Ambipolar Ballistic Electron Emission Microscopy Studies of
Gate-field Modified Schottky Barriers

Dissertation

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ABSTRACT

In this thesis, we present two separate studies: (1) The development and use of “amibipolar” ballistic electron emission microscopy (BEEM), which allows the measurement of Schottky barrier heights (SBHs) for *both* electrons and holes at the same location on the same metal/semiconductor contact with nm-scale spatial resolution and meV-scale energy resolution. A significant accomplishment of this study is the successful development of a new method that can monitor lateral variations of the local interface electric field and local interface dipoles at metal/semiconductor contacts by monitoring local variations in the electron- and hole SBHs. (2) Ion milling and inductively coupled plasma reactive ion etching (ICP-RIE) of vertical silicon nanowires, in order to increase the fraction of vertical vs. non-vertical nanowires.

In the first experiment, novel four-terminal back-gated Schottky contact sample structures (similar in ways to field effect transistors) were fabricated from

silicon-on-insulator (SOI) substrates and used to successfully measure the Schottky barrier heights for both electrons and holes at the same location on the same metal/semiconductor (M/S) contact by using a four-terminal BEEM technique. This measurement *cannot* be done using conventional three-terminal BEEM on regular metal/bulk silicon contacts, which do not allow the interface electric field under the M/S contact to be modified by an applied gate voltage. With our back-gated Schottky diode structures, by applying a back-gate voltage to the SOI substrate, the Si film could be made either effectively n-type or p-type depending on the polarity of the gate voltage.

Using this gated SOI sample structure, we demonstrated ambipolar BEEM measurements in which BEEM and BHEM (ballistic hole emission microscopy) measurements were performed at the same location on the same Au/Si and Cu/Si contacts at $T=80$ K. After accounting for image force lowering (IFL), the local Schottky barrier heights for electrons and holes sum to approximately the silicon band gap, indicating that we can accurately probe both the conduction band and valence bands at the same location. Hence, we demonstrated that this technique is sensitive to local variations in the metal/Si interface dipole and/or the interface electric field. While the individual n- and p-SBHs varied by more than 200 meV between the Au/Si and Cu/Si contacts, for a given sample they sum to within 15 meV of the same value, indicating that the individual variations are due to

variations in a local surface dipole as compared with tip effects or variations in local composition.

The second study presents a method to increase the ratio of vertical silicon nanowires (grown by chemical vapor deposition (CVD) with dispersed colloidal Au particles as catalyst) by ion milling and RIE etching. By choosing the correct ion milling thickness of silicon, we found that it is possible to remove most or all of the non-vertical silicon nanowires leaving mostly or only vertical silicon nanowires standing on the substrate. This is an important achievement which opens up a new opportunity for researches on high density vertical nanowires. Our method may be useful for studies that require samples with a large fraction of vertical nanowires.

Dedicated to my parents and my wife

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CHAPTER 1

MOTIVATION AND OVERVIEW

In this work, we present the results of two different studies: (1) ambipolar ballistic electron emission microscopy (BEEM) studies on gated silicon-on-insulator (SOI) sample, and (2) ion milling of silicon nanowires to increase the yield of vertical nanowires. The main accomplishments of the first study are: (1) The successful development of a new method that can monitor the energy (relative to the metal Fermi energy) of *both* the conduction band minimum and the valence band maximum of a thin semiconductor film *at the same location*. (2) By comparing these two energies, this technique can be used as a method to monitor and quantify lateral variations of (i) the local interface electric field, (ii) local interface dipoles, and (iii) the local bandgap at metal/semiconductor contacts. The main accomplishment of the second study is the development of a method to increase the ratio of vertical silicon nanowires that are grown epitaxially on a Si substrate.

I. Amibipolar ballistic electron emission microscopy (BEEM) studies on gated silicon-on-insulator (SOI) sample. There is an increasing interest in nm-size electronic device structures in which current flow is controlled by internal tunnel barriers that are modified by an applied gate bias. For example, it has been argued that carbon nanotube field effect transistors (FETs) [1] can behave as Schottky barrier FETs [2] in which the current is controlled by gate-field modulated tunneling through a Schottky barrier. One characteristic of Schottky barrier FETs is ambipolar transport [2], in which either electrons or holes are the primary carriers that tunnel through a gate-field controlled tunnel barrier. Gate-field controlled tunneling is also the basis of Tunneling FETs [3,4], which have been proposed to have better scalability and demonstrated to have a lower sub-threshold swing than possible in conventional FETs. Since locally-enhanced electric fields (for example at the edges of a gate or the channel region) can strongly impact the local tunneling in Schottky barrier and Tunneling FETs, it is important to be able to measure the effects of an applied field on the local barrier properties for both electron and hole transport. However, how the Schottky barriers are modified by the gate field can't be determined by conventional methods such as I_{SD} (source-drain current) versus V_G (gate voltage) measurement. For example, in carbon nanotube FETs, the gate voltage affects the source-drain current by modulating both the nanotube channel conductance and the Schottky barriers at the source/drain end, so it is difficult to extract the effect of the gate voltage on the Schottky barrier from $I_{SD} - V_G$

measurement. In this study, we take advantage of the high spatial resolution (nm-scale) and high energy precision (several meV) of the technique of BEEM and modified it from a three-probe technique to a four-probe technique. By applying this modified BEEM technique on a novel sample structure fabricated on SOI wafers, we succeeded in varying the electric-field under the Schottky contacts by applying a gate voltage and measuring how the Schottky barriers are modified by this electric-field.

II. Ion milling of vertical Si nanowires. This study presents a method to increase the yield of vertical silicon nanowires by ion milling. Vertical silicon nanowires have been used to fabricate some novel devices such as silicon vertically integrated nanowire FETs or Surround-gate FETs silicon nanowire photodetectors, and silicon nanowire solar cell. These devices were claimed to have some better performance than conventional structures. And end-on metal contacts to vertical Si nanowires can also be used to study the role of Fermi level pinning in nano-scale metal-semiconductor contacts, which is one of the critical issues in nanowire or carbon nanotube FETs. Our method may be found useful by someone who wants to conduct research on vertical Si nanowires but has difficulty in obtaining samples that do not have a high density of vertical nanowires.

Background information and experimental results of our work are presented in the following chapters:

Chapter 2 is an introduction to silicon and silicon-on-insulator properties. Several topics important to our studies are covered: energy bands of silicon, carrier concentration at thermal equilibrium, Si/SiO₂ interface, and structure and fabrication of SIMOX (Separation by IMplantation of Oxygen) SOI.

Chapter 3 covers several concepts related to Schottky barriers: formation of Schottky barriers, Fermi level pinning, image force lowering, inhomogeneity of the Schottky barriers, and ohmic contacts.

In Chapter 4, the technique of BEEM is described in detail. The basic idea of BEEM and theoretical models for extracting barrier heights are presented.

Chapter 5 describes the preparation methods of our samples used in our measurements, including chemical cleaning, photolithography, dry-etching, and metal evaporation, etc..

In Chapter 6, we demonstrate our ambipolar BEEM measurements in which BEEM and BHEM measurements were performed at the same location on the same Au/Si and Cu/Si contacts at $T = 80\text{K}$. After accounting for image force lowering, the local SBHs for electrons and holes sum to approximately the Si bandgap, indicating that we can accurately probe both the conduction band and valence bands at the same location. While the individual n- and p-SBHs varied by more than 200 meV between the Au/Si and Cu/Si contacts, for a given sample they sum to within 15 meV of the same value, indicating that the individual variations are due to variations

in a local surface dipole as compared with tip effects or variations in local composition.

Chapter 7 is our results on using ion milling to increase the yield of vertical silicon nanowires. We found that the fraction of vertical NWs can be increased, but some damage does occur to the remaining (vertical) NWs if the milling is done too long. By choose the correct ion milling thickness of silicon, all of the non-vertical silicon nanowires can be removed leaving only vertical silicon nanowires standing on the substrate.

CHAPTER 2

SILICON AND SILICON-ON-INSULATOR MATERIALS

2.1 Silicon

In this section, some properties of Si and Si/SiO₂ interfaces will be discussed.

2.1.1 Crystal structure

Silicon belongs to Group IV A and has an atomic configuration of [Ne]3s²3p² [5]. The crystal structure of silicon is the diamond lattice structure in which each silicon atom is surrounded by four equidistant nearest silicon atoms which lie at the corners of a tetrahedron, and the lattice constant is $a = 5.43\text{\AA}$, as shown in Figure 2.1 [6]. In crystalline silicon, the four outermost shell electrons (3s²3p²) form four equivalent sp³ hybrid orbitals which are directed at an angle of 109.5° relative to each other as shown in Figure 2.2 [6]. The bond between two nearest silicon

Figure 2.1: Diamond lattice structure where **a** is the lattice constant (figure taken from Ref. [6]).

Figure 2.2: sp^3 hybrid orbitals (figure taken from Ref. [7]) .

atoms is a covalent σ bond formed by head-to-head overlapping of two sp^3 hybrid orbitals with opposite spins.

Since the diamond lattice can be considered as two interpenetrating face-centered cubic (FCC) lattices which are shifted by $\sqrt{3}a/4$ along the diagonal [5], the Bravais lattice of silicon crystal is the FCC lattice and the reciprocal lattice is the body-centered cubic (BCC) lattice. The first Brillouin zone for the diamond lattice is the truncated octahedron as shown in Figure 2.3 in which the most important symmetry points and symmetry lines are indicated: zone center Γ : $2\pi/a(0,0,0)$; X: $2\pi/a(0,0,1)$; L: $2\pi/a(1/2,1/2,1/2)$; K: $2\pi/a(3/4,3/4,0)$; Δ : $\langle 100 \rangle$ axes; Σ : $\langle 110 \rangle$ axes; and Λ : $\langle 111 \rangle$ axes [4].

Figure 2.3: Brillouin zone for the diamond lattice (figure taken from Ref. [8]).

2.1.2 Energy bands

The energy band structure describes the relationship between the energy E and the momentum $\mathbf{k}$ which can be obtained by solving the Schrödinger equation with the aid of group theory [9]. Figure 2.4 shows the energy bands in silicon along the [100] and [111] directions [10]. The upper part shows the conduction bands and the lower part shows the valence bands. The separation is the silicon band gap $E_g = 1.12\text{eV}$ at room temperature. The lowest conduction band has a minimum at a point along the [100] direction. For the valence bands, two degenerate bands meet at $\Gamma(0,0,0)$, giving the maximum of the valence bands. These two valence bands have different curvature at point Γ and are called the light-hole band and the heavy-hole band respectively. The third valence band is separated from the other two bands by roughly 0.044 eV because of the spin-orbital coupling. Since the conduction band minimum and the valence band maximum occur at different points in $\mathbf{k}$ -space, silicon is an indirect band-gap semiconductor.

At the conduction band minimum $(k_x^{\min}, k_y^{\min}, k_z^{\min})$, the energy of electron can be written as

$$E(\vec{k}) = E_c + \frac{\hbar^2}{2} \left(\frac{(k_x - k_x^{\min})^2}{m_x} + \frac{(k_y - k_y^{\min})^2}{m_y} + \frac{(k_z - k_z^{\min})^2}{m_z} \right) \quad (2.1)$$

Figure 2.4: Energy bands in silicon along [111] and [100] directions (figure taken from Ref. [10]).

Figure 2.5: Constant-energy surface near the conduction band minima (figure taken from Ref. [5]).

where E_C is the energy at the bottom of the conduction band, and m_x , m_y and m_z are the effective masses of electrons along x, y and z axis. We can see the constant energy surfaces are ellipsoidal in shape and for silicon there are six ellipsoids along the $\langle 100 \rangle$ axes due to the symmetry of the first Brillouin zone as shown in Figure 2.5 [5]. The effective mass along the $\langle 100 \rangle$ axes (the longitudinal effective mass) is $m_l^* = 0.98m_0$, and the effective mass perpendicular to the $\langle 100 \rangle$ axes (the transverse effective mass) is $m_t^* = 0.19m_0$, where $m_0 = 9.11 \times 10^{-31}$ kg is the free electron mass [5]. At the valence band maximum the two degenerate valence bands are spherically symmetric and the energy can be written as

$$E(\vec{k}) = E_V - \frac{\hbar^2}{2} \frac{k_x^2 + k_y^2 + k_z^2}{m_h} \quad (2.2)$$

where E_V is the maximum energy of the valence bands, m_h is the effective mass of holes which is equal to $0.16m_0$ for the light-hole band and $0.49m_0$ for the heavy-hole band [5].

Figure 2.6: Temperature dependence of the energy band gap of silicon.

As for most semiconductors, the energy band gap of Si decreases with increasing temperature and has a temperature dependence of

$$E_g(T) = E_g(0) - \alpha T^2 / (T + \beta) \quad (2.3)$$

as shown in Figure 2.6 , where $E_g(0) = 1.170$ eV is the Si band gap at $T = 0$ K, $\alpha = 4.83 \times 10^{-4}$ eV/K and $\beta = 636$ K [6]. This temperature dependence is due to the thermal expansion of the periodic crystal lattice and the effect of lattice vibration on the band structure and energy band gap [5].

2.1.3 Carrier concentration at thermal equilibrium

For intrinsic (undoped) silicon at zero temperature, the conduction band is empty and the valence band is fully filled with electrons. When $T > 0$ K, some electrons will be thermally excited from the valence band to the conduction band which leaves an equal number of holes in the valence band, so the free electron density n and the free hole density p are equal, $n = p = n_i$ where n_i is the intrinsic carrier density which is $\sim 1.45 \times 10^{10}/\text{cm}^3$ at room temperature for silicon [6]. Using the Fermi-Dirac distribution, the electron density in the conduction band and the hole density in the valence band are given by

$$n = N_c \frac{2}{\sqrt{\pi}} F_{1/2} \left(\frac{E_F - E_c}{k_B T} \right) \quad (2.4)$$

Figure 2.7: Energy levels for silicon with donor and acceptor impurities.

$$p = N_v \frac{2}{\sqrt{\pi}} F_{1/2} \left(\frac{E_V - E_F}{k_B T} \right) \quad (2.5)$$

where N_C (N_V) is the effective density of states in the conduction (valence) band (at room temperature, $N_C = 2.8 \times 10^{19}/\text{cm}^3$, and $N_V = 1.04 \times 10^{19}/\text{cm}^3$), $F_{1/2}(x) = \int_0^\infty dy \sqrt{y} / (1 + \exp(y - x))$ is the Fermi-Dirac integral, and E_F is the Fermi energy which can be determined by $n = p$. At thermal equilibrium, $np = n_i^2 = N_C N_V \exp(-E_g / k_B T)$, which is called the law of mass action.

In doped silicon, donor or acceptor impurities will introduce impurity level inside the band gap as shown in Figure 2.7, where E_D (E_A) is the donor (acceptor) impurity level, which is equal to $E_C - 0.044 \text{ eV}$ ($E_V + 0.046 \text{ eV}$) for Phosphorus (Boron) in silicon. At $T = 0 \text{ K}$, a donor (acceptor) level is occupied by an electron (a hole) and is neutral. At elevated temperatures, the electron (hole) at a donor (acceptor) level will be excited to the conduction (valence) band, so the density of electrons (holes) in the conduction (valence) band is different from n_i , but can still be evaluated by Equation (2.4) (Equation (2.5)). However, in this case the Fermi energy E_F is not the same as it is in intrinsic silicon, and should be determined by the neutrality condition

$$n + N_A^- = p + N_D^+ \quad (2.6)$$

In the above equation (2.6), N_A^- (N_D^+) is the ionized donor (acceptor) density

$$N_A^- = \frac{N_A}{1 + 4 \exp((E_A - E_F)/k_B T)} \quad (2.7)$$

and

$$N_D^+ = \frac{N_D}{1 + 2 \exp((E_F - E_D)/k_B T)} \quad (2.8)$$

where N_A (N_D) is the donor (acceptor) density and the number 4(2) in the denominator is the degeneracy factor of the acceptor (donor) levels[6].

2.1.4 Carrier transport

The basic equations which describe the carrier transport phenomena in semiconductors are the Maxwell equations, the current-density equations, and the continuity equation, which are discussed in detail in section 1.5 of Reference.6. Here, the three equations which are used most frequently in semiconductor device simulations are listed below.

(1) The Poisson equation:

$$\nabla \cdot (-\varepsilon \nabla \psi) = q(p + N_D^+ - n - N_A^-) \quad (2.9)$$

where ε is the material permittivity and ψ is the electric potential.

(2) The current-density equations:

$$\vec{J}_n = q\mu_n n \vec{E} + qD_n \nabla n \quad (2.10)$$

$$\vec{J}_p = q\mu_p p \vec{E} - qD_p \nabla p$$

where μ_n (μ_p) is the mobility of electrons (holes), $\vec{E} = -\nabla\psi$ is the electric field, and $D_n = (k_B T/q)\mu_n$ ($D_p = (k_B T/q)\mu_p$) is the diffusion constant of electrons (holes). In Equations (2.10), it is assumed that the drift velocity is equal to $\vec{v}_d = \mu_n \vec{E}$ or $\mu_p \vec{E}$. At sufficiently high field, $\mu_n \vec{E}$ or $\mu_p \vec{E}$ should be replaced by the saturation velocity $\vec{v}_s$.

(3) The continuity equations:

$$\frac{\partial n}{\partial t} = G_n - R_n + \frac{1}{q} \nabla \cdot \vec{J}_n \quad (2.11)$$

$$\frac{\partial p}{\partial t} = G_p - R_p - \frac{1}{q} \nabla \cdot \vec{J}_p$$

where G_n (G_p) is the generation rate of electrons (holes), and R_n (R_p) is the recombination rate of electrons (holes) [6].

2.1.5 SiO₂ and Si/SiO₂ interface

One reason that silicon became the dominant semiconductor material used in integrated circuits is that its oxide SiO₂ is a stable and high-quality insulator and

is easy to grow. In a stoichiometric SiO_2 , each silicon atom is bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms as shown in Figure 2.8. Thermally grown SiO_2 is an amorphous silicon dioxide structure (shown in Figure.2.9) which is a continuous random network of the basic structure shown in Figure 2.8 [11].

The interface between thermally grown SiO_2 and the bulk silicon is a complicated structure, and has been studied extensively because the quality of Si/SiO_2 interface affects the performance of MOSFET (Metal-Oxide-Semiconductor Field-Effect-Transistor) devices. It was proposed that at a Si/SiO_2 interface, between the single-crystal Si and the stoichiometric, strain-free, amorphous SiO_2 ,

Figure 2.8: Schematic bonding structure in SiO_2 . (In crystalline SiO_2 , the bond angle is 109.5°).

Figure 2.9: Amorphous SiO₂ structure (figure taken from Ref. [11]).

there is a monolayer of nonstoichiometric SiO_x ($1 < x < 2$) and then a 10-40 Å strained stoichiometric amorphous SiO₂ area as shown schematically in Figure 2.9 [11].

Interface traps and/or oxide charge exist at Si/SiO₂ interfaces and in thermally grown SiO₂. These interface traps and oxide charges can be classified as the following (Figure 2.10) [12]: (1) interface traps and interface trapped charge Q_{it} which come from the silicon dangling bonds at the interrupted silicon surface. These interface traps may be created by the chemical reaction

where $\equiv Si \cdot$ is the dangling bond and the $(Si - O)^+$ gives rise to the fixed oxide charge Q_f [13]. These traps can be donor-like or acceptor-like and can exchange electron with the bulk silicon very quickly. These interface traps and interface trapped charges may decrease the carrier mobilities, change the surface potential, and can act as recombination/generation centers. Usually interface traps at Si/SiO₂ interfaces have a density of 10^{11} - 10^{12} /cm²/eV and can be reduced to the order of 10^{10} /cm²/eV by annealing in H₂ at 450° [6]; (2) The fixed oxide charges (represented by Q_f) are located within 30Å of the Si/SiO₂ interface and are not mobile [14]. They cannot be charged or discharged. The density is around 10^{10} - 10^{12} /cm² and depends on the silicon crystal orientation: Si(111) > Si(110) > Si(100) [15]; (3) oxide trapped charges (represented by Q_{ot}) may be created by irradiation of X-rays, γ rays and hot-electron injection; (4) mobile ionic charges Q_m . Q_m are mainly due to ions such as Na⁺, K⁺ and H⁺, which are introduced unintentionally during the processing steps. For example, Na⁺ can come from chemical-cleaning solutions, cleaning glassware, and the oxidation furnace wall. Since these charges are mobile and can redistribute under an applied field, they affect the flat-band potential [6, 16] in a time-dependent way.

Figure 2.10: Terminology of charges associated with thermal SiO_2 [12].

2.2 Silicon-on-Insulator (SOI)

Silicon-on-insulator is a three-layer wafer structure as shown in Figure 2.11. For CMOS (complementary metal-oxide semiconductor) based devices fabricated on a bulk silicon, all the devices are connected by the bulk substrate. This can cause some problems such as parasitic capacitance between the source and drain and the

Figure 2.11: Silicon-on-insulator wafer structure.

substrate, and the interaction between the devices [17]. Silicon-on-insulator (SOI) technology is able to avoid these problems by isolating the n-well structures, the p-well structures, and the substrate by an insulating silicon oxide. Compared to bulk devices, SOI devices also have the advantages such as higher speed, lower power dissipation, high radiation tolerance, etc. [17]. SOI technology is also compatible with most conventional fabrication processes.

Several methods of fabricating SOI wafers have been developed, such as SIMOX (Separation by IMplantation of Oxygen), wafer bonding and epitaxial growth. Since the SOI wafers used in our experiment is SIMOX SOI, we will only talk about SIMOX in this section.

SIMOX technology includes two steps which are shown in Figure 2.12 [18]. The first stage is implanting a large dose of reactive O^+ ions into single

Figure 2.12: The basic SIMOX process (figure taken from Ref. [18]).

Figure 2.13: Cross-section TEM images of SIMOX samples before and after high temperature annealing at 1360 °C for 6hours (figure taken from Ref. [19]).

Figure 2.14: Oxygen precipitation, growth and precipitate coalescence during SIMOX annealing with different oxygen doses (figure taken from Ref. [18]).

crystal silicon. The second stage is a high temperature annealing (HTA) step which is aimed at annihilating the lattice defects created during the implantation step and redistributing the implanted oxygen to form a buried layer of homogeneous, stoichiometric SiO_2 with abrupt Si/SiO_2 interfaces by the thermally driven physical processes of precipitate growth and precipitate coalescence. Figure 2.13 shows two cross-section transmission electron microscope (TEM) images of SIMOX samples implanted at 65KeV with a dose of $2.0 \times 10^{17} \text{ O}^+ / \text{cm}^2$ before and after HTA at 1360 °C for 4 hours in Ar (O_2) without any protective cap on the surface [19]. What makes SIMOX wafers commercially available is two major breakthroughs in

SIMOX technology: the discovery of low-dose SIMOX [19] and the discovery that internal thermal oxidation [20] occurs during the HTA step.

It was found that for certain implantation energy there is an optimum implantation dose (Izumi window) for the formation of a continuous buried oxide (BOX) [19]. The mechanism is illustrated in Figure 2.14 [18]. When the oxygen dose is above this optimum dose window, too many nucleation sites exist over a wide range. This will result in formation of silicon islands within the BOX film. When the oxygen dose is below this optimum dose window, individual SiO₂ islands will form instead of a continuous BOX film. Only when the oxygen dose is within this window, will a continuous BOX form without any silicon island trapped inside [18]. Within the Izumi dose window, the concentration of implanted oxygen atoms is lower than that in stoichiometric SiO₂. After the low-dose oxygen implantation, the wafers are annealed in an oxygen rich atmosphere Ar + x O₂ (10% < x < 70%) at high temperature (over 1300 °C), which will lead to internal thermal oxidation. Under these conditions, oxygen will be driven by the concentration gradient from the free surface to the BOX and internal thermal oxidation will occur there and predominantly at the SOI/BOX interface [21]. Figure 2.15 shows a set of TEM micrographs of samples implanted at a dose of 1.5, 2.0, 2.5, 3.5, 4.5, and 5.0×10¹⁷ O⁺/cm², respectively, but all annealed at 1350°C for 6 h in Ar (O₂) with a protective cap [21]. We can see the existence of an optimum dose for the formation of Si island free BOX layer.

Figure 2.15: A set of TEM micrographs shows the existence of an optimum dose for the formation of Si island free BOX layer. Images (a)–(f) represent samples implanted at a dose of 1.5 , 2.0 , 2.5 , 3.5 , 4.5 , and $5.0 \times 10^{17} \text{ O}^+/\text{cm}^2$, respectively but all annealed at 1350°C for 6 h in Ar (O_2) with a protective cap (figure taken from Ref. [21]).

The quality of SOI wafers can be evaluated by the following parameters: SOI thickness and thickness uniformity, BOX thickness and uniformity, HF etch defect density, dislocation density, surface roughness, carrier mobilities, BOX short density, fixed charge density in the BOX, and interface state density at the Si/BOX interfaces. Table 2.1 summarizes typical physical and electrical properties of commercial SIMOX compared with those of bonded SOI [18].

Parameters	Unit	SIMOX SOI	Bonded SOI
SOI thickness uniformity	Å	6-9	10-15
HF defects	cm ⁻²	<0.5	<0.5
Surface roughness	Å	4-7	1.0-2.0
Electron mobility	cm ² /V/s	550-650	500-600
Hole mobility	cm ² /V/s	200-230	200-230
BOX short density	cm ⁻²	<0.5	<0.5
BOX breakdown field	MV/cm	7-8	>8
BOX charge	cm ⁻²	3.0×10 ¹¹	<3.0×10 ¹¹
Interface charge	cm ⁻²	3.0×10 ¹¹	<3.0×10 ¹¹

Table 2.1: Physical and electrical properties of modern commercial SIMOX [18].

CHAPTER 3

METAL-SEMICONDUCTOR INTERFACE

3.1 Schottky Barriers

When a metal makes abrupt contact with a semiconductor, often the metal Fermi energy falls within the bandgap of the semiconductor. In this case there are energy offsets between the Fermi energy and the conduction band and valence band of the semiconductor. For an n-type semiconductor, the Fermi energy/conduction band offset represents an energy barrier (called an electron Schottky barrier) that majority electrons must overcome to move between the metal and semiconductor. For a p-type semiconductor, the Fermi Energy/valence band offset represents a hole Schottky barrier for majority holes. For an ideal metal/semiconductor interface (i.e., with no interface states), the formation of an electron or hole Schottky barrier can be understood using simple energy-band diagrams. Consider for example an ideal metal/n-semiconductor contact. When the metal and the n-semiconductor are

Figure 3.1: The energy band diagram of metal-semiconductor contacts.

isolated, the vacuum levels of the metal and semiconductor are equal causing the energy band alignment as shown in Figure 3.1(a). If charge transfer is permitted, then electron transfer between the metal and semiconductor cause their Fermi

energies to line up at thermal equilibrium. Figures 3.1(b) and (c) show the case when the distance between the metal and the semiconductor is finite. We can see the contact potential due to the difference between the metal work function $q\phi_m$ and the semiconductor work function $q\chi + (E_C - E_F)$ (where $q\chi$ is the semiconductor electron affinity) is shared by the voltage drop ΔV across the space between the metal and the semiconductor and the band bending V_{bi} in the semiconductor. The voltage drop ΔV decreases as the spacing decreases and eventually goes to zero when the metal makes intimate contact with the semiconductor as show in Fig. 3.1(d). Based on the above arguments, the barrier height can be easily obtained from the band diagram:

$$q\phi_{Bn} = q\phi_m - q\chi . \quad (3.1)$$

This is called Schottky-Mott model.

3.2 Fermi Level Pinning

According to the Schottky-Mott model, the change of the barrier height should scale exactly with the change of metal work function, i.e., $q\Delta\phi_{Bn} = q\Delta\phi_m$ for different metal contacts to the same semiconductor. However experimental measurements showed that for many metal/semiconductor contacts (including those made to Si and GaAs) the dependence of the barrier height on the metal work

function is weaker: $q\Delta\phi_{Bn} = \alpha * q\Delta\phi_m$, where $\alpha \ll 1$ (e.g. $\alpha = 0.27$ for Si and $\alpha = 0.074$ for GaAs - see Figure 3.2) [22].

To explain this, Bardeen proposed that between the metal and the semiconductor there exists an *interfacial layer* which is of atomic dimensions ($\delta \sim 4\text{\AA}$) (Figure 3.3). Bardeen assumed that this interfacial layer can withstand a potential drop ΔV across it but is transparent to electrons. In this interfacial layer,

Figure 3.2: Experimental results of barrier height for metal-semiconductor contacts (figure taken from Ref. [22]).

Bardeen proposed that there is a large density of *interface states* which can become charged according to

$$\sigma_s = qD_s(q\phi_{CNL} - E_F), \quad (3.2)$$

where D_s is the interface-state density in unit of $1/\text{cm}^2/\text{eV}$ and $q\phi_{CNL}$ is called the *charge neutrality energy level*. When $E_F = q\phi_{CNL}$, there is no surface charge; when

Figure 3.3: Energy band diagram with interface states [23].

E_F is above $q\phi_{CNL}$, interface charge is negative, and when E_F is below $q\phi_{CNL}$, interface charge is positive. This interface charge and its image charge inside the metal form a planar charge- dipole sheet. If the contact size is $\gg \delta$ (which is always true for large planar contact to bulk semiconductors), the size of this dipole sheet can be considered as infinite, so the potential drop across the interfacial layer due to this infinite dipole sheet is equal to $\Delta V = \sigma_s \delta / \epsilon_0 = qD_s (q\phi_{CNL} - E_F) \delta / \epsilon_0$. If D_s is very large, then only a small deviation of E_F from $q\phi_{CNL}$ would create a large density of interface charge. The net effect is that a change in the metal work function causes a change in the interface charge that produces a potential drop ΔV across the interfacial layer which can accommodate the change of the metal work function. In this case, the Fermi level is completely pinned at the charge neutrality level $q\phi_{CNL}$, so the barrier height doesn't depend on the metal work function and is equal to

$$q\phi_{Bn} = E_C - q\phi_{CNL}. \quad (3.3)$$

When D_s is equal to zero, the Schottky barrier is determined by Equation (3.1). For real semiconductors such as Si and GaAs, D_s is large but finite, causing partial pinning with:

$$q\phi_{Bn} = a(q\phi_m - q\chi) + b(E_C - q\phi_{CNL}), \quad (3.4)$$

where $a = 2q\epsilon_s N_D \delta^2 / \epsilon_i^2$ and $b = 1 - \epsilon_s / (\epsilon_i + q^2 \delta D_s)$ are two constants determined by the semiconductor and the interface states (ϵ_i is the permittivity of the interface layer, and ϵ_s is the permittivity of the semiconductor, and N_D is the doping of the semiconductor) [6]. Actually several models have been proposed to explain the physical origin of these interface states, (for example surface states [6], MIGS (Metal-Induce-Gap-States) [24] and impurity states [25]), but none of them can explain all of the experimental results. However, their basic effect on the Schottky barrier is the same: interface states, an interfacial layer, and a charge neutrality level $q\phi_{CNL}$ provide a “negative feedback” for the movement of Fermi level responding to the change of the metal work function.

3.3 Image Force Lowering

Since the metal in a metal-semiconductor contact has a very high free carrier density, the effective electrical potential $V(x)$ that an electron inside the semiconductor feels is modified so that there is an “image force” induced lowering of the Schottky barrier height that depends on the electric field near the metal-semiconductor interface. Let’s use a metal-vacuum system shown in Figure 3.4 as an example to explain the basic idea of image-force-induced lowering. When an

Figure 3.4: Energy band diagram between a metal and a vacuum [6].

electron is placed at a distance x from the metal, the force between the electron and the metal is attractive and is easy to be calculated using the image charge method [26]. For an infinite flat metal, the force is equal to that generated by an equal positive charge q^+ at position $-x$, so the image force is

$$F = \frac{-q^2}{16\pi\epsilon_0 x^2}, \quad (3.5)$$

where $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the vacuum permittivity. And the potential due to this image force is

$$V(x) = \frac{q}{16\pi\varepsilon_0 x}. \quad (3.6)$$

If an external field E exists at the interface, the total potential energy is

$$qV(x) = -\frac{q^2}{16\pi\varepsilon_0 x} - qEx. \quad (3.7)$$

The maximum of $qV(x)$ can be found by the condition $dV(x)/dx = 0$. And the image force lowering of the Schottky barrier can be found to be

$$q\Delta\phi_{IFL} = q\sqrt{\frac{qE}{4\pi\varepsilon_0}}. \quad (3.8)$$

For a semiconductor, ε_0 should be replaced the semiconductor dielectric constant, and experimental results showed that for metal-silicon contacts the ε_0 should be replaced by the static dielectric constant of silicon $\varepsilon_s = 11.7\varepsilon_0$ [27].

3.4 Current Transport

The current transport through a thick Schottky barrier can be described by the thermionic emission theory which assumes that only carriers with a kinetic energy greater than the energy barrier can pass over the barrier, and that there is no transport through the barrier via tunneling or generation-recombination processes. Using the density of states and the Fermi distribution function, the current density from metal to semiconductor J_{m-s} and the current density from semiconductor to metal J_{s-m} can be calculated. The net current density is $J_{TE} = J_{m-s} + J_{s-m}$ and can be calculated to be

$$J_{TE} = A^* T^2 \exp\left(-\frac{q\phi_B}{k_B T}\right) \left[\exp\left(\frac{qV}{k_B T}\right) - 1\right] \quad (3.9)$$

where A^* is the effective Richardson constant and V is the applied voltage [28]. Figure 3.5 shows the theoretical and experimental values of current-voltage characteristics for Au/Si barrier [29].

In the thermionic emission theory, the current component due to the tunneling through the barrier is neglected, which is not a valid approximation for heavily doped semiconductors and low temperature operation. For heavily doped semiconductors, the Schottky barrier can be so thin that carriers can tunnel through the barrier. At low temperature, the number of carriers which have a higher kinetic

Figure 3.5: Theoretical and experimental values of current-voltage characteristics for Au/Si barrier (Figure taken from Ref. [29]).

energy than the energy barrier will become too small. So in these cases the tunneling current density may dominate and it can be written as

$$J_t \propto \exp(-2\phi_B / \hbar / \sqrt{N_D(or N_A) / (\epsilon_s m^*)}), \quad (3.10)$$

where $\hbar$ is the reduced Plank constant and m^* is the tunneling effective mass of the carriers [30].

For a real device, the current density can be written as

$$J = J_s [\exp(\frac{qV}{nk_B T}) - 1], \quad (3.11)$$

where J_s is the saturation current density, and n is the ideality factor which is equal to 1 for an ideal Schottky diode and is between 1 and 2 for a real Schottky diode because of the reasons such as image force lowering, tunneling, surface imperfection, recombination in depletion region, etc. [6].

3.5 Ohmic contacts

In semiconductor devices, ohmic contacts are usually needed and are defined as contacts which have a negligible contact resistance and give a linear and symmetric I - V curve. Figure 3.6 (a) and (b) show two ways which are used to fabricate ohmic contacts: low barrier and/or high doping [6]. In the case of low barrier height, due to thermal excitation, the number of carriers which can transport over the barrier by the thermionic emission mechanism is very large, so the resistance is small. In the case of high doping, the density of ionized dopants is high and the bands bend steeply. This gives rise to a very thin barrier so the carriers can easily tunnel through it. In practice, it may be difficult to fabricate a metal/semiconductor contact with a low barrier height, so high doping is the most frequently used method for making an ohmic contact to semiconductors.

3.6 The Tung Model: inhomogeneous Schottky Barriers

In the above discussion, a uniform Schottky barrier height was assumed at the metal/semiconductor interface. However, *small-scale lateral variations* of the Schottky barrier height should produce different current-voltage behavior than predicted for a uniform barrier. Such local variations in Schottky barrier height have been observed in several studies using ballistic electron emission microscopy (BEEM) [31-34]. For example, Niedermann et al. saw a lateral variation of more than 0.2eV in barrier height in their BEEM studies of Pt/n-Si(100) [31]. Palm et al.

(a) LOW BARRIER HEIGHT

(b) HIGH DOPING

Figure 3.6: Low barrier height and/or high doping for ohmic contacts (Figure taken from Ref. [6]).

studied the distribution of barrier heights of Au/n-Si(100) contacts for two different dopant concentration and found that the width of the distribution is larger for the sample with higher doping [32]. One possible reason for this barrier height inhomogeneity is the presence of semiconducting or insulation interlayers at the interface due to interfacial reactions or contaminations.

A general theoretical treatment of the barrier height inhomogeneity has been done by Tung [35,36]. In Tung's model, the metal/semiconductor interface consists of patches each of which has a different local Schottky barrier height, and the conduction band minimum potential inside the semiconductor is obtained by solving Poisson's equation with the boundary condition determined by the barrier heights at the interface. Simulation results showed that due to the interaction between neighboring patches with different barrier heights the conduction path beneath a small patch with a low barrier height is "pinched-off" by the presence of high barrier height patches in its close proximity. This is illustrated in Fig. 3.7, which plots the calculated conduction band minimum potential in an n-type semiconductor near a circular patch based on Tung's model [31]. The radius of the circle is 10nm and has a barrier height of 0.4eV. The area outside the circle has a barrier height of 0.6eV and a depletion width of 1 μ m. We can see beneath the lower barrier patch the conduction band minimum increases to a saddle point about 25nm away from the interface inside the semiconductor. When pinch-off occurs, the potential at a saddle point beneath the low barrier height area determines the transport properties [35]. The effect of such a saddle point on electrical transport

Figure 3.7. Conduction band minimum potential in an n-type semiconductor near a circular patch of radius = 10nm with a 0.2eV lower barrier height. The outside barrier height is 0.6eV and the depletion width is 1 μ m. (figure taken from Ref. [31]).

across the Schottky barrier should become significant if the size of a low-barrier patch is smaller than the characteristic depletion width of the semiconductor [35,36].

3.7 Characterization of Schottky Barrier Height

The experimental method for measuring the Schottky barrier height includes current-voltage measurement, activation energy measurement, capacitance-voltage measurement, photoelectric measurement and BEEM (Ballistic Electron Emission Microscopy). The method of BEEM will be discussed in the next chapter, and a summary of the other five methods mentioned above can be found in reference [6].

CHAPTER 4

BALLISTIC ELECTRON EMISSION MICROSCOPY

4.1 Schematics of BEEM

The technique of Ballistic Electron Emission Microscopy (BEEM) was invented by W.J.Kaiser and L.D.Bell in 1988 to investigate metal/semiconductor interfaces with high spatial ($\sim$ few nm) and energy ($\sim$ 10meV) resolution [37]. This is a three-terminal technique modified from Scanning Tunneling Microscopy (STM) and has been mainly used to measure Schottky barrier heights and hot carrier transportation at metal/semiconductor interfaces. BEEM has also been applied to study energy band offsets [38], quantum-size effects [39] using semiconductor heterostructures, and spin-dependent electron scattering and spin-filtering effects [40] using magnetic metal/semiconductor interfaces. BEEM has also been applied to study electron transport in insulator using metal/insulator/semiconductor structures

Figure 4.1: (a) Schematic representation and (b) Energy band diagram of BEEM .
(Figure taken from Ref. [46]).

[41-43]. Reference [44] and [45] are two good comprehensive reviews of BEEM technique.

The basic experimental setup of BEEM measurements is illustrated in Figure 4.1(a) [46]. The energy band diagram of BEEM measurements is shown in Figure 4.1(b) using a metal/n-semiconductor interface as an example [46]. In typical BEEM measurements, small size (diameter $\sim 500\mu\text{m}$) Schottky contacts are fabricated by evaporating a thin ($\sim 10\text{nm}$) and clean metal film on a clean semiconductor surface (usually with native oxide removed). With the metal film grounded, if a negative bias V_T is applied on the STM tip and the tip is brought close ($\sim 1\text{nm}$) to the metal film, electrons can tunnel through the barrier between the tip and the metal film and enter the metal films as hot electrons with an average energy about qV_T higher than the metal Fermi energy. Because the metal film is very thin, a small portion of these hot electrons can survive thermalization and reach the metal/semiconductor interface without losing significant energy. There the Schottky barrier works like an energy filter: only electrons with energy higher than the Schottky barrier height can cross the interface and contribute to the BEEM current I_c . (Actually only a fraction of the electrons with enough energy can cross due to mechanisms such as defect, scattering or because lateral momentum is not conserved). The barrier height at the metal/semiconductor interface can be determined as qV_{th} where qV_{th} is the threshold tip voltage above which the BEEM current will start to increase from zero.

4.2 BEEM Spectrum

The most important application of the BEEM technique is the determination of the Schottky barrier height at a metal/semiconductor interface by taking BEEM spectra measurements in which the BEEM current I_c is measured as a function of the tip voltage V_T . Figure 4.2 shows a spectrum measured on an Au/n-Si Schottky contact. The black arrow indicates the fitted Schottky barrier height using the method discussed in the next section. Due to the statistical distribution of the

Figure 4.2: Typical BEEM spectrum on Au/n-Si.

injected hot electrons according to the temperature and the Fermi energy inside the tip, the BEEM current actually starts to increase from zero at a voltage which is smaller than the indicated threshold voltage.

4.3 Theoretical Models

In order to extract a Schottky barrier height from BEEM measurements, several theoretical models have to be proposed to describe the spectral shape of the BEEM current around the threshold voltage region. Among them, the Bell-Kaiser (BK) model [37, 47] and the Ludeke-Prietsch (LP) model [48,49] are the most commonly used models. In these two models, a thermally broadened power-law ($n = 2$ for the BK model and $n = 5/2$ for the LP model) is assumed to describe the BEEM current at the threshold voltage region.

The transport of electrons in the BEEM process can be divided into four independent steps: (1) tunneling from the tip to the metal film; (2) transport of the hot electrons through the metal film; (3) transmission across the interface from the metal into the semiconductor; (4) transport inside the semiconductor. The general expression of the BEEM current can be written as

$$I_{BEEM}(V_T) = \int_{-\infty}^{\infty} dE \iint_{2\pi} d\Omega D(E, V_T, \vec{u}, T) \exp[-l(\vec{u})/\lambda(E)] C(E, \vec{u}). \quad (4.1)$$

In Equation (4.1), $D(E, V_T, \mathbf{u}, T)$ describes the distribution of tunneling current from the tip to the metal film where $\mathbf{u}$ is the tunneling direction; $\exp[-l(\mathbf{u})/\lambda(E)]$ describes the transmission through the metal film where $l(\mathbf{u})$ is the electron-path length through the metal film and $\lambda(E)$ is the energy-dependent mean-free path of the electrons; and $C(E, \mathbf{u})$ describes the transmission coefficient across the metal-semiconductor interface. In the following parts of this section, we will discuss how to calculate BEEM current using Equation (4.1) in the BK model and the LP model.

(1) Tunneling current distribution.

Here a planar tip approximation has been assumed to describe the tunneling between the tip and the metal film [50]. The distribution of the tunneling current can be written as

$$D(E, V_T, \vec{u}, T) \propto \rho_T(E - qV_T) \rho_M(E) [f(E - qV_T) - f(E, T)] |M|^2. \quad (4.2)$$

In Equation (4.2), $\rho_T(E - qV_T)$ and $\rho_M(E)$ are the density of states in the tip and the metal film, $f(E - qV_T, T)$ and $f(E, T)$ are the Fermi distribution functions in the tip and the metal film respectively, where the Fermi distribution is defined as $f(x, T) = 1/(1 + \exp(x/k_B T))$, and $|M|^2$ is the tunneling probability (Figure 4.3). For a square tunneling barrier, using the Wentzel-Kramers-Brillouin (WKB) approximation, the tunneling probability can be estimated as

$$|M|^2 \cong \exp\left(-\frac{2\sqrt{2m}}{\hbar} \beta d \sqrt{W_A + qV_T/2 - (E - E_{//})}\right), \quad (4.3)$$

where m is the free electron mass, $\beta \sim 1$ is a correction factor, d is the vacuum gap, $W_A = (W_T + W_M)/2$ is the average of the work functions of the tip and the metal film, $E_{//}$ is the incident electron's kinetic energy parallel to the metal surface, and $W_A + qV_T/2 - (E - E_{//})$ is the average potential barrier height.

Figure 4.3: Schematic energy diagram of the tunneling process.

Compared to the strong energy variation of the tunneling probability defined as Equation (4.3), the densities of states $\rho_T(E-qV_T)$ and $\rho_M(E)$ can be assumed to be constant in the energy region of BEEM measurements, so the spatial and energy distribution of the tunneling current is mainly determined by Equation (4.3). And it can be shown that the energetic and spatial distribution of the tunneling current is approximately described by

$$D(E, V_T, \vec{u}, T) \propto f(E - qV_T) \exp(E / \Delta E) \exp((- \varphi_T / \Delta \varphi_T)^2 / 2), \quad (4.4)$$

where $\Delta E \cong 0.2\text{eV}$, φ_T is the tunneling angle relative to the normal direction of the metal film, and $\Delta \varphi_T \cong 20^\circ$ [44]. $\Delta E \cong 0.2\text{eV}$ means the tunneling probability increase by $e=2.718$ times when the energy is increased by 0.2eV . $\Delta \varphi_T \cong 20^\circ$ describes the angular distribution of the tunneling probability, which means most of the tunneling happens within an angle $\leq 20^\circ$ relative to the surface normal. This average opening angle of the tip-emission cone is derived from a sharp tip and is larger than the value estimated for planar tunneling ($\Delta \varphi_T \cong 11^\circ$ for Au film), since in reality a laterally infinite tip is not a good approximation.

(2) Transport through the metal film.

During the transport through the metal film, the hot electrons will suffer from inelastic scattering and elastic scattering: inelastic scattering will result in a background of secondary electrons, and elastic scattering will result in a larger

effective path length and a more isotropic angular distribution [44]. The main contribution to the inelastic scattering is coming from the electron-electron scattering which gives rise to a mean-free path of $\lambda(E) \cong (E-E_0)/E^2$ where E_0 is the conduction band minimum in the metal film. Both of inelastic scattering and elastic scattering will broaden the momentum distribution of the hot electrons and reduce the lateral spatial resolution of BEEM [44].

In the BK model and the LP model, the mean-free path of the electrons in the metal film $\lambda(E)$ is assumed to be energy- independent, and the factor $\exp[-l(\mathbf{u})/\lambda(E)]$ in Equation (4.1) is replaced by unity.

(3) Transmission across the interface.

In the following discussion about the transmission of hot electrons across the metal/semiconductor interface, two assumptions have been made: (1) free-electron like behavior in both the metal and the semiconductor and (2) conservation of both energy and transverse momentum of electrons. So just before and after the electrons cross the interface,

$$E = \frac{\hbar^2 k_{\perp,M}^2}{2m} + \frac{\hbar^2 k_{\parallel,M}^2}{2m} - E_F = q\phi_B + \frac{\hbar^2 k_{\perp,S}^2}{2m_{\perp}} + \frac{\hbar^2 k_{\parallel,S}^2}{2m_{\parallel}} \quad (4.5)$$

and

$$k_{\parallel} = k_{\parallel,M} = k_{\parallel,S}, \quad (4.6)$$

where m is the electron mass in the metal film, $m_{\perp}$ and $m_{//}$ are the longitudinal and transverse effective mass of electrons in the semiconductor, and the superscript M and S mean the values in the metal and in the semiconductor respectively (Figure 4.4). It will only be possible for an electron with an energy E to cross the interface if the Equations (4.5) and (4.6) have real number solutions for $k_{\perp,M(S)}$ and $k_{//,M(S)}$. It can be shown using Figure 4.4 that only when the incident angle θ_M inside the metal film satisfies

$$\sin^2 \theta_M \leq \frac{m_{//}}{m} \frac{E - q\phi_B}{E + E_F}, \quad (4.7)$$

an electron with an energy E can cross the interface. Equation (4.7) defines an acceptance cone with an opening angle

$$\theta_{C,M} = \arcsin \sqrt{\frac{m_{//}}{m} \frac{E - q\phi_B}{E + E_F}}. \quad (4.8)$$

If transverse momentum is indeed conserved, then all the electrons with angles larger than $\theta_{C,M}$ should be reflected back to the metal film at the interface and can't enter the semiconductor. For Au/Si contacts if we assume $m_{//} \cong m$, $\theta_{C,M}$ is equal to 7° for $E - q\phi_B = 0.1\text{eV}$ and 16° for $E - q\phi_B = 0.5\text{eV}$ [44].

Figure 4.4: k -space diagram of electrons crossing the interface.

In the BK model, it is assumed that for all the electrons which satisfy the condition (4.7) the transmission coefficient across the metal-semiconductor interface $C(E, \mathbf{u})$ is constant. But in the LP model, the Schottky barrier is assumed to be an abrupt potential step, and the transmission coefficient $C(E, \mathbf{u})$ can be calculated using quantum mechanics to be

$$C(E, \vec{u}) = \frac{4k_{\perp,M}k_{\perp,S}}{(k_{\perp,M} + k_{\perp,S})^2} . \quad (4.9)$$

Based on the discussion in (1)-(3), the total BEEM current in the threshold region is approximately given by

$$I_{BEEM}(V_T) \propto \int_{q\phi_B}^{\infty} dE \frac{-df(E - qV_T, T)}{dE} (E - q\phi_B)^n \quad (4.10)$$

where $n = 2$ for the BK model and $n = 5/2$ for the LP model. This equation represents a thermally broadened n -power law. The difference $1/2$ in the power n comes from the difference in the transmission coefficient $C(E, \mathbf{u})$.

Since in our experiment we use the BK model to fit our results, here we will say a little more about the BK model. The discussion below follows the reference [51] with the symbols modified to be consistent with the discussion above. For the case of $m_{//} < m$, using Equations (4.5) and (4.6), it can be shown that electrons which can cross the Schottky barrier and enter the semiconductor need satisfy the following two equations:

$$E_{//} \leq \frac{m_{//}}{m - m_{//}} (E_{\perp} - E_F - q(V_T + \phi_B)) \equiv E_{//}^{\max} \quad (4.11)$$

and

$$E_{\perp} \geq E_F + q(V_T + \phi_B) \equiv E_{\perp}^{\min} . \quad (4.12)$$

So the BEEM current can be written as

$$I_{BEEM}(V_T) = RI_{t0} \frac{\int_{E_{\perp}^{\min}}^{\infty} dE_{\perp} D(E_{\perp}) \int_0^{E_{\parallel}^{\max}} dE_{\parallel} (f(E - qV_T, T) - f(E, T))}{\int_0^{\infty} dE_{\perp} D(E_{\perp}) \int_0^{\infty} dE_{\parallel} (f(E - qV_T, T) - f(E, T))}. \quad (4.13)$$

To extract barrier heights, experimental spectra are fitted by Equation (4.13) with ϕ_B and R as adjusting parameters. This model in general fits our data in the near-threshold pretty well as shown in Figure 4.2. And even if it is not exactly correct for our experiments, it is still a well-defined fitting formula that should accurately reveal changes in the Schottky barrier height if they exist.

(4) *Transport in the semiconductor.*

After electrons enter the semiconductor, several things can happen: (1) some electrons can be reflected back to the metal due to elastic scattering; (2) energy-dependent back reflection in the region between the interface and the potential maximum due to the inelastic scattering by optical phonons will decrease the overall transmission coefficient [52]; and (3) impact ionization can result in a larger BEEM current than given in Equation (4.10) by generating electron-hole pairs [53-55].

4.4 Equipment Setup

Our BEEM measurements were performed in an ultra high vacuum (UHV) system with a base pressure of $1-2 \times 10^{-10}$ Torr. This UHV system was modified from a commercially available Omicron variable temperature STM. Details about this setup are available in the Ph.D thesis of Eric Heller [56].

This UHV system is composed of an airlock and two main chambers (an analysis chamber and an STM chamber). The airlock is equipped with a magnetically coupled horizontal transfer arm which allows the transfer of samples in and out of the UHV system without breaking the vacuum of the main chambers. The analysis chamber is connected to the airlock and has one horizontal arm and one vertical arm that allow the sample transfer from the airlock to the STM chambers. The horizontal arm can also allow direct and indirect heating samples up to ~ 1400 K for direct heating and ~ 750 K for indirect heating. A Varian Vac-Ion Plus 500 ion pump with a pumping speed of 500 liters/sec is connected to the analysis chamber in order to maintain a $\sim 1-2 \times 10^{-10}$ Torr pressure inside the system. Inside the analysis chamber, there is also a tip/sample carousel which can hold up to six tips/samples. The STM chamber has one CCD (charge-coupled device) camera which is used to locate the sample and position the tip or the grounding Au wires. The STM chamber also has a liquid helium flow cryostat which is connected to the sample stage with a copper braid. This allows the sample to be cooled down to ~ 25

Figure 4.5: Schematic of our Omicron variable temperature STM system.

K. A current preamplifier is built inside the STM chamber so it is very close to the sample stage to reduce electronic noise. A tip voltage up to 10 V and a tunnel current up to 25 nA can be used to scan areas as large as $100 \mu\text{m}^2$.

Camelia Marginean and I modified the system to add a second grounding Au wire. This Au wire is not easy to manipulate as the Au wire on the left side since the motion in x and y direction is not independent.

CHAPTER 5

SAMPLE FABRICATION

In this chapter, we will discuss our SOI sample structure and the process procedures used in our sample fabrications in details.

5.1 Sample structure

In our studies, we want to modify the electric field at a metal/semiconductor interface in a sample geometry so that the top metal surface can be accessed by an STM tip. To do this, we take advantage of the three-layer structure of SOI wafer and fabricated a sample structure as shown in Figure 5.1. The Au electrode on the substrate is used to apply a gate voltage to modify the electric field at a metal/semiconductor interface on the top SOI film.

Our SOI samples were fabricated using SIMOX SOI wafers from Simgui Technology Co., China. These SIMOX SOI wafers have a three-layer structure of

(a)

(b)

Figure 5.1: Top view and side view of our SOI sample.

35nm-Si/150nm-SiO₂/p-Si substrate, where the starting silicon wafer was boron doped at $0.6\text{-}1.2 \times 10^{15}/\text{cm}^3$. The detail of our SOI sample structure is illustrated in Figure 5.1. To reduce leakage current between the top silicon film and the p-Si substrate, the top silicon film was etched into $\sim 3.5\text{mm} \times 0.9\text{mm}$ rectangular islands using plasma etching or RIE etching. For measurements on Au/Si contacts, four separate $450\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$ Au/Si Schottky contacts were deposited on each silicon island with Au film thickness = 7 nm. The ohmic contact for BEEM measurements is a $950\text{ }\mu\text{m} \times 600\text{ }\mu\text{m}$ size Ti/Si contact with 20 nm Ti capped with 100 nm Au, and the ohmic contact for BHEM measurements is a $950\text{ }\mu\text{m} \times 600\text{ }\mu\text{m}$ size Pt/Si contact with 20 nm Pt capped with 100 nm Au. For measurements on Cu/Si contacts, four separate $450\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$ Cu/Si Schottky contacts were deposited on each silicon island with 20 nm Cu capped with 10 nm Au. The top Au layer presents to protect the Cu film from oxidation. A much larger contact ($950\text{ }\mu\text{m} \times 600\text{ }\mu\text{m}$) of the same composition was found to be a sufficiently leaky “ohmic” contact to collect both electrons and holes from each Si island. A large-area 100 nm thick Au film electrode was deposited on the backside of the substrate for the back gate bias. Prior to depositing these contacts, the native oxide was removed by dipping in a 10:1 buffered HF (hydrofluoric acid) solution for $\sim 20\text{-}30\text{s}$. A standard lift-off process was used for each metal contact pad, with metals deposited by thermal or electron beam evaporation.

At room-temperature, the resistance between each Si island and the substrate was measured, and samples with one or more islands with $> 1\text{ T}\Omega$ resistance were introduced into our UHV Omicron variable temperature STM/BEEM chamber (base pressure $\sim 1 \times 10^{-10}$ Torr) for BEEM/BHEM measurements [57]. Such a large island/substrate resistance is necessary to reduce stray current from the Si island when a large (up to 17 V) substrate back-gate bias is applied.

In our sample fabrications, we need to do wafer cleaning, photolithography, dry etching, metal deposition, lift-off, and wet etching. The details of these process procedures are discussed in the following sections.

5.2 Chemical cleaning

Depending on the fabrication jobs and the available facilities, different cleaning methods were used during our sample preparation. In our labs (Smith Laboratory and the Physics Research Building (PRB) at Ohio State University), three-solvent cleaning was used to degrease the wafers. In the cleanroom in the Nanotech West fabrication facility at Ohio State University, either piranha cleaning or four-chemical cleaning was used.

5.2.1 Three-solvent cleaning

In this cleaning method, three solvents Trichloroethylene (TCE), Acetone (ACE), and Methanol (ME) are used to clean the sample to remove organic contaminations or dusts on the wafer surface. This cleaning process was mainly used to clean silicon or GaAs wafers in our lab for evaporating Au/Si or Au/GaAs Schottky contacts and we found this is good enough for us. The cleaning procedure is

- (1) Place the sample in a clean glass beaker.
- (2) Ultra-sonic clean in ~50ml TCE for 5 minutes. Drain TCE from beaker.

This step removes organic contaminations (such as oil, grease or wax) from the wafer surface.

- (3) Ultra-sonic clean in ~50ml ACE for 5 minutes. Drain ACE from beaker.

ACE in this step removes the TCE residue and acts as a further cleaning solvent.

- (4) Ultra-sonic clean in ~50ml ME for 5 minutes. Drain ME from beaker.

This step removes the ACE residue.

- (5) Rinse with deionized (DI) water and blow dry with compressed nitrogen gas.

This step removes the ME residue.

All used solvents should be disposed in the proper solvents waste can and should not be left in the fume hood to evaporate!

5.2.2 Piranha cleaning

Piranha cleaning was used to clean our silicon or SOI wafers before the photolithography step in the cleanroom of Nanotech West. This step removes organic contaminants and leaves a thin and clean SiO₂ film on the Si surface. The cleaning procedure is

- (1) Ultra-sonic clean in ~50ml ACE for 5 minutes.
- (2) Rinse with DI water.
- (3) Piranha cleaning (H₂SO₄ : H₂O₂ = 3 - 4 : 1) @ 110°C-130°C or room temperature for 5-10 minutes.
- (4) DI water rinse and N₂ blow dry.

5.2.3 Four-chemical cleaning

For silicon oxide growth, silicon wafers with a diameter ≤ 3 inches are cleaned using four-chemical clean which is an industry standard and is a sequence of four chemical solutions cleaning. This cleaning process was done in the

cleanroom of Nanotech West. In this process, three hotplates are used to heat solutions, three high-purity fused silica (commonly known as quartz) 3-inch dishes are used for Piranha cleaning, SC(Standard Cleaning)¹ and SC2 cleaning, and a high purity PTFE (polytetrafluoroethylene) dish is used for the HF dip. The cleaning procedure is

- (1) Piranha cleaning ($98\% \text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 4 : 1$) @ 110°C - 130°C for 3-10 minutes. This step removes organic contaminants.
- (2) DI water rinse and N_2 blow dry.
- (3) HF dip (DI water: $49\% \text{HF} = 50 : 1$) @ room temperature for 30-60 seconds. This step removes the SiO_2 layer on the wafer and leaves a fresh silicon surface.
- (4) DI water rinse and N_2 blow dry.
- (5) SC1 clean (DI water : $29\% \text{NH}_4\text{OH} : \text{H}_2\text{O}_2 = 20 : 4 : 1$) @ $65^\circ\text{C} - 80^\circ\text{C}$ for 3-10 minutes. Also called RCA1 or APM. This procedure removes particulate contaminants, and desorbs trace metals (Au, Ag, Cu, Ni, etc.). Some metals (e.g. Al) are insoluble in this oxidizing, highly basic solution and tend to precipitate on the surface of Si wafers. After this SC1 clean, the wafer surface is contaminated by Fe ions and is rough.
- (6) DI water rinse and N_2 blow dry.

- (7) SC2 Clean (DI Water : 37 % HCl : 30% H_2O_2 = 5 : 1 : 1) @ 65°C – 80°C for 90 seconds. Also called RCA2 or HPM. This procedure dissolves alkali ions and hydroxides of Al^{3+} , Fe^{3+} , Mg^{3+} .
- (8) DI water rinse and N_2 blow dry.

This method also consumes ~20 nm silicon because the SC1 clean step cleans the silicon surface by etching some silicon material away. So it is not good for cleaning SIMOX SOI wafers with a thin silicon film.

5.3 Photolithography

In our experiments, photolithography was used to define areas where we want to deposit metal contacts or etch away the exposed silicon film of SOI wafers. For metal contact deposition, we tried two methods: lift-off with dual-layer resists and lift-off with single layer resist. The lift-off process with dual-layer resists (explained in the next section) was the first method we tried but we found that we couldn't see BEEM signals on most of the samples fabricated using this method. We thought the reason may be that there was still some lift-off resist (LOR) 2A left on the wafer surface after the photolithography process. Then we tried a lift-off process with single layer resist and we found this worked well for us. Photolithography was done in the cleanroom of Nanotech West.

The spin coating and hotplate baking of photoresist films were done using a Cost Effective Equipment (CEE) 100CB spin coater with programmable spin, ramp, bake and exhaust sequences, and auto-dispense capabilities with syringe or cartridge. The alignment and UV exposure were done using an EV Group EV620 Mask Aligner with accuracy to 0.5 microns and resolution to 0.7 microns.

5.3.1 Lift-off with dual-layer resists.

In this method, first one layer of MicroChem LOR 2A is coated on the wafer and soft-baked (Figure 5.2(a)). Then one layer of Shipley Microposit photoresist S1813 is coated on top of the LOR 2A layer and soft-baked (Figure 5.1.a). After UV exposure (Figure 5.2(b)), the sample is insert into MF-319 developer and because LOR 2A develops isotropically an undercut will form (Figure 5.1(c)). This should result in a discontinuous metal film during evaporation (Figure 5.1(d)) and clear edge profiles after lift-off (Figure 5.1(e)) [58]. The procedure detail is

- (1) Clean the wafer using Piranha cleaning for 20minutes.
- (2) Bake at 200 °C for 30 minutes using a hot plate to remove moisture.
- (3) Coat with LOR 2A (using Program #9 in the spin coater).

Final speed = 3000RPM and time = 45 seconds.

The LOR thickness is about 200nm.

Figure 5.2: Lift-off process with dual-layer resists: (a) spin-coat and soft-bake LOR 2A and S1813; (b) Expose to UV; (c) Develop LOR 2A and S1813; (d) Metal deposition; and (e) Lift-off.

- (4) Prebake at 190 °C for 15 minutes using a hot plate.
- (5) Coat with photoresist S1813 (using Program #4 in the spin coater).
Final speed = 3000RPM and time = 60 seconds.
The LOR thickness is about 1.4um.
- (6) Softbake at 115 °C for 1minute.
- (7) Expose to UV for 6 seconds.
- (8) Develop in MF-319 for 2 minutes.
- (9) Metal deposition.
- (10)Lift-off using NMP and Acetone.

5.3.2 Lift-off with single layer resist.

In this method, only one layer photoresist is used: Shipley S1813. Since there is no undercut, a continuous metal film may form during metal evaporation and this may result in ragged edges (Figure 5.3). These ragged edges may be a problem for other researchers but they are not a problem for us since we usually measure STM/BEEM away from the contact edge. The procedure detail is

- (1) Clean the wafer using Piranha cleaning for 20minutes.
- (2) Coat with photoresist S1813 (using Program #4 in the spin coater).
Final speed = 3000RPM and time = 60 seconds.

Figure 5.3: Lift-off process with single-layer resists: (a) spin-coat and soft-bake S1813; (b) Expose to UV and develop S1813 in MF-319; (c) Metal deposition; and (d) Lift-off.

The LOR thickness is about 1.4 μ m.

- (3) Softbake at 115 °C for 1minute.
- (4) Expose to UV for 5-6 seconds.
- (5) Develop in MF-319 for 1 minute.
- (6) Metal deposition.
- (7) Lift-off using Acetone.

5.4 Dry etching

Because current leakage paths sometimes exist in the BOX of SIMOX SOI wafer, we etched the SOI film to small rectangles to reduce the possibility that our sample structure has substantial leakage to the substrate. We used plasma etching or reactive ion etching (RIE) to etch the SOI film into small ($\sim 3.5\text{mm} \times 0.9\text{mm}$) rectangles. In these etching processes, photoresist S1813 was used as a mask, and was patterned using the method discussed in Section 5.3.2 with steps (a) and (b). The photoresist S1813 was hard-baked at 115°C for 30 minutes in the BlueM Oven #1.

5.4.1 Plasma etching

The equipment we used is Lam 590 Oxide Etcher in Nanotech West. The recipe is

Gasses: $\text{O}_2 + \text{He} + \text{CF}_4 = 8\text{sccm} + 10\text{sccm} + 133\text{sccm}$;

Pressure: 425 mTorr;

Power: 300W;

Gap between electrodes: 1.2cm;

Time: 100s.

After this plasma etching, for SIMOX SOI (35nm) samples, about 130nm of the original 150 nm SiO₂ is left. For this piece of equipment all of the above parameters are controlled by the user. The details of this recipe are listed in Table 5.1.

	Step 1	Step 2	Step 3	Step 4	Step 5
Pressure (mTorr)	425	425	425	0	0
RF Power(W)	0	0	300	0	0
Gap(cm)	1.2	1.2	1.2	1.2	1.35
O ₂ (sccm)	8	8	8	0	0
He (sccm)	10	10	10	50	0
CF ₄ (sccm)	133	133	133	0	0
Other chemicals (sccm)	0	0	0	0	0
COMPL	Time 10s	Time/stability 15s	Time 100s	Time 15s	RECIPE

Table 5.1: Details of the recipe for plasma etching 35nm SIMOX SOI wafers.

5.4.2 Reactive ion etching

The equipment we used was the Technics Micro-RIE (Series 800-II) in Nanotech West. Because the gas lines connected to this equipment are switched between $\text{CF}_4 + \text{O}_2$ or $\text{CHF}_3 + \text{O}_2$ depending on the users' requests, we developed one recipe for each of these two connections. These two recipes are

(1) Gasses: $\text{CF}_4 + \text{O}_2 = 30\text{sccm} + 10\text{sccm}$;

Power = 80-90 W;

Pressure $\approx 233\text{mTorr}$;

Time = 150s.

About 102-114 nm of the original 150 nm SiO_2 BOX layer is left for the 35nm SIMOX SOI samples.

(2) Gasses: $\text{CHF}_3 + \text{O}_2 = 30\text{sccm} + 10\text{sccm}$;

Power = 85-92 W;

Pressure $\approx 233\text{mTorr}$;

Time = 150s.

About 110-120 nm SiO_2 is left for the 35nm SIMOX SOI samples.

For this piece of equipment, only the flow rate of the reactive chemicals, the RF power and the process time can be controlled by users. The RF power fluctuates

during the etching so a power range was shown in the above recipes instead of a specific number.

5.5 Wet etching

Before the silicon wafer is transferred into the evaporation chamber for metal depositions, we need to remove the native oxide on the silicon wafer. This is done by a 20-30 seconds dip in a diluted hydrofluoric acid solution (10:1 or 7:1 buffered oxide etch) and then a 1 minute DI water rinse. 49% HF is not good since it attacks the photoresist S1813. After this HF dip, the silicon wafer is transferred into the evaporation chamber very quickly and the chamber is pumped down just after this transfer to avoid oxide growth. After the HF dip, the silicon surface is passivated with H-Si bonds which make the surface oxidation rate very slow [59].

5.6 Metal evaporation

In our ambipolar BEEM experiments, we need to do four metal depositions: one for ohmic contacts on the backside of the wafers, two for ohmic contacts on the top SOI film, and one for the Schottky contacts on the top SOI film. The first three contacts were deposited using the e-beam evaporator DV(Denton Vacuum)-502A in Nanotech West, and the Schottky contacts were deposited using our own custom-made thermal evaporator.

For making a Au/GaAs reference sample, the native oxide on GaAs is removed by dipping in a $\text{NH}_4\text{OH} : \text{DI} = 1:1$ solution for 1 minute followed by a 1-minute rinse in DI water and N_2 blow dry.

5.6.1 E-beam evaporation

In this evaporation process, an electron beam is used to heat the source material and causes it to evaporate.

Using the e-beam evaporator DV(Denton Vacuum)-502A in Nanotech West, we deposited the ohmic contacts (Au, Ti and Pt) on the backside and on the SOI film. The deposition rate is around $0.3\text{-}0.5\text{\AA}/\text{s}$, and the pressure before evaporation is around $1\text{-}4 \times 10^{-6}$ Torr. The source materials are from Kurt J Lesker: Au (purity = 99.99%), Ti (purity = 99.995%) and Pt (purity = 99.99%). The deposited film thickness is monitored by a crystal monitor.

5.6.2 Thermal evaporation of Schottky contacts

The Schottky contacts (Au/Si and Cu/Si) are deposited using our own thermal evaporator [60]. In this thermal evaporator, the metal sources (Au and Cu) are placed in two tungsten boats which are separated with a piece of plate to avoid contaminating each other. The metal source is heated using a high-power current source until the metal starts to evaporate. The deposition rate is around $0.3\text{-}0.5\text{\AA}/\text{s}$. The pressure before evaporation is typically $\leq 1\text{-}2 \times 10^{-7}$ Torr, which can be

achieved after 4-5 hours of pumping. Also the evaporator allows the heating or cooling of samples during evaporation to modify the grain structure of the deposited metal [46]. The metal contacts can be patterned using photolithography or a metal shadow mask with an array of 450um diameter holes. The deposited film thickness is monitored by a crystal monitor. The source materials we used are Au (purity = 99.999%) from Kurt J Lesker and oxygen-free Cu (purity = 99.995%) from Alfar Aesar.

5.7 Fabrication steps for one complete SOI sample

Here, we give a general procedure for fabricating a complete SOI sample without repeating the details of each process step.

- (1) Cleave a piece of SOI wafer with a size of $1.1\text{cm} \times 1.5\text{cm}$.
- (2) Clean it using ultrasonic cleaning in Acetone and then clean it using piranha cleaning.
- (3) Evaporate 100nm Au on the backside of the wafer.
- (4) Do photolithography and plasma or RIE etch the silicon islands.
- (5) Do photolithography and evaporate ohmic contacts and lift-off.
- (6) Scribe lines using a diamond scribe for the cleaving in Step (8). The goal for this step is to protect the metal film of the Schottky contacts and the SOI film during the cleaving in Step (8). By scribing the

cleaving lines in this step, the SOI wafer can be broken into four pieces before the liftoff Step (9), so the SOI wafer is covered with $\sim 1.4\mu\text{m}$ photoresist. This will protect the metal film of the Schottky contacts and the SOI film.

- (7) Do photolithography and evaporate Au or Cu Schottky contacts.
- (8) Break this piece of wafer into four pieces. The size of each cleaved sample should be smaller than $5\text{mm}\times 5\text{mm}$ because the space on the STM sample holder is $5\text{mm}\times 5\text{mm}$. According to my experience, it is better to make the sample size around $4.5\text{mm}\times 4.5\text{mm}$, so the sample size is not too small and it is easy to place it on the sample holder.
- (9) Lift-off in acetone and ultra-sonic clean in methanol
- (10) Rinse in DI water and blow dry with N_2 gas.

CHAPTER 6

AMBIPOLAR BEEM MEASUREMENTS

In this chapter, we report measurements using ballistic electron/hole emission microscopy (BEEM/BHEM) on device structures fabricated SOI wafers to investigate how the local electron (n-type) and hole (p-type) Schottky barrier heights (i.e., local valence-maximum and conduction-minimum band energies at the metal/Si interface) are modified by an applied gate field. We demonstrate the first nm-resolution *ambipolar n-BEEM/p-BHEM* measurements performed at the same location on Au/Si and Cu/Si Schottky contacts at temperatures down to 80K. The local Schottky barrier heights for electrons and holes at particular locations were measured and, when corrected for image force lowering, were found to sum to nearly the same value (approximately the silicon bandgap). While the individual n- and p-SBHs varied by more than 200 meV between the Au/Si and Cu/Si contacts, for a given sample they sum to within 15 meV of the same value, indicating that the

individual variations are due to variations in a local surface dipole as compared with tip effects or variations in local composition. This method could be a platform for studying the band gap of different epitaxial layers and band offset in heterostructures.

6.1 Previous BEEM results on Au/Si and Cu/Si contacts

Before describing the details of our ambipolar BEEM measurements, we briefly review previous BEEM/BHEM results on metal/Si interfaces. Since the Schottky barriers in our ambipolar BEEM experiments are Au/Si(100) and Cu/Si(100), in this section we only discuss previous BEEM/BHEM results on Au/Si(100) and Cu/Si(100).

6.1.1 Au/Si(100)

In their initial work, Kaiser and Bell measured the barrier height of Au/*n*-Si(100) (doping $\cong 2 \times 10^{15}/\text{cm}^3$) using BEEM at room temperature [47]. The average Schottky barrier height they measured was 0.82 eV determined from BEEM spectrum fitted with a thermally-broadened square law ($n = 2$, see Section 4.3). At $T = 77$ K, Bell et al. measured the Schottky barrier heights of Au/*n*-Si(100) (doping $n = 2 \times 10^{15}/\text{cm}^3$) and Au/*p*-Si(100) (doping $p = 3 \times 10^{15}/\text{cm}^3$) using BEEM/BHEM [61-63]. The barrier heights were determined to be 0.82 eV for *n*-Si and 0.35 eV for *p*-Si using a square law. The measured Schottky barrier height using BEEM by different groups was found to vary slightly with sample preparation and measurement conditions, in the range from 0.75 to 0.87 eV [37, 47, 61-67].

Figure 6.1 shows our measured BEEM/BHEM spectra on Au/n-Si(100) and Au/p-Si(100) at $T = 80\text{K}$, using the equipment discussed in Section 4.4. The red curves are the experimental results and the blue ones are the fits using the BK model. The average measured barrier height is $0.818(2)\text{ eV}$ for $n\text{-Si}$ and $0.332(2)\text{ eV}$ for $p\text{-Si}$. The doping of the Si wafer used in these experiments is $n \cong 0.2\text{-}1.0 \times 10^{16} / \text{cm}^3$ for the $n\text{-Si}$ and $p \cong 3 \times 10^{16} / \text{cm}^3$ for the $p\text{-Si}$.

6.1.2 Cu/Si(100)

Labella et al. measured the Schottky barrier height of Cu/n-Si(100) (doping $\cong 0.3\text{-}4.0 \times 10^{15} / \text{cm}^3$) using BEEM at $T = 80\text{K}$ and the value they obtained was 0.64 eV [68]. Banerjee et al. measured the Schottky barrier height of Cu/p-Si(100) using BHEM at $T = 150\text{K}$ and the value they obtained was 0.48 eV [69].

6.2 Ambipolar BEEM studies

For the BEEM/BHEM measurements mentioned in Section 6.1, the Schottky contacts were fabricated by depositing Au or Cu on regular n-type or p-type silicon substrate. Due to the band bending inside the silicon substrate, only BEEM can be performed on Au(Cu)/n-Si contacts and only BHEM can be performed on Au(Cu)/p-Si contacts. For an Au(Cu)/n-Si contact, starting from the metal/silicon interface, the energy bands bend downward towards into the silicon as shown in Figure 6.2 (a). In this case, if hot electrons are injected across the metal/silicon interface, they will be

Figure 6.1: BEEM/BHEM spectrum measured on (a) Au/n-Si(100) and (b) Au/p-Si(100) at $T = 80\text{K}$. Red - experimental results and blue - fitted results using the BK model.

swept away from the interface and into the substrate by the electric field due to the band bending, so they can be collected as BEEM current by the ohmic contact on the substrate. However, if hot holes are injected across the metal/silicon interface, they will be swept back towards the interface and back into the metal by the electric field because they have positive charge, so they cannot be collected as BHEM current by the ohmic contact at the other end of the substrate. So for an Au(Cu)/n-Si contact, only electrons can be collected, i.e. only BEEM measurements can be performed and only the Schottky barrier height for electrons can be measured. For an Au(Cu)/p-Si contact, similar argument can show that only holes can be collected, so only BHEM measurements can be performed and only the Schottky barrier height for holes can be measured. Therefore, for conventional BEEM or BHEM measurement, separate samples have to be used to measure the Schottky barrier heights for electrons and holes. This makes it difficult to directly compare the electron- and hole-SBHs.

Here we will demonstrate the first nm-resolution *ambipolar n-BEEM/p-BHEM* measurements which can measure the local Schottky barrier heights for electrons and holes at the same location on the same metal/silicon contact, allowing for the first time a direct comparison between the electron- and hole-SBHs on a particular sample.

So

Figure 6.2: Energy band diagrams of (a) Metal/n-Si and (b) Metal/p-Si.

6.2.1 Sample geometry and basic idea of Ambipolar BEEM

Figures 6.3 and 6.4 illustrate the basic idea of how to measure the local Schottky barrier heights for electrons and holes at the same location on the same metal/silicon contact using SOI structures.

The schematic diagram of sample geometry and wiring for our ambipolar BEEM measurements is shown in Figure 6.3. Electrons or holes are injected from the Schottky contact, and then they conduct laterally and are collected at the ohmic contact. The electrode on the backside of the substrate is used to apply a back-gate voltage which can make the same metal/silicon Schottky barrier either effectively n-type (Figure 6.4(a)) or p-type (Figure 6.4(b)) depending on the polarity of the substrate gate bias. Since the top silicon film has a doping of $\sim 1 \times 10^{15}/\text{cm}^3$ and the corresponding bulk depletion width is $\sim 1 \text{ }\mu\text{m}$, the dopant-related band bending in the 35 nm-thick silicon film should be negligible. Then if a positive substrate bias is applied to the substrate, the energy bands in the top silicon film will bend downward (similar to an n-type Schottky barrier) as shown in Figure 6.4(a). If the applied positive bias is large enough so that the conduction band minimum approaches the silicon film Fermi level $E_{F,\text{Si}}$ at the Si/SiO₂ interface, then electrons will accumulate near the Si/SiO₂ interface and allow the Si film to become laterally conductive. When the silicon film is conducting enough, hot electrons injected from a negatively-biased tip can be swept to the Si/SiO₂ interface, then conduct laterally and be collected as BEEM current at the ohmic contact. This allows BEEM measurements to be performed and the Schottky barrier height for electrons can be determined. In contrast,

Figure 6.3: Schematic diagram of sample geometry and wiring for ambipolar BEEM measurements.

Figure 6.4: Energy band structures for Au/Si barriers (a) SOI sample with a positive substrate bias, and (b) SOI sample with a negative substrate bias. Here $e\phi_{n0}$ and $e\phi_{p0}$ are intrinsic Schottky barrier heights.

if a negative substrate bias is applied to the substrate, the energy bands in the top silicon film will bend upward (similar to a p-type Schottky barrier) as shown in Figure 6.4(b). If the applied positive bias is large enough so that the valence band maximum approaches the silicon film Fermi level $E_{F,Si}$ at the Si/SiO₂ interface, then holes will accumulate near the Si/SiO₂ interface. When the silicon film is conducting enough due to hole accumulation, holes injected from a positively-biased tip can be swept to the Si/SiO₂ interface, then conduct laterally and be collected as BHEM current at the ohmic contact. This allows BHEM measurements to be performed and the Schottky barrier height for holes can be determined. Therefore, using this SOI structure, the local Schottky barrier height for both electrons and holes can be measured at the same location on the same metal/silicon contact.

6.2.2 Ambipolar BEEM measurement results

Before describing the details of the ambipolar BEEM measurement results, the general procedure of how to get the barrier heights from BEEM/BHEM measurements is first discussed. In the following discussion, we use BEEM measurement as an example and note that an analogous procedure applies for BHEM measurements. During BEEM spectra measurements, the scan area was set to be a square whose sides had a size of 300-400nm. In a particular scan, a BEEM spectrum was measured at about 10-20 locations which were randomly chosen. At each of these 10-20 locations, 10 BEEM IV curves were measured and these 10 curves were averaged to give one BEEM spectrum which was then fitted using BK model to give

one local Schottky barrier height. On one Schottky contact, at least two groups of measurements were done: one with the tip voltage swept from low to high and the other with the tip voltage swept from high to low (to reduce the effect of time delay in BEEM IVs at low temperature). Then all of barrier heights measured with the tip voltage swept from low to high were averaged to give the Schottky barrier height $q\phi_{L-H}$, and all of barrier heights measured with the tip voltage swept from high to low were averaged to give the Schottky barrier height $q\phi_{H-L}$. Finally these two measured barrier heights $q\phi_{L-H}$ and $q\phi_{H-L}$ were averaged to give the average barrier height of the Schottky contact. And the standard deviation of measured barrier heights was also determined and was used to calculate the uncertainty in the average barrier height. Typical ambipolar BEEM spectra at 80 K with $V_{\text{Sch}} = 0$ on a gated Au(Cu)/Si (SOI) contact are shown in Figure 6.5 (see Fig. 6.3 for the definition of V_{Sch}).

In Figure 6.5 (a), the blue curve is a typical BEEM spectrum measured at 80 K on a Au/Si (SOI) contact with a positive gate bias of 7.0 V applied to the substrate and with the Ti/Si contact used as the ohmic contact to collect the BEEM current. For comparison, the red curve shows a typical BEEM spectrum for a regular Au/n-Si (doping $\sim 0.2\text{-}1.0 \times 10^{16} \text{ cm}^{-3}$) also measured at 80 K. The dotted curves are the experimental results and the solid lines are the corresponding Bell-Kaiser fits. For the Au/Si (SOI) contact, the average barrier height was found to be 0.787(2) eV, while for the regular Au/n-Si contact, the average barrier was found to be 0.818(2) eV (here the number inside the bracket is the uncertainty in the average). We see the Schottky

Figure 6.5: (a) BEEM and BHEM spectra at $T = 80\text{K}$. Red ($\square$), blue ($\circ$), and green (Δ) data points correspond to regular Au/n-Si, Au/SOI and Au/Cu/SOI. Solid lines are corresponding Bell-Kaiser fits.

barrier height is ~ 31 meV lower on the gated SOI sample as compared with the Schottky barrier height on the regular silicon. This can be explained by the mechanism of image force lowering discussed in Section 3.3. To estimate the electric field inside the silicon film near the interface, we can assume that the conduction band minimum in the silicon film is very close to the Fermi level at the interface and the slope of the band bending is constant (due to the low doping of the Si film and the small 35 nm thickness of the Si film), so the electric field inside the silicon film near the interface can be estimated by

$$E = \frac{\phi_{n0}}{d}, \quad (6.1)$$

where $q\phi_{n0}$ is the intrinsic Schottky barrier and d is the silicon film thickness. From this the interface electric field in the gated SOI sample is estimated to be $\sim 2 \times 10^5$ V/cm. Using Equation (3.8), the image force lowering due to this field is found to be ~ 49 meV in the gated SOI sample. The interface electric field in the regular Au/n-Si sample can be estimated by

$$E = \sqrt{\frac{2qN_D}{\epsilon_s} \left(V_{bi} - \frac{k_B T}{q} \right)}, \quad (6.2)$$

where N_D is the doping of the silicon substrate, $\epsilon_s = 11.7\epsilon_0$ is the silicon permittivity and V_{bi} is the built-in voltage inside the silicon [6]. The built-in voltage V_{bi} and can be estimated by

$$V_{bi} = q\phi_n - (E_C - E_F), \quad (6.3)$$

where $(E_C - E_F)$ can be determined using Equation (2.6) [6]. For a phosphorous doped silicon with a doping level of $\sim 0.2-1.0 \times 10^{16} / \text{cm}^3$, $(E_i - E_F)$ is around 0.52eV, so the depletion field can be estimated to be $\sim 4 \times 10^4$ V/cm. This will produce an image force lowering of ~ 22 meV. The difference between these image force lowering is ~ 27 meV which is close to the difference between the measured Schottky barrier heights ~ 31 meV.

We can also notice that the amplitude of the BEEM current is slightly smaller in the gated SOI sample than in the regular silicon sample. The smaller BEEM amplitude in the gated sample may result if some of the injected electrons *cross back* over the barrier into the Au film (and hence are not collected) as they move laterally towards the ohmic contact. And also because of the reflection due to the band structure of the BOX under the silicon film, the transmission coefficient $C(E, \mathbf{u})$ may be much smaller in the SOI sample than that in the regular sample.

We note that at lower gate bias the resistance of the Si film becomes much larger (due to reduced electron accumulation at the Si/SiO₂ interface - see Figure 6.4 (a)) causing the BEEM current to be greatly reduced. At larger gate bias, the

resistance of the Si film becomes smaller (due to greater electron accumulation) and the BEEM current becomes significantly noisier due to increased leakage between the Au and the electron accumulation layer at the Si/SiO₂ interface. As a consequence, the best BEEM signal-to-noise ratio was obtained for a substrate bias V_{sub} in the range of 6 to 8 V.

For hole-BHEM on the gated Schottky contact (blue curve in Figure 6.5(b)), a negative bias of -17.0 V was applied to the substrate and Pt/Si contact was used as the ohmic contact to collect the BHEM current. The comparison red curve in Figure 6.5(b) is from a regular Au/p-Si (doping $\sim 3 \times 10^{16} / \text{cm}^3$) contact at 80K. The measured average barrier height is 0.323(2) eV for the gated SOI sample and 0.332(2) eV for the regular silicon sample. We can see the measured average barrier height is ~ 9 meV lower on the gated sample as compared with the regular Au/p-Si sample, and also the amplitude of the BHEM current is smaller on the SOI sample, most likely for the same reasons as discussed above for the n-type BEEM measurements. In the p-type case, the best signal-to-noise was found for the gate bias range of -16 to -18 V. We note that in general, the p-type Schottky zero-bias resistance was smaller than the n-type zero-bias resistance, resulting in noisier BHEM as compared to BEEM measurements.

Using the measured barrier heights and the mechanism of image force lowering, the intrinsic Schottky barrier height $q\phi_{n(p)0}$ can be extracted self-consistently from

$$q\phi_{n(p)} = q(\phi_{n(p)0} - \sqrt{qE/4\pi\epsilon_s}), \quad (6.4)$$

where the electric field is determined by $E = \phi_{n(p)0}/d$. The intrinsic barrier heights for Au/SOI sample were determined to be 0.841(2) eV for electrons and 0.359(2) eV for holes. These sum to 1.200(3) eV which is close to the expected Si bandgap $E_g \sim 1.17$ eV at 80K [6]. The ~ 30 meV difference may be due to systematic errors in fitting the data or inaccurate estimates of the interface electric fields.

Similar measurements were also made using gated Cu/Si Schottky contacts (green data points in Figure 6.5), which are expected to have a smaller n-type and a larger p-type Schottky barrier height as compared to Au/Si. Previous experiments on Cu/Si contacts conducted by regular BEEM or BHEM reported a barrier height of 0.64(2) eV for electrons at 80K [68] and 0.48(3) eV for holes at $T = 150$ K [69], respectively. Using our gated Cu/Si contacts, at 80K we found a measured barrier height of 0.570(2) eV for electrons and 0.551(7) eV for holes respectively, which yield corresponding intrinsic barrier heights of 0.617(2) eV and 0.597(7) eV respectively, when self-consistently corrected of image force lowering using Equation (6.4). These sum to 1.214(4) eV, which is quite close to the sum of the measured barrier heights for electron and holes on our gated Au/Si SOI sample (1.20 eV) measured at the same temperature, even though the individual barrier heights differ by more than 200 meV from their Au/Si counterparts. On a second gated Cu/Si sample, the measured intrinsic barrier heights at 80K (0.646(2) eV for electrons and 0.558(10) eV for holes respectively) varied somewhat from the first Cu/Si sample, but

their sum (1.204(5) eV) is again quite close to that of the Au/Si and other Cu/Si samples. This demonstrates that the large variations in individual electron- and hole-Schottky barrier heights are due to variations in the local surface dipole at the Au/Si or Cu/Si contacts, and not due to tip artifacts or variations in local composition (such as a thin oxide layer on the Si), which would have the effect of increasing the sum.

6.3 Explanation of the applied gate voltages for Cu/SOI and Au/SOI

We notice that the gate voltages for BEEM and BHEM measurements on Au/SOI and Cu/SOI are different: for Au/SOI they are +7V for BEEM and -17V for BHEM and for Cu/SOI they are +12V for BEEM and -14V for BHEM. We believe this difference comes from the interface state or fixed charge at the Si /SiO₂ interfaces.

First, we believe that most of the applied gate voltage is across the SiO₂ layer, since the voltage drop across the thin top Si film or the substrate can't be much larger than the Si bandgap. This follows by assuming that the top Si film is in equilibrium with the front-side ohmic contact and that the substrate is in equilibrium with the back-side ohmic contact. In this case free carrier accumulation or strong inversion at the SOI film/SiO₂ and SiO₂/Si substrate interfaces will limit the band bending in the Si film or Si substrate to be not much larger than the Si bandgap. For a p-Si with a doping of $\sim 10^{15}/\text{cm}^3$, $E_F - E_V \approx 0.05\text{eV}$ and $E_C - E_F \approx 1.12\text{eV}$ at $T=80\text{K}$ [6], so we think the bending in the substrate will not be much larger than $\sim 0.1\text{ V}$ for

BEEM (with a positive substrate bias) and $\sim 1.1\text{V}$ for BHEM (with a negative substrate bias).

Using Gauss's law and assuming no interface state or fixed charge at the Si/SiO₂ interfaces or in the SiO₂, and also assuming the E-field inside the SOI film is equal to $E = \phi_{n(p)0}/d$, we can estimate how large the gate voltage is. For measurements on Au/SOI, the estimated gate bias is $\sim +13\text{V}$ for BEEM and $\sim -8\text{V}$ for BHEM, which are much different from the applied gate voltage in our measurements ($+7\text{V}$ for BEEM and -17V for BHEM). And in Cu/SOI case, the estimated gate voltages are $\sim +9\text{V}$ for BEEM and -10V for BHEM.

The gate voltages used in our experiment could be explained by assuming there is interface charge (due to interfaces states) in the order of $\sim 10^{12} \text{ q/cm}^2$ at Si/SiO₂ interfaces, in combination with some fixed charge at Si/SiO₂ interfaces and/or in the SiO₂ bulk. Previous studies have reported the existence in SIMOX wafers of “acceptor-like” interface states above E_i (the intrinsic level in Si) and “donor-like” interface states below E_i with a density in the order of $D_{it} = 10^{11}\text{-}10^{12}/\text{cm}^2/\text{eV}$, and fixed charge in the order of $D_f = 10^{11}\text{-}10^{12} \text{ q/cm}^2$, and these numbers may be larger for SIMOX wafers with thinner Si film [18,70]. To estimate the density of interface states and fix charge in our SOI sample, we assume at Si/SiO₂ interfaces the density of interface states is constant across the silicon band gap and the fix charge is at the Si/SiO₂ interfaces and there is no charge inside the BOX. Then using Gauss's law we can get

Figure 6.6: Energy band diagram for (a) positive substrate bias and (b) negative substrate bias.

$$\varepsilon_{Si} E_{Si} - \varepsilon_{ox} E_{ox} = D_f - q D_{it} E_g / 2 \quad (6.5a)$$

for BEEM measurements and

$$\varepsilon_{ox}E_{ox} - \varepsilon_{Si}E_{Si} = D_f + qD_{it}E_g / 2 \quad (6.5b)$$

for BHEM measurements (Figure 6.6) . In Equations (6.5), $\varepsilon_{Si} = 11.9\varepsilon_0$ ($\varepsilon_{ox} = 3.9\varepsilon_0$) is the dielectric constant of silicon (silicon oxide), and E_{Si} (E_{ox}) is the E-field in the silicon (oxide) near the interface. Since we assume the conduction band minimum (valence band maximum) and the Fermi level coincide at the SOI/BOX interface for BEEM (BHEM) measurements, the interface charge is $-qD_{it}E_g/2$ ($+qD_{it}E_g/2$) for BEEM (BHEM) measurements. The E -field inside the silicon film can be estimated by $E_{Si} = \phi_{n(p)0}/d$, and the electric field inside the BOX can be estimated by $E_{ox} = (\text{gate voltage} - E_g / q)/d_{ox}$ where $d_{ox} = 150$ nm is the BOX thickness and it is assumed that the sum of voltage drops across the SOI and the substrate is $\sim E_g/q$. In order to explain our measurements, for the Au/SOI samples we then would need to assume an average interface state density of $1.5 \times 10^{12}/\text{cm}^2/\text{eV}$ and fixed charge density of $1.2 \times 10^{12} q/\text{cm}^2$, while for the Cu/SOI samples the interface state density would need to be $1.9 \times 10^{12}/\text{cm}^2/\text{eV}$ and the fixed charge density $0.2 \times 10^{12} q/\text{cm}^2$. These numbers agree with the numbers mentioned in Ref.[18] and Ref.[70].

We simulated the gate voltages for BEEM and BHEM measurements on our sample structure using a numerical simulation tool COMSOL Multiphysics. The details about this simulation is listed in Appendix A. Figure 6.7 is the simulation results on Au/SOI and Cu/SOI assuming there is no interface states at the Si/SiO₂ interfaces and no fix charges at the Si/SiO₂ or inside the BOX, where the conduction

band minimum and the valence band maximum are plotted relative to the Fermi level in the metal of the Schottky contacts on the SOI film. The dark blue curve is the conduction band minimum in the SOI film of Au/SOI sample when the gate voltage is +13V, and the green curve is the valence band maximum in the SOI film of Au/SOI sample when the gate voltage is -8V. The blue curve is the conduction band minimum in the SOI film of Cu/SOI sample when the gate voltage is +9V, and the red curve is

Figure 6.7: COMSOL Multiphysics simulation without interface states or fix charges.

the valence band maximum in the SOI film of Cu/SOI sample when the gate voltage is -10V. We can see this simulation results are in good agreement with our estimation above. Figure 6.8 is the simulation results on Au/SOI sample structure assuming there are interface states with a density of $1.5 \times 10^{12} \text{ /eV/cm}^2$ and a fix charge with a density of $1.2 \times 10^{12} q/\text{cm}^2$ at the Si/SiO₂ interfaces. The dark blue curve is the conduction band minimum in the SOI film when the gate voltage is +7V, and the red

Figure 6.8: Simulation results on Au/SOI sample structure assuming there are interface states with a density of $1.5 \times 10^{12} \text{ /eV/cm}^2$ and a fix charge with a density of $1.2 \times 10^{12} q/\text{cm}^2$ at the Si/SiO₂ interfaces.

curve is the valence band maximum in the SOI film when the gate voltage is -17V. For comparison, the green curve is the conduction band minimum in the SOI film when the gate voltage is +7V assuming there is no interface states or fix charge, and the blue curve is the valence band maximum in the SOI film when the gate voltage is -8V. Figure 6.9 is the simulation results on Cu/SOI sample structure assuming there are interface states with a density of $1.9 \times 10^{12} \text{ /eV/cm}^2$ and a fix charge with a

Figure 6.9: Simulation results on Cu/SOI sample structure assuming there are interface states with a density of $1.9 \times 10^{12} \text{ /eV/cm}^2$ and a fix charge with a density of $0.2 \times 10^{12} q/\text{cm}^2$ at the Si/SiO₂ interfaces.

density of $0.2 \times 10^{12} q/\text{cm}^2$ at the Si/SiO₂ interfaces. The dark blue curve is the conduction band minimum in the SOI film when the gate voltage is +12V, and the red curve is the valence band maximum in the SOI film when the gate voltage is -14V. For comparison, the green curve is the conduction band minimum in the SOI film when the gate voltage is +9V, and the blue curve is the valence band maximum in the SOI film when the gate voltage is -10V. We can see adding interface states in the order of 10^{12} /eV/cm^2 and a fix charge in the order of $10^{12} q/\text{cm}^2$ can explain the gate voltages in our BEEM and BHEM measurements qualitatively.

It is not clear why there should be a lower fixed charge density for the Cu/SOI samples, but we do note that a much larger power was needed to thermally deposit the Cu film than the Au films (due to the lower vapor pressure of Cu compared to Au), and that the sample likely became significantly hotter during the Cu deposition, which may have had an annealing effect (no intentional annealing of these samples was done). It will be nice if all of the gate voltages can be explained by assuming an interface state density and a fixed charge density with the same values. But this is really difficult or even impossible due to the following facts present in a real device. First, the interface state density is not a uniform function of energy as shown in reference [70]. Second, the alignment of the conduction or valence band relative to the Fermi energy at the Si film/SiO₂ interface is not easy to estimate. The assumption we made in our paper is just a simple way to estimate the E field under the Schottky contacts. Third, processing can cause variations from sample to sample.

6.4 Image Force Lowering Measurements

We note that for a given V_{Sch} (the applied voltage between the Schottky contact and the ohmic contact to the Si film, see Figure 6.3), the measured SBH was found to be essentially independent of the substrate bias V_{sub} . This is expected since varying charge accumulation at the Si/SiO₂ interface in response to varying V_{sub} will effectively “pin” the conduction (valence) band minimum at the Si/SiO₂ interface to the silicon Fermi energy, causing the electrical field (and hence the Schottky barrier

Figure 6.10: Energy band diagrams when there is bias between the Schottky contact and the ohmic contact.

Figure 6.11: Schottky barrier heights measured on Au/SOI samples at $T = 80\text{K}$ with $V_{\text{Sch}} = 0\text{ V}$ (SBH = 0.794(2)), -0.4 V (SBH = 0.782(4)) and -0.7 V (SBH = 0.778(3)).

height) to be nearly independent of V_{sub} , since the same electric field should produce the same image force lowering (see Section 3.3). All the BEEM/BHEM measurements discussed earlier in this chapter were made with $V_{\text{Sch}} = 0\text{ V}$. However, a non-zero value of V_{Sch} should change electric field according to

$$E = (V_{\text{Sch}} + \phi_{n(p)0})/d \quad (6.5)$$

(as shown in Figure 6.10), and so should have a measurable effect on the Schottky barrier height (see Equation 3.8). Figure 6.11 shows the measured electron Schottky barrier height vs V_{Sch} (data points) on Au/Si SOI sample along with the predicted variation (based on Equations 6.5 and 3.8), where we see a good agreement. Therefore, we demonstrated that BEEM can monitor changes in the SBH due to variations in the interface electric field, and so should be able to quantify local variations in Schottky barrier heights with high spatial resolution.

6.5 Wet etch SOI silicon film

This work is aimed to develop a recipe for etching a $\sim 10\text{nm}$ step on the 35nm SIMOX SOI wafer. With such a recipe, we can fabricate a structure as shown in Figure 6.12. Using this structure, we can test how the Schottky barrier height can be modified by the E-field $E = \phi_{n(p)0}/d$ by varying the film thickness d . And also in this structure, the electric field will be larger at the corner (marked by the red circles) than other places due to the “lightning rod effect” [26], so a lower Schottky barrier height should be seen at these corners because of image force lowering.

Since the SIMOX SOI only has a 35nm silicon film, the ideal recipe should give a very slow etch rate so that it can be precisely controlled. And after etching the silicon surface should be very smooth in order to have good tip-metal tunneling characteristics in order to see BEEM signals. It has been demonstrated by Tang et al. that the standard clean 1 (SC-1, see Section 5.2) can be modified to etch the silicon

Figure 6.12: SOI sample structure with sharp corners.

film on a SIMOX wafer slowly and smoothly [71]. Their recipe is:

Solution: $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 1:8:64$;

Temperature: 70 °C.

The etch rate they measured was 0.12 Å/s and the roughness of the silicon film after etching was 4-5Å.

We tried this recipe and found that for our laboratory conditions and for our SIMOX wafers the etch rate was about 0.01 Å/s, which is about 10 times smaller than reported by Tang *et al.* To increase the etch rate, we modified this recipe by

increasing the solution density and the ratio of $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$. The recipe which we found to be good for us is:

Solution: $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 1:2:16$;

Temperature: 70 °C.

For our 35nm SIMOX SOI, with a 15-minute etching in a mixture of 20ml NH_4OH + 40ml H_2O_2 + 320ml H_2O at 70 °C, about 10nm SOI film was etched away. The RMS roughness of the silicon film after this etching was measured to be 2-3 Å using AFM (Atomic Force Microscopy), which is similar to the roughness of Si film before the etch (see Fig. 6.13). So we see this wet etching method leaves an extremely smooth surface.

In order to etch a step as shown in Figure 6.12, we have to find a mask material that will not be etched. We found that photoresist S1813 does not work because it starts to pearl off after ~10-minute dipping in our SC-1 solution. Since the etch rate of thermal oxide using the SC-1 etch is about ~5 times slower than the etch rate of silicon [18,71], we decided to use a thermally grown thin oxide film (4-5nm) as a mask. This thin oxide film was grown by Paul Steven in Nanotech West. The growth condition was

Dry thermal oxidation at 850°C for 25 minutes.

Figure 6.13: AFM images of the silicon surface (a) before and (b) after SC-1 etching.

Figure 6.14: AFM images of the silicon surface after SC-1 etching (a) covered and (b) not covered by the thermal oxide.

Figure 6.15. Step on the sample etched using our SC-1 recipe with 4-5nm thermal oxide as a mask.

The SIMOX SOI wafer was cleaned using Piranha cleaning (see Section 5.2) and then after a 10-20s 10:1 buffered HF dip the wafer was transferred to the oxide furnace for oxide film growth. After a 4-5 nm oxide film was grown, photolithography with S1813 was used to define areas where this thin oxide film was removed by a 10:1 buffered HF dip. Then photoresist S1813 was removed by an ultrasonic clean in Acetone and the sample was etched using our SC-1 recipe for 15 minutes. After the etching, the sample was dipped in 10:1 buffered HF for 20-30 seconds to remove all the oxide film. Figure 6.14 shows two AFM images taken on one of our SC-1 etched SIMOX SOI sample with 4-5nm thermal oxide as a mask. Figure 6.14 (a) is the AFM image taken on the area which is covered by the thermal oxide during SC-1 etch and Figure 6.14 (b) is the AFM image taken on the area which is not covered by the thermal oxide during etching. We can see the roughness ($5\text{\AA}$) is a little bigger than the roughness ($2-3\text{\AA}$) on samples etched without oxide growth, but it is still small and the surface after etching is very smooth. Figure 6.15 is the AFM image across the step, from which we can see the step height is $\sim 9-10\text{nm}$.

6.6 Conclusions and future works

In summary, we developed a new method to monitor the energy (relative to the metal Fermi energy) of *both* the conduction band minimum and the valence band maximum of a thin semiconductor film *at the same location*. By comparing these two energies, this technique can be used to monitor and quantify lateral variations of (i) the local interface electric field, (ii) local interface dipoles, and (iii) the local bandgap

at metal/semiconductor contacts. In our measurements, we performed BEEM and BHEM measurements at the same location on the same Au/Si and Cu/Si contacts at $T=80$ K. After accounting for image force lowering, the measured local Schottky barrier heights for electrons and holes sum to approximately the Si band gap, indicating that we can accurately probe both the conduction band and valence bands at the same location, and hence are sensitive to local variations in the metal/Si interface dipole and/or interface electric field. The gate voltages used in our experiment were explained by assuming there is interface charge (due to interface states) in the order of $\sim 10^{12} \text{ eV/cm}^2$ in combination with some fixed charge) in the order of $\sim 10^{12} \text{ q/cm}^2$ at Si/SiO₂ interfaces. We also demonstrated that BEEM can monitor changes in the SBH due to variations in the interface electric field, and so should be able to quantify local variations in Schottky barrier heights with high spatial resolution. By modifying an SC-1 recipe, we found a method to etch a thin layer of silicon from our 35nm SIMOX SOI wafer that leaves a very smooth surface (RMS roughness $\approx 5 \text{ \AA}$) and with a very slow etch rate ($\approx 0.1 \text{ \AA/s}$) so it is easy to control how much silicon is etched away.

In the future, we will apply our ambipolar BEEM technique to study the energy band structure of some epitaxial layers such MgO. A thin layer of MgO can be grown epitaxially on a silicon substrate and can be used as a tunneling barrier for spin injection. The energy band structure of thin MgO is not well known. Our method is a promising way to measure this.

CHAPTER 7

ION MILL AND RIE ETCHING OF SILICON NANOWIRES

7.1 Introduction

Vertical Si nanowires have been used to fabricate some novel devices such as Si vertically integrated nanowire FETs or Surround-gate FETs [72, 73], Si nanowire photodetectors [7.4], and Si nanowire solar cell [75]. These devices were claimed to have some better performance than conventional structures. For example, FETs with a surrounding gate have been proposed and demonstrated to have excellent subthreshold behavior due to the high gate coupling efficiency and a 35% reduction of short-channel effects compared to double-gate (Fin FET) devices [76-79]. End-on metal contacts to vertical Si nanowires can also be used to study the role of Fermi level pinning in nano-scale metal-semiconductor contacts, which is one of the critical issues in nanowire or carbon nanotube FETs [80].

In this chapter, we will first give a brief introduction on the methods for fabricating vertical silicon nanowires. Then we will discuss our experiments that use

ion milling to increase the yield of vertical nanowires on a nanowire sample in which the yield of vertical nanowires is not 100%.

7.2 Vertical Si nanowire fabrication

Two groups of methods have been used to fabricate vertical Si nanowires: the “bottom up” approach and the “top down” approach. In the bottom up approach, Si nanowires are synthesized by one-dimensional epitaxial crystal growth using the vapor-liquid-solid (VLS) mechanism [81]. In this process, metal nanoclusters are used as catalyst and are spin-coated or deposited using photolithography/e-beam lithography on the semiconductor substrate surface. Then after the substrate is heated above the eutectic temperature, liquid droplets of metal/semiconductor alloy will form on the substrate surface. In the presence of a vapor-phase source of the semiconductor, the continuous feeding of the semiconductor reactant into the liquid droplet will supersaturate the eutectic. This leads to nucleation of the solid semiconductor at the liquid-solid interface and the nanowire grows. Figure 7.1 shows an SEM image of vertical Si nanowire array grown by Atwater’s group from Caltech [82]. In their experiment, a 300nm thermal oxide was grown on Si (111) substrates and then was patterned using photolithography. The oxide within the patterned photoresist holes was removed by HF dip, then 500nm Au or Cu was thermal evaporated on the substrate. After lift-off of the photoresist, these patterned Au or Cu dots form an array of catalyst islands separated by a buffer oxide layer. Then these samples were annealed and Si nanowires were grown using SiCl_4/H_2 . With this

Figure 7.1: SEM views of a Cu-catalyzed Si wire array having nearly 100% fidelity over a large 1 cm^2 area. The scale bar in the inset is $10 \text{ }\mu\text{m}$. (figure taken from Ref. [82]).

method, they attained excellent control of the size, position, and uniformity of vertically aligned, large-area Si wire arrays. The epitaxial growth on Si(111) substrate guarantees most of nanowires are vertical. Also Lieber et al. found that the silicon nanowire growth direction is related to the diameter for silicon nanowires grown by VLS method [83]. They demonstrated that for small silicon nanowires (diameters between 3 and 10 nm) 95% grew along the $\langle 110 \rangle$ direction and for large silicon nanowires (diameters between 20 and 30 nm) 64% grew along the $\langle 111 \rangle$ direction.

Figure 7.2: SEM of vertical-etched Si NW array device. The wires are 200 nm in diameter and 2.7 μm in length with 1 μm spacing. Scale bar is 1 μm . (figure taken from Ref. [74]).

In the top-down approach, vertical Si nanowires are usually fabricated using anisotropic ICP-RIE (inductively coupled plasma reactive ion etching) etching. In this process, an array of mask material with nano-scale size is patterned on Si substrates using e-beam lithography/photolithography. Then vertical Si nanowires can be fabricated by etching away the Si material not covered by the mask using RIE etching. The undercut and side-wall slope can be controlled by the pressure, RF bias, the composition of reactive chemicals [see the reference 84 for more details]. For example, for silicon etching using $\text{SF}_6 + \text{O}_2$, when $\text{SF}_6/\text{O}_2 = 1$, the sidewalls are nearly

vertical [84]. Figure 7.2 shows an SEM image of vertical Si nanowire array fabricated using ICP-RIE etching by Wang's group from UCSD [74]. In their experiment, an array of nano-scale Ni dots was patterned on a *p*-type Si wafer using e-beam lithography with PMMA as a resist. Then an ICP-RIE process at room temperature was used to anisotropically etch Si nanowires from the Ni dots.

7.3 Vertical ion milling of Si nanowires

As has been discussed in Sec.7.2, high quality vertical Si nanowires (with controllable size, position, uniformity and high fidelity) can be fabricated using both bottom-up and top-down approaches. However, finding the right recipe for growing or fabricating this kind of high quality vertical Si nanowires is not easy. In most cases the vertical Si nanowire samples we received from collaborators had Si nanowires lying on the substrate, some were tilted at an angle (but were not perpendicular to the substrate), and the rest were perfectly vertical. It seems that small changes in growth parameters (temperature, nanowire doping, substrate orientation, diameter of catalyst particles, etc.) caused many of the nanowires to grow in a non-vertical orientation.

Here we discuss a method to increase the yield of vertical Si nanowires on such "imperfect" samples using ion milling or RIE. This method may be useful to those who need to increase the fraction of vertical nanowires on samples with a high density of non-vertical nanowires.

Before discussing the details of ion milling vertical Si nanowire, we first discuss the equipment used for performing the ion milling and measuring scanning

electron microscope (SEM) images of the samples before and after the ion milling. The equipment used for these experiments is the FEI Helios Nanolab 600 Dual Beam Focused Ion Beam/Scanning Electron Microscope [85]. This piece of equipment has both an electron beam for SEM imaging and a Ga^+ ion beam for ion milling. The range of beam energy is 50eV-30keV and 500eV-30keV for the electron and Ga^+ beams respectively. The size of both particle beams can be adjusted by the user, and both particle beams can be raster-scanned over the sample surface. The electron beam and the ion beam form an angle of 52 degrees [Figure 7.3]. The sample stage can be rotated up to an angle of 52 degrees so that an SEM image can be taken at any angle

Figure 7.3: Dual Beam Focused Ion Beam/Scanning Electron Microscope.

Figure 7.4: An SEM of Si nanowire sample taken at 52 degree.

between 0 to 52 degrees to the surface normal. The sample surface can be oriented perpendicular to the ion beam for “vertical” ion milling by the high energy heavy Ga^+ ions.

In our experiments, the vertical Si nanowire samples were obtained from Lauhon’s group in Northwest University [86]. These vertical Si NWs were epitaxially grown on an n-Si (111) substrate by chemical vapor deposition (CVD) at 450 °C with dispersed colloidal Au particles as catalyst and silane as Si source. Figure 7.4 shows

an SEM image of this Si nanowire sample measured with the electron beam at 52° from the surface normal. We can see from Fig. 7.4 that there are some vertical Si nanowires, but that most of the Si nanowires are lying flat on the substrate or are tilted at an angle less than 90° from the surface. We found that the highly anisotropic ion milling from the focused Ga^+ ion beam oriented normal to the sample surface can

Figure 7.5: A 52° SEM image of Si nanowire sample after ion milling expected to etch 10nm of Si.

be a good tool to remove non-vertical Si nanowires, while leaving the vertical nanowires largely intact.

To do the ion milling, we first followed the standard operation procedure of the SEM to focus the electron beam on the sample surface and to bring the sample surface to a distance of 4.1mm away from the electron gun. Then the stage was carefully rotated by 52° so that the ion beam was perpendicular to the sample surface. Then ion milling over an area of $5\mu\text{m}\times 5\mu\text{m}$ was done by an amount that was expected to etch about 10 nm of Si. Another SEM image was then taken with the sample still

Figure 7.6: A 52° SEM image of Si nanowire sample after ion milling expected to etch 30nm of Si.

Figure 7.7: A 52° SEM image of Si nanowire sample after ion milling expected to etch 200nm of Si.

facing the ion beam, as shown in Figure 7.5. From this image we can see that most of the Si nanowires which survived from the ion milling are vertical Si nanowires, and that most of the non-vertical Si nanowires were milled away. We can also notice that some nanowires seem to be etched more than others, which could be a problem for some applications. Figure 7.6 shows an SEM image of an area after an ion milling expected to etch roughly 30nm of Si, and here we can see essentially only vertical Si nanowires remaining, with essentially all the non-vertical Si nanowires removed. For

comparison, an SEM image of an area with an expected 200nm of Si ion milling is shown in Figure 7.7 from which we can see all of the Si nanowires were milled away.

7.4 ICP-RIE etch silicon nanowires.

We also tried to use low temperature ICP-RIE etching to increase the yield of vertical silicon nanowire in a large area, since ICP-RIE etching is a more common etching tool for Si processing than ion milling, and because it produces more uniform etching over large areas. The reactive gases we used were a mixture of SF_6 and O_2 , which was reported to produce high aspect ratio etching of silicon because O_2 in SF_6 plasma can form a thin fluorinated silicon oxide passivation layer on the (vertical) sidewalls (which can prevent chemical etching of the Si on the sidewalls), while the physical etching of the ions (which are mainly moving in the vertical direction) removes the passivation layer on horizontal surfaces [84]. Cooling the substrate can also slow down the lateral etching, resulting a high aspect ratio etching.

The RIE etcher used for these experiments was the Oxford 180 ICP-RIE in the Dreese Lab cleanroom. In this system, there are two RF power sources: one is the “ICP power” which is mainly used to create the plasma, and the other is mainly used to accelerate ions in the “vertical” direction (normal to the sample surface) (Figure 7.8). The sample stage temperature can varied from -150 °C to +400 °C by liquid N_2 cooling or electrical heating.

Figure 7.8: Schematic of ICP-RIE.

We found a recipe which can give nearly vertical etching of a bulk silicon sample. The recipe is

SF₆:O₂ = 25sccm:25sccm;

ICP power = 500W;

RF power = 90W;

Pressure = 15mTorr;

Temperature = -110°C.

However, we found two problems with this recipe. First, even though the average etching is almost vertical the sidewalls after etching were found to be rough. Second, the etch rate of ~18nm/s for bulk Si was found to be too fast, making it very hard to control the etch depth. At present we are working on finding a recipe which can give a high aspect ratio etch (sidewall angle $\approx 90^\circ$) and a slow etch rate ($< 2\text{nm/s}$). We do not yet know if ICP-RIE etching can effectively remove non-vertical Si nanowires while leaving vertical Si NWs largely intact.

7.5 Conclusions and future work

From the above discussion, we can conclude that by choose the correct ion milling thickness of silicon essentially all of the non-vertical silicon nanowires can be removed, leaving essentially only vertical silicon nanowires standing on the substrate. While this method is not able to fabricate a highly-uniform array of vertical silicon nanowires from a highly non-uniform starting sample (such as that shown in Fig. 7.4), but may be useful as a means to remove most non-veritical nanowires if they exist. In the future, we will try to use low-temperature ICP-RIE (Inductively Coupled Plasma Reactive Ion Etching) to do the same work, since ICP-RIE can etch a larger area than Ion Milling and is a more common tool for Si processing.

APPENDIX A

NUMERICAL SIMULATION OF GATE VOLTAGES

The gate voltages needed for our BEEM and BHEM measurements on SOI samples was simulated using a commercial numerical simulation tool COMSOL MultiPhysics 4.0 which can solve coupled differential equations using finite element methods.

Figure A.1 shows the geometry and symbols used in this simulation.

1. Parameters:

1) Bandgap E_g :

- a. Silicon: $E_{g_{Si}} = 1.17\text{eV}$.
- b. SiO_2 : $E_{g_{ox}} = 9\text{eV}$

2) Electron affinity χ :

- a. Silicon: $\chi_{Si} = 4.05\text{eV}$

b. SiO_2 : $\chi_{\text{ox}} = 0.95\text{eV}$

3) Schottky barrier height (SBH) for electrons

a. Au/Si : $\text{SBH} = 0.84\text{eV}$

b. Au/Si : $\text{SBH} = 0.62\text{eV}$

4) Dielectric constant ϵ :

a. Silicon: $\epsilon_{\text{Si}} = 11.9\epsilon_0$.

b. SiO_2 : $\epsilon_{\text{ox}} = 3.9\epsilon_0$.

5) Geometry:

a. Silicon film thickness: $d_{\text{Si}} = 35\text{nm}$.

b. BOX thickness: $d_{\text{ox}} = 150\text{nm}$.

c. Silicon substrate thickness: $d_{\text{sub}} = 3000\text{nm}$.

6) Doping:

$$N_A = 1.0 \times 10^{15} / \text{cm}^3 \text{ in Regions R1 and R3}$$

$$N_A = 0 \text{ in Region R2.}$$

7) Temperature: $T = 80\text{K}$.

8) Boltzmann constant: $k_B = 1.381 \times 10^{-23} \text{J/K}$.

9) Elementary charge: $q = 1.602 \times 10^{-19} \text{C}$.

10) Permittivity in vacuum: $\epsilon_0 = 8.854 \times 10^{-14} \text{F/cm}$.

11) Intrinsic carrier density $n_i = 6.07 \times 10^{-14} / \text{cm}^3$ at 80K .

12) Charge neutrality level (CNL) $\phi_{\text{CNL}} = E_i$.

2. Variables:

- a. Applied substrate voltage: V_a (V).
- b. Interface state density at Si/SiO₂ interface: D_{it} (1/cm²/eV).
- c. Fixed charge density at Si/SiO₂ interface: D_f (q/cm²).

3. Model: AC/DC modeling→ electrostatics interface.

Equation: $-\nabla \cdot (\epsilon \nabla \psi) = \rho$

$$\rho = q(p - n - N_A)$$

a. Region R1:

$$n = n_i \exp((q\psi + E_{g_{Si}}/2 - SBH1)/k_B T)$$

$$p = n_i \exp((SBH1 - q\psi - E_{g_{Si}}/2)/k_B T)$$

b. Region R2: $p = 0, n = 0, N_A = 0$.

c. Region R3:

$$n = n_i \exp((q\psi + E_{g_{Si}}/2 - SBH1 - qV_a)/k_B T)$$

$$p = n_i \exp((SBH1 + qV_a - q\psi - E_{g_{Si}}/2)/k_B T)$$

Boundary conditions:

a. B1: $\psi = 0$

b. B2: Surface charge

$$\sigma_s = (SBH1 - q\psi - E_{g_{Si}}/2)D_{it} + D_f$$

c. B3: Surface charge

$$\sigma_s = (SBH1 + qV_a - q\psi - Eg_{si}/2)D_{it} + D_f$$

d. B4: $\psi = (SBH1 - SBH2)/q + V_a$.

4. ψ is the potential of the vacuum level. So the conduction band minimum

$Ec = q(\psi - \chi_{si})$ in regions R1 and R3, and $Ec = q(\psi - \chi_{ox})$ in the region R2.

And the valence band maximum $Ev = (q\psi - q\chi_{si} - Eg_{si})$ in regions R1 and

R3, and $Ev = (q\psi - q\chi_{ox} - Eg_{ox})$ in the region R2.

Figure A.1: Geometry for COMSOL numerical simulation.

REFERENCES

- [1] J.Appenzeller, J.Knoch, V.Derycke, R.Martel, S.Wind, and Ph.Avouris, *Phys. Rev. Lett.* **89**, 126801 (2002).
- [2] H.-C. Lin, K.-L.Yeh, T.-Y.Huang, R.-G.Huang, and S.M.Sze, *IEEE Trans. Electron Devices* **49**, 264 (2002).
- [3] W.Y.Choi, B.-G.Park, J.D.Lee, and T.-J.King Liu, *IEEE Electron Device Lett.*, **28**, 743 (2007).
- [4] J.Knoch and J.Appenzeller, *Phys. Stat. Sol. (A)* **205**, 679 (2008).
- [5] N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Brooks/Cole Thomson Learning,1976.
- [6] S.M.Sze, *Physics of Semiconductor Devices*, 2nd Ed, Wiley, New York, 1981.
- [7] www.wiredchemist.com/chemistry/instructional/intro_chem_valencebond.
- [8] D.G.Thomas,ed., *II-VI Semiconducting Compounds*, W.A.Benjamin, New York,1967.
- [9] YP.Y.Yu and M.Cardona, *Fundamentals of Semiconductors - Physics and Materials Properties*, 3rd Ed, Springer-Verlag, Berlin, 2001.

- [10] C.A.Hogarth, ed., *Materials Used in Semiconductor Devices*, Interscience, New York, 1965.
- [11] Y. Tu and J. Tersoff, *Phys. Rev. Lett.* **84**, 4393 (2000).
- [12] B.E.Deal, *IEE Trans. Electrons Devices* **27**, 606 (1980).
- [13] S.I.Raider and A.Berman, *J. Electronchem. Soc.* **125**, 629 (1978).
- [14] E.H.Nicollian and J.R.Brews, *MOS Physics and Technology*, Wiley, New York, 1982.
- [15] B.E.Deal, M.Sklar, A.S.Grove, and E.H.Snow, *J. Electronchem. Soc.* **114**, 266 (1967).
- [16] X.G.Zhang, *Electrochemistry of Silicon and its oxide*, Kluwer Academic/Plenum Publishers, New York, 2001.
- [17] J.-P. Colinge, *Silicon-on-Insulator Technology: Materials to VLSI*, 3rd Ed., Springer, New York, 2004.
- [18] M.J.Anc, ed., *SIMOX*, The Institution of Electrical Engineers, London, 2004.
- [19] S.Nakashima and K.Izumi, *J. Mater. Res.* **8**, 523 (1993).
- [20] S.Nakashima, T.Katayama, Y.Miyamura, A.Matsuzaki, M.Imai, K.Izumi, and N.Ohwada, *Proc.IEEE SOI Conf.*, 71 (1993).
- [21] J.Jiao, B.Jonhson, S.Seraphin, M.J.Anc, R.P.Dolan, and B.F.Cordts, *Mater. Sci. Eng. B* **72**, 150 (2000).
- [22] A.M.Cowley and S.M.Sze, *J. Appl. Phys.*, **36**, 3212 (1965).
- [23] D. A. Neamen, *Semiconductor Physics and Devices: Basic Principles*, Richard D. Irwin, Boston, (1992).

- [24] V.Heine, *Phys. Rev.*, **138**, A1689, (1965).
- [25] W.E.Spicer, P.W.Chye, P.R.Skeath, C.Y.Su and I.Lindau, *J. Vac. Sci. Technol.* **16**, 1422 (1979).
- [26] J.D.Jackson, *Classical Electrodynamics*, Wiley, New York, 1975.
- [27] S.M.Sze, C.R.Crowell, and D.Hahng, *J. Appl. Phys.*, **35**, 2534 (1964).
- [28] H.A.Bethe, *MIT Radiat. Lab. Rep.* **43**,12 (1942).
- [29] C.Y.Chang and S.M.Sze, *Solid State Electron.*, **13**, 727 (1970).
- [30] F.A.Padovani and R.Stratton, *Solid State Electron.*,**9**, 695 (1966).
- [31] P.Niedermann, L.Quattropani, K.Solt, A.D.Kent, and Ø.Fischer, *J. Vac. Sci. Technol. B*, **10**, 580 (1992).
- [32] H.Palm, M.Arbes and M.Schulz, *Phys. Rev. Lett.* **71**, 2224 (1993).
- [33] A.E.Fowell, R.H.William, B.E.Richardson, A.Cafolla, D.I.Westwood, and D.A.Woolf, *J. Vac. Sci. Technol. B*, **9**, 581 (1991).
- [34] A.A.Talin, R.S.William, B.A.Morgan, K.M.Ring, and K.L.Kavanagh, *J. Vac. Sci. Technol. B*, **12**, 2634 (1994).
- [35] R.T.Tung, *Appl. Phys. Lett.*, **58**, 2821 (1991).
- [36] R.T.Tung, *Phys. Rev. B*, **45**, 13509 (1992).
- [37] W.J.Kaiser and L.D.Bell, *Phys. Rev. Lett.* **60**, 1406 (1988).
- [38] T.-H.Shen, M.Eliott, A.E.Fowell, A.Cafolla, B.E.Richardson, D.Westwood and R.H.Williams, *J. Vac. Sci. Technol. B* **9**, 2219 (1991).
- [39] C.Tivarus, J.Pelz, M.K.Hudait and S.A.Ringel, *Phys. Rev. Lett.* **94**, 206803 (2005).

- [40] W.H.Rippard and R.A.Buhrman, *Phys. Rev. Lett.* **84**, 971 (2000).
- [41] M.T.Cuberes, A.Bauer, H.J.Wen, M.Prietsch, and G.Kaindl, *J. Vac. Sci. Technol. B* **12**, 2646 (1994).
- [42] R.Ludeke, A. Bauer, and E. Cartier, *Appl. Phys. Lett.* **66**, 730 (1995).
- [43] B.Kaczer and J.P.Pelz, *J. Vac. Sci. Technol. B* **14**, 2864 (1996).
- [44] M.Prietsch, *Phys. Rep.* **253**, 163 (1995).
- [45] V.Narayanamurti and M.Kozhevnikov, *Phys. Rep.* **349**, 447 (2001).
- [46] Cristian Tivarus, *Ph.D Thesis* (The Ohio State University, Columbus, 2005).
- [47] L.D.Bell and W.J.Kaiser, *Phys Rev. Lett.* **61**, 2368 (1998).
- [48] R.Ludeke and M.Prietch, *J. Vac. Sci. Technol. A* **9**, 995 (1991).
- [49] R.Ludeke and M.Prietch, *Phys. Rev. Lett.* **66**, 2511 (1991).
- [50] J.G.Simmons, *J. Appl. Phys.* **34**, 1793 (1963).
- [51] J.A.Stroschio and W.J.Kaier, ed., *Scanning Tunneling Microscopy*, Academic Press, San Diego, 1993.
- [52] E.Y.Lee and L.J.Schowalter, *J. Appl. Phys.* **70**, 2156 (1991).
- [53] R.C.Alig, S.Bloom, and C.W.Struck, *Phys. Rev. B* **22**, 5565 (198).
- [54] E.Cartier, M.V. Fischetti, E.A.Eklund, and F.R.McFeely, *Appl. Phys. Lett.* **62**, 3339 (1993).
- [55] E.A.Eklund, P.D.Kirchner, D.K.Shuh, F.R.McFeely, and E.Cartier, *Phys. Rev. Lett.* **68**, 831 (1992).
- [56] Eric Heller, *Ph.D Thesis* (The Ohio State University, Columbus, 2003).
- [57] B. Kaczer, Z. Meng, and J. P. Pelz, *Phys. Rev. Lett.* **77**, 91 (1996).

- [58] <http://www.microchem.com>
- [59] <http://snf.stanford.edu/Process/Characterization/NativeOx.html>
- [60] Benjamin Kaczer, *Ph.D thesis*, The Ohio State University.
- [61] L.D.Bell, W.J.Kaiser, M.H.Hecht, and L.C.Davis, *J. Vac. Sci. Technol. B* **9**, 594 (1991).
- [62] L.D.Bell, M.H.Hecht, W.J.Kaiser, and L.C.Davis, *Phys. Rev. Lett.* **64**, 2679 (1990).
- [63] M.H.Hecht, L.D.Bell, W.J.Kaiser, and L.C.Davis, *Phys. Rev. B* **42**, 7663 (1990).
- [64] E.Y.Lee and L.J.Schowalter, *Phys. Rev. B* **45**, 6325 (1992).
- [65] A.Davies and H.G.Craighead, *Appl. Phys. Lett.* **64**, 2833 (1994).
- [66] M.T.Cuberes, A.Bauer, H.J.Wen, D.Vandré, M.Prietsch, and G.Kaindl, *J. Vac. Sci. Technol. B* **12**, 2422 (1994).
- [67] A.Fernandez, H.D.Hallen, T.Huang, R.A.Huhrman, and J.Silcox, *Appl. Phys. Lett.* **57**, 2826 (1990).
- [68] J.J.Garramone, J.R.Abel, I.L.Sitnitsky, R.L.Moore, and V.P.Labella, *J. Vac. Sci. Technol.B* **27**, 2044 (2009).
- [69] T.Banerjee, E.Haq, M.H.Siekman, J.C.Lodder and R.Jansen, *IEEE Transactions on Magnetism* **4**, 2642 (2005).
- [70] Y.Nakajima et al., *Jpn. J. Appl. Phys.* **42**, 2004 (2003).
- [71] X.H. Tang, N.Rechinger, G.Larrieu, E.Dubois, D.Flandre, J-P.Raskin, B.Nysten, A.M.Jonas, and V.Bayot, *Nanotechnology* **19**, 165703 (2008).

- [72] Josh Goldberger, Allon.I.Hochbaum, Rong Fan, and Peidong Yang, *Nano Lett.* **6**, 973 (2006).
- [73] Volker Schmidt, Heike Riel, Stephan Senz, Siegfried Karg, Walter Riess, and Ulrich Gösele, *Small* **2**,85 (2006).
- [74] Arthur Zhang, Sifang You, Cesare Soci, Yisi Liu, Deli Wang, and Yu-Hwa Lo, *Appl.Phys.Lett.***93**,121110 (2008).
- [75] Michael D. Kelzenberg, ShannonW. Boettcher, Jan A. Petykiewicz, Daniel B. Turner-Evans, Morgan C. Putnam, Emily L.Warren, Joshua M. Spurgeon, Ryan M. Briggs, Nathan S. Lewis, and Harry A. Atwater, *Nature Materials* **9**, 239(2010).
- [76] J. M.Hergenrother, S.H.Oh, T.Nigam, D.Monroe, F. P Klemens, A.Kornblit, *Solid-State Electron.***46**, 939 (2000).
- [77] S.H.Oh, Physics and Technologies of Vertical Transistors. Thesis, Stanford, Palo Alto, CA, 2001.
- [78] S.H.Oh, D.Monroe, J.M.Hergenrother, *IEEE Electron Device Lett.***21**, 397 (2000)
- [79] A.K.Sharma, S.H.Zaidi, S.Lucero, S.R.JBrueck, N.E.Islam, IEE Proc.sCirc. DeV. Syst. **151**, 422 (2004).
- [80] F.Leonard and J.Tersoff, *Phys.Rev.Lett.* **84**, 4693 (2000) and *Phys.Rev.Lett.* **97**, 026804 (2006).
- [81] R.S.Wagner and W.C.Ellis, *Appl.Phys.Lett.***4**, 89 (1964).

- [82] Brendan M. Kayes, Michael A. Filler, Morgan C. Putnam, Michael D. Kelzenberg, Nathan S. Lewis, and Harry A. Atwater, *Appl. Phys. Lett.* **91**, 103110 (2007).
- [83] Y. Wu, Y. Cui, L. Huynh, C. J. Barrelet, D. C. Bell, and C. M. Lieber, *Nano Lett.* **4**, 433 (2004).
- [84] Sergi Gomez and Rodolfo Jun Belen, Mark Kiehlbauch, Eray S. Aydil, *J. Vac. Sci. Technol.* **22**, 606 (2004).
- [85] <http://www.fei.com/products/dualbeams/helios-nanolab.aspx>
- [86] J. E. Allen, E. R. Hemesath, D. E. Perea, J. L. Lensch-Falk, Z. Y. Li, F. Yin, M. H. Gass, P. Wang, A. L. Bleloch, R. E. Palmer, and L. J. Lauhon, *Nature Nanotechnology* **3**, 168 (2008).