum of graphene that has been exposed to rubidium and in a graphene sample that has been exposed to rubidium oxide. This additional peaks might be useful for tuning the properties of graphene for electronic circuits like graphene-based transistors by doping it intentionally with rubidium or rubidium oxide.

Spatial detection of microwaves

Not only the detection of DC or low AC electric fields is possible with Rydberg atoms, they can also be used for the detection of microwave electric fields. Detection of microwaves is especially interesting for near-field imaging of microwave fields with a spatial resolution below the microwave wavelength. A high sensitivity of this method [15] as well as a spatial detection of the magnetic part of microwaves [89] with a similar system has been shown elsewhere. During this thesis a spatial detection of the microwave electric field with a resolution of $\lambda_{MW}/650$ using Rydberg atoms as non-invasive sensors has been shown. This resolution, corresponding to 65 µm was only limited by the imaging setup and can be improved further. Microwave electric fields can be detected when two Rydberg states are resonantly coupled by the microwave, and the electric field strength of the microwave field can be determined with high sensitivity. The transition frequency between two neighboring Rydberg states in the range of n = 30 - 60 is on the order of $\nu = 5 - 30 \,\mathrm{GHz}$. In contrast to commonly used detection methods with standard antennas alkali atoms are not disturbing the microwave field itself. This method is especially useful for imaging near-fields close to small microwave circuits or metamaterials. In combination with the previously described anodic bonding technique for the fabrication of alkali vapor cells, they offer the possibility to implement microwave waveguide structures directly inside vapor cells. By that not only the creation of arbitrary microwave field distributions are possible, waveguides could also be used to transmit a resonant signal from the atoms via microwave striplines to other vapor cells far apart from each other.

Outlook

This vapor cell fabrication method can now be used to realize more complex vapor cell designs, without changing the fabrication method. In this thesis we already showed, that also thinner vapor cells are possible. This technique, with similar design can easily be scaled down to vapor cell thicknesses of below $10 \,\mu\text{m}$. These are interesting for single photon devices based on Rydberg atoms. The electrodes can then be used for addressing or tuning the atomic vapor. Also surface interactions between Rydberg atoms and metallic surfaces, that are well described in theory [90] and up to now usually observed in vacuum chambers can now be observed in vapor cells. New surface materials like graphene can then be investigated more easily.

During this thesis only simple electrode structures have been implemented inside the vapor cells. However it opens the possibility to implement more complex electronic circuits, including transistors and other electronic components inside the cell for improvement or even evaluation of the detected signals. The possibility of integrated circuits can be used for spatial addressability of the alkali vapor. One can implement arbitrary spatial dependent electric fields, only limited by the resolution of the structuring method of the thin-film structures.

This vapor cell fabrication technique also offers the possibility to integrate not only microwave waveguides, but also optical waveguides into alkali vapor cells. Spectroscopy can then either be done in the evanescent field around the waveguide or in hollow core waveguides to maximize the overlap of the light field and the atomic vapor.

Appendix

Level schemes of cesium and rubidium

Here the level schemes of cesium (Fig. 9.1) and rubidium (Fig. 9.2) from the ground to the first excited state are shown with values for all hyperfine levels. The first excited state is then coupled in all experiments to a Rydberg state, which is not shown here. The hyperfine splitting of the Rydberg state is not resolved in our measurements.



Figure 9.1: Level scheme of cesium of the $6S \rightarrow 6P$ transition.



Figure 9.2: Level scheme of rubidium of the $5S \rightarrow 5P$ transition.

Abbreviations and materials

Notation	Description
AC	alternating current
Al	aluminum
Al_2O_3	aluminum oxide
$lpha_0$	polarizability
AOM	acusto-optical modulator
Ar	argon
Au	gold
AZO	aluminum zinc oxide
B_2O_3	boron trioxide
CCD	charge-coupled device
CNT	carbon nanotubes
CO	carbon monoxide
Cr	chromium
CVD	chemical vapor deposition
DAVLL	dichroic atomic vapor laser lock
DC	direct current
EIT	electromagnetically induced transparency
Fe	iron (ferrum)
FWHM	full width half maximum
GaAs	gallium arsenide
Ge	germanium
H_2	hydrogen
Не	helium
HF	high frequency
ITO	indium tin oxide
K_2O	potassium oxide

Notation	Description
Kr	krypton
LO	longitudinal optical
MCP	multi channel plate
MEMS	micro electro mechanical systems
Mo	molybdenum
MW	microwave
N_2	nitrogen
Na ₂ O	sodium oxide
Ne	neon
NH_3	ammonium
Ni	nickel
NO_2	nitrogen dioxide
PCB	printed circuit board
PECVD	plasma-enhanced chemical vapor deposition
PMMA	poly-methyl-methacrylate
PRS	photoresist stripper
R_y	Rydberg constant
Rb	rubidium
$\rm Si_3N_4$	silicon nitride
σ	cross-section
SiO_2	silicon oxide
SOI	silicon on insulator
Та	tantalum
Ti	titanium
ТО	transversal optical
UHV	ultra high vacuum
UV	ultra violett
Xe	xenon
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Erklärung

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbständig und ohne fremde Hilfe verfasst und keine anderen als die von mir angegebenen Quellen und Hilfsmittel verwendet habe.

Ich habe mich anderwärts nicht um einen Doktorgrad beworben und besitze einen entsprechenden Titel nicht.

Ich erkläre die Kenntnissnahme der dem Verfahren zugrundeliegenden Promotionsordnung der Fakultät 8 (Mathematik und Physik) der Universität Stuttgart.

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