

THESIS





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SCANNING PROBE SPECTROSCOPY OF INDIVIDUAL DOPANTS IN SILICON

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SCANNING PROBE SPECTROSCOPY OF INDIVIDUAL DOPANTS IN SILICON

By

Morewell Gasseller

A DISSERTATION

Submitted to Michigan State University In partial fulfillment of the requirements For the degree of

DOCTOR OF PHILOSOPHY

Physics

2010

ABSTRACT

SCANNING PROBE SPECTROSCOPY OF INDIVIDUAL DOPANTS IN SILICON

By

Morewell Gasseller

I have applied a novel scanned probe method called Charge Accumulation Imaging technique (CAI) to study the electronic states of individual boron dopants in silicon. In particular, I used the Charge Accumulation Imaging technique to image boron acceptors buried about 15 nm below the surface of a p-type silicon substrate and I was able to determine the binding energy of the B^+ state on an atom-by-atom basis for 20 such acceptors with millivolt precision. The data shows that acceptors with more distant neighbors exhibit weaker binding than those with close by neighbors. Hence I was able to discern both the average binding energy and the trend, which shows that binding energy increases with decreasing nearest neighbor distance. Comparing our data to a simple hydrogenic model that combines the effective mass approximation and configuration-interaction calculation show a general agreement. Thus our technique has proved to be an ideal tool to study directly individual and small clusters of dopant atoms.

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This thesis is dedicated to my family.

ACKNOWLEDGEMENTS

My PhD work would never have been possible without the help, support and encouragement I have received from various people. I want to take this opportunity to express my heartfelt thanks and gratitude to all those people. First of all, I would like to thank my thesis adviser Professor Stuart Tessmer for his continuous advice, encouragement and support. I thank him for giving me the chance to join his nano group and guiding me to complete my thesis work starting from scratch. The discussions I have had with him over the years have not only helped to expand my interest in physics but have also left an enduring impression in my mind. His encouragement and support has been the most critical driving force throughout my student career. The advice and positive criticism of the drafts of my thesis I got from him had a major impact on the final outcome of this thesis. I consider myself very fortunate to have the chance to work under his supervision.

I am also thankful to Prof. Golding for agreeing to proof read a draft of this thesis. His advice and comments have helped to make the final outcome of this thesis better. I am thankful to Prof. Zelevinsky, Prof. Dykman, and Prof. Tollefson for agreeing to serve in my committee. I am very grateful to Professors Carlo Piermarocchi, Tom Kaplan and S.D Mahanti for their interest in my research. Their expert theoretical input was very helpful in the process of understanding the interesting physics of my experimental findings. Many thanks are due to Dr. Sven Rogge of Delft University for his collaboration and to R. Loo and M Caymax of IMEC, Belgium for providing us with the sample. I would like to attribute my special thanks to all members of our group starting with Irma Kuljanishvil who taught me many tricks which made my experiments easier. Aleksandra Tomic, with whom I shared a lab room, was always very considerate and helpful. I would like to say thanks to Cemil Kayis, Josh Veazey, and Christopher Lawrence, my lab-mates and good friends who were always ready to assist not only with the lab related tasks but any day-to-day life issues. A number of undergraduate students passed through our lab over the years, but two of them left a lasting impression on me because of their work rate and commitment to their projects. These two are John Raguse and Jessica Muir. It was a great pleasure to have these two young students as my coworkers and friends

I am very grateful to Mrs. Debbie Barratt for her constant assistance on different occasions, always ready to give a timely advice or reminder of something important that one may forget to do. Her professionalism and responsibility for her work are truly remarkable. I should thank Dr. Reza Lolee for his help with the timely purchase of helium whenever I was running my experiments. He was always flexible with us when we have ordered too little or too much helium. I am very thankful to all the staff members of the machine shop, particularly James Muns, Thomas Hudson, and Thomas Palazzolo for their help and assistance during the initial stages of my research.

Lastly and by no means least, I would like to thank my wife Pauline. She has been very supportive and patient with me during all these years, always encouraging me and always believing in me.

This work was supported by the National Science Foundation grants DMR-0305461 and the Institute for Quantum Sciences.

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Chapter 1

Introduction

1.1 Motivation and thesis outline

As the size of conventional semiconductor components is reduced to nanometer scales, the improvement in their performance is determined by ever fewer numbers of impurity atoms known as dopants. The ultimate limit is a single dopant, and numerous devices have been proposed based on manipulating the charge and spin of small numbers of dopant atoms [1, 2, 3, 4, 5]. Identifying the position and quantum state of an individual dopant in a semiconductor is a key step and a difficult technical challenge. Here we present measurements that extend the reach of scanned-probe methods to discern the properties of individual dopants in silicon, tens of nanometers below the surface. Using a capacitance-based approach we have both spatially-resolved individual subsurface boron acceptors and detected spectroscopically single holes entering and leaving these atoms. By directly measuring the quantum levels and the influence of dopant interaction, this method represents a valuable tool for the development of future atomic scale semiconductor devices.

This thesis is organized as follows: In the introduction I give a brief outline of the current trends in semiconductor device technology including the difficulties and challenges it faces as the device size approaches the quantum limit. A brief introduction to the effective mass approximation theory of shallow dopants in bulk semiconductors is also given. Finally an overview of scanning probe techniques as a tool to probe and manipulate small clusters of dopants is discussed. Chapter 2 represents a brief review of two experiments that inspired this project. One experiment was done by Kuljanishvili and

1

coworkers [6, 7, 8]. In this study they were able to observe donor layer charging in a GaAs heterostructured sample using a technique called subsurface charge accumulation imaging (CAI) [9]. The other experiment was performed by Caro and coworkers [10], who observed resonant tunneling through the B^+ state of boron dopants in a silicon sample. Both experiments are concerned with the characterization of dopants at the atomic level. Chapter 3 reviews some general aspects of doped silicon samples and describes specifically the details of the sample that I used, which is a silicon crystal doped with boron. Chapter 4 describes the design and construction of my CAI microscope and gives the details of the other apparatus used in my experiments. Chapter 5 describes the methods and experimental techniques and Chapter 6 describes the testing and calibration of the CAI microscope. Results, analysis and discussions are presented in Chapter 7. Concluding remarks and possible directions for further work are given in Chapter 8.

1.2 Semiconductor technology

Semiconductors refer to a class of materials whose electrical properties are between conductors and insulators. Semiconductor devices are critical components in the electronics industry and they affect people in all facets of life. The industry has sustained a rapid growth in the past 40 years [11]. Over these years the industry has taken advantage of the fact that decreasing the device size not only reduces cost but also improves performance in terms of speed, functionality and power dissipation. This trend is often referred to as Moore's law, an expression coined in 1965 that prescribes that the number of transistors on a silicon chip will double every two years. Maintaining this

growth for as long as possible is the primary goal of many of those involved in semiconductor device technology, from university researchers to industry.

However it now appears that the industry is rapidly approaching the formidable quantum limit consisting of an unprecedented number of technical challenges, which threaten the continuation of this miniaturization process. The current line widths in stateof-the-art microprocessors are as small as ten nanometers, for which quantum mechanical effects become apparent and in some cases dominant. The key atoms that control electrical activity in semiconductor devices are called dopants; these are deliberately added impurity atoms that supply electrons (from donors) or holes (from acceptors) to the semiconductor. With line widths on the nanometer scale a few misplaced dopants can completely change the way the device is supposed to work [12]. Hence, the physical properties of these systems can no longer be determined by simply scaling down from large sizes. New techniques are required for characterization of such small devices. Projections of future device performance and key challenges to be overcome are discussed in a biannual Semiconductor Industry Association (SIA) document called the "National Technology Roadmap for Semiconductors" [13]. In the 2007 version the SIA identified two and three-dimensional dopant profiling as key needs for future device technology. Scanning capacitance microscopy (SCM) provides a direct method for mapping the dopant distribution in a semiconductor device on a 10 nm scale [14]. This capability is critical for the development, optimization and understanding of future nanometer size devices [15].

1.3 Classification of impurities

The electronic effects of dopant atoms are easily described when they are from adjacent columns of the periodic table. For example, phosphorous has one more electron in the outer shell available for chemical bonding than silicon. When a phosphorous atom is inserted into a crystal of silicon atoms, the extra donated electron can move in the crystal lattice and carry an electric current. Because the electron carries a negative charge, using phosphorous as a dopant produces an n-type semiconductor. On the other hand, boron has one electron fewer than silicon; so boron atoms can accept electrons form the host crystal, leaving spaces or holes where the electrons could have been. These holes are also free to move and when they do they act like positive charges moving through the solid. Hence, boron-doped silicon is a p-type semiconductor. Fig. 1.1 shows a sketch of p-type and n-type silicon.

1.4 Shallow and deep level defects

In a semiconductor, the energy region that is free of electronic states and separates the valence band from the conduction band is called the band gap. Fig. 1.2 shows the energy band diagram of a typical semiconductor. Dopants modify the electrical conductivity of semiconductors by adding states in this band gap. These added states provide electrical charge carriers (electrons for donors or holes for acceptors) to the conduction or valence band respectively. Fig. 1.3 shows the band diagram of a doped semiconductor.

Shallow donors or acceptors have energy levels within a few tens of millielectron volts from the respective band edges, whereas deep defects reside closer to the center of the band gap [16]. Deep levels have highly localized wave functions whereas shallow

level wave functions are more extended. The boron acceptors in my experiment are shallow level acceptors.



Figure 1.1 Substitutional dopants in silicon. Phosphorus (P) behaves as a donor and boron (B) as an acceptor, shown schematically within a covalently bound Si lattice with the extra or missing electron (line) at P or B.



the conduction band E_C and the top edge of the valence band E_V . E_C and E_V are separated by the band gap energy E_g .



Figure 1.3 Band diagram of a typical semiconductor showing the added states due the presence of donor and acceptor dopants.

1.5 The effective mass approximation

Here we discuss the effective mass approximation (EMA) to describe the electronic structure of shallow level dopants. The electronic structure of shallow impurity states in semiconductors has been widely investigated with EMA [17, 18]. The dopant atom is modeled essentially as a single charge with one or more electrons or holes bound to it [19]. The eigenstates of this donor or acceptor can be described approximately as those of a hydrogen atom with a modified field reduced by the dielectric constant, κ , and with an electron or hole of effective mass m^* . The combined effect of the effective mass and dielectric constant causes the charge to be bound much less tightly than the actual hydrogen atom with an effective radius of several lattice constants.

The key assumptions of EMA are that the electron or hole wave functions of shallow dopants extend over several lattice constants of the host semiconductor and that short wavelength oscillations are not important. With respect to spatial coordinate r, where r=0 is the location of the dopant, the wave function $\psi(r)$ can be expressed as a product: $\psi(r) = F(r)\phi(r)$, where $\phi(r)$ is a function that oscillates with a wavelength comparable to the lattice spacing of the host crystal, a, and F(r) is an envelope function, as shown in Fig. 1.4. The envelope function satisfies an appropriately modified hydrogen-like Schrödinger equation.

Two important parameters for EMA are the effective Bohr radius a_0^* and the effective Rydberg energy R^* , both of which are defined with respect to the ground state of a single electron (or hole) bound to an isolated donor (or acceptor): a_0^* gives the size of the envelope wave function and R^* gives the binding energy. These parameters can be expressed as

$$a_{0}^{*} = \frac{4\pi\varepsilon_{0}\kappa\hbar^{2}}{m^{*}e^{2}} = \frac{\kappa m_{0}}{m^{*}}a_{0},$$

and

$$R^* = \frac{e^2}{8\pi\varepsilon_0 \kappa a_0^*},$$

where ε_0 is the permittivity of free space, \hbar is the reduced Planck constant, m_0 is the free electron mass and a_0 is the hydrogen atom Bohr radius, $a_0=0.592$ Å. For common semiconductors such as silicon and gallium-arsenide, a_0^* is typically 1-10 nm and R^* is typically 5-100 meV. This model has been confirmed to hold approximately over a broad range of electrical and optical studies of a vast number of dopants in numerous semiconductor materials [20].



Figure 1.4 Relationship between the envelope function F(r) and the wave function $\psi(r)$ for the effective mass approximation. A shallow dopant is located at r=0; a denotes the lattice constant of the host semiconductor and a_0^* is the effective Bohr radius [19].

With regard to the silicon system, in general the effective mass approximation for acceptors does not give as good a description as it does for donors. As discussed in Section 3.0, the valence band in silicon consists of two degenerate bands and a third spin-split band. The two degenerate bands interact to distort the ideal spherical symmetry and the parabolic distribution upon which the effective mass is based. This distortion leads to a poor agreement between theoretically derived and measured properties of the holes [21, 22, 23]. For example, for an isolated boron acceptor with one bound hole, EMA calculations yield $R^*=37.1$ meV for the ground-state binding energy; however measurements give 45.7 meV, a discrepancy of 20% [10, 20, 21].

For my experiment, I probed holes tunneling into boron acceptors in a silicon host. Both light and heavy holes tunnel. Therefore, an average mass for tunneling, which takes into account the directionality of the tunneling process actually applies here. However, due to the bending of the bands and the uncertainty in the Fermi energy, a determination of this mass is not trivial. Therefore following the method of Ref. [10], I estimated an effective Bohr radius from the empirical relation $a_0^* N_{B,c}^{1/3} = 0.26$, where $N_{B,c}$ is the critical hole carrier density at the metal-to-insulator transition point. This relation is referred to as the Mott criterion for the metal-to-insulator transition. For this system, $N_{B,c} = 4.0 \times 10^{18}$ cm⁻³, which gives an effective Bohr radius $a_0^* = 1.6$ nm.

In light of the above considerations, clearly there are many approximations involved with applying EMA to my system. While EMA-based modeling may be used as a guide for our understanding of long-wavelength effects, we should keep in mind that we do not expect quantitative agreement measurements to a precision of a few percent.

1.6 Subsurface charge accumulation imaging

A number of different techniques have been developed for two-dimensional dopant profiling. These techniques include scanning probe microscopy (SPM) and other electron/ion beam approaches. See Reference 14 for a detailed review. Of all these techniques, SPM has been identified as a leading approach for obtaining twodimensional dopant profiles of semiconductor devices and is currently being modified and adapted to a variety of problems by many researchers and industrial users.

Scanning probe microscopy is based on the interaction between an ultra sharp tip and a sample. Measurements described in this thesis are based on a special type of the scanned probe technique. This technique can resolve features down to the atomic level. There are many types of SPM techniques, including scanning tunneling microscopy (STM), scanning capacitance microscopy (SCM), atomic force microscopy (AFM), force modulation microscopy and many others. In the case of scanning capacitance microscopy, a conducting tip is scanned across a sample and small changes in the tipsample capacitance are measured. These changes can be caused by topographic changes, dielectric variations or by local variations in carrier density. The volume probed by SCM is determined by several factors, including the tip radius, the gap between tip and surface, the local dielectric constant and the voltage between the tip and sample [24, 25]. Below I will give a brief review of the development and adaptations of SCM techniques up to our charge accumulation imaging (CAI) technique.

One of the early scanning capacitance microscopes was developed by Mately and Blanc in 1984 [26]. Their microscope demonstrated the capability of detecting variations of surface topography on the order of 0.3 nm over areas of the order of 2.5 μ m². This great sensitivity to height changes is achieved by the placement of a capacitance probe some 20 nm above the sample surface. In 1988 Bugg and King demonstrated imaging on a scale of 2μ m lateral resolution with an unguided scanning system similar to SCM [27]. Williams and co-workers then demonstrated capacitive imaging on a 25 nm scale and showed that the limit for capacitive imaging was below 10 nm. Various other systems were developed as described in reference [28]. Central to all these systems is the fact that capacitive interaction is used to control the height of the tip above the surface during scan. This was accomplished by modulating the height of the tip at a fixed frequency and measuring the capacitance change at that frequency with a lock-in amplifier. Since the capacitance change increases as the tip approaches the sample, a feedback loop is used to adjust the height of the tip to keep the capacitance changes constant as the tip is scanned over the surface. A generic example of SCM system with a force feedback is shown in Fig. 1.5.

In order to achieve high spatial resolution, ultra high capacitance sensitivity is required. The typical tip/sample capacitance is in the atto-farad range $(10^{-18} F)$. While it is extremely difficult to measure such a small static capacitance, measuring a dynamic change in capacitance on this scale is possible. In fact the first sensor used in SCM was capable of measuring capacitance changes on the order of $10^{-21} F$ [29].

The techniques mentioned above are predominantly room temperature measurements. A special type of SCM called charge accumulation imaging (CAI) has the unique advantage of being able to operate at low temperatures. Low temperature operation enables the probing of quantum systems with energy level spacing on the millivolt scale. Moreover, the technique enables the direct imaging of electronic systems buried tens of nanometers beneath the surface of semiconductor materials. An adaptation of this technique is the one we used for measurements described in this thesis. This method is described in detail in Chapter 5.



Figure 1.5 System drawing of a generic SCM with an atomic force microscopy topographic control system (adapted from Ref. 14)

Chapter 2

Review of Previous Experiments

The next generation semiconductor devices will be so small that their functionality will likely be determined by the presence of only a few dopant atoms. Hence the need and ability to control and detect single dopants with atomic resolution and identify their electronic states has become vital [30, 31, 32, 33, 34, 35]. In this chapter we will review two experiments that probed dopant atoms with atomic precision. One experiment was done by Kuljanishvili and coworkers [6]. This experiment successfully detected donor layer charging in a GaAs heterostructured sample. The broad spectroscopic peaks obtained there were attributed to dozens of electrons tunneling into clusters of donors. The other experiment by Caro and coworkers measured resonant tunneling through an acceptor quantum level in a boron-doped silicon sample. Related to these two experiments are optical experiments on single impurity states. For example, a photoconductance spectroscopy experiment on silicon samples with low doping density by Burger and Lassman measured the binding energy of an isolated B^+ ion to be 2.0 meV [36, 37, 38].

2.1 Resonant tunneling experiment on a delta-doped silicon sample

Resonant tunneling experiments offer an opportunity for detailed investigations of both the tunneling process through an impurity state and the local properties of a two dimensional electron gas (2DEG) [39, 40, 41]. Caro and coworkers used a resonant tunneling device with a metal-insulator-metal structure to probe the characteristic of a delta-doped layer. Delta-doping refers to dopants confined approximately to a single atomic layer, as opposed to bulk doping where the dopants are everywhere in the material. The layering sequence of the device was:

$$p^+Si(500nm)/p-Si(20nm)/\delta/p^-Si(20nm)/p^+(500nm)$$
.

Boron was the dopant for the bottom and top p^+ layers and the δ layer. The p^+ layers were heavily doped at 1.0×10^{19} cm⁻³ and hence acted metallic, whereas the p^- layers were intrinsic silicon and formed barriers. The areal density of boron in the delta layer was 1.7×10^{11} cm⁻², which gives an average spacing of 25 nm between boron atoms. The doping profile of the device using secondary ion mass spectroscopy (SIMS) is shown in Fig. 2.1 (a). The δ layer, the barrier and the metallic layers are clearly discernible on the diagram. The profile of the valence band edge of the device is shown in Fig. 2.1 (b), where E_0 is the ground state energy of the neutral boron atom (B^0) and E^+ is the binding energy of the B^+ state. The B^+ state is the acceptor counterpart of the generally known D^- state. It forms when a second hole is weakly bound to a neutral boron atom. The SIMS method and details of delta doping are further discussed in Chapter 3.

Fig. 2.2 shows the differential conductance of such a device as function of the bias voltage. Measurements were taken for temperatures in the range of 0.5 K to 12.5K. A tunneling resonance is clearly seen as a peak at $\pm 10mV$. The silicon wafer was patterned into micron-size mesas; hence the transport current can interact with millions of boron dopants. The heavily doped p^+ layers at the bottom and top of the sample acted as the contact layers to which wire leads were attached. The conductance peak shown in Fig. 2.2 is attributed to resonant tunneling through the B^+ states of the boron impurities in the δ layer. The resonant peaks cannot be due to tunneling through E_0 because it is too

deep below the Fermi level so that it is permanently occupied for the voltage ranges permitted by this measurement. Resonant tunneling refers to tunneling in which the electron transmission coefficient through a structure is sharply peaked about certain energies. This happens when the electron has an intermediate state to tunnel into. In this case the B^+ state provides the intermediate step. Since the measured resonance comes from the δ layer, equal parts of the bias drop across the barriers at either side of the potential well associated with the boron impurity. Thus the resonance voltage is $V_{res} = 2[\phi_B - E^+]/e$. With $\phi_B = 11.7$ meV and the measured value of $V_{res} = 10$ mV, the value of E^+ is found to be 6.7 meV.

•


Figure 2.1 (a) Secondary Ion Mass Spectroscopy profile (SIMS) of the boron concentration in the device used by Caro and co-workers. Details of SIMS technique are discussed in Section 3.1. (b) Valence band edge diagram of the device. The barrier height is $\phi_B = \Delta E_V - E_F$ [10].



Figure 2.2 Conductance characteristic of the resonant tunneling device used by Caro and co-workers. The peaks are clearly seen at $\pm 10 \text{ mV}$ [10].

The main result from this experiment is the observation of resonant tunneling through B^+ states of the boron dopants in the delta layer. From their measurements Caro and coworkers determined that the binding energy E^+ of the extra hole on an isolated B^+ ion is 6.7 meV. This value deviates from the 2.0 meV which was obtained from photo conductance spectroscopy experiments on Si samples with low doping levels [42, 43, 44, 45]. The most plausible explanation for this discrepancy is that at this concentration, the boron dopants cannot be considered to be isolated. This issue will be the major focus of my experiment.

2.2 Charge accumulation imaging (CAI) experiment on a GaAs sample

Charge accumulation imaging (CAI) is a powerful tool to probe mobile charges in many experiments. The method will be described in detail in Chapter 5. Kuljanishvili and coworkers used CAI to probe the electron addition spectra of a system of silicon donors in AlGaAs. Fig. 2.3 (a) shows the schematic of the CAI method for this experiment, which essentially measures the capacitance between the sample and a sharp metal tip. For this measurement, the key sample parameters are the surface-to-delta layer distance of 60 nm and the dopant density within the delta layer of 1.25×10^{16} m⁻². The key tip parameters are the radius of curvature of the apex of 50 nm and its distance from the sample surface of about 1 nm. The measurement had rather poor spatial resolution of about 60 nm; in other words, with the tip at a fixed location, it interacted with a circular area of the donor layer of radius ~60 nm, which contained about 150 dopants. Fig. 2.3 (b) shows the representative data for this measurement. The capacitance curves consistently showed three broad peaks over a tip voltage range of 0-1.0 V. Fine structure

measurements on the millivolt scale showed sharp peaks which are consistent with single-electron peaks. These are shown in Fig. 2.3 (c). The broader peaks labeled A, B and C are interpreted as bundles of \sim 15 electrons entering "donor molecules" formed by nearest-neighbor silicon atoms.

For both of these experiments discussed in this chapter, the electronic structure of the dopants is inferred from spectroscopic measurements of systems which give the average behavior of 100 to several million dopants. However, as devices size shrink knowledge of the behavior of small numbers of dopants become increasingly vital. In my experiment I combine both spectroscopic single-electron measurements and actual imaging of dopants to examine the electronic structure of individual dopants *one by one*.



Figure 2.3 (a) Schematic of the CAI measurement for the Kuljanishvili experiment [6]. (b) Spectroscopic data showing broad peaks, labeled A, B and C. Each peak corresponds to roughly 15 electrons. These peaks were interpreted as electrons entering clusters of donor, effectively forming "donor molecules". The rms amplitude of the excitation voltage was 15 mV. (c) A subsequent measurement acquired with tip voltages indicated by the rectangular box in (b) showing single-electron peaks. In this case, the rms amplitude of the excitation voltage was 3.8 mV, as indicated.

Chapter 3

Silicon Samples

Silicon is the best known and most frequently used semiconductor [46]. Under exposure to oxygen a silicon surface oxidizes to form silicon dioxide (SiO₂). The stability of the native oxide and silicon's large band gap led to it being the dominant semiconductor material used in electronic devices [47]. The sample used in my experiment was grown by chemical vapor deposition on a silicon substrate. The dopant in all the layers is boron which forms an electron acceptor. This means that my sample is a p-type semiconductor. In this chapter I will first discuss the silicon band structure and then talk about the general aspects of silicon samples such as growth by chemical vapor deposition, delta doping and dopant profiling by secondary ion mass spectroscopy. After this I will give specific details of the sample used in my experiment.

3.0 Silicon band structure

The electronic properties of silicon are completely determined by the comparatively small number of electrons excited into the conduction band and holes left behind in the valence band. The electrons will be found in the levels near the conduction band minima while the holes are confined in the neighborhood of the valence band maxima. The band structure of silicon, which is the energy (E) versus wave vector (k) diagram, is shown in Fig. 3.0. The conduction band has three minima, the lowest of which is away from k=0 (called the Γ point) along the [100] direction. Hence silicon is said to be an indirect semiconductor. The electrons in this minimum have a 6-fold degeneracy. With regard to holes, there are two degenerate valence band maxima, both located at k=0 which are

spherically symmetric. These two bands give rise to light holes and heavy holes. There is also a third band (not shown in the Fig 3.0) about 44 meV below the valence band maximum. This band is separated from the other two by the spin-orbit coupling. At temperatures on the order of room temperature ($k_BT=0.025 \text{ eV}$) it too can be a significant source of carriers.



Figure 3.0 The band structure of silicon. The horizontal axis shows the k=0 point (Γ) and two directions in k-space: [111] (L) and [100] (X). The energy band gap of 1.12 eV is indicated. The conduction band minimum is displaced in k-space away from the valence band maximum, making silicon an indirect semiconductor. The valence band shows two degenerate bands and a third band called the split-off hole band (not shown).

3.1. Chemical vapor deposition

My sample was grown using chemical vapor deposition (CVD); in this section I briefly describe the method. CVD is a synthesis process in which the chemical constituents react in the vapor phase near or on a heated substrate to form a solid deposit. The technique is used for depositing thin films of a large variety of materials. The substrate is placed inside a reactor to which a number of precursor gases are supplied. Fig. 3.1 shows a simplified schematic picture of a CVD horizontal epitaxial reactor chamber.

A CVD reaction is governed by the thermodynamics and the growth kinetics of the system. The thermodynamics of the system determines the direction the reaction is going to proceed while the growth kinetics defines the transport process and determines the rate control mechanisms [48]. Chemical thermodynamics deals with the interrelation of various forms of energy and the transfer of the energy from one chemical system to another. In the case of CVD, this transfer occurs when the gaseous compounds react to form the solid deposit. A desired CVD reaction will only take place if the thermodynamics is favorable. This happens when the free energy of the reaction is negative [49].

Another important aspect of CVD is the growth kinetics and mass transport mechanisms. In a CVD process the precursor gases are transported from the location where the gases are supplied to the surface on which deposition must occur. The rate of deposition can be controlled by the surface reaction rate or the mass transport or diffusion rate. The boundary layer model has been widely accepted for the description of mass transport from bulk gas to the substrate surfaces [50, 51, 52, 53]. Fig. 3.2 shows the formation of a boundary layer above the substrate in a horizontal epitaxial reactor. The

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gas velocity is zero at the substrate and rapidly increases to a value identical to the velocity of the bulk gas. The distance in which the gas velocity increases from zero to the bulk value is referred to as the thickness of the boundary layer σ . This layer thickness is determined by the flow dynamics of the gas mixture in the reactor. In open tube reactors, such as the one shown in Fig. 3.1, the gas flows by forced convection.



Resistive heaters

Figure 3.1 Simplified schematic diagram of a horizontal epitaxial reactor chamber showing the wafers stacked in vertical slots and the motion of the precursor gases.



Figure 3.2 Schematic representation of the formation of a boundary layer of thickness σ above the substrate in a horizontal epitaxial reactor [52].

3.2 Delta-doped semiconductors

In delta doping, the dopant atoms are confined to a single atomic layer in the host semiconductor. Such a situation is illustrated schematically in Fig. 3.3. A δ -doping profile is characterized by the location of the dopant plane and the density of the doping atoms in the plane. Assuming that the dopants are located at $z = z_d$ in the x-y plane, then the doping profile is given by

$$N(z) = N^{2D} \delta(z - z_d),$$

where the two-dimensional (2D) density denoted by N^{2D} is the number of doping atoms in the plane per cm².

In Section 3.1 we discussed the growth of samples by chemical vapor deposition (CVD). Here we summarize briefly the basic procedure for the growth of δ -doped samples. The first step involves the suspension of the epitaxial growth of the semiconductor. The surface should be atomically flat with minimal atomic terrace steps. In the second stage this flat surface is exposed to either a flux of elemental doping atoms or to a flux of the doping precursor gas. The doping atoms would then form bonds with the host semiconductor atoms. Ideally, all doping atoms occupy substitutional lattice sites on the semiconductor surface. In the final stage of δ -doping the deposition of the dopants is stopped and the epitaxial growth of the host semiconductor is resumed.

The density of doping atoms in the monolayer can be determined by the flux of dopant atoms in the doping precursor and the time that the semiconductor surface is exposed to the dopant flux. In practice, for most δ -doped semiconductors, the dopants are not perfectly confined to a single atomic layer. There is often a distribution on the depth

of the δ -layer. Surface roughness and other processes such as diffusion, drift and segregation may contribute to the doping redistribution.



Figure 3.3 Schematic illustrations of a semiconductor substrate and an epitaxial film containing a delta-doped layer [54].

3.3 Secondary ion mass spectroscopy

The doping profile of any delta-doped sample can be measured by secondary ion mass spectroscopy (SIMS). In SIMS, primary ions with energies between 1 and 15 keV are made to impinge on the surface of the material to be analyzed. Part of the energy of the primary beam goes into ejecting atoms and clusters of atoms from the surface of the material under consideration (Fig. 3.4). A small fraction of these sputtered-off particles leave the sample either positively or negatively charged. These secondary ions are then identified using a mass spectrometer and counted as a function of their mass. Over time the ejected atoms leave a pit in the sample. Hence data collected as secondary ion counts versus time can be converted to concentration versus depth [55, 56, 57]. An example of a SIMS plot is shown in Fig. 2.1(a).



Figure 3.4 The SIMS process. An incoming primary ion generates a variety of secondary particles from a narrow escape region [54].

3.4 Strain issues in boron doped silicon

As strain can lead to energy shifts in semiconductors, its effects on the B-doped samples studied in this thesis should be considered. Under a strain, the symmetry of a crystal is lowered in general, resulting in the lifting of degeneracies associated with the energy levels of dopant atoms [58, 59]. Substitutional boron dopants in silicon exert strain in the following way: As the smaller boron atom replaces a silicon atom, there is a tendency for the lattice to contract locally and change the unit cell. However, the silicon lattice resists contracting, resulting in a tensile strain, as shown in Fig. 3.5 [60, 61]. The amount of this kind of strain in the lattice is dependent upon the density of the boron dopants. In our sample the boron dopants make up only 0.02% of the lattice. For example, impurity defects in silicon also introduce strain to the lattice. For example, impurity defects such as oxygen or carbon can create some local strain which may cause the shifting of the ground state energy of the boron dopants [58, 59, 63]. Possible effects of strain on our measurements are discussed in Chapter 7.



Figure 3.5 A local tensile strain is generated as a boron atom substitutes into a silicon lattice. AL is the change in the lattice constant due to the replacement of a silicon atom with a boron atom. (Figure adapted from Reference 6.)

3.5 Specifics of my sample

The silicon sample used in this experiment was grown by Roger Loo and Matty Caymax at the IMEC facility in Belgium [62, 64]. Boron is the dopant for the bottom layer and the delta-layer. The active structure was deposited by chemical vapor deposition in an ASM Epsilon 2000 reactor on a Si (001) substrate. It is a layered structure whose active part is (top to bottom) $Si(15nm)/\delta/Si(20nm)/p^+Si(500nm)$, where Si denotes intrinsic undoped silicon and p^+Si denotes boron doped silicon with a dopant density of 1.0 x 10^{19} cm⁻³; as shown in Fig. 3.6 (b). The overall dimensions of the sample are $10 \times 2 \times 1$ mm. Fig. 3.6 (a) shows a schematic of the sample showing the boron dopants randomly distributed in the delta-layer and Fig. 3.6 (c) shows a photograph of the sample.

3.5.1 Sample growth

The sample was grown at 700° C at a pressure of 40 torr using hydrogen as the carrier gas. B_2H_6 was used as the dopant precursor gas. The dopant atoms were introduced using the vapor phase doping technique (VPD) [62]. In this technique the dopant atoms are deposited on the Si surface through the thermal decomposition of the gaseous precursor (B_2H_6) in a standard chemical vapor decomposition reactor. The dopant dose increases linearly with dopant flow and time. With regard to silicon growth, the bottom p^+ layer ~500 nm was grown with SiH₄; for the other layers SiCl₂H₂ was used. The δ -layer has an areal density of 1.7 x 10¹¹ cm⁻² and is almost centered in a 35 nm layer of intrinsic silicon. This areal density corresponds to a mean distance of ~25 nm between the boron dopants. The width of the δ -layer is about 2 nm wide and it has a peak bulk

concentration of ~5 x 10¹⁷ cm⁻³. The p^+ layer is heavily doped, $N_A^{3D} = 10^{19}$ cm⁻³ and serves as a bottom contact layer, where N_A^{3D} is the 3D density of the boron acceptor atoms. The doping profile of our sample was measured by secondary ion mass spectroscopy (SIMS). This measurement was done by the sample growers and is shown in Fig. 3.6 (b).

The background contamination of oxygen or carbon during growth was not measured for our particular sample. However the sample growers carried out weekly systematic process control tests (SPC-tests) during production. For samples grown under identical conditions to our sample, the measured background contamination of oxygen and carbon is far below the SIMS detection limit [64].



Figure 3.6 (a) Schematic of my sample showing the random distribution of boron dopants in the delta-layer as blue dots. The area of interaction with the tip is indicated in red. The silicon layer above the delta layer is 15 nm thick (1); the silicon layer below the delta layer is 20 nm thick (2) and the heavily-doped p⁺ substrate layer is 1000 nm thick (3). (b) SIMS plot of our sample showing that the δ -layer is about 15 nm from surface. (c) A photograph of the actual sample. The sample is a rectangular silicon crystal of dimensions 10 x 2 x 1 mm; the gold wires shown bring the bias voltage to the heavilydoped p⁺ layer.

3.5.2 Valence band diagram of sample

A boron dopant is an acceptor atom in silicon. In other words, when a boron atom replaces a silicon atom in the lattice, it readily gains an electron, or equivalently, loses a hole; this state is denoted as the B^- state. Can the hole be reunited with the acceptor? The answer is "yes". In fact the negative *B* ion can bind one or two holes. When occupied by one hole, the acceptor becomes neutral and the energy of the hole can be approximated as a hydrogen-like atom. The ground state in this case is known as B^0 state. The binding energy of the hole in the B^0 state is $E^0 = 45.7$ meV [10, 20] this state is sufficiently deep such that it is far below the Fermi level of the bottom contact layer. The system can also accommodate a second hole; this hole will experience a repulsive energy with the first hole, thus forming a state with reduced binding energy, E^+ , known as the B^+ state. The goal of my experiment is to probe locally holes entering the B^+ state. (This state is the acceptor counterpart of the donor state known the D^- state.) The state can be described with the following equation: $B^0 + h = B^+$.

Figure 3.7 shows a semi-quantitative schematic of the expected valence band for our sample relative to the Fermi levels of the tip and bottom contact layer, labeled as metallic substrate. We see that the weakly-bound B^+ state is expected to be only a few meV from the Fermi level of the substrate. An important parameter is the effective tunneling barrier height though which the hole must tunnel. This parameter is denoted as ϕ_B in Fig. 3.7. It is given by the valence-band contribution to the band-gap narrowing of the bottom contact layer, minus the Fermi energy E_F . The value is expected to be 11.7 meV [10, 65].



Figure 3.7 Schematic of the profile of the valence band edge of my sample. The heavilydoped bottom contact layer acts as a metallic substrate. Holes can tunnel onto the boron atoms from this layer, as indicated by the red arrow. The gap between the tip and the sample forms a second higher barrier, inhibiting charge from tunneling directly onto the tip. E^0 is the binding energy of the neutral boron state (B^0) with one bound hole; E^+ is the binding energy of the of the positive boron (B^+) state with two bound holes; ϕ_B is the effective work function or tunnel-barrier height.

Chapter 4

Design and Construction of Microscope

This chapter describes the design and construction of the scanning unit and top loading probe of my CAI microscope. This construction was done with the help of staff at the physics machine shop. The design of my scanner is based on the Besocke-type scanning tunneling microscope. The CAI microscope can be operated in three different modes. These modes, which will be discussed in detail in Chapter 5, are the STM mode, the capacitance mode and the Kelvin probe mode.

The main components of the scanning unit are the base plate, body, door and the sample holder, all of which are made from stainless steel. The main goal of the design is to have a microscope that is stable and has little thermal drift. The scanning unit is compact and rigid which makes it less sensitive to external vibrations. The combined effect of mechanical vibrations and thermal drift of the system must be extremely small to allow the tip to stay above a single dopant atom for many hours. The scanning unit is rigidly attached to the top loading probe. The top loading probe can be divided into three main parts; the vacuum lock, the sliding insert and the top cone. These parts are also constructed from stainless steel.

4.1 Scanning unit

This section describes the scanning unit in detail. Fig. 4.0 (a) shows a blown out drawing of the scanning unit and Fig. 4.0 (b) is a photograph.

4.1.1 The base plate

The base plate is a rigid steel plate of diameter 3.00 cm and thickness 0.50 cm. At the top side of this plate we machined four sockets that hold four identical piezotubes. Each piezotube has four quadrants to which electric signals could be applied, as described in detail in Section 5.2. On one end, the piezotubes are soldered to the bottom plate while on the other end they are free and can be actuated in x, y and z directions by applying appropriate electric signals. We used indium solder to bond the piezotubes to the base plate. Fig. 4.0 (a) shows the base plate and the arrangement of the piezotubes on the base plate.

The three outer piezotubes are arranged in a triangular configuration and act as the sample carriers. The fourth piezotube is located at the center of the triangle and acts as the scanning piezotube. We used custom-made piezotubes made from lead-zirconiumtitanate (type PZT-5A). The tubes are of length 1.91 cm, diameter 0.48 cm, with a wallthickness of 0.09 cm. The scanning and carrier piezotubes are all of equal length. Equal length piezotubes are important for thermal stability of the scanning unit, as they expand and contract identically as the temperature changes.

The free end of each of the three carrier piezotubes are soldered to copper feet with stainless steel balls attached to them. We used a stycast mixture for bonding the steel balls to the copper feet. The balls are highly polished for low friction performance during the approach of the sample. The scanning piezotube has a miniature L-shaped copper cap soldered to it. This copper piece holds the sensor circuit chip with the tip rigidly attached to it. Details of the sensor circuit will be given in Section 4.6. On each of the four piezotubes we soldered six thin Kapton-coated copper wires which carry electrical



Figure 4.0 (a) A blown out schematic of the scanning unit showing the main parts. The diameter of the scanning unit is 3.00 cm and the total length of the compact assembly is 8.04 cm. The sample holder sketch shows the sample and the slopped ramps. It is a stainless steel disk of outer diameter 2.70 cm and thickness 0.70 cm. The base plate schematic shows how the four piezotubes are arranged. (b) A photograph of the scanning unit; the door is removed to show the copper feet onto which the sample holder rests.

signals. Four of the wires are for each of the four outer quadrants; the fifth wire is for the interior, which is held at ground, and the sixth wire goes to the copper foot on top of the piezotube. For the three carrier piezotubes, this sixth wire brings the bias voltage to the sample, whereas on the scanning piezotube the wire is connected to ground. Great care must be taken when soldering the wires to the piezotube quadrants. Any stray soldering flux that lands on the space between the quadrants is a potential source of an electric short and must be thoroughly cleaned. Fig. 4.1 is a photograph of the top and bottom sides of the base plate. The top and bottom of the base plate has grooves that are 0.30 cm deep into which all the 24 wires from the piezotubes are neatly packed. The wires are then routed into a vertical groove on the side of the body of the scanning unit and ultimately run the length of the probe to the top cone.



Figure 4.1 Photograph of the base plate (diameter 3.00 cm and thickness 0.50 cm) showing the top and bottom sides. In this photograph, only a few of the connecting wires are shown and one carrier piezotubes is missing.

4.1.2 Body of scanning unit

The base plate is attached with three screws to the body, which is a solid cylindricalshaped piece as shown in Fig. 4.0 (a). Due to the compact design of the scanning unit, it can be difficult to route and attach the four coaxial wires that control the sensor circuit. In my design the body is tailored to provide easy access to the sensor circuit and to these wires. The length of the body is 7.54 cm and the inside diameter is 3.10 cm. In Fig. 4.2 two of the cooper feet on the carrier piezotubes are clearly shown and the L-shaped copper foot of the scanning piezotube is also visible. The small GaAs chip that holds the sensor circuit and the tip is shown together with the four wires that connect the sensor to the control electronics.

The sample holder is a stainless steel disk of thickness 0.70 cm and outer diameter 2.70 cm which rests on the three carrier piezotubes. It has a Teflon ring on the outside which prevents electrical contact between the sample and the body. On the bottom of the sample holder are three sloped ramps as shown in Fig. 4.0 (a). Each ramp is tilted an amount of about two degrees with respect to the horizontal. Fig. 4.2 shows a picture of the sample holder sitting on top of the carrier piezotubes. Also shown in the picture are the Teflon ring and two 0.3 cm deep grooves on opposite's sides of the sample holder. The purpose of the grooves is to provide for easy handling of the sample holder using a two-pronged fork. To keep the sample holder in place and also for the purposes of protecting the sensor circuit, we machined a stainless steel door which is screwed onto the body. The door is shown in Fig. 4.0 (b).

When all the different parts of the scanning unit are assembled, the whole scanning unit is then rigidly attached by a connecting flange to a 2.00 m long top-loading probe for subsequent positioning of the unit inside the ³He cryostat.

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Fig. 4.2 A close-up image of the tip holder and sample holder. In this picture the copper feet and the steel balls on top of two of carrier piezotubes are clearly shown. A Teflon ring surrounds the sample holder, preventing it from making electrical contact to the body of the scanning unit. The tip is mounted at the top corner of a GaAs chip that also holds the sensor circuit. The sensor circuit is controlled by four coaxial wires which emerge from small holes to the left and right of the tip holder (not discernable in the picture).

4.2 Top-loading probe

The top-loading probe can be divided into three main parts: a vacuum lock, a sliding insert and a top cone. Fig. 4.3 (a) shows a schematic of the probe. The vacuum lock is a stainless steel cylinder of length 47.50 cm and inner diameter 5.00 cm. On the top end of the vacuum lock there is a sliding seal and a pumping port. The seal ensures that no air enters during the sliding of the insert. At the bottom end of the vacuum lock there is an oring that locks to the gate valve of the commercially purchased ³He cryostat. A sliding insert of length 2.00 m and inner diameter 1.30 cm runs through the vacuum lock. The scanning unit is attached to the bottom end of this sliding insert. Just above the scanning unit there is an important part of the top loading probe. This is a copper disk called the 1 K pot wedge. Its purpose is to make a good thermal contact between the scanning unit and the 1 K pot. Details of the 1 K pot will be given in Section 4.5. On top of the probe is a cone which houses 36 electrical feedthroughs (a 24 pin Fisher connector and 12 coaxial SMA connectors). Fig. 4.3 (b) and Fig. 4.3 (c) show photographs of the cone and the top loading probe respectively.



Figure 4.3 (a) Schematic of the top loading probe. The total length of the vacuum lock and the sliding insert is about 2 m. (b) A photograph of the top cone showing the 12 SMA connectors attached to it. (c) A photograph of the top loading probe placed on top of the ³He cryostat ready for positioning of scanning unit into cryostat.

4.3 Wiring and electronics

The wiring of the system is divided is into three parts: outside cables connecting microscope to control electronics, wires in the top-loading probe and wires in the scanning unit. Since wires connected to the microscope should not transmit vibrations, all the outside wires are thin and flexible. The 24 wires that go to the piezotubes are Constantine wires of thickness 0.6 mm. They are all put together in the form of a 12 twin-pair ribbon cable that starts at the Fisher connector on the side of the cone and terminate at a connector inside the vacuum lock. From this connector, thin Kapton-coated coppers wires were used to make the connection to the piezotubes. The wires for the tunneling current and sensor circuit connections are all shielded stainless steel coaxial cables. They start from SMA connectors at the top of the cone and terminate at some connectors inside the probe. All together there are 28 wires that go into the scanning unit. The intermediate connectors inside the probe allow the scan head to be dismounted without the disruption of any cables. Our microscope is operated using a commercially purchased scanning control and data acquisition system from RHK Technology, Inc.

4.4 Noise isolation

Noise isolation is one of the main challenges we faced in our measurements. The noise can be electrical or mechanical. With regard to electrical noise, I carefully shielded the charge sensor control and measurement leads, all of which are coaxial; moreover ground loops were eliminated from the microscope and control system. The following section addresses the issue of mechanical noise.

4.4.1 Mechanical stability of the microscope

Mechanical noise, e.g. vibrations, originates from external building vibrations as well as acoustic waves in the air. When operating the microscope in tunneling mode the mechanical vibrations should not produce variations in tunneling current of more than a few percent of the set value. This requires tip-sample mechanical stability of much better than ~ 0.1 Å. Our scanning unit design coupled with two stages of vibration isolation achieves this stability. The compact scanning unit design gives high normal mode vibration frequencies of roughly 2 kHz which are not easily excited by room vibrations. Moreover, the two-stage vibration isolation platform that supports the system decouples the scanning unit from floor vibrations. The first stage of the isolation platform consists of four pressurized rubber springs and the second stage consists of four optical table legs as shown in Fig. 4.4. These two stages result in the lowest normal-mode vibration frequency of the platform of about one hertz. This is sufficiently far from room vibrations \sim 10-20 Hz. Acoustic vibrations transmitted through the air also affect the stability of the tunneling current. In order to counter this, the room in which the experiments were performed is cushioned with sound absorbing padding on the walls. The padding consists of patterned sheets of foam rubber material arranged in checkerboard pattern, which significantly attenuates reverberation.

These precautions allowed me to eliminate any extra noise while performing the capacitance measurements. In other words, I achieved noise levels consistent with the intrinsic noise of the charge sensor amplifier, as discussed further in Chapter 7.

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Figure 4.4 Schematic of the two-stage vibration isolation system used in our measurements. The hatched bars represent two rigid platforms.

4.5 Cryogenic system

The ³He cryogenic system we used for our experiments can be operated at room temperature as well as other selected low temperatures. Most of the data discussed here were obtained at the liquid ⁴He boiling temperature of 4.2 K. However some preliminary and testing data was obtained at room temperature and at 77 K. The probe which carries the scanning unit, the sample and the charge sensor is loaded onto the top of the ³He cryostat and is inserted slowly. The process of lowering the probe takes approximately 5-6 hours. It is important to protect the fragile ceramic material of the piezotubes from thermal stress; otherwise the piezotubes may break or become depolarized. The schematic picture of the cryostat is shown in Fig. 4.5

The principle of operation of a ³He cryostat is relatively simple. The whole cryostat is cooled in stages from room temperature to 4.2 K. First, we cool the cryostat down to 77 K with liquid nitrogen. Then we remove the liquid nitrogen and fill the cryostat with liquid ⁴He. The sample space is kept under vacuum (~4.7 x10⁻⁶ mbar) during the cool-down procedure and for the subsequent measurements. Outside the sample space and attached to its outer wall is a small donut like chamber called the 1 K pot. The 1 K pot is filled with liquid ⁴He and it can be pumped to maintain a temperature of about one Kelvin. For most of my experiments it was maintained at a pressure of one atmosphere and a temperature of 4.2 K. This allowed me to eliminate vibrations induced by the mechanical pump. The sliding insert has a copper wedged plate that makes good thermal contact with the 1 K pot (see Fig. 4.3 (a)). The temperature of the sample equilibrates to that of the 1 K pot, 4.2 K for most of my measurements.



Figure 4.5 Schematic of the cryostat. The cryostat is about 60 cm wide and 1.5 m long and can hold up to 60 L of liquid ⁴He. During the experiment, the probe resides inside the cryostat and the scanning head is situated at the bottom of the cryostat surrounded by superconducting magnet.

4.6 The cryogenic charge sensor circuit

At the heart of the charge accumulation imaging technique is the cryogenic charge sensor. Our charge sensor is made from high electron mobility transistors (HEMTs), which are field-effect transistors. The HEMTs that we used are unpackaged commercial devices (model FHX35X) manufactured by Fujitsu. The active channel is formed at the interface of GaAs and AlGaAs. In general to allow conduction, semiconductors need to be doped with impurities to generate mobile electrons in the channel. However the presence of the dopants lowers the mobility, as the charges collide with impurities that were used to generate them in the first place. The HEMT use modulation doping to resolve this contradiction. This is accomplished using the heterojunction of a highly-doped supply layer of AlGaAs and a non-doped channel layer of GaAs. The electrons generated in the n-type AlGaAs move into the GaAs layer, falling in the potential well created by the different band gaps of the two materials. The electrons are confined in this quantum well, typically ~20 nm away from the doped AlGaAs. The effect of this is to create a very thin layer of highly mobile conducting electrons. This layer is called a two-dimensional electron gas.

As with all other types of FETs, a voltage applied to the gate alters the conductivity of this layer. We chose the HEMT as our active device due to their superior low temperature performance as well as low input capacitance (channel-gate mutual capacitance). HEMTs do not suffer from carrier freeze out at low temperatures because the carriers are not thermally generated. Field-effect transistors are typically operated in saturation mode for which the current is approximately independent of voltage. However the power dissipated in this regime is typically in the miliwatt range. This would be large

enough to heat up the sample surroundings and may cause thermal instabilities. We operate our circuit in the low voltage regime (ohmic region) far from saturation, indicated by the circle in Fig. 4.6. In this region, the power dissipation is decreased by 2-3 orders of magnitude compared to saturation mode operation [66]. For my typical operating parameters the power dissipated is about 0.3 μ W. Figure 4.6 shows the drain I-V characteristics of our HEMTs, indicating the regime in which we operated. Fig. 4.7 (a) shows the schematic picture of the cross section of the HEMT and Fig. 4.7 (b) is a photograph of the device.

Our charge sensor circuit uses two HEMTs, the measurement HEMT and the bias HEMT, as shown in Fig. 4.8 (a). The gate of the measurement HEMT is biased through the bias HEMT. The role of the bias HEMT is to act as a very high resistor, preventing the charge induced on the tip from leaking to the left. The inclusion of the bias HEMT is the major improvement from the original design, which used an on-chip thin film resistor [67, 68, 69]. The bias HEMT couples less than 0.1 pF of additional capacitance to the tip electrode. In contrast the thin-film resistor added 1.0 pF of stray capacitance; this significantly reduces the circuit's gain, as discussed on the following pages.



Drain-source Voltage (V)

Figure 4.6 Drain-source I-V characteristics at different gate voltages V_{GS} of our HEMT [70]. The circles mark the voltage range in the linear regime in which we operate the device.





Figure 4.7 (a) Schematic picture of the cross section of a HEMT [70]. (b) A photograph of the Fujutsi model FHX35X HEMT. The size of the device is $\sim 500~\mu m$ across.

The signal of interest which I want to measure originates from charge moving below the apex of the tip in response to an excitation voltage V_{exc} applied to the base of the sample. The standard capacitor C_S is used to subtract away the stray (or background) capacitance, arising mostly from the electric fields from the sample which do not terminate on the apex of the tip. This is accomplished by applying an AC voltage, $V_{balance}$ to C_S . $V_{balance}$ is of the same amplitude as V_{exc} but exactly 180⁰ out of phase. The typical value of the C_S is about 20 fF (femtofarad). We can model our circuit with a simple voltage divider as shown in Fig. 4.8 (b). We assume that bias HEMT is tuned to assure that no current leaks to the left. If we consider now only the measurement HEMT, we see that the circuit acts like a simple voltage divider. Here V_{in} is the input voltage, in our case V_{exc} , and V_{out} is proportional to the measured voltage V_{meas}/G . Here G is a gain factor.

To construct the voltage divider equation, we label C_{in} as the input capacitance, the capacitance between the gate and the source-drain channel of the HEMT. C_{meas} is the tip-sample capacitance, proportional to the tip charge, which is the quantity that we need to measure. We can write the following expression:

$$\frac{V_{out}}{V_{in}} = \frac{V_{meas}}{GV_{exc}} = \frac{Z_2}{Z_1 + Z_2},$$
(4.1)

where
$$Z_1 = \frac{1}{i\omega C_{meas}}$$
 and $Z_2 = \frac{1}{i\omega C_{in}}$.



Figure 4.8 (a) Schematic of the charge sensor circuit. The charge sensor circuit uses two HEMTs, the measurement HEMT is to the right and the bias HEMT is to the left. The gate of the measurement HEMT is biased through the bias HEMT. The role of the bias HEMT is to act as a very high resistor, preventing the charge induced on the tip from leaking to the left. C_S is the standard capacitor and V_{in} is the rms value of the applied AC excitation to the sample. The AC excitation applied to C_S , is of the same amplitude but 180° degree out of phase with the excitation voltage that is applied to the sample. The charge sensitivity of the circuit is 0.15 electron/ \sqrt{Hz} . (b) The sensor circuit can be modeled as a simple voltage divider.

 C_{meas} is typically about 1 aF, whereas C_{in} is a much larger 0.4 pF. Hence the typical value for Z_2 is much smaller than Z_1 therefore we can neglect Z_2 in the denominator of above equation. The voltage measured by the lock-in amplifier V_{meas} is given by the following relationship.

$$V_{meas} = GV_{exc} \frac{C_{meas}}{C_{in}}.$$
 4.2

The gain of the circuit G depends on the electronics external to the circuit. For my setup G is 1.0; therefore I can write

$$\frac{V_{meas}}{V_{exc}} \approx \frac{C_{meas}}{C_{in}}.$$
4.3

The key point is that low input capacitance means larger signal. The input capacitance of the HEMT is only 0.3 pF. It is important to keep in mind that the stray capacitance adds to this parameter. In other words, the geometric self-capacitance of the entire device must be less than \sim 0.1 pF. This sets the 1 mm as the size limit of the tip plus circuit system. Finally, it is straightforward to convert from the measured capacitance to the rms charge induced on the tip:

$$q_{tip} = C_{meas} V_{exc} = V_{meas} C_{in}, \qquad 4.4$$

where we have assumed an equality for Eq. 4.3.

Our circuit is ultimately limited in sensitivity by the Johnson noise in the bias HEMT, which gives a charge sensitivity of 0.15 electrons/ \sqrt{Hz} at 4.2 K [66]. However, if the input capacitance is too large it directly reduces the value of the signal so that other sources of noise will start to dominate, decreasing the sensitivity.

Chapter 5

Methods and Experimental Techniques

5.0 Introduction

In my experiment, I study the electronic structures of dopants which are buried about 15 nm below the surface of silicon. The usual STM method cannot probe subsurface dopants. However a modification to the STM, utilizing the same scanning unit, can be used to probe structures below the surface. This technique is called Charge Accumulation Imaging (CAI) [9, 71, 72, 73, 74]. The measurement basically consists of monitoring the image charge induced on a metallic tip due to an excitation voltage applied to the sample. Unlike the STM tip, our tip is connected to a charge sensor. Some fraction of electric field lines emerging from charges entering the subsurface dopants are terminated on the apex of the sharp tip, hence inducing charges of opposite sign on the tip. In this way charge flowing in and out of the sample induces charge to flow in and out of the tip. By monitoring this signal, we

can locally map out the charging of the dopants inside the dopant layer. This chapter describes the methods and experimental techniques used in all our measurements.

5.1 Voltage lever arm

An important aspect of the CAI measurement is the voltage lever arm of the sample (also referred to as the α -parameter). Changing the voltage of the tip relative to the substrate shifts the potential in the dopant layer. However the potential shift is less than the full voltage applied to the tip. The value of the lever arm parameter depends on geometry of the sample and it sets the reduction factor between the voltage applied to the tip and the voltage actually felt at the dopant site. As a simplified example, let's suppose that the dielectric constant of the material is one and that a dopant is located below the tip and midway between the substrate and the tip. Lastly, let's assume here that the tip acts as a parallel plate. Now if one volt is applied to the tip, i.e., $V_{tip}=1$ V, with the substrate grounded, the potential at the dopant is $V_{dopant}=0.5$ V. In this case, one-half of the voltage drop occurs between the tip and the dopant and one-half of the drop occurs between the dopant the dopant and one-half of the drop occurs between the tip and the voltage lever arm is $\alpha = V_{dopant}/V_{tip} = 1/2$.

A realistic model must consider that the dopant is actually immersed in a dielectric which partially screens the electric field. With regard to the tip, this electrode can be modeled as a sharp needle with a radius of curvature at the apex of tens of nanometers, positioned 1-2 nm above the dielectric surface. Such a model is considered in detail by Tessmer and Kuljanishvili [75]. Applying the model to my sample, given the Si dielectric constant of 11.5, the 15 nm depth of the dopant layer, and the 20 nm separation between the dopant layer and substrate electrode, yields $\alpha \sim 0.15$. The precise value of α depends on the distance between the tip and the dopant in question, and the size of the gap between the tip and the surface. (The lever arm is 11.5 times more sensitive to variations of the gap compared to distance variations within the sample; essentially the absence of the dielectric in the gap means the electric field gradient is 11.5 times greater.)

5.2 Nulling voltage

Another key parameter of the system is the contact potential between the tungsten tip and silicon sample which arises from the work function difference of the two materials. This

parameter represents an offset voltage for which we must compensate. For clarity, I shall refer to the parameter as the nulling voltage, V_{null} . This is the effective zero voltage of the tip for which there is no electric field terminating on it. In principle, V_{null} can be calculated by taking the difference of work function measurements for the two materials, which can be found in the literature. (For my system, this approach yields a nulling voltage of about 280 mV). However, in practice for layered semiconductors the quantity must be measured as it can vary considerably depending on the density of permanently trapped charges [76]. Our measurement of the nulling voltage is discussed in Section 7.2.

5.3 Control of tip-sample separation

The motion of the sample holder with respect to the tip, which is attached to the central piezotube, is achieved by the applying a saw tooth wave to the appropriate quadrants of the carrier piezotubes. During the fast part of the pulse the sample holder slides with respect to the steel balls due to inertia. During the slow part of the saw tooth pulse the sample holder moves along with the supporting elements due to the friction between the ramps and the steel balls. Depending on the signs of the pulses applied to the different quadrants, the sample holder can be made to move in the vertical and horizontal directions. The amplitude and frequency of the saw tooth signal control the step size of the sample motion from a few nm up to a μ m per step. Coarse movement on a scale of millimeters can be achieved horizontally. Coarse movement on a scale of hundreds of microns can be achieved in the vertically direction by applying the saw-tooth in a rotational sense, causing the sample holder to rotate. Figure 5.1 shows the quadrants of piezotubes and the sequence for vertical motion.

5.4 Modes of operation of microscope

Our microscope can operate in three totally independent modes. These are the tunneling mode, capacitance mode and Kelvin probe mode. Figure 5.2 shows a schematic of the three modes. Our microscope is designed to operate inside a standard ³He refrigerator manufactured by Oxford Instruments. All capacitance mode measurements were done at a temperature of 4.2 K as described in Section 4.5 (some calibration and testing measurements were done at 77 K). For every data run we start by scanning the tip in the tunneling mode to check that the surface is clean and there are no major electronic defects. If any defects or dirt on the surface are found, we can easily move the tip to a different part of the surface.



Figure 5.1 (a) Schematic representation of a typical scanning probe piezotube with four quadrants. (b)The top view. The quadrants denoted with +X, +Y, -X, and -Y are used for mechanical control. (c) Schematic of the three carrier piezotubes indicating motion in a rotational sense.



Figure 5.2 Three modes of operation of the microscope: charge accumulation mode (left), Kelvin-probe mode (middle) and tunneling mode (right).

5.4.1 Tunneling mode

The microscope can be operated in the conventional STM mode by suspending all AC voltages. To do this we bypass the charge sensor and attach the tip wire to a standard STM DC current-to-voltage converter. In the surface topographic imaging mode, the tip is scanned over the surface of the sample while the tunneling current is maintained constant. A fixed bias voltage is applied and the desired tunneling current is set. As the tip is scanned across the surface of the sample, variations in the topography of the sample and the underlying electronic structure affect the tunneling current [77, 78]. In order to keep the pre-selected value of the tunneling current constant, a feedback loop provided by the microscope control electronics is used to adjust the position of the tip above the sample surface. The feedback voltage, corresponding to the vertical position of the tip is recorded, reflecting the surface topography. The set current and the set bias voltage depend on the nature of the sample. The tunneling current is typically set to a range of 0.1-1.0 nA for graphite or silicon samples.

The tunneling mode proves useful for finding any defects or absorbed particles on the surface of the sample. It can also accurately determine the tilt of the sample plane relative to the horizontal so that one may apply the appropriate plane compensation parameters to the scan piezotube to correct for this effect. This is particularly important when we wish to proceed to the capacitance mode since in this mode the microscope scans at a constant tip height with the feedback loop turned off. Any uncompensated slope may cause the tip to crash into the sample.

5.4.2 Capacitance mode

Charge Accumulation Imaging technique is done in the capacitance mode. With the tip positioned a few nanometers from the sample, the sample and tip system can be thought of as a parallel plate capacitor. Any movement of charge in the sample results in a changing image charge on the tip, which we monitor. Figure 5.3 shows aspects of the CAI technique.

Positioning of the tip is first achieved in tunneling mode, where a constant tip sample distance is controlled by a tunneling current feedback loop. Once the tip is in range (i.e. a tunneling current is observed), we use the z off-set of our piezotubes to move the tip away from the sample for about 30-40 nm and then move it laterally sufficiently far from the tunneling location to an unperturbed location. Then with the feedback off, the tip is brought closer to the surface using manual fine approach. The measurement proceeds by recording the signal in phase with the AC excitation voltage with the aid of a lock-in-amplifier. If the measurement is obtained while the tip is scanned close to the sample surface one obtains a charging map. The dopants sites can be in principle marked by the increase in image charge as shown in the sketch of Fig. 5.4 (b).

We may also carry out a different measurement by keeping the tip at a fixed position above the surface while varying the bias voltage. This measurement yields capacitance-voltage curves. The resonance voltages will be found as peaks in the charging as a function of the bias voltage. A sketch of a resonance peak is shown in Fig. 5.4 (a). To be clear, our plotted C-V curves represent the change in capacitance as a function of voltage. In other words, we subtract away the background capacitance from

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Figure 5.3 (a) Schematic of Charge Imaging method. Charge entering the sample induces image charge $q_{i\mu}$ on the tip, which is monitored using a cryogenic charge sensor. The charge sensor has a sensitivity of 0.15 electrons/Hz. (b) An example of charging structure measured in a GaAs-AlGaAs two-dimensional electron system using this technique. The dark spot is an area of reduced charging which resulted from an effective reduction in the concentration of Si dopants [9].



Figure 5.4 A schematic representation of the anticipated charge accumulation data. (a) Spectroscopic data. The sharp peak represents the voltage for which an energy level in the dopant layer is in resonance with the Fermi level of substrate. (b) A representation of scanning capacitance image with the tip voltage fixed near the peak voltage. Yellow indicates a high capacitance and dark red indicates a relatively low signal. We anticipate that distinct high-capacitance features will mark the locations of the subsurface dopant sites within the plane.

the plotted curves using the bridge circuit described in Chapter 4. To compensate for electronic noise and drift effects in both types of measurements, several curves and capacitance images are averaged together to achieve an acceptable signal-to-noise ratio. At the end of every capacitance image data run we convert to the tunneling mode to study the surface of the sample; this allows us to check if there are any features in the topography that may lead to artifacts in the capacitance images.

5.4.3 Kelvin probe mode

The Kelvin probe measurement is a technique used to measure the contact potential between two surfaces that are brought in close proximity [9, 79, 80]. This method requires the tip to oscillate in order to modulate the tip-sample separation; this in turn modulates the tip's charge giving a signal Δq_{tip} . Ideally, one can find V_{null} from the tip voltage for which Δq_{tip} vanishes. Unfortunately, for my system I have found that the stray electric field emanating from the electrodes of the oscillating piezoelectric tube results in an artifact in the measurement. As an alternative, we have developed a method to measure the nulling voltage that does not require the tip to oscillate. Instead, we rely on the step structure that appears in the capacitance measurement, as described in Section 7.2.

5.5 Procedure for analyzing the C-V curves

As part of my analysis, I compare the capacitance peaks in the C-V curves with calculated fitting curves. These fitting curves are based on single-electron capacitance peaks, which are essentially the convolution of semi-elliptical peaks with the derivative of the Fermi distribution function scaled by the lever arm parameter α [72, 81, 82]. As

mentioned in the previous section, the measurement here utilized an amplifier output low-pass filter with time constant τ , which tends to further broaden the peaks. This can be incorporated into a calculation by performing a simple integration. To generate the fitting curves, we used a modeling routine that superposes 4-6 single-electron peaks and then integrates the resulting curve appropriately. The excitation amplitude, temperature and time constant were fixed parameters, set to the experimental values of $V_{exc} = 3.7$ mV and T=4.2 K, $\tau = 3.0$ s. The parameters α and V_{tip}^{peak} were considered as free and hence varied to achieve the best fit. We find that this procedure reproduces the measured curves well. (See for example, Fig. 7.6 in Chapter 7.)

Chapter 6

Testing and Calibration of the Microscope

6.1 Calibration of the scanning unit

After putting our scanning unit together, the first thing to do is to test if the microscope can achieve simple STM atomic resolution. A graphite sample was used for this purpose. Obtaining atomic resolution images of graphite demonstrates that the scanning unit is stable. Graphite crystals consist of layers of carbon atoms. In each layer, carbon atoms are covalently bonded into hexagons, while different layers are connected together by weak van der Waals forces. Carbon atoms on the graphite surface appear in the STM images as a triangular lattice which contains every other atom, not as honeycomb rings as would be expected. This asymmetry was explained by Tomanek as a purely electronic effect due to the interlayer interactions [83]. Essentially there are two nonequivalent carbon atom types in each layer. Carbon atoms of one type have neighbors directly beneath them in the underlying atomic layer as shown in Fig. 6.0 (a). Carbon atoms of the second type do not have neighbors directly beneath them. Band structure calculations predict that atoms visible in the STM image are ones that do not have the subsurface atom beneath them. In Fig. 6.0 (a), open circles represent atoms that appear in an STM image. Fig. 6.0 (b) shows carbon atoms in the STM image of graphite I obtained at a tunneling current of 0.5 nA and bias voltage of 50 mV. The scan range is 2.00×1.80 nm. This image clearly demonstrates that our scanning unit is stable at the atomic level.

Once atomic resolution is obtained, the next step is to calibrate the scanning unit's scan range. The purpose of the calibration is to know the sensitivity of the piezotubes. This calibration was done at room temperature with the system in the

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tunneling mode. For the lateral sensitivity of the piezotubes graphite samples were used. An STM image of graphite with good atomic resolution is used to obtain the correct value for the x and y scan range, knowing that graphite plane lattice constant is 2.46 Å. The STM image of graphite used for the x and y calibration is shown in Fig. 6.1 (a). This image was obtained at the tunneling current of 0.5 nA and bias voltage of 60 mV. The scan range was 1.10×1.25 nm. For a particular STM image, the applied voltage to the scanning piezotube for motion in the lateral direction is known. The lateral sensitivity of the piezotube is then determined as a measure of lateral displacement per unit volt.

A standard calibration sample, provided by Veeco Instruments was used for vertical z calibration. This sample is silicon patterned into a mesh of squared pits and covered with platinum. The value used for z calibration is the actual depth of the platinum pits which is 180 nm. The squared pits are 5 μ m in size, with the same size of separation between them. As the room temperature scan range of the scanning unit is 5 μ m, we can only hope to find an edge of the pits as shown in Fig. 6.1 (b). Using the same method as for the lateral calibration, the z sensitivity of the piezotubes can be obtained. The sensitivity values I obtained for our scanning unit at room temperature are: x sensitivity = 29.31 nm/V, y sensitivity = 36.22 nm/V and z sensitivity = 1.04 nm/V. As the piezo response is known to be reduced by a factor of 1/5.60 at helium temperatures [84], from these values we were able to determine that the sensitivities at 4.2 K as 5.23 nm/V, 6.46 nm/V and 0.19 nm/V respectively for the x, y and z directions.

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Figure 6.0 (a) Schematic drawing of two successive layers of hexagonal graphite. Open solid circles represent atoms that appear in an STM image. (b) Carbon atoms in the STM image of graphite obtained at the tunneling current of 0.5 nA and bias voltage of 50 mV. The scan range is 2.00×1.80 nm. Obtaining image (b) demonstrates the scanning unit is sufficiently stable.



Figure 6.1 Images used for calibration of scanner. (a) An STM image of graphite obtained at the tunneling current of 0.5 nA and bias voltage of 50mV with a scan range of 1.10×1.25 nm. (b) STM image of platinum sample showing the edge of one of the pits. From these images the *x*, *y* and *z* sensitivity of the piezotubes were obtained.

6.2 Testing of microscope

Before I started work on my sample at 4.2 K, I performed some preliminary tests at 77 K using my sample and also a GaAs sample. For my sample the first test was to scan the surface at various places in STM mode in order to find the best place to do the capacitance measurements. From these measurements we see that the sample surface is generally flat with some small undulations of less than 5 nm. Figure 6.2 (a) shows a typical topography image of my sample. The scan range for this image is about 500 nm x 500 nm. Fig. 6.2 (b) is a cross-section along the path marked by the double arrow in Fig. 6.2 (a). I also scanned the surface of a GaAs sample, shown in Fig. 6.2 (b), in order to compare the topography of the two samples. The topographic image of GaAs show the typical growth features in the form of surface mounds which are $\sim 1 \mu m$ long and $\sim 5 nm$ high. These STM images were taken at 77 K.

I also performed the capacitance-mode C-V measurements at 77 K. When I averaged as many as 32 curves I could discern peaks and a capacitance step; these features were similar to data obtained at 4.2K, shown in the next chapter. Although the data were relatively noisy and contained some artifacts related to tip instabilities, the curves indicated that the experiment was working, encouraging me to perform the measurement at 4.2 K.



Figure 6.2 Topography images of silicon and GaAs samples. (a) A typical STM image of the silicon sample surface, the scan range for this image is about 500 nm x 500 nm. (b) A cross-section along the path marked by the double arrow in (a). (c) The topographic image of GaAs showing the typical growth features of the GaAs surface of $\sim 1 \mu m \log and \sim 5 nm$ high. These STM images were taken at 77 K.

Chapter 7

Single Dopant Charging Results and Discussions

7.1 Introduction

We start here by reviewing the procedure for performing my measurements. All measurements were performed at 4.2 K which was achieved by direct immersion of the whole microscope in liquid ⁴He. A chemically-etched tungsten tip of ~25 nm radius was positioned within a few nanometers of the sample surface. Positioning of the tip is first achieved in tunneling mode, where a constant tip sample distance is controlled by a tunneling current feedback loop. Once the tip is in range (i.e. a tunneling current is observed), we use the z off-set of our piezo tubes to pull the tip away from the sample for about 30-40 nm and then move it laterally sufficiently far from the tunneling location to an unperturbed location. Then with the feedback off, the tip is brought closer to the surface using manual fine approach.

With the system in capacitance mode, the capacitance curves (C-V) are acquired by positioning the tip about 1 nm from sample surface and holding it at the fixed location while sweeping the tip voltage. To acquire the capacitance images, we scan the tip over the sample surface while maintaining a fixed bias voltage. This bias voltage is selected to correspond to the peaks that appear on the capacitance curve. To compensate for noise and drift effects in both types of measurements, several curves and images are averaged together to achieve an acceptable signal-to-noise ratio.

As described in Chapter 4, our sensor circuit includes a bridge that allows us to subtract away the background mutual capacitance of the tip and sample, which is approximately 20 fF. This means that our plotted C-V curves represents the change in capacitance as a function of voltage. As a reminder, we can convert from the measured capacitance C_{meas} to the charge induced on the tip using the equation,

$$q_{tip} = C_{meas} V_{exc}$$
,

where V_{exc} is the excitation voltage applied to the sample.

In the analyses that follow we refer to charges as holes entering and exiting states of the acceptor atoms. However, this is an interpretation of the data; the measurement is not sensitive to the sign of the charge carrier. Moreover, conceptually a hole entering an acceptor is equivalent to an electron exiting the state. With regard to the noise in the images and *C*-*V* curves, the charge sensor itself attains a sensitivity of $0.15 \ e/\sqrt{Hz}$. As will be shown on the following pages, I find that vibrations in my system are sufficiently small such that the achieved noise level is consistent with this value. An experimental challenge for these measurements is the long data acquisition time required to achieve single-hole sensitivity. Essentially the rate of data acquisition must be of order 1 s⁻¹. For the data presented here, we used a rate of 0.33 points per second for the *C*-*V* curves, and ~5 pixels per second for the capacitance images. In contrast to STM methods, we do not use feedback to maintain the tip position. This puts a stringent demand on the stability of the tip position.

7.2 Observed capacitance curves and determination of the nulling voltage

C-V curves acquired with our probe consistently showed the two types of features indicated by the arrows in Fig. 7.1 (a), which is a representative capacitance curve. The horizontal axis is the raw tip voltage V_{raw} , which is the actual voltage on the tip with respect to the substrate, without compensating for the contact potential (see Sec. 5.2). Two types of structures are evident: The green arrow marks a step structure that reproducibly occurred near -0.30 V, with little dependence on the lateral position of the tip. The red arrow indicates a peak structure, which was found to occur in the voltage range of -0.150 \pm 0.075 V. We find the magnitude and voltage of these peaks varies as the tip is moved from one position to another.

Before analyzing the peaks, we turn our attention to the step structure, which is similar in appearance to capacitance steps observed in previous capacitance measurements [6, 72]. We interpret the step structure (green arrow in Fig. 7.1) as the capacitance increase due to the accumulation of charge in a surface potential well. Although a detailed description of the formation of this layer is complicated by the fringing nature of the tip's electric field, we can estimate the threshold potential using a parallel-plate picture. The first charge will enter the surface accumulation layer at a tip potential of

$$V_{lip} = V_{raw} - V_{null} = -(\phi_B + \Delta) / \alpha e, \qquad 7.1$$

where V_{null} accounts for the contact potential, e is the elementary charge, Δ is the quantum level spacing between the bottom of the well and the first hole state to appear, and α in this case is the voltage lever arm with respect to the surface (see Sec. 5.1).



Fig 7.1 (a) Representative capacitance data, plotted with respect to the raw tip voltage. Two types of features were consistently observed: peaks near V_{raw} =0.15 V (red arrow) and a step near -0.30 V (green arrow). The peaks are consistent with single charges entering the dopant layer. The step is consistent with the formation of an accumulation layer at the sample surface. (b) Valence-band diagram (reproduced from Fig. 3.7) showing our interpretation of the peaks as holes entering acceptor atoms, and the step as an accumulation layer formed at the semiconductor surface.

We expect α to be about 0.15 directly below the apex [75, 81], and ϕ_B =11.7 meV [10]. With regard to Δ , the accumulation layer will initially form a quantum dot below the apex of the tip of radius ~25 nm, determined mostly by the tip radius. From a simple estimate based on a quantum box of this size, and using a hole effective mass of half of the free electron mass, we find $\Delta \approx 10$ meV. These values give a threshold voltage of about -150 mV. As V_{tip} increase further, the dot will grow in size and more charges will enter. As a result, a conducting surface layer is expected to form, giving rise to the characteristic step-like C-V curve [81].

We can extract V_{null} for my sample and tip by comparing two or more C-V curves that are acquired with the tip positioned at different distances from the sample surface. This is shown schematically in Fig. 7.2. For example, suppose for Curve 1 the tip is a distance from the surface of $d_{gapl}=2.0$ nm and for Curve 2 the tip is a distance of $d_{gap2}=1.0$ nm. From a parallel-plate picture, we expect that the lever arm parameters follow $\alpha_2/\alpha_l=(d+\kappa d_{gap1})/(d+\kappa d_{gap2})$, where d is the distance from the surface to the conducting substrate and κ is the dielectric constant. Plugging in the values for my sample, we get $\alpha_2/\alpha_l=(35 \text{ nm} + 11.5*2.0 \text{ nm})/(35 \text{ nm} + 11.5*1.0 \text{ nm})= 1.25$. Hence the threshold voltage will be higher for Curve 1 compared to Curve 2 by a factor of 1.25.

Of course, due to the fringing field emanating from the tip, we do not expect the parallel-plate expression to strictly apply. However, the lever-arm parameter must decrease as the tip distance increases, and the threshold voltage will increase accordingly. More generally, the entire C-V curve will expand with respect to voltage as the tip distance increases. If we account for this scale factor, the functional form of the curve should not change as long as the tip-surface distance is small compared to the radius of



Figure 7.2 Schematic of capacitance technique to extract the nulling voltage V_{null} . This is the effective zero voltage, the potential for which no electric field terminates on the tip. The method uses the step feature that correspond to the tip-surface separation and the lever-arm, respectively. (top) Two capacitance curves acquired at different tip positions, plotted as a function of the raw tip-voltage. (bottom) The same two curves plotted with a new voltage scales V^* . In principle, the two curves will only coincide if they are rescaled with respect to the nulling voltage, as indicated.

curvature of the tip and the distance from the surface to the substrate electrode. Because the effective tip voltage is $V_{tip} = V_{raw} - V_{null}$, the voltage expansion should be centered on $V_{tip} = V_{raw} - V_{null} = 0$, or with respect to the raw tip voltage, $V_{raw} = V_{null}$. In other words, if we compare C-V curves acquired at different tip distances, with voltage plotted on the horizontal axis, we expect to find similar curves except that they are scaled horizontally with respect to the nulling voltage. This is illustrated in Fig. 7.2.

To extract the most accurate value for the nulling voltage from my measurements, I focus on data acquired with an especially blunt tungsten tip. In this case, the amplitudes of the C-V curves were eight times greater in magnitude than the curves acquired with the sharpest tips, yielding a favorable signal-to-noise ratio. The large amplitude indicates a radius of curvature of tip's apex of ~120 nm. Fig. 7.3 (a) shows two especially stable curves acquired with this tip at distances of 2 nm and 1 nm, as indicated. (Other data were also acquired at different distances with this tip, however these curves exhibit more scatter).

As a guide to determine the scaling factor, the two curves of Fig. 7.3(a) are fit with the following step-function:

$$y = P_2 + \frac{P_1 - P_2}{1 + e^{(V - P_3)/P_4}} + P_5(V - P_6)^2, \qquad 7.2$$

where y is the normalized capacitance, V is the tip voltage, and the P's are free parameters, varied to achieve the best least-squares fit. The first term is a constant; the second term has the same form as the familiar Fermi function; the third term is parabola. Figure 7.3 (a) Two capacitance curves acquired with a blunt tip at nominal distances from the surface d_{gap} of 1 nm and 2 nm, as indicated. The clear step-like curve is consistent with charge accumulating on a surface conducting layer. The data were acquired at a temperature of 4.2 K. The solid curves are least-squares fits, using the step function shown in Eq. 7.2. For the solid Curve 1, the fitting parameters are P₁=-0.63822, P₂ =1.0374, P₃=-0.10295, P₄=0.03251, P₅=10.07723 and P₆=0.04011; for the solid Curve 2, the fitting parameters are P₁=-2.61947, P₂ =1.08667, P₃=-0.13956, P₄=0.03600, P₅=45.71289 and P₆=0.01299. (b) The same two curves normalized and plotted with voltage scales V* for which V_{null} and α_2/α_1 were chosen to yield the best agreement. The best-fit parameters are V_{null}=-0.068 and α_2/α_1 =1.295.



(a)






We include the third term to allow for asymmetry about the inflection point and thus produce a better fit. (If we use only the best-fit Fermi function without the third term and then apply the same procedure to find nulling voltage, in the end we arrive at a nearly identical value for V_{null} .) We see from Fig. 7.3 (b) that the data are well-fit with this function, shown as the solid curves.

Figure 7.3 (c) shows the data with the voltages shifted and rescaled, following Fig. 7.2, so that the two curves coincide. The best fit is achieved with a nulling voltage of V_{null} =-0.068 V, as shown. To estimate the accuracy of this value, we consider the fact that if we try to fit the two curves with V_{null} =0.048 V or V_{null} =0.088 V, then for the best fit that can be achieved the solid curves have a maximum deviation of about 0.20 in the normalized units. This is comparable to the average scatter in the data. To be specific, we define the rms scatter of the measured data M as $\sqrt{\frac{1}{N}\sum_{i}(M_{i} - y_{i})^{2}}$, where M_{i} is an individual data point, y_{i} is the corresponding point from the step-function curve, and N is the number of data points. For both of the curves this equals 0.018 in the normalized units. Hence we estimate the uncertainty in the nulling voltage to be 0.020 V; i.e., V_{null} =-0.068 \pm 0.020 V. The 20 mV uncertainty in the nulling voltage is a source of uncertainty for the E^{+} values extracted from my data. However, due to the lever arm factor which scales the tip potential to the dopant layer, the 20 mV contributes about 2 meV to the uncertainty in E^{+} . This is comparable to other sources of uncertainly, as

discussed in Sec. 7.4.

Returning to Fig. 7.3(b) we see the best fit was achieved with a scale factor of $\alpha_2/\alpha_1=1.295$. This is close to the value of 1.25 expected from the parallel-plate

expression. The parallel plate model also predicts that the capacitance should scale with the lever arm. Hence in the un-normalized units, Curve 2 should be 25% taller than Curve 1; however it is actually only 10% taller. This discrepancy reflects the limitations of the parallel-plate model applied to the tip-sample system.

All subsequent data that I will present in this thesis were acquired with a sharper tungsten tip with a radius of curvature at the apex ~25 nm. Here I show data acquired with this sharper tip, and I give more details of the data acquisition and processing. Fig. 7.4 shows data similar to Fig. 7.3, acquired with the sharp tip held at the indicated distances from the surface. Each curve displays the average capacitance of eight consecutive voltage sweeps. The individual data points for each sweep were acquired with a three-second time increment, which was equal to the time constant setting of the amplifier output filter. Hence the effective averaging time for each data point in Figure 7.4 is 24 seconds. No additional filtering or processing was performed. Unless otherwise noted, capacitance data presented in this thesis were acquired with a similar procedure, with a nominal tip-surface distance of 1 nm. The curves display clear peak and step-like structure, indicated by the red and green arrows, respectively. We see that a reasonable agreement is achieved if the two curves are plotted with rescaled voltages, with respect to a nulling voltage of $V_{null} = -0.068 V$; this is consistent with the nulling voltage found with the blunt-tip data set.

With regard to the noise level, we see from Fig. 7.4 that the scatter in the data is about 1 aF, which corresponds in charge units to about 0.03 electrons (this is found by simply scaling with the 3.7 mV excitation amplitude). For comparison, the noise level of our charge sensor is 0.15 electrons/ \sqrt{Hz} . For this measurement, we therefore expect a

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Figure 7.4 (a) Two capacitance curves acquired with a sharp tip at nominal distances from the surface d_{gap} of 1 nm and 2 nm, as indicated. The 1 nm curve is shifted vertically by 5 aF for clarity. The curve displays clear peak and step-like structure, indicated by the red and green arrows, respectively. The data were acquired at a temperature of 4.2 K. (b) The same two curves normalized and plotted with voltage scales V*. In this case a nulling voltage of 0.068 V is used, consistent with the blunt-tip data set (Fig. 5.6); α_2/α_1 was chosen to yield the best agreement, which in this case is $\alpha_2/\alpha_1=1.200$. We see that a reasonably good fit is achieved. The same tip was used for all subsequent measurements presented in this thesis.

noise level of about $0.15/(\sqrt{24}) e = 0.031 e$, in agreement with the approximate scatter in the data. In comparison to the blunt-tip data set, these data exhibit a considerably reduced signal-to-noise ratio. For this reason, for the nulling voltage parameter, I will rely on the analysis presented in Fig. 7.3 which yielded a value of V_{null} =-0.068 ± 0.020 V.

Section 7.3 Capacitance images and further analysis

Figure 7.5 (a) reproduces the representative data from Fig. 7.1; in this case we have compensated for the contact potential by displaying the voltage axis with respect to V_{tip} . Fig. 7.5 (b) shows a representative 70 x 50 nm capacitance image, acquired by fixing the voltage at V_{tip} =-0.076 V while scanning the tip. The data are unfiltered and minimally processed (a standard line-wise correction was performed to remove drift effects in the vertical direction). Bright high-capacitance features are clearly present, as indicated by the red dots.

Do the bright spots correspond to boron dopants? If we consider the density of boron dopants in the delta-layer, 1.7×10^{11} cm⁻², then the number of dopants expected in a 70 x 50 nm area is about five. Indeed, here we observe six bright spots. Several similar capacitance images were acquired and confirm that the number of bright features approximately agrees with the expected number of boron acceptors. Moreover, comparisons to topographical images of the surface, acquired by using our method in tunneling microscopy mode, consistently show no correlation between the surface topography and the capacitance features. Fig. 7.5 (c) shows the cross section of a



Figure 7.5 (a) Representative capacitance data reproduced from Fig. 7.1. Here we have compensated for the contact potential by displaying the voltage axis with respect to V_{up} . (b) A representative 70 x 50 nm capacitance image, acquired by fixing the voltage at V_{up} =-0.076 V while scanning. The data are unfiltered and unprocessed, other than a standard line-wise correction to remove drift effects in the vertical (slow scan) direction. Bright high-capacitance features are indicated by the red dots. (c) The capacitance profile of an individual dopant; r=0 corresponds to the center of the bright spot. To reduce scatter, we have averaged three paths as indicated. This averaging does not change the general shape compared to an individual path through the dopant. In this case the measured curve (black dots) is well described by a Lorentzian-squared $[1+(r/15)^{-12}$ (blue curve).

relatively isolated bright spot. We see that the feature is well reproduced by the square of a Lorentzian peak of width 15 nm, $[1+(r/15 \text{ nm})^2]^{-1}$. This functional form arises essentially from a convolution of two Lorentzians [15, 75, 85] and is consistent with charge entering a single atom. Hence considering both the *C-V* curves and capacitance image data, we conclude that we are observing the B^+ state of individual boron dopants; the peaks in the *C-V* curves correspond to the binding energies of the B^+ state of the boron dopants and the imaged high-capacitance bright spots mark the locations of the boron dopants. We find that these peaks shift on the scale of tens of millivolts and often resembled multiple peaks, depending on the location of the probe.

Figure 7.6 shows a data set for which I obtained a high-quality capacitance image and subsequently acquired several C-V curves at two locations within the imaged area. The scatter plots to the right show the measured peak structure at the high-capacitance features A and B, as indicated. The C-V curves marked 1 and 2 show data taken at the same place (A) but separated by 16 hours. The lower curve was taken when the tip was moved to location marked B. The solid curves show calculated fits based on singleelectron capacitance peaks, introduced in Sec. 5.5, which are essentially the convolution of semi-elliptical peaks with the derivative of the Fermi function [72]. In these C-V curves, we focus on the peak structure. To examine the details of the peaks, we have subtracted away a linear background from each curve, similar to the grey line shown in Fig. 7.5 (a). The vertical axis is converted to charge and displayed in units of e.



Figure 7.6 Data set showing an integrated capacitance image and spectroscopy. The image is to the left. The plots on the right display C-V curves in charge units acquired at the indicated locations, A and B. To emphasize the peak structure, I have subtracted a fits from the model based on the assumption that each peak corresponds to a single hole entering the system (as discussed in Sec. 7.4). The top panel shows two curves nominally acquired at the same location A, but with a time delay of 16 hours. The top curve is shifted vertically by 0.12e for clarity. The curves show similar peak structure, but some of the features have shifted in voltage by as much as 10 mV. These lead to -1 meV shifts in the extracted quantum energies (as discussed in Sec. 7.4). The arrow indicates the tallest or primary peak. The lower panel shows the measurement and fit for location B. We see that the C-V curve exhibits two prominent peaks of nearly equal magnitude. This most likely arises from two closely spaced acceptors at location B.

7.4 Determination of addition energy of individual boron dopants

To analyze the peak structure, we consider a quantum state with energy E^+ with respect to the valence band edge (see Fig. 7.1(b)). The resonance tip voltage for this state will be

$$V_{tip}^{peak} = -\frac{(\phi_B - E^+)}{\alpha e}; \qquad 7.3$$

this is a similar expression to Eq. 7.1, which described the threshold voltage for the capacitance step. In this case α is the lever arm parameter with respect to the particular dopant. To extract the values of E^+ from our data we used α parameters determined for each peak by its observed charge magnitude. In other words, we perform a case-by-case measurement of the lever arm; this is desirable as the parameter depends on both the lateral (x, y) and vertical (z) distance between the dopant and the apex of the tip. Specifically, we scale the vertical axis of the C-V curve by V_{exc} to convert to charge units, and then examine the peak height, which must equal αe due to the quantization of charge [15, 86].

As an example, consider the three peaks shown in Fig. 7.7(a) which were taken from three different locations; these peaks are similar to the ones shown in Fig. 7.6, except that they are relatively well isolated from neighboring peaks. The measured α parameters for the peaks labeled 1, 2 and 3 are 0.067, 0.0833 and 0.0971 respectively and the extracted E^+ energies from Equation 7.3 are 10.26 meV, 6.65 meV and -0.49 meV respectively. By probing different areas on the sample, we have observed 20 peaks of sufficient quality to apply this procedure. Fig. 7.7(b) shows the resulting histogram of the extracted energies, which have a mean value of $E^+ = 4.3 \pm 3.1$ meV, where the uncertainty is determined by the standard deviation. This compares well to the average B^+ energies of 6.7 meV observed for a similar sample by Caro and coworkers [10]. Fig. 7.7(c) is a table showing the peak voltages, α parameters and the extracted E^+ for all the 20 distinct peaks.



Figure 7.7 (a) Data showing three distinct peaks that are relatively isolated. The measured α parameters for the peaks labeled 1, 2 and 3 are 0.067, 0.0833 and 0.0971, respectively. (b) A histogram of the quantum state energies E^+ , extracted from measurements of 20 distinct peaks. The mean value and standard deviation of the distribution are 4.3 meV and 3.1 meV, respectively. (c) A table showing the peak voltages, α parameters and the extracted E^+ for all of the peaks.

As to the widths of the peaks, we find that these are indeed consistent with the model for single charges as described below. For unfiltered data, four parameters determine the functional form of single-electron peaks: the excitation amplitude V_{exc} , the temperature T, the local lever arm α , and the peak voltage V_{lip}^{peak} . The measurement here utilized an amplifier output low-pass filter with time constant τ , which tends to further broaden the peaks. This can be incorporated into a calculation by performing a simple integration. The fitting curves were generated as discussed in Section 5.5. The parameters α and V_{tip}^{peak} were considered as free and hence varied to achieve the best fit. We see that this procedure reproduces the measured curves well. For example, the top solid curve of Fig. 7.6 (location A) invokes five peaks for which V_{tip}^{peak} ranges from -30 mV to -130 mV. The lever-arm varies significantly from peak to peak; $\alpha = 0.156$ for the primary peak (red arrow) and α =0.091 for the relatively short leftmost peak. We interpret the primary peak as a charge entering an acceptor directly below the tip's apex whereas the other peaks correspond to the charging of more distant acceptors within the plane.

To see the reproducibility of our data, we go back to Fig. 7.6 where two curves labeled (1) and (2) are shown which were nominally acquired at the same location A, but with a time delay of 16 hours. We see that the curves have similar features, but the amplitudes and voltages of the peaks have changed somewhat. We attribute these changes to drift of the actual tip location, which alters the lever arm parameter for each acceptor atom. Applying Equation 7.2 to each curve to extract the energy of the acceptor state corresponding to the primary peak, we find $E_A^+(1)=0.2$ meV and $E_B^+(2)=1.05$

meV. This comparison indicates that our analysis method is accurate to about 2 meV. The lower panel shows the measurement and fit for location *B*. We see that the *C-V* curve exhibits two prominent peaks of nearly equal magnitude, marked by two arrows. A careful analysis indicates that the peak on the left is the primary peak in that it is closer to the tip's apex; the extracted energy is E_B^+ =3.24 meV. The extracted energy from the right peak is 2.21 meV. We attribute the double peak to two closely spaced dopants near location *B*. In contrast, the dopants in the vicinity of *A* are likely more dispersed. This idea is explored in detail below.

1 2

7.5 Analysis of secondary peaks

For the data sets that show multiple peaks, thus far we have implied that the focus is on the tallest or primary peak, which corresponds to the dopant closest to the tip's apex. However, it is equally useful to examine the other peaks as well; these secondary peaks likely originate from neighboring acceptors not directly below the tip. In general, due to the decreased lever arm, more distant dopants will exhibit charging peaks of reduced magnitude and of greater peak voltage. As shown in Ref. [75], the lever arm for a subsurface dopant laterally displaced from the tip's apex is given by a Lorentzian function

$$\alpha(r)/\alpha_0 = [1 + (r/w)^2]^{-1}, \qquad 7.4$$

where r=0 corresponds to the location in the dopant plane directly below the apex, $\alpha_0=\alpha$ (0), and w is approximately equal to the depth of the underlying conducting layer, which is 35 nm for our sample. If we assume that $r\approx 0$ for the primary peak, we can rewrite the expression as

$$\frac{\alpha_S}{\alpha_P} = \left[1 + \left(\frac{r}{w}\right)^2\right]^{-1},$$
7.5

where α_P is the primary peak lever arm and α_S is the lever arm corresponding to a particular secondary peak. Fig. 7.8 (a) displays a table of the lever-arm fitting parameter, α for the *C-V* curves of Fig. 7.6 at locations *A* (curve 1) and B. The bottom two rows of the table in Fig. 7.8 show α_S / α_P for each secondary peak and the estimated distances to the respective acceptors, based on Equation 7.5. In Fig. 7.8 (b) the triangles mark the likely locations of dopants based on the local maxima of the capacitance image. The dashed circles show the approximate area of interaction for the tip while positioned at *A* and *B*. A comparison of the distances of the triangles from the center of the respective circles and the distances extracted from the *C-V* curves shown in the bottom row of the table shows rough agreement. The agreement is especially good, to a precision of about 5 nm, for location *B*, for which the extracted distances are all 25 nm or less.

In order to gain more insight into the physics involved when two dopants are close together, in the following section we compared our data to a simple hydrogenic model that combines the effective-mass approximation and configuration-interaction calculations of the electronic energies of a two acceptor molecule.

Curve B Peaks	Peak type	Р	S	S	S	S		
	Lever arm	0.156	0.114	0.097	0.091	0.071		
	$\alpha_{\rm S}/\alpha_{\rm P}$		0.73	0.62	0.58	0.46		
Curve B Peaks	Dist.from P (nm)		21	27	30	38		(.
	Peak type	Р	S	S	S	S	S	(a
	Lever arm	0.100	0.095	0.087	0.080	0.067	0.067	
	$\alpha_{\rm S}/\alpha_{\rm P}$		0.95	0.87	0.80	0.67	0.67	
	Dist.from P (nm)		8	14	18	25	25	

(b)

Figure 7.8 Estimating the nearest neighbor distance. (a) Tables of the fitting parameter, α for the *C-V* curves at locations *A* (top curve) and *B* shown in Fig. 7.3. The primary peak, *P*, corresponds to the resonance with the greatest lever arm, other peaks are referred to as secondary, *S*. The bottom two rows show $\alpha_S'\alpha_P$ for each secondary peak and the estimated distances to the respective acceptors, based on Eq. 7.5. (b) The capacitance image with triangles marking the likely locations of dopants. The hollow triangles correspond to dopants most likely too far from locations *A* and *B* to contribute to the respective *C-V* curves. The dashed circles are of fradius 25 nm to show the approximate area of interaction for the tip at the two locations

7.6 Configuration-interaction calculation

To explore theoretically the effect of neigboring dopants on the B^+ state, Professor J. F. Harrison of the Chemistry Department at Michigan State University calculated the energy needed to add a third hole to a system of two neutral acceptors separated by a distance R. The two acceptor model is shown in Fig. 7.9. The model incorporates two neutral acceptors and finds the binding energy of a third-hole; E^+ is positive if the third charge results in a lower electronic energy for the system, i.e., if the third hole is bound.

The calculations were performed using the configuration-interaction method in the effective mass approximation [87, 88, 89]. As discussed in Sec. 1.5, EMA is very much an approximate method for my system. While EMA-based modeling may be used as a guide for our understanding of long-wavelength effects, we do not expect a high degree of quantitative agreement between modeling and experiment.

The results of this calculation are shown as the red curve in the insert Fig. 7.10. The data points in Fig. 7.10 were extracted from measurements of dopants at different locations, including the data from A and B in Fig. 7.6. The blue line is the best fit line for our primary peak quantum energies plotted as a function of nearest-neighbor distance R. The error bars show the estimated uncertainty of the energy and distance. With regard to energy uncertainty, the error bars do not include the contribution from the nulling voltage (see Sec. 7.2), which gives a systematic 2 mV uncertainty to the labels on the vertical axis. For the calculation (red), for $R>9a_0^*$, we show the asymptotic solution of E^+ , which equals that of an isolated acceptor with two holes, equivalent to the binding energy of the H^- ion. We see that E^+ is predicted to be positive for separations $R>3a_0$, indicating that the third hole is bound. In the range of separations $5a_0^* < R < 16a_0^*$ we see that the



Figure 7.9 Schematic of our modeling method which uses the effective mass approximation and the configuration-interaction method. At large separations the molecule can hold three holes, similar to the H-state, but for small separations only two holes can be accommodated. The intuitive picture is that the neutral system can polarize and weakly bind the third hole; but this is prohibited for small separations for which the direct Coulomb repulsion dominates.

calculated curve has a small negative slope. Our data are consistent with this trend, and qualitatively consistent with the resonant tunneling measurements by Caro and coworkers,. However the data show greater-than-predicted slope compared to our model. Moreover, the calculation shows a maximum near $R=5a_0^*$ which is not apparent in the measured data.

The behavior for large separations, $R > 5a_0^*$, can be understood as a consequence of basic quantum-mechanics of molecules. Considering our measurement range of $5a_0^* < R < 16a_0^*$, for $R >> 10a_0^*$, each B^0 is effectively isolated; here it is well established that an additional hole experiences a weak attraction to each of the neutral acceptors due to polarization. Hence either one can bind the third hole to form the B^+ state. For the isolated B^+ the size of the wave function is large as the root mean square distance of the hole to the acceptor is $\bar{r}_2 = 5.80 a_0 * [10]$. If we now allow the two neutral acceptors to be separated by $R \sim 10 a_0^*$, the third hole has some probability to be found on either location. Hence the corresponding wavefunction resembles a molecule with two peaks centered at each atom. Fig. 7.11(a) shows an analogous system where the state is represented by the ground-state wave function of two delta-function potentials. As the separation decreases, the gradient of the wavefunction decreases along the line joining the two atoms as shown in Fig. 7.11(b). Schrödinger's equation immediately tells us that effect will decrease the energy, or correspondingly increase the binding energy of the state. However at sufficiently close separations this behaviour breaks down as the system will be poorly described as a two-acceptor molecule, instead behaving more as a single atom with double the nuclear charge [90].



Figure 7.10 E^+ binding energy versus nearest-neighbor distance. Primary-peak binding energy plotted as a function of nearest-neighbor distance R. The parameters were extracted from measurements of dopants at different locations, including the data from Fig. 7.6 A and B. The error bars show the estimated uncertainty of the energy and distance. Also shown in blue is a least-squares linear fit. The inset shows in red the results of a simple-hydrogenic model which incorporates two neutral acceptors and finds the binding energy of a third-hole; E^+ is positive if the third charge results in a lower electronic energy for the system, i.e., if the third hole is bound.



Figure 7.11 The ground state wave function potential well. (a) The two potentials are well-separated compared to the wave function width of an isolated well. (b) The two potentials are close together compared to the width of an isolated well. This state has a lower energy due to reduced gradient.

To further compare the calculations to our measurements, it is instructive to calculate the statistical nearest neighbor distances for the acceptor atoms in our sample. Fig. 7.12 shows the statistical nearest neighbor distances for donors randomly dispersed within a 2D layer. Nearest neighbor distances essential follow the Poissonian distributions [78]. For any randomly selected acceptor atom, it can be shown that the probability to find its m^{th} nearest neighbor at a distance between R and R+dR is

$$\frac{(\pi R^2 \rho)^{m-1}}{(m-1)!} 2\pi R \rho \exp(-\pi R^2 \rho) dR$$
7.6

where ρ is the 2D density. For the curves shown in Fig. 7.9 we used the nominal acceptor density of our sample, $\rho = 1.7 \times 10^{11} \text{ cm}^{-2}$. The statistically expected mean distance of the first nearest neighbor is ~12 nm. Professor Harrison's calculations show that the average binding energy of the acceptors with a nearest neighbor close to the statistically expected mean distance is about 4 meV. This agrees very well with the mean value of the twenty resonances of 4.3 meV, shown in Fig. 7.7 (b).

Returning to the trend shown in Fig. 7.10 of decreasing binding energy with nearest neighbor distance, it is possible that the greater-than-expected slope may result from strain effects. To be specific, my measurements are consistent with an increase in E^+ binding energy of about 4 meV as the nearest neighbor distance decreases by about 20 nm; however, our calculations show only about a 1 meV effect. As introduced in Section 3.4, both the substitutional boron acceptor atoms and any interstitial defects such as



Figure 7.12 Statistical nearest neighbor distances for the boron dopants in our system, calculated using the nominal growth density of boron dopants in our system.

oxygen or carbon can create strain that will affect the binding energies [58, 59, 63, 91]. In particular, Calvet and coworkers observed a ground state energy splitting of about 0.8 meV for the first hole on an isolated boron acceptor atom in silicon [58]. Their analysis indicated that the splitting of the excited states would be comparable to that of the ground state. Hence it is likely that the binding energy of additional holes, e.g. the B^+ state, would be similarly affected. Although the density of the acceptor atoms in this sample was two orders of magnitude higher than in my sample, it is plausible that an individual acceptor in my sample with an especially close boron neighbor or defect could experience a meV-scale increase in E^+ energy. To the best of our knowledge, there is no complete theory for the effect of strain on the B^+ state.

In summary, I have applied a scanning probe method to image and discern the energy levels of subsurface boron acceptors in silicon. The analysis supports the picture of increasing B^+ binding energies due to interactions with neighboring dopants. Moreover, we find rough agreement between the experiment and a model calculation in the range of separations between $5a_0^*$ and $16a_0^*$. The level of agreement between our measurements and calculated curve is not surprising in light of the highly simplified nature of the model, which incorporates only one neighbor and neglects effects arising from the host crystalline potential such as the multivalley structure of the Si conduction band and strain. Additional comments on this matter are included in Section 8.2.

Chapter 8

Summary and Future Directions

8.1 Summary

The major technical innovation of this thesis is the demonstration that individual subsurface dopants can be both imaged and characterized electronically at the singleelectron level. Specifically, I have used the Charge Accumulation Imaging technique to image boron acceptors buried about 15 nm below the surface of a silicon crystal, and I was able to determine the binding energy of the B^+ state on an atom-by-atom basis for 20 such acceptors with millivolt precision. The data show that acceptors with more distant neighbors tend to exhibit weaker binding than those with close neighbors. The data were compared to a simple hydrogenic model that combines the effective mass approximation and configuration-interaction calculations.

8.2 Future directions

We believe this work opens the door to a plethora of atomic-scale experimental studies of subsurface dopants. Our very simple theoretical model neglected, among other things, effects arising from the periodic crystalline potential, the multivalley structure of the Si and strain. Indeed we expect such considerations to become more pronounced for dopants separated by less than a few nanometers, in which case the separation becomes comparable to several lattice constants. Recent calculations by the Das Sarma group focusing on closely spaced pairs of P donors in Si predict that the precise separation and orientation of the dopant pair with respect to the crystalline axis are crucial parameters in determining the ground state wave functions [92, 93].

Thus far we have probed systems for which the lateral positions of the dopants are random. The logical future direction for this research is to probe controlled arrangements of donor or acceptor atoms. Adjacent clusters will be separated by a distance greater than the spatial resolution of the probe and much greater than the effective Bohr radius. This way measurement will effectively probe isolated donor or acceptor molecules instead of ensembles of many donor molecules. The main purpose would be to study the basic quantum mechanics governing the addition spectra of such systems. The motivation for this work is three-fold. Firstly, exciting applications beyond the well-known Kane quantum computer [93, 94, 95] have emerged for which single dopant atoms form the functional part of the device. For example, Lansbergen and coworkers have recently constructed three-dimensional field-effect transistors (FinFETs) for which the electron of a single donor atom could be made to hybridize with a nearby quantum well in a controlled way [1]. Secondly, as conventional state-of-the-art transistors scale down to below the 32 nm level, understanding the role of individual dopants and the interactions with neighbors is becoming increasingly important [96, 97, 98]. Thirdly, the ability to probe the quantum levels of single dopant atoms and dopant-dopant interactions at the atomic level paves the way for the development of new experiments and theories of fewbody quantum mechanical systems.

Preparations for this work have already started in our group. This effort will feature collaboration with Professor Michelle Simmons of the University of New Wales in Australia. Professor Simmons's group has developed a method to control the placement of subsurface phosphorus donors in silicon based on STM lithography and *in situ* molecular beam epitaxy [99, 100].

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