Nanoscale characterization of metal/dielectric/semiconductor interfaces using ballistic electron emission microscopy

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2012

Qin, H. (2012). Nanoscale characterization of metal/dielectric/semiconductor interfaces using ballistic electron emission microscopy. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/50608>

<https://doi.org/10.32657/10356/50608>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**NANOSCALE CHARACTERIZATION OF
METAL/DIELECTRIC/SEMICONDUCTOR
INTERFACES USING BALLISTIC ELECTRON
EMISSION MICROSCOPY**

QIN HAILANG

**SCHOOL OF ELECTRICAL AND ELECTRONIC
ENGINEERING**

2012

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METAL/DIELECTRIC/SEMICONDUCTOR
INTERFACES USING BALLISTIC ELECTRON
EMISSION MICROSCOPY**

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A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of

Doctor of Philosophy

2012

ACKNOWLEDGEMENTS

It has been a long trip. It is a trip filled with frustration, but also with excitement. I would not have gone this far without the support of many who gave me advice, encouragement, ideas, and also those who helped me throughout this journey in one way or another.

This thesis would not have been possible without the continued guidance and support from Professor PEY Kin Leong. I appreciate him for his great patience and constant encouragement for the last few years, especially during the hard time. I am also grateful to my co-supervisor Dr. Cedric Troadec (Institute of Materials Research and Engineering, IMRE), for his sharing of the UHV experience and for help in setting up the UHV system, and various others.

My first real introduction of STM and BEEM probably went to Dr. Amin Bannani, who was so nice, patient and willing to teach me all the STM and BEEM basics, BEEM data analysis and all other stuff. I would also like to thank Dr. Johnson Goh Kuan Eng and Dr. Michel Bosman, for all the discussions we had and for all the suggestions they have given.

A lot of thanks also go to Dr. Chandrasekhar Natarajan, Justin SONG Chien Wen, Dr. Sunil Singh KUSHVAHA, Dr. Wulf HOFBAUER, Dr. Carlos MANZANO and Dr. We-Hyo SOE. I would also like to thank Dr. Zheng Yi for his introduction of RHK BEEM system.

There are many of Professor Pey Kin Leong's collaborators I am really grateful to, especially Mr. TUNG Chih Hang for his sharing of knowledge and technical discussions;

Professor Hiroshi Iwai and Professor Kuniyuki Kakushima from Iwai Laboratory, Frontier Research Center, Tokyo Institute of Technology, for providing samples and also for fruitful discussions.

I would also like to acknowledge all the group members from Professor Pey's group: Dr. Lo Vui Lip, Dr. Li Xiang, Chen Yining, Shubhakar, Wu Xing, Nagarajan Raghavan, Zin Zar Lwin and Liu Wenhui, for discussions during the group meetings, sharing ideas, and for helping me in various other ways.

Last, but not the least, I would like to express my gratitude to my parents, sister and brother for their constant support and encouragement all the years.

So finally I made it. It is time to take a break and get ready to move on.

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ABSTRACT

Ballistic electron emission microscopy (BEEM) was employed to study metal/dielectric/semiconductor devices with high spatial resolution. A comprehensive study of the subthreshold characteristics of the BEEM spectra shows that the BEEM current in the subthreshold region decreases at a rate of ~ 60 mV/decade. A comparative BEEM study of Au/SiO₂/n-Si devices with *in-situ* and *ex-situ* deposited metal suggests that an ultraclean metal surface is critical for the BEEM studies of the devices with high electron barriers. Investigation of the ultrathin native oxide and high- κ dielectrics shows that an ultrathin dielectric (probably no thicker than 6–8 Å) does not exhibit the same electronic properties as a thicker dielectric. Spatial non-uniformity of these oxides on the nanometer scale was also observed by BEEM. We also determined the electron barrier height for a few important dielectrics (oxidized GaAs, Al₂O₃ and HfO₂) on GaAs.

An analytical equation describing the subthreshold BEEM behavior is derived from the basic BEEM model, i.e., the Bell-Kaiser model. This analytical equation shows that the BEEM current in the subthreshold region decreases exponentially with a subthreshold swing of about 60 mV/decade as the tip bias decreases. The equation is further verified by simulated and experimental BEEM spectra. Realizing the subthreshold characteristics, a new simplified model was proposed for the BEEM spectrum fitting. This proposed model takes the subthreshold behavior into account and it is to the best of our knowledge the first simplified analytical BEEM model that considers the temperature dependence. This model is shown to significantly improve the fitting of the BEEM

spectrum compared with using the well-known simplified square model. It also provides a quick method to estimate the BEEM current at and below the threshold.

It is shown that the BEEM measurement of samples with high barriers (~ 3.0 eV or above), cannot be performed properly if the metal base electrode is deposited *ex-situ*, while it can be performed consistently if the metal is deposited *in-situ* in an ultra-high vacuum. We further show that the main reason is that contamination of the Au surface strongly affects the tunneling between the tip and Au base in the high bias range, thus affecting the BEEM spectroscopy.

Electronic properties of ultrathin dielectrics are investigated. BEEM studies are carried out for both native oxides on Si and high- κ dielectrics on Si. Both measurements show that a dielectric of less than a certain thickness ($6\text{--}8$ Å) in a metal/dielectric/semiconductor structure does not have the same electronic properties as the corresponding thicker bulk dielectric. However, these ultrathin dielectrics still strongly attenuate ballistic electron transport. We also find that native oxide on silicon does not grow uniformly on the nanoscale.

We determine the barrier height of a few important dielectrics on GaAs substrate. For a Au/3 nm oxidized GaAs/n-GaAs device, the BEEM spectra have two thresholds of 1.4 and 3.55 eV, respectively. Through an in-depth study, we show that the first threshold arises from the scanning tunneling microscopy photocurrent signal and thus determine the barrier height of Au/oxidized GaAs to be ~ 3.55 eV. We next determine the barrier heights of Au/Al₂O₃/n-GaAs and Au/HfO₂/n-GaAs. We hope these barrier heights can serve as a good reference for other studies.

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LIST OF ABBREVIATIONS

BEEM	Ballistic electron emission microscopy
BEES	Ballistic electron emission spectroscopy
EDX	Energy-dispersive X-ray spectroscopy
EELS	Electron energy loss spectroscopy
MIM	Metal/insulator/metal
MOS	Metal/oxide/semiconductor
RBEEM	Reverse-bias ballistic electron emission microscopy
RBEES	Reverse-bias ballistic electron emission spectroscopy
STM	Scanning tunneling microscopy
STM-PC	Scanning tunneling microscopy photocurrent
TEM	Transmission electron microscopy
UHV	Ultra-high vacuum
XPS	X-ray photoelectron spectroscopy

Chapter 1 Introduction

1.1 Introduction

The performance of integrated circuits has improved mainly through the continued scaling of silicon oxide (SiO_2) or nitrided silicon oxide (SiON) gate dielectric. In recent years, however, the SiO_2 -based gate dielectric thickness has approached the scaling limit of 1.0–1.4 nm [1, 2]. This scaling limit of SiO_2 (or SiON) is generally believed to be related to gate leakage current due to the direct tunneling of electrons through the SiO_2 [1, 2].

One solution is to use a physically thicker high-dielectric-constant (high- κ) material as the gate insulator [1–3]. In this case, the gate capacitance can be maintained at the same level but the tunneling current can be reduced. High- κ /metal gate transistors have already been demonstrated in high-volume manufacturing [4]. As one would expect, the scaling of high- κ dielectrics cannot go on forever. A similar bottleneck arises when high- κ dielectrics reach a certain thickness. Therefore, it is important to study the intrinsic properties of ultrathin dielectrics and understand the scaling limit from a fundamental point of view. In addition, when the dielectric thickness is ~ 1 nm or less, small spatial variation can affect the device performance significantly. Studying ultrathin dielectrics at high spatial resolution is therefore also critical.

On the other hand, high-electron-mobility III–V semiconductors such as GaAs have also been explored for implementation in future metal-oxide-semiconductor field-effect transistors [5, 6]. However, various challenges remain in understanding and realizing GaAs metal-oxide-semiconductor devices. In particular, the poor quality of their

native oxides often results in a poor oxide/semiconductor interface. Fermi-level pinning has also been found to exist for both metal/dielectric and dielectric/semiconductor interfaces [6, 7]. Clarifying Fermi-level pinning largely depends on experimentally determining band offsets of both metal/dielectric and dielectric/semiconductor interfaces. While various experimental methods can be employed to investigate the dielectric/semiconductor interface, there are limited experimental methods available to accurately determine the barrier height of the meta/dielectric interface [6, 8, 9].

Ballistic electron emission microscopy (BEEM) is a scanning tunneling microscopy (STM)-based technique that was developed by W. J. Kaiser and L. D. Bell at Jet Propulsion Laboratory, California Institute of Technology, in 1988 [10, 11]. It not only has all the functions of STM, but also the ability to probe the metal/semiconductor and metal/dielectric/semiconductor interfaces and their related devices. One unique advantage of BEEM is that it has high spatial resolution (typically a few nanometers).

1.2 Motivation and Objectives

To clarify the scaling limit of SiO₂ and high- κ dielectrics, it is necessary to know the properties of ultrathin dielectrics (~ 1 nm or less). To date, there have been few studies on ultrathin SiO₂ and other dielectrics thinner than 1 nm. Tang *et al.* [12] and Muller *et al.* [13] evaluated the minimum thickness for an ideal SiO₂ gate oxide to be around 0.7 nm. A few first-principles calculations indicated that the band edges at the SiO₂-Si interface change gradually instead of abruptly and the bandgap of SiO₂ decreases on the SiO₂ side near the interface [14–17].

In this study, we employ BEEM to study the electronic properties of dielectrics with thicknesses of ~ 1 nm or less. By comparison with electronic properties of relatively thick dielectrics, we determine whether there is a significant difference in terms of the electronic barrier. We also investigate the causes of any such differences.

To advance the application of GaAs devices, it is vital to understand and determine the Fermi-level pinning at the metal/dielectric interface. To clarify the Fermi pinning, it is essential to accurately determine the barrier height of metal/dielectric interfaces. With the unique advantage of the BEEM technique, we determine the barrier height of Au and various important dielectrics.

1.3 Organization of the Thesis

This work is organized as follows:

Chapter 2 introduces STM and BEEM techniques. Following an introduction to the history and basic principle of STM, we focus on planar tunneling theory in STM. The basic BEEM principle and two working modes are then introduced, followed by the discussion of the basic BEEM theory. Finally, a comprehensive literature review of BEEM studies on metal/dielectric/semiconductor devices is presented.

The experimental setup and procedures are introduced in Chapter 3. We first introduce ultra-high vacuum (UHV) chambers and the capabilities of each component of the apparatus. We then concentrate on the *in-situ* thermal evaporator assembly and the electrical setup of the system. Toward the end of the chapter, experimental procedures are introduced, and trouble-shooting tips for commonly encountered problems are given.

Chapter 4 presents a comprehensive study of the subthreshold characteristics. An analytical equation is first derived from the basic BEEM theory, and then experimentally verified. A new simplified BEEM model is then proposed, and discussed.

Chapter 5 addresses the experimental issues in BEEM studies in the high tip-bias range for metal/dielectric/semiconductor devices. By comparing the BEEM measurements of 5-nm Au/5-nm SiO₂/n-Si(100) samples with Au deposited *in-situ* and *ex-situ*, we find that the BEEM measurement of *ex-situ* prepared samples does not give a reliable barrier height (in the high tip-bias range); in contrast, the BEEM measurement of *in-situ* prepared samples can be performed consistently and reliably. A detailed study is then carried out to determine the main difference between the two cases.

Chapter 6 investigates the electronic properties of ultrathin dielectrics. A comparative BEEM study of the native oxide with different thicknesses is first discussed. The electron barrier height of the ultrathin high- κ dielectrics is then investigated.

Chapter 7 determines the barrier height of a few important GaAs-based metal/oxide/semiconductor devices: Au/3-nm oxidized GaAs/n-GaAs, Au/Al₂O₃/n-GaAs and Au/HfO₂/n-GaAs.

Finally, conclusions and recommendations are given in Chapter 8.

1.4 Contributions

This study employs ballistic electron emission microscopy/spectroscopy to study the properties of metal/dielectric/semiconductor devices with high spatial resolution.

In terms of BEEM technique, we studied the subthreshold characteristics of ballistic electron emission spectra. A simple analytical equation describing the

subthreshold behavior of the BEEM spectrum was first derived. This equation shows that the BEEM current in the subthreshold region decreases by ~ 60 mV/decade, which has been verified by both simulation and experiment. Using the subthreshold equation, we proposed a new simplified analytical model for the BEEM spectrum fitting. This model significantly improves the fitting near and below the threshold compared with the simplified square model. More importantly, the model provides a method to quickly estimate the BEEM current at and below the barrier height according to the BEEM current above the barrier height.

We showed that BEEM measurement of samples with high barriers (~ 3.0 eV or above) cannot be performed properly if the metal base electrode is deposited *ex-situ*, even though there is no problem if the metal is deposited *in-situ* in a UHV. We further showed that the main reason is that contamination of the Au surface strongly affects tunneling between the tip and Au base, thus affecting the BEEM spectroscopy.

Electronic properties of ultrathin dielectrics—both native oxides on Si and high- κ dielectrics on Si—were investigated. We showed that a dielectric with less than a certain thickness ($6\text{--}8$ Å) in a metal/dielectric/semiconductor structure does not have the same electronic properties as the corresponding thicker bulk dielectric. However, these ultrathin dielectrics still strongly attenuate the ballistic electron transport. In addition, we found that native oxide on silicon does not grow uniformly on the nanoscale. This, on the other hand, suggests that BEEM is able to distinguish the minute dielectric thickness variation on the nanoscale for special devices.

For GaAs-based metal/oxide/semiconductor devices, we determined the barrier height of a few important dielectrics. For the Au/3 nm oxidized GaAs/n-GaAs device, the

BEEM spectra shows two thresholds of 1.4 and 3.55 eV. In an in-depth study, we showed that the first threshold arises from the STM photocurrent (STM-PC) signal and thus determines the barrier height of Au/oxidized GaAs as ~ 3.55 eV. We next determined the barrier height of Au/Al₂O₃/n-GaAs and Au/HfO₂/n-GaAs. We hope that these determined barrier heights can serve as a good reference for other studies.

Finally, in BEEM studies of Au/native oxide/n-Si and Au/3-nm oxidized GaAs/n-GaAs devices, we recorded spectra having two thresholds: one low and the other one much higher. Our in-depth studies showed, however, that the origins of the first threshold differ for the two devices. For the Au/native oxide/n-Si sample, the first threshold is due to the native oxide being too thin locally, while for the oxidized GaAs sample, the first threshold is due to the STM-PC signal.

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Chapter 2 Scanning Tunneling Microscopy and Ballistic Electron Emission Microscopy

In the first part of this chapter, some basis of scanning tunneling microscopy (STM) will be introduced. This includes STM history, the basic principle and most importantly the planar tunneling theory. In the second part, we focus on ballistic electron emission microscopy (BEEM), which is the main technique used in this study. After a brief introduction of the basic principle of BEEM, we present a detailed derivation of the basic BEEM model, Bell-Kaiser model, followed by a brief introduction of the BEEM theory on metal/dielectric/semiconductor devices. An introduction of reverse BEEM will also be given. Lastly, we will give a literature review of BEEM studies on metal/dielectric/semiconductor devices.

2.1 Scanning Tunneling Microscopy

2.1.1 STM history

In the historical talk entitled “There’s Plenty of Room at the Bottom” given by Richard P. Feynman on December 26, 1959, at the annual meeting of the American Physical Society at the California Institute of Technology [1], Richard P. Feynman considered the possibility of “to see individual atoms distinctly” and “to arrange the atoms the way we want” and had virtually introduced us into the world of nanoscience and nanotechnology. More than 20 years later, the invention of scanning tunneling microscopy [2-5] by G. Binnig and H. Rohrer at the IBM Zurich Research Laboratory had finally realized P. Feynman’s prediction.

However, the understanding of quantum tunneling began as early as the 1920s, notably the work about α -radioactivity by Gamow and Gurney and Condon [6-7]. Fowler and Nordheim then developed the theory of field emission [8]. After that, in the last half of the 20th century, four Nobel prizes were awarded to discoveries and inventions related to tunneling: the tunneling junction experiment of Giaever, the discovery of the Josephson Effect, the invention of tunnel diode by Esaki, and STM [9].

In 1971, Young *et al.* demonstrated an instrument called “Topografiner”, which had much in common with the basic principle of operating the STM, except that it was based on field emission rather than quantum tunneling and the tip had to be rather far away from sample surface [10].

Then finally in 1981, it took 27 months for Binnig and Rohrer to make the scanning tunneling microscope born from its conception [2]. STM did not really become so popular until they observed the 7×7 reconstruction on Si(111) resolved in real space in 1982 [2, 5].

Now STM, as a member of the scanning probe microscopy (SPM), is one of the most important techniques not only in nanoscience and nanotechnology, but also in surface science, physics, electronics, biology, *etc.*

2.1.2 Basic Principle

When a very sharp metallic tip is brought close (usually a few angstroms) to a conductive sample, the electron wavefunctions of the tip and the sample overlap. If a bias is applied between the tip and sample, a tunneling current will be generated. A STM usually uses piezoelectric driver (scanner) to control the tip to do a raster scan in the X-Y

directions over the sample and with a feedback mechanism to drive the scanner to retract or extend the tip in the Z-direction to keep the tunneling current constant. The tip height can be recorded at each (X, Y) position to form a sample surface topography. This is usually called the constant current mode, as shown in Figure 2.1. STM can also operate in constant height mode, in which the tunneling current is recorded while keeping the tip height constant during scanning.

Figure 2.1 A schematic showing how a scanning tunneling microscope works.

2.1.3 Planar Tunneling Theory

There are a few theories about quantum tunneling phenomena in STM. In 1961, Bardeen developed the tunneling theory from a many-particle point of view [11]. Tersoff and Hamman further modified the Bardeen theory and applied it to STM [12, 13]. In

1963, John G. Simmons developed a generalized formula for the tunneling current in a metal-insulator-metal (MIM) structure [14, 15], which is called planar tunneling theory. The development of the basic Bell-Kaiser theory in BEEM is based on the planar tunneling theory [16]. In this section, we derive the general formula for the tunneling current in the STM configuration, i.e., the MIM structure, based on References 7, 14, and 17. Later in this chapter, we use these results to derive the well-known Bell-Kaiser formula.

Figure 2.2 A schematic of the band diagram of metal/insulator/metal structure with a bias of $-V$ at metal 1.

As shown in Figure 2.2, we consider two metal electrodes which are made of the same material with the Fermi energy of E_F and separated by an insulator with a thickness of d . A voltage of $-V$ (we consider the case of V as positive here) may be applied to the left electrode while the other electrode is grounded.

We assume that the insulator forms a potential barrier which impedes the flow of electrons between two metals. When the barrier is thin enough and a voltage is applied

between the two metals, the electrons can tunnel through the barrier, which will be considered as the main source of the electric current.

The tunneling current is the net current of the current flow from metal 1 to metal 2 and that from metal 2 to metal 1. We will first derive the current from metal 1 to metal 2.

In order to know the number of electrons flowing from metal 1 to metal 2, we need to know the density of states and the occupation probability of the electrons, the probability that the electrons hitting the barrier can tunnel through and the probability of having unoccupied states in metal 2.

The density of states can be calculated in the following way: consider a cubic metal with a side of L . By matching the wave functions with periodic boundary conditions, one can find that the wave vectors (k_x, k_y, k_z) can only have the values of

$\frac{2\pi}{L}n$, where $n = 0, \pm 1, \pm 2, \dots$. Thus, in k -space, each state has the volume of $\left(\frac{2\pi}{L}\right)^3$

(two spin states will be included later). In a volume of $dk_x dk_y dk_z$ in the k space, the

density of states is then $\frac{dk_x dk_y dk_z}{\left(\frac{2\pi}{L}\right)^3}$. The density of states (in a volume of $dk_x dk_y dk_z$ in k

space) per unit volume in real space after including two spin states is then

$$2 \frac{dk_x dk_y dk_z}{\left(\frac{2\pi}{L}\right)^3} \frac{1}{L^3} = \frac{2}{(2\pi)^3} dk_x dk_y dk_z. \quad (2.1)$$

Electrons belong to Fermions, so they obey Fermi-Dirac distribution function:

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}, \quad (2.2)$$

where k is the Boltzmann constant, T is the temperature in Kelvin, and E_F is the Fermi energy.

The number of occupied states between (k_x, k_y, k_z) and $(k_x+dk_x, k_y+dk_y, k_z+dk_z)$ is the number of states multiplied by occupation function

$$f(E) \frac{2}{(2\pi)^3} dk_x dk_y dk_z . \quad (2.3)$$

The number of electrons between (k_x, k_y, k_z) and $(k_x+dk_x, k_y+dk_y, k_z+dk_z)$ reaching the barrier at the left side per second is

$$v_x f(E) \frac{2}{(2\pi)^3} dk_x dk_y dk_z . \quad (2.4)$$

Now we need to consider the probability that an electron can tunnel through a barrier potential of $V(x)$, i.e., transmission coefficient $T(E_x)$. This can be calculated by the Wentzel-Kramers-Brillouin (WKB) approximation [7]:

$$T(E_{xm}) = \frac{e^{-2\sigma}}{(1 + \frac{1}{4} e^{-2\sigma})^2} , \quad (2.5)$$

$$\sigma = \int_{x_1}^{x_2} \sqrt{\frac{2m}{\hbar^2} [V(x) - E]} dx , \quad (2.6)$$

where x_1 and x_2 are the turning points as shown in Figure 2.2, m is the free electron mass,

$\hbar = \frac{h}{2\pi}$ is the reduced Planck constant, h is Planck constant, $V(x)$ is the potential barrier,

and E_x is the energy component of the incident electron in the x direction. The number of electrons between (k_x, k_y, k_z) and $(k_x+dk_x, k_y+dk_y, k_z+dk_z)$ that can tunnel through the insulator per second is:

$$T(E_x)v_x f(E) \frac{2}{(2\pi)^3} dk_x dk_y dk_z, \quad (2.7)$$

where v_x is the x-component of the electron velocity.

The electrons can only reach the other side of the barrier provided that there are unoccupied states in metal 2. The probability of having unoccupied states in metal 2 is given by $1-f(E+eV)$, where $-V$ is the bias applied to metal 1. So, the number of electrons between (k_x, k_y, k_z) and $(k_x+dk_x, k_y+dk_y, k_z+dk_z)$ that can finally reach metal 2 will be

$$T(E_x)v_x f(E) [1-f(E+eV)] \frac{2}{(2\pi)^3} dk_x dk_y dk_z. \quad (2.8)$$

By integrating Equation (2.8) over all the k-space (only those electrons with $k_x \geq 0$ are able to reach the barrier) and multiplying by elementary charge of one electron e and effective tunneling area a , we get the current contribution from the electrons tunneling from metal 1 to metal 2:

$$\begin{aligned} I_{12} &= ae \int_0^\infty \left[\int_{-\infty}^\infty \int_{-\infty}^\infty T(E_x)v_x f(E) [1-f(E+eV)] \frac{2}{(2\pi)^3} dk_y dk_z \right] dk_x \\ &= \frac{2}{(2\pi)^3} ae \int_0^\infty \left[\int_{-\infty}^\infty \int_{-\infty}^\infty f(E) [1-f(E+eV)] dk_y dk_z \right] T(E_x)v_x dk_x \end{aligned} \quad (2.9)$$

Similarly, we can easily write down the current flow from metal 2 to metal 1:

$$\begin{aligned} I_{21} &= ae \int_0^\infty \left[\int_{-\infty}^\infty \int_{-\infty}^\infty T(E_x)v_x f(E+eV) [1-f(E)] \frac{2}{(2\pi)^3} dk_y dk_z \right] dk_x \\ &= \frac{2}{(2\pi)^3} ae \int_0^\infty \left[\int_{-\infty}^\infty \int_{-\infty}^\infty f(E+eV) [1-f(E)] dk_y dk_z \right] T(E_x)v_x dk_x \end{aligned} \quad (2.10)$$

The net tunneling current between metal 1 and metal 2 is then

$$\begin{aligned}
I_t &= I_{12} - I_{21} \\
&= \frac{2}{(2\pi)^3} ae \int_0^\infty \left[\int_{-\infty}^\infty \int_{-\infty}^\infty [f(E) - f(E + eV)] dk_y dk_z \right] T(E_x) v_x dk_x
\end{aligned} \tag{2.11}$$

Now let us try to write the tunneling current in terms of energy components of E_x and E_t , which are defined below:

$$v_x = \frac{\hbar k_x}{m}$$

$$E_x = \frac{\hbar^2 k_x^2}{2m}$$

In polar coordinate system,

$$k_t^2 = k_y^2 + k_z^2$$

$$\tan \varphi = \frac{k_z}{k_y}$$

$$E_t = \frac{\hbar^2 k_t^2}{2m}$$

Then,

$$v_x dk_x = \frac{\hbar k_x}{m} dk_x = \frac{1}{\hbar} dE_x \tag{2.12}$$

$$dk_y dk_z = k_t dk_t d\varphi = \frac{m}{\hbar^2} d\left(\frac{\hbar^2 k_t^2}{2m}\right) d\varphi = \frac{m}{\hbar^2} dE_t d\varphi . \tag{2.13}$$

Inserting Equations (2.12) and (2.13) into Equation (2.11), we have

$$\begin{aligned}
I_t &= \frac{2}{(2\pi)^3} ae \int_0^\infty \left[\int_{-\infty}^\infty \int_{-\infty}^\infty [f(E) - f(E + eV)] dk_y dk_z \right] T(E_x) v_x dk_x \\
&= \frac{2}{(2\pi)^3} ae \frac{1}{\hbar} \frac{m}{\hbar^2} \int_0^{2\pi} d\varphi \int_0^\infty \left[\int_0^\infty [f(E) - f(E + eV)] dE_t \right] T(E_x) dE_x \quad (2.14) \\
&= \frac{4\pi ame}{\hbar^3} \int_0^\infty \left[\int_0^\infty [f(E) - f(E + eV)] dE_t \right] T(E_x) dE_x
\end{aligned}$$

Therefore, the tunneling current in planar tunneling theory can be expressed as:

$$I_t = C \int_0^\infty T(E_x) dE_x \int_0^\infty [f(E) - f(E + eV)] dE_t, \quad (2.15)$$

where $C = \frac{4\pi ame}{\hbar^3}$. As we can see, the tunneling current of a MIM structure depends on the bias V , the metal/dielectric (vacuum) interface barrier φ and dielectric (vacuum gap) thickness d , and also the tunneling area a .

2.2 Ballistic Electron Emission Microscopy and Spectroscopy

Ballistic electron emission microscopy is a STM-based technique developed by W. J. Kaiser and L. D. Bell at Jet Propulsion Laboratory, California Institute of Technology in 1988 [18, 16]. It not only has all the functions of STM but also the capability of probing the interfaces of thin metal film (from a few nanometers to tens of nanometers) and underlying semiconductor or insulators with high spatial resolution (typically a few nanometers).

Two excellent early reviews of BEEM studies were given by Mario Prietsch [19] and L. D. Bell and W. J. Kaiser [20]. The studies of metal-oxide-semiconductor (MOS) structures with BEEM were reviewed by R. Ludeke [21]. An overview on BEEM theories was given by P.L. de Andres *et al.* [22]. Some more recent reviews can be found in References 23–25.

Figure 2.3 (a) Basic BEEM configuration and (b) corresponding band diagram for a metal/semiconductor device. (c) An example of a BEEM spectrum (red circles) on a 5-nm Au/n-Si sample, while the blue dotted line corresponds to the extracted barrier height.

In this section, we give an overview of the basic principle of BEEM. In the next section we discuss the basic Bell-Kaiser BEEM theory.

Figure 2.3 (a) is a schematic of BEEM experimental setup for metal/semiconductor device. The metal base is grounded and a bias is applied to the STM tip via a biased current-voltage preamplifier. The biased preamplifier also measures the tunneling current. The backside of the semiconductor is connected to another current-voltage preamplifier via ohmic contact to measure the BEEM current (or collector current).

When the tip is negatively biased and brought close to the metal base, electrons from the tip can tunnel through the vacuum barrier to the thin metal film. After transport in the metal film, some of the electrons can reach the metal-semiconductor interface without losing significant energy. If the energy of the electrons is higher than the interface barrier (see Figure 2.3 (b)), they have a finite probability to cross the interface into the conduction band of the semiconductor substrate and are collected as BEEM current.

BEEM can work in two basic modes: In spectroscopy mode, the tip stays at one location. By varying the tip bias V_{Tip} with the STM feedback on (so tip height will change), the BEEM current I_{BEEM} can be recorded to form ballistic electron emission spectroscopy (BEES), i.e., I_{BEEM} versus V_{Tip} . An example of the BEES is shown in Figure 2.3 (c). When the tip bias (strictly the corresponding energy) is below the interface barrier height, the measured BEEM current is zero or negligible. When the tip bias is higher than the barrier height, a BEEM current can be detected. A theoretical description of the behavior of the spectrum is discussed later. In imaging mode, the tip scans across the

metal base in constant current mode with a bias higher than the interface barrier, revealing topography of the metal surface and the corresponding image (BEEM image) of the collector current.

2.3 Basic BEEM Theory

2.3.1 Bell-Kaiser Model for Metal/Semiconductor

A similar expression can be written for the BEEM current based on the tunneling current Equation (2.15) after taking into account a few restrictions [17, 19, 24], such as energy restriction on E_x and E_t for injected electrons from the tip.

Assume the electron effective mass in metal base is equal to the free electron mass m , while the “transverse” effective mass in semiconductor is m_t . The perpendicular and parallel (transverse) components of the electron momentum are k_{xm} and k_{tm} in metal and k_{xs} and k_{ts} in semiconductor, respectively. The perpendicular and parallel (transverse) components of the electron energy are E_{xm} and E_{tm} in metal and E_{xs} and E_{ts} in semiconductor, respectively. Then we have

$$E_s = E_{xs} + \frac{\hbar^2 k_{ts}^2}{2m_t} = E + eV - E_F - \Phi_{BH} , \quad (2.16)$$

where E is the electron energy with reference to the conduction band minimum of the tip, $-V$ is the bias at the tip, and Φ_{BH} is the interface barrier height.

If we assume the parallel momentum is conserved at the interface of the metal and the semiconductor [16], i.e., $k_{tm} = k_{ts}$, we can replace k_{ts} in Equation (2.16) with k_{tm} to get

$$E_{xs} + \frac{\hbar^2 k_{tm}^2}{2m_t} = E + eV - E_F - \Phi_{BH} . \quad (2.17)$$

Since $E_{xs} \geq 0$, then

$$k_{tm}^2 \leq \frac{2m_t}{\hbar^2} (E + eV - E_F - \Phi_{BH}) . \quad (2.18)$$

As $E_{tm} = \frac{\hbar^2 k_{tm}^2}{2m}$ and $E = E_{xm} + E_{tm}$, then from Equation (2.18), we have

$$mE_{tm} \leq m_t (E_{xm} + E_{tm} + eV - E_F - \Phi_{BH}) , \text{ i.e.,} \\ E_{tm} \leq \frac{m_t}{m - m_t} (E_{xm} + eV - E_F - \Phi_{BH}) . \quad (2.19)$$

Therefore,

$$E_{tm}^{\max} = \frac{m_t}{m - m_t} (E_{xm} + eV - E_F - \Phi_{BH}) . \quad (2.20)$$

In addition, we have the minimum energy requirement for the perpendicular energy component so that the electrons can cross the interface:

$$E_{xm}^{\min} = E_F - eV + \Phi_{BH} . \quad (2.21)$$

With the restrictions of Equations (2.20) and (2.21) for the electrons to be able to reach the collector, we can write the BEEM current as:

$$I_{BEEM} = RC \int_{E_{xm}^{\min}}^{\infty} T(E_{xm}) dE_{xm} \int_0^{E_{tm}^{\max}} (f(E) - f(E + eV)) dE_{tm} , \text{ i.e.,} \\ I_{BEEM} = RC \int_{E_{xm}^{\min}}^{\infty} T(E_{xm}) \left[\int_0^{E_{tm}^{\max}} (f(E) - f(E + eV)) dE_{tm} \right] dE_{xm} , \quad (2.22)$$

where $C = \frac{4\pi ame}{h^2}$ and R is an attenuation factor accounting for the electron of transport through the metal and the metal/semiconductor interface.

Strictly speaking, Equation (2.22) is to describe a BEEM spectrum acquired at constant tunneling gap. However, BEEM spectra are usually taken at constant tunneling current condition, during which the tunneling gap changes. In addition, the prefactor C includes an effective tunneling area, which is usually hard to determine. Therefore, Bell and Kaiser proposed to treat the tunneling gap as a constant and normalize the BEEM current by the tunneling current for each voltage [16]. Combining Equations (2.15) and (2.22), we get the Bell-Kaiser formula for BEEM spectra at constant tunneling current:

$$I_{BEEM} = RI_t \frac{\int_{E_{xm}^{\min}}^{\infty} T(E_{xm}) \left[\int_0^{E_{tm}^{\max}} (f(E) - f(E + eV)) dE_{tm} \right] dE_{xm}}{\int_0^{\infty} T(E_{xm}) \left[\int_0^{\infty} (f(E) - f(E + eV)) dE_{tm} \right] dE_{xm}}. \quad (2.23)$$

Various simple models have been derived from Equation (2.22) or Equation (2.23), either through simplification or considering some additional physical effects. When Equation (2.22), the constant gap Bell-Kaiser model, is evaluated at $T = 0$ K, the BEEM current near the threshold is found to have a $(eV - \Phi_{BH})^n$ (where $n=2$) dependence on the tip bias [16, 20]. Prietsch and Ludeke proposed the $n = 5/2$ model by considering a square-root dependence of the quantum mechanical transmission at the interface [26]. For Equation (2.23), if we assume the tunneling current has a linear dependence on the tip bias, we will have another simple model: the “ $n = 2$ model divided by eV ”, which was proposed by Bannani *et al.* [27].

Thus far, different groups have been using different models to extract the barrier height from the experimental spectra. The extracted barrier height may be slightly different for different models. A comprehensive comparison on the fitting of the BEEM spectra with different models is given in Chapter 4.

2.3.2 BEEM Theory on Metal/Insulator/Semiconductor

In the previous section, we have discussed the BEEM theory on metal/semiconductor (MS) structure. Now we will briefly discuss the BEEM theory on the metal/insulator (mainly oxide)/semiconductor (MIS) structure.

BEEM has been mainly used to study metal/semiconductor systems; however, it has also been demonstrated useful in studying metal/insulator/semiconductor systems, especially metal (Au, Pt)/CaF₂/Si [28-32], metal (Pd, Pt, W, Au, and Ir)/SiO₂/Si [21, 33], metal (W)/Al₂O₃/Si [34, 35], metal (Pd, Pt)/SiO₂/Si [36–40], metal (Pt, Al)/Sc₂O₃/Si [41], and Au/HfO₂/SiO₂/Si [42, 43].

Figure 2.4 is a schematic of BEEM configuration and the corresponding band diagram for a MOS structure. With a negative tip bias, electrons are injected from the tip into the thin metal film. Some of the electrons can reach metal-oxide interface without losing significant energy. If the tip bias is higher than the barrier height at the metal/oxide interface, some of the electrons are able to enter the conduction band of the oxide, reach the oxide-semiconductor interface and finally be collected at the semiconductor substrate. Therefore, for a metal/oxide/semiconductor device, the barrier height extracted from the BEEM spectra is the difference between the Fermi level of the metal and the conduction band minimum of the oxide.

Figure 2.4 (a) Basic BEEM configuration and (b) corresponding band diagram for a metal/oxide/semiconductor device. (c) An example of a BEEM spectrum (red circles) on 5-nm Au/5-nm SiO₂/n-Si, while the blue dotted line corresponds to the extracted barrier height.

2.4 Reverse-bias BEEM

The tip can also be positively biased, in which the spectroscopy is called reverse-bias BEES (RBEES) or ballistic hole emission spectroscopy (BHES). With a positive bias at the tip, electrons tunnel from the metal thin film into the tip. Effectively, it is injecting holes into the metal. For metal/p-type semiconductor, the injected holes can enter the valence band of the semiconductor and be collected as collector current. RBEES studies on metal/p-type semiconductor have been shown to be able to probe the hole barrier [44–45]. However, RBEES studies on oxide-based samples have so far not yielded much information related to the electron barrier or hole barrier at the metal/oxide interface.

RBEES can be useful for identifying some competing signal with the real ballistic electron signal, for instance, STM photocurrent. STM photocurrent (STM-PC) is a signal that can appear in the BEEM spectra for certain devices [46]. While it is a very weak signal for most devices, it can be significant for certain devices, especially for oxide-based samples. STM-PC is commonly believed to be due to the electron-hole pairs generated in the semiconductor substrate by the photons emitted at the STM tunnel junction during tunneling [47, 48]. We will have more discussions on the features of the STM-PC signal in Chapter 6.

2.5 Spatial Resolution of BEEM

From Equation (2.18), the parallel momentum of the electrons at the metal/semiconductor interface has a maximum value, which means that an electron whose parallel momentum is larger than a critical value cannot enter the semiconductor

substrate. As a result, only electrons with their angle of incidence smaller than a critical angle can contribute to the BEEM current. This critical angle θ_c is determined by

$$\sin^2 \theta_c = \frac{k_m^2}{k_m^2} = \frac{m_t}{m} \frac{E + eV - E_F - \Phi_{BH}}{E + eV},$$

where $k_m = \sqrt{\frac{2m}{\hbar^2}(E + eV)}$ is the electron momentum in the metal base. For Au-GaAs interface, the critical angle is calculated to be only a few degrees at relatively low electron energies [24]. The small critical angle results in a high spatial resolution.

Experimentally, a high spatial resolution of 1.5 nm was observed for Au films of 10–15 nm in the Au/Si system [23]. Atomic resolution was also obtained on certain samples, such as epitaxial CoSi₂ layers on Si(111) substrates [49].

For our studies on metal-oxide-semiconductor devices, a high tip bias is typically used. The spatial resolution at a high tip bias is worse and can be as large as 10 nm [23].

With the high spatial resolution, BEEM has the potential to detect the lateral variations of the barrier height and electron transport on the nanoscale. For a metal-semiconductor system, Prietsch [19] showed that the minimum length scale to be able to observe a barrier-height variation reduces considerably when a substrate with a high doping concentration is used. In practice, a few limitations exist in detecting the lateral variations in electron transport, such as the scattering in the metal and at the metal-semiconductor interface. Another challenge lies in the extraction of the barrier height from the spectra, which will be discussed in Chapter 4.

2.6 Literature Review

As mentioned earlier, BEEM has been employed to study metal/semiconductor devices extensively. However, there are not many reports on BEEM studies of metal/insulator/semiconductor devices. Some reviews on BEEM studies of metal/semiconductor devices can be found in References 19–25. In this section, we will give a review of the BEEM studies of the metal/insulator/semiconductor devices.

For insulators of non-oxides, CaF_2 is by far one of the few that have been successfully studied with BEEM [28–32]. For insulators of oxides, various devices have been studied on silicon substrate, notably metal (Pd, Pt, W)/(SiO_2 , Al_2O_3)/Si by Ludeke's group [21] and metal (Pd, Pt, and Al)/(SiO_2 , Sc_2O_3)/Si by Pelz's group [36–41]. Quattropani *et al.* [33] and Zheng *et al.* [42–43] have also reported some studies on metal (Au, Ir)/ SiO_2 /Si and Au/ HfO_2 / SiO_2 /Si, respectively. There have been no BEEM studies of oxides on other semiconductor substrates.

While one of the most important results on metal/oxide/semiconductor devices has been the accurate determination of the metal/oxide interface barrier height, there are also other findings like the charge trapping in the oxide film.

Kaczer *et al.* [50] studied charge trapping in thick (25 nm and 10 nm) SiO_2 films extensively with BEEM. They reported the current suppression with the injection of hot electrons into the oxide and obtained three-dimensional profile of the trapped charge in buried SiO_2 films from these thick SiO_2 devices. They also observed quantum-mechanical resonance of hot electrons in the oxide film on thin (2.7 nm) SiO_2 device.

Ludeke *et al.* also studied SiO_2 -based samples with BEEM considerably and has summarized his work in a review paper [21]. They studied mainly on the charge trapping

in the oxide film and also on the extraction of certain parameters, such as effective dielectric constant and effective electron mass in SiO_2 layer. They also reported BEEM studies on SiO_2 degradation with time.

Cai *et al.* [51] used BEEM to study SiO_2 samples and also high-k dielectrics of epitaxial Sc_2O_3 and Lu_2O_3 samples. They found the lateral inhomogeneous of the metal/oxide interface of $\text{Pt}/\text{Al}/\text{SiO}_2/\text{Si}$ by comparing it with $\text{Pt}/\text{SiO}_2/\text{Si}$. They also found that the “tail states” conduction band can support the hot electron transport across the thick Sc_2O_3 film even against an applied electric field. It was found that some differences in the $\text{Pt}/\text{Lu}_2\text{O}_3$ interface barrier extracted from BEEM and that from internal photoemission measurement existed, but not for $\text{Pt}/\text{Sc}_2\text{O}_3$ interface.

Quattropani *et al.* [33] reported BEEM investigation on $\text{Au}/\text{SiO}_2/\text{Si}$ and $\text{Ir}/\text{SiO}_2/\text{Si}$ samples with SiO_2 thicknesses of 3 nm and 1 nm. On the 3-nm SiO_2 sample, they extracted the interface barriers of Au/SiO_2 and Ir/SiO_2 to be 4.1 eV and 5.6 eV, respectively. On the sample of $\text{Au}/1\text{-nm SiO}_2/\text{n-Si}$, they observed a linear BEEM current component below the ~4 eV barrier of Au/SiO_2 interface. For the sample of $\text{Ir}/1\text{-nm SiO}_2/\text{n-Si}$, they have observed a smaller threshold of ~1.5 eV and a broad peak in the BEEM current around 4 eV. On the same sample they also found a similar behavior in reverse BEEM spectra compared to the BEEM spectra in terms of current flow direction, the threshold and intensity.

While the BEEM measurements on metal/dielectric/semiconductor devices summarized above were almost all performed in ultra-high vacuum with *in-situ* metal deposition, BEEM measurements on metal/dielectric/semiconductor samples in high vacuum and/or without *in-situ* metal deposition were also reported in a few publications.

Zheng *et al.* [42, 43] reported some BEEM studies on Au/HfO₂/SiO₂/Si. They have extracted the interface barrier heights of Au/SiO₂ and also Au/HfO₂. They also carried out breakdown studies on the same sample. However, as they pointed out, no BEEM signal was observed at most locations of the sample. This is not the case for BEEM studies in UHV and with *in-situ* metal deposition. Lee *et al.* [52] also documented some BEEM studies on Pd/SiO₂/Si samples with *ex-situ* Pd deposition. However, they did not observe the expected barrier height of ~4 eV for Pd/SiO₂ interface; instead, they observed a barrier height much higher than ~4 eV. They concluded that the lift-off processing altered the metal/oxide interface properties or contaminated the interface. Kaczer *et al.* [39] also reported BEEM measurement with *ex-situ* deposited Pd. However, after transferring into the UHV system, the sample was degassed at 350–400 °C for 10 min, which might have produced a cleaner Pd surface.

2.7 Summary

In this Chapter, we gave an introduction of the basic principle of STM and BEEM. We discussed the STM planar tunneling theory and the basic BEEM theory. Finally, a comprehensive literature review of BEEM studies on metal/dielectric/semiconductor devices is presented.

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Chapter 3 Experimental Setup and Procedure

In this chapter, we introduce the ultra-high vacuum (UHV) STM/BEEM system which was set up during the period of Jan, 2010–Aug, 2010. The system also has the capability of *in-situ* metal deposition, which was demonstrated to be critical for the BEEM measurement of metal/insulator/semiconductor devices. We will then introduce the major procedures to perform the BEEM experiment. In addition, we discuss some problems that may occur during the experiment together with some trouble-shooting tips.

The current system was upgraded from an existing high vacuum BEEM system, which was basically the STM/BEEM chamber with an ion pump and a rotary pump. With this high vacuum system, the typical procedures for BEEM experiment were as follows: preparing sample in a separate evaporator, transferring it through air via a quick-access door, pumping, and performing the experiment at a typical pressure of $\sim 6 \times 10^{-8}$ mbar.

In order to perform the experiment in a significantly better environment and in a much better controlled manner, we have upgraded it into a UHV STM/BEEM system with the capability of *in-situ* metal deposition.

3.1 UHV STM/BEEM System

Figure 3.1 show some photographs of the STM/BEEM setup. The UHV STM/BEEM system consists of three main parts: STM/BEEM control system, UHV chambers, and various power supplies and controllers. In this section we will mainly discuss the UHV chambers.

(a)

(b)

(c)

Figure 3.1 Photographs of the UHV STM/BEEM system during the setup process: (a) table frame and other parts before installing, (b) the STM/BEEM chamber, preparation chamber and the load-lock are all in place, and (c) the completed system with all parts installed and tested.

The UHV chambers have three main parts: the load-lock chamber, the STM/BEEM chamber, and the preparation chamber.

The load-lock chamber is an intermediate chamber for the introduction of sample to the preparation chamber. It is a six-way cross chamber with a transfer arm, a pressure gauge, a turbomolecular pump with a rotary backing pump, and a nitrogen venting valve.

The STM/BEEM chamber has the capability of tip cleaning by electron bombardment, sample heating/cooling, and *in-situ* metal grounding without breaking the vacuum.

The preparation chamber has a XYZ manipulator for transferring the sample from the load-lock chamber to the STM/BEEM chamber. It also has the setup for sample heating/cooling. More importantly, it has an evaporator for thin metal film deposition.

Both of the STM/BEEM and preparation chamber have one ion pump and one titanium sublimation pump (TSP). These two chambers are isolated by a UHV gate valve. The pressures in both of these chambers are typically in the range of 3×10^{-10} mbar.

3.1.1 STM/BEEM Chamber

Figure 3.2 shows the electrical connections from the sample in the vacuum to the Bayonet Neill–Concelman (BNC) connectors in the air side. In order to perform the BEEM experiment, the original internal connections have been modified so that the two BNC connectors are now connected to the two spring contacts (which were originally connected to thermocouple wires), respectively. Depending on the connection of the sample to the spring contacts, either of the two BNC connectors can be connected to a current-voltage preamplifier to measure the BEEM current.

Figure 3.2 A schematic showing the electrical connections from sample in vacuum to the BNC connectors in air side.

The thermocouple wires are inside but electrically isolated from the sample holder. Usually the first step is to load the sample onto the sample holder. By sliding the sample holder onto the sample stage, the thermocouple wires will be in electrical contact with the existing spring contacts, and thus the BNC connectors in the air side. The thermocouple wires on the sample holder are mainly for measuring the sample temperature when the sample is being heated on the XYZ manipulator in the preparation chamber.

There are three ways to heat the sample in the STM/BEEM chamber. First, the sample can be heated with the tungsten filament below the sample stage. Second, the sample can be heated with electron-beam bombardment. In this configuration, a direct current (DC) flows through the tungsten filament below the sample stage and the high voltage is applied to one of the BNC connectors. However, with these two methods, the sample temperature is difficult to measure, as there is no more thermocouple in the STM/BEEM chamber. Another way to heat the sample is to use direct current heating. To use direct current heating, the thermocouple on the sample holder has to be replaced with two tantalum or tungsten wires. Two tantalum foils connected to these two wires are also needed to clamp the sample (sample size about 3 mm $\times$ 6 mm) inside the sample holder. With a proper DC power supply (typically 20–70V, 0.1–10A) connected to the two BNC connectors, the sample can be heated by direct current heating. In this way, the sample can be heated to more than 1200 °C while the temperature can be monitored with a pyrometer.

For the metal grounding during *in-situ* BEEM measurement, a thin gold wire was attached to a BNC feedthrough which can be manipulated by a mini XYZ manipulator. This is shown in Figures 3.3 (a) and (b). When the sample is ready in place, the gold wire can be moved in three dimensions to gently touch the metal dot by manually controlling the XYZ manipulator. With the *in-situ* metal grounding, the sample does not need to be exposed to air after metal deposition to maintain the cleanness of the sample. In addition, possible oxidation can be avoided.

(a)

(b)

Figure 3.3 (a) Photos showing the sample, tip, thin Au wire for grounding, and various other parts. (b) A close-up view of the sample with metal grounded and the tip close to the sample.

3.1.2 Preparation Chamber

The preparation chamber has an evaporator installed, which will be discussed in more detail later. In addition, a XYZ manipulator from RHK Technology based on Omniax from VG Scienta was installed. It is used for receiving the sample from the load-lock chamber and transferring it to the STM/BEEM chamber. The manipulator also has the capability of heating (if the sample holder has a built-in heater) and cooling for the sample. With the radiative heating on the manipulator, the advantage is that there is an existing thermocouple on the manipulator to measure the sample temperature.

3.2 *In-situ* Metal Deposition

One great improvement of the upgraded STM/BEEM system is the *in-situ* metal deposition, which to a large extent eliminates or minimizes the possible contamination of the metal/oxide interface and the metal surface. Typical filament current to reach a deposition rate of 0.01 nm/s for Au is around 11.5–12.5 A.

Figure 3.4 (a) shows the schematic of the evaporation assembly, including a thermal evaporator, a quartz crystal microbalance, a shadow mask, and a mask holder. Figure 3.4 (b) is the photo of the thermal evaporation assembly. We will discuss each part separately.

3.2.1 Thermal Evaporator

For Au deposition, we use a thermal evaporation method as shown in the schematic of Figure 3.4. Basically a 0.25 cc (cubic centimeter) pyrolytic boron nitride (PBN) crucible is wrapped by a tungsten filament of a diameter of 0.4 mm. A certain amount of the metal source can be put in the crucible.

Figure 3.4 (a) Schematic showing the configuration of the thermal evaporation assembly.

(b) Photo of the thermal evaporation assembly.

3.2.2 Quartz Crystal Microbalance

The quartz crystal microbalance (QCM) is positioned above the evaporator and directly above the evaporation source. It is attached to a linear motion feedthrough. Due to space and some other limitations, the QCM cannot see the evaporation source when the sample is in place during the evaporation. Therefore, it has to be tested from time to time to determine the key parameters (filament current, *etc.*) needed to get a specific deposition rate. During a test of the evaporation rate, the sample is pulled away from the place and the QCM is pushed to the same height as the sample and will be retracted away after the test. The QCM accuracy was double checked with a surface profiler in our experiment.

3.2.3 Shadow Mask and Mask Holder

In order to deposit some metal dots (to reduce the area and thus the leakage current of the device), we fabricated a special shadow mask made of stainless steel with a few 0.5-mm diameter holes and one 0.2-mm diameter hole. In order to make sure the mask can be very close to the sample and to better align the mask to the sample/sample holder by simply looking through the viewport, a mask holder of a special shape instead of a simple flat plate was designed.

3.3 Electrical Setup

Figure 3.5 Block diagram of the BEEM experimental setup.

Figure 3.5 is a block diagram of the electrical setup of the STM/BEEM system. It is based on the variable temperature UHV STM from RHK Technology, Inc. The STM operation is controlled by a SPM 1000 (control electronics), PPC 100 and XPMPPro software from RHK Technology, Inc.

The tunneling current is measured through a biased-preamplifier with a gain of 100 mV/nA. This amplifier also provides the bias to the tip.

The BEEM current measurement has a few stages: the first and second stages are IVP-300 with a bandwidth of 5 kHz and IVP-PGA with a bandwidth of 500 Hz with an overall gain of 1V/nA. Both of these amplifiers are from RHK Technology, Inc. After these two stages, the BEEM current usually has a peak-to-peak noise of 5–10 pA, which is too high for most BEEM measurements. In order to reduce the noise level, the BEEM current is then routed to a SR560 preamplifier (Stanford Research Systems). At this stage, the BEEM current can be further filtered and amplified. A cut-off frequency of 30 Hz or 10 Hz is usually used.

With the old control software of SPM32, a 12-bit analog-to-digital converter (ADC) was used. The electrical resolution of the ADC converter was $\frac{20}{8 \times 2^{12}} \approx 0.61$ mV, where $\frac{20}{8}$ is the output range of the ADC. Thus, with a gain of 1 nA/V in the current-voltage preamplifier, the electrical resolution in the BEEM current would be 0.61 pA, which was too high for most BEEM measurements, especially for oxide samples. If the amplification of SR560 is set to $\times 100$, the electrical resolution can improve to 0.0061 pA. However, the measurement range will be limited to ± 12.5 pA. In October, 2009, we upgraded the SPM32 software to XPMPPro 2.0 together with an adaptor box, which can

acquire 16 bit resolution data over a 20 V range (or as small 2.5 V). With the new software and the gain of the SR560 set to $\times 10$, the electrical resolution in the BEEM current can be as small as 0.00381 pA, which is small enough for almost all BEEM measurements.

3.4 Tip Preparation

In all the experiments carried out prior to the setup of the *in-situ* UHV system, we used mechanically cut PtIr (90% Pt, 10% Ir) tips, as we could not clean etched tips in vacuum. After the installation of the UHV system, we used etched tungsten tips. Here we mainly describe the preparation steps of etching and cleaning tungsten tips. For more details on tip etching and cleaning, one can refer to Reference 1.

3.4.1 Tip Etching

Tungsten tips of 0.25 mm diameter were etched with a 5-g NaOH/50-mL deionized (DI) H₂O solution by initially applying 15 mA current, which suddenly dropped to 0–0.03 mA. Immediately after etching, the tip was cleaned with isopropanol (IPA) and DI water thoroughly and checked under an optical microscope.

3.4.2 Tip Cleaning

An etched tip is usually not immediately ready for use because of contamination and the formation of tungsten oxide. It is advisable to clean the tip further with electron bombardment (i.e., electron-beam heating) after the tip has been transferred to a vacuum chamber.

To clean the tip with electron bombardment, the original tip exchange holder was modified by tightening a 0.4-mm diameter tungsten wire onto it. After this modification, the tungsten wire was inserted into one of the spring contacts when the tip exchange holder was inserted into the sample stage. Since the tip in the tip holder is in electrical contact with the exchange holder, the BNC connector on the air side is in electrical contact with the tip. Once the tip is in place, the tungsten filament below the sample stage is raised until it is about 1–2 mm from the W tip end as observed through a viewport with the help of a charge-coupled device (CCD) camera. (Note that it is not necessary to move the filament close to the tip. It works equally well to leave the filament far from the tip.) The filament is connected to a DC power supply, and at the same time, the BNC connector is connected to the output of a high-voltage power supply. Since the outer layer of the output BNC is already grounded by the high-voltage power supply, it has a common ground with the DC power supply. Before connecting the high voltage BNC connector to the BNC connector on the chamber and applying any current or high voltage, it is necessary to check the following items:

- The inner conductor of the BNC connector on the chamber should be in electrical contact with the STM heating/cooling stage thermocouple;
- The inner conductor of the BNC connector on the chamber and the ground should be insulated. It is important to ensure there is nothing on the thermocouple of the sample stage;
- The BNC connector and tungsten filament should be insulated;
- The tungsten filament and outer layer of the BNC output of the high voltage power supply should have a common ground.

Once everything has been checked, the DC power supply is set in constant-current mode and a current of ~ 4.0 A is applied. We then slowly ramp up the high voltage to ~ 800 V while observing the emission current and chamber pressure. If the emission current is still much less than 0.02 mA, we slowly increase the filament current until the emission current reaches 0.03–0.05 mA. At the same time, we observe the pressure carefully and ensure that it does not increase too quickly. We then leave the system for about 10 min. The high voltage should not exceed 1000 V owing to the limitation of the BNC connector. The filament current is typically around 4.5 A. The typical pressure during cleaning is in the low range of 10^{-9} mbar.

3.5 Experimental Procedures

3.5.1 Substrate Cleaning

In the Au/n-Si(111) experiment, the silicon substrate (doping concentration of $\sim 1 \times 10^{15} \text{ cm}^{-3}$) was first heavily ion-implanted with arsenic (dose of $\sim 1.0 \times 10^{15} \text{ cm}^{-2}$) at the backside and annealed at 1000°C for ~ 5 s. Before loading into the vacuum for metal deposition and BEEM measurement, the substrate can be cleaned in different ways. One way is standard RCA cleaning, in which 1) the silicon substrate is first cleaned with a solution of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 3:1$), 2) the substrate is etched by dipping it into a 10% HF solution for 3 minutes and rinsed in DI water for 5 s; 3) the substrate is cleaned with a solution of DI H_2O , hydrogen chloride (HCl), and H_2O_2 (6:1:1), and 4), the sample is hydrogen terminated by etching with a commercial buffered oxide etch solution (40% NH_4F :49% HF = 7:1). Another method is to clean the sample with acetone, IPA, and DI water. The sample is then also etched with

a commercial buffered oxide etch solution for ~20 s. The sample is finally dipped in DI water and blown with dry nitrogen.

For oxide samples on silicon substrate, the backside was either heavily ion implanted and annealed or coated with a layer of aluminum deposited by electron-beam evaporation. The samples were then sequentially cleaned with acetone and IPA while being ultrasonically vibrated for several minutes.

For the oxide samples on GaAs substrate, a backside ohmic contact was made by electron-beam evaporation of a composite layer consisting of Ni(5 nm)/Ge(25 nm)/Au(100 nm)/Ni(20 nm)/Au(200 nm), and this was followed by annealing in N₂ ambient at 450 °C.

3.5.2 Substrate Degassing

After the substrate was cleaned, it was loaded into the load-lock and the chamber was pumped down for several hours. The substrate was then transferred into the preparation chamber. Depending on the specific purpose of the experiment, the substrate might be degassed to remove possible contamination at the surface.

Two methods were used for the sample degassing: direct current heating or radiative heating. If the sample was to be degassed below 360 °C, either of the two methods could be used. However, if it was to be degassed above 360 °C, we employed direct current heating. During degassing, the chamber pressure was typically in the 10⁻⁹ mbar range or in the low 10⁻⁸ mbar range. After degassing, the sample was left in the vacuum to cool to room temperature before metal deposition.

3.5.3 Metal Deposition

Before deposition, the filament current was determined by positioning the quartz crystal microbalance (QCM) at the same height as the sample to achieve a deposition rate of 0.01 nm/s. The QCM was then retracted. The sample and shadow mask were next moved into place. After all alignments were carried out, the filament current was raised slowly to the desired value as just determined, and kept stable for around 1 minute before the shutter was opened. Once the required thickness was reached, the shutter was closed and the filament current was decreased to zero quickly. The pressure during Au deposition was typically around 2×10^{-8} mbar and the pressure decreased to the low 10^{-9} mbar range within ~30 s of the filament current falling to zero.

The metal deposition could also be carried out while the sample was being cooled with liquid nitrogen. In this case, once the sample and mask were in place, the sample was first cooled with liquid nitrogen flowing through the XYZ manipulator, and the temperature of the sample on the manipulator was measured by an existing thermocouple. Once the temperature was relatively stable, deposition commenced in the same way as above. Once the deposition was complete, the liquid nitrogen flow was slowly cut off. The sample was left to warm to room temperature before being transferred to the STM/BEEM chamber for the measurement.

3.5.4 BEEM Measurement

All the amplifier connections were first checked with the sample on the STM/BEEM stage. With the aid of light and a CCD camera, the thin gold wire was then

gently moved to touch the metal dot of interest by manually controlling the mini XYZ manipulator.

3.6 Tip Sharpening and Evaluation

3.6.1 Tip Sharpening

In most cases, a fresh mechanically cut PtIr tip is immediately ready for scanning and spectral measurement without further treatment. This is also true for an etched tungsten tip after cleaning by electron-beam bombardment. However, after a period of scanning or spectral measurement, the tip quality may degrade as the tip picks up some material from the sample, drops atoms from the tip, or is involved in an accidental crash. Whenever these situations occur, routine treatments have to be applied in order to regain a sharp tip.

There are various ways to sharpen the tip either *ex-situ* or *in-situ* and they have been well documented in the literature [1]. One of the most frequently used methods is to apply a higher pulse voltage to the tip or the sample (with the feedback control turned off) when the tip is in the tunneling range at a lower tunnel voltage. The effectiveness of this method depends on many parameters, such as the pulse amplitude, width, and voltage polarity. Another way is to manually drive the tip to gently touch the sample surface (or vice versa) by applying a voltage to the piezoelectric scanner when the feedback is off. This approach is usually used when the tip is in a terrible condition. Other methods such as fast scanning also work.

3.6.2 Evaluation of Tip Quality

Since the tunneling involves the tip, air/vacuum gap, and sample, unstable tunneling can arise from any of these factors. For instance, an STM working in air ambient typically cannot achieve stable tunneling with bias of more than 3 V, which is why STM in air is normally restricted to a bias of not more than 2.5 V. However, most of the experiments described here were carried out under UHV condition, and the air gap should therefore not be a large problem. Unstable tunneling thus narrows down to the tip and sample. If we assume that the sample surface is sufficiently clean, any unstable tunneling must be due to the tip.

A common way to check the quality of a tip is to check the topography after scanning. If the topography is clear and the same as expected, then the tip is normally in good condition.

Another quick yet uncommon way to check the quality of a tip is to take the spectroscopy of tip height versus tip bias in the constant-current mode [2]. Usually the bias should be ramped up to a high value (e.g., -0.3 V to -10.0 V) to better evaluate the tip condition. Basically, the change in tip height in such a large range of the bias is quite small such as 1.0 nm or less. If the tip (or sample surface) is not in good condition, the change in tip height is normally much larger, around a few nanometers or possibly more. This method is typically used for the UHV condition and a clean sample, as otherwise it is difficult to tell whether a large change in the tip height is due to a bad tip or the sample. One example is that if the experiment is done in a high vacuum and the sample is not UHV clean, scanning at low bias can give a good topography for a tip in good condition;

however, the change in tip height over a large bias range (e.g., -0.3 V to -8.0 V) can still be significantly large (8 nm or so).

3.7 Trouble-shooting

There are a few critical aspects of a practical BEEM experiment:

- After grounding the metal dot, it is usually advisable to check the noise level of the tunneling current and BEEM current (by observing the spectrum analyzer at the highest sampling frequency or by observing the oscilloscope), especially the noise at ~ 50 Hz and in the range of 60–70 kHz. There are several methods to eliminate or reduce such noise. One approach is to set the STM100 controller far from the ion pump controllers. A high level of noise around 60–70 kHz can be induced when the STM100 controller is close to the ion pump controllers, owing to the switching mode of the ion pump power supply. Another way is to turn off the CCD camera and light, and to cover all viewpoints. Finally, it also helps to position the IVP-PGA preamplifier at different locations. The peak-to-peak noise of the BEEM current should be typically no more than 1 pA.
- When the thin gold wire touches the metal dot, the BEEM current offset usually suddenly goes out of range of the SR560 preamplifier (in the case of a device that is very light-sensitive) or changes a little bit (in the case of a device that is not very light-sensitive). This is a good way to check if the gold wire is in good electrical contact with the metal dot.
- We find that the noise level is closely related to the BEEM current offset: the lower the BEEM current offset (the absolute value), the lower the noise level. One

of the main reasons is that the BEEM current offset after all the viewports are covered is a good indication of the zero-bias resistance of the device. With higher zero-bias resistance, the BEEM current offset will be smaller. Thus, the noise in the BEEM current will also be less. For instance, the peak-to-peak noise level corresponding to a BEEM current offset of around 0 pA could be as low as 0.5 pA, while it could be as high as 5 pA for a BEEM offset of around 150 pA.

3.8 Summary

The UHV STM/BEEM system was briefly described in this chapter. The details of the *in-situ* metal deposition and the electrical setup of the system were then discussed. We next introduced the main experimental procedures. Finally, we gave some troubleshooting tips for the BEEM measurements.

References

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Chapter 4 Subthreshold Characteristics of Ballistic Electron Emission Spectra and a New Simplified Model for BEES Fitting

4.1 Introduction

Ballistic electron emission spectroscopy (BEES) is a powerful technique for determining the Schottky barrier height of metal/semiconductor devices with nanometer spatial resolution [1]. The Bell-Kaiser model, based on the planar tunneling theory in STM, has been successful in modeling the near threshold behavior of BEEM spectra and extracting the barrier height to a large extent [2]. A simplified power law model (power, $n = 2$) [2] based on the Bell-Kaiser model has been widely used to fit the spectra, largely due to its simplicity [3]. However, the $n = 2$ model is usually based on the assumption of temperature, $T = 0$ K. At non-zero temperatures, there are still electrons above the Fermi energy of the STM tip, as governed by the Fermi-Dirac distribution. When the tip bias is lower than the interface barrier height, these electrons still have a finite probability to reach the metal/semiconductor interface and are collected as BEEM current. Therefore, it is expected that there will be a non-zero BEEM current when the tip bias is a few kT (k is Boltzmann's constant and T is the temperature) below the barrier height. Deviations in the fitting of the near (both below and above) threshold [4] region are thus expected when using the $n = 2$ model to fit the spectra acquired at a non-zero temperature. Despite these deviations, so far there has been little detailed quantitative study on this subthreshold behavior [5].

In this chapter, we will first present a quantitative study on the subthreshold characteristics of the BEEM spectra, based on a simplified analytical model derived from the Bell-Kaiser formula. It will be analytically and experimentally shown that the BEEM current in this region decreases at a subthreshold swing (SS) of ~ 60 mV/decade, i.e., the BEEM current decreases one order of magnitude when the tip bias decreases by ~ 60 mV. It will also be shown that significant deviations could exist when the experimental BEEM spectra are fitted using the simplified $n = 2$ model. Next, we will introduce a simple, but more accurate analytical model for the BEEM spectra fitting. As an extension of the $n = 2$ model, the proposed model includes a temperature dependence and takes into account subthreshold characteristics. We will show that this model significantly improves the fitting accuracy in the near-threshold region, and the extracted barrier heights are very similar to those extracted from the full Bell-Kaiser model. We will also show that this model provides a method to quickly estimate the BEEM current in the subthreshold region based on the BEEM current at $10kT$ above the extracted barrier. Finally, we will have a comprehensive and complete comparison on the BEES fitting with various BEEM models.

4.2 Subthreshold Characteristics-Theoretical Description

The Bell-Kaiser model for the BEEM spectra of a metal/n-type semiconductor device at constant tunneling gap based on the planar tunneling theory can be written as [2],

$$I_{BEEM} = RC \int_{E_{xm}^{\min}}^{\infty} T(E_{xm}) \left[\int_0^{E_{tm}^{\max}} (f(E) - f(E + eV)) dE_{tm} \right] dE_{xm} \quad (4.1)$$

where I_{BEEM} is the BEEM current, R is an attenuation factor accounting for the electron transport through the metal and the metal/semiconductor interface, C is a constant, $f(E)$ is

the Fermi-Dirac distribution function, $T(E_{xm}) = \frac{e^{-2\sigma}}{(1 + \frac{1}{4}e^{-2\sigma})^2}$ is the tunneling probability

through the vacuum gap based on the Wentzel–Kramers–Brillouin (WKB) approximation

[6], with $\sigma = -\frac{2}{3} \frac{d}{eV} \sqrt{\frac{2m}{\hbar^2}} \left[(E_F + \phi - eV - E_{xm})^{\frac{3}{2}} - (E_F + \phi - E_{xm})^{\frac{3}{2}} \right]$. Here d is the vacuum

gap width, $\hbar$ is the reduced Plank's constant, ϕ is the average workfunction of the tip

and the metal base, E_{xm} and E_{tm} are the perpendicular and transverse energy components

of the electrons in the metal base, respectively, $E_{xm}^{\min} = E_F - eV + \Phi_{BH}$,

$E_{tm}^{\max} = \frac{m_t}{m - m_t} (E_{xm} + eV - E_F - \Phi_{BH})$, E_F is the Fermi energy of the tip, $e = + 1.6 \times 10^{-19}$

C is the elemental charge, V is the absolute value of the tip bias, Φ_{BH} is the interface

barrier height, m_t is the transverse electron effective mass parallel to the interface in the

semiconductor, and m is the free electron mass.

To compensate for the change in the tunneling gap during the acquisition of the BEEM spectra under constant tunneling current condition, Bell and Kaiser [2] proposed the following formula which basically modified Equation (4.1) by dividing it by tunneling current at each tip bias at the same tunneling gap,

$$I_{BEEM} = R \frac{\int_{E_{xm}^{\min}}^{\infty} T(E_{xm}) \left[\int_0^{E_{tm}^{\max}} (f(E) - f(E + eV)) dE_{tm} \right] dE_{xm}}{\int_0^{\infty} T(E_{xm}) \left[\int_0^{\infty} (f(E) - f(E + eV)) dE_{tm} \right] dE_{xm}}, \quad (4.2)$$

where R is a constant to be determined from the fitting. Note also that the tunneling current setpoint I_t has been dropped here for convenience of discussion.

To derive an analytical model for the subthreshold characteristics of the BEEM spectra, we first consider Equation (4.1): for eV much larger than kT , $f(E + eV)$ can be neglected compared to $f(E)$, thus the inner integral of Equation (4.1) can be written as,

$$\begin{aligned} \int_0^{E_{tm}^{\max}} [f(E) - f(E + eV)] dE_{tm} &\approx \int_0^{E_{tm}^{\max}} f(E) dE_{tm} \\ &= \int_0^{E_{tm}^{\max}} \frac{1}{1 + \exp(\frac{eV - \Phi_{BH}}{kT})} dE_{tm} \\ &= kT \ln \frac{\exp(-\frac{E_{xm} - E_F}{kT}) + 1}{\exp(-\frac{E_{tm}^{\max} + E_{xm} - E_F}{kT}) + 1}. \end{aligned} \quad (4.3)$$

Note that we are considering $eV \leq \Phi_{BH}$, so $E_{xm}^{\min} = E_F - eV + \Phi_{BH} \geq E_F$, i.e., $E_{xm} - E_F \geq 0$. In addition, the inner integral we are considering will be later integrated with respect to E_{xm} from $E_{xm}^{\min}$ to infinity (in practice, to a value larger than a few kT above E_F , e.g., 1). The minimum value for $E_{tm}^{\max}$ is zero, however, for the majority of the E_{xm} values in the interval of $[E_{xm}^{\min}, E_F + 1]$, $E_{tm}^{\max}$ is much larger than kT . For these E_{xm} values, $\exp(-\frac{E_{xm} - E_F}{kT})$ are much larger than $\exp(-\frac{E_{tm}^{\max} + E_{xm} - E_F}{kT})$. Thus, Equation (4.3) can be written as,

$$\int_0^{E_{tm}^{\max}} f(E) dE_{tm} \approx kT \ln \left[\exp(-\frac{E_{xm} - E_F}{kT}) + 1 \right]. \quad (4.4)$$

Note that these E_{xm} values satisfy the condition of $E_{xm} - E_F$ being much larger than kT , i.e., $\exp(-\frac{E_{xm} - E_F}{kT})$ being much less than 1, therefore Equation (4.4) can be further simplified as follows:

$$\int_0^{E_{tm}^{\max}} f(E) dE_{tm} \approx kT \exp(-\frac{E_{xm} - E_F}{kT}) \quad (4.5)$$

With the above approximation, Equation (4.1) can be written as,

$$I_{BEEM} = RCkT \int_{E_{xm}^{\min}}^{\infty} T(E_{xm}) \exp(-\frac{E_{xm} - E_F}{kT}) dE_{xm} . \quad (4.6)$$

Since $T(E_{xm})$ changes much more slowly compared to the exponential term (this can be easily verified by plotting the $T(E_{xm}) \sim E_{xm}$ curve), it can be approximated to be a constant, then Equation (4.6) can be written as,

$$\begin{aligned} I_{BEEM} &\approx C_1 kT \int_{E_F - eV + \Phi_{BH}}^{\infty} \left[\exp(-\frac{E_{xm} - E_F}{kT}) \right] dE_{xm} \\ &= C_1 (kT)^2 \exp(\frac{eV - \Phi_{BH}}{kT}), \end{aligned} \quad (4.7)$$

where C_1 is a constant. This suggests that the BEEM current in the subthreshold region increases exponentially with the tip bias with a subthreshold swing of

$$SS = \left(\frac{d \log_{10} I_c}{dV} \right)^{-1} = \ln 10 \frac{kT}{e} \approx 60 \text{ mV / decade at room temperature.}$$

In other words, the BEEM current in the subthreshold region decreases one order of magnitude when the tip bias (the absolute value) decreases by ~ 60 mV.

Now we consider the subthreshold characteristics of BEEM spectra described by Equation (4.2), i.e., the Bell-Kaiser model for constant tunneling current. The tunneling

current at a constant tunneling gap usually changes only about one order of magnitude or less under normal experimental spectrum conditions. Thus, the normalization by the tunneling current does not significantly change the overall exponentially increasing behavior of the BEEM current in the subthreshold region, except that it will slightly change the subthreshold swing. This will also be further verified by the simulation results later.

In order to further verify that the approximations made previously are indeed reasonable, we will consider the simulated BEEM spectra based on Equations (4.1) and (4.2). Figure 4.1 (a) is a simulated BEEM spectrum for a Au/n-Si system plotted in both linear and logarithmic-linear scale based on the constant gap BEES described by Equation (4.1). Here we used the average workfunction of the tip and the metal base $\phi = 4.7$ eV, as determined from our experimental tunneling current versus the relative tunneling gap distance spectrum [7]. For the tunneling gap distance, we used a value of $7.6 \text{ \AA}$, which was determined by fitting the experimental scanning tunneling spectroscopy on the same Au/n-Si sample with tunneling current formula in the denominator of Equation (4.2). The blue dotted line is the tip bias corresponding to the barrier height of 0.856 eV used in the simulation. The black solid line in the range of 0.356 V – 0.856 V in the logarithmic-linear scale curve is a linear fitting of $\log_{10}(I_{\text{BEEM}}) \sim V$. The fitting gave a subthreshold swing of 61.2 mV/decade , very close to 60 mV/decade as predicted from the analytical equation previously derived. This gives us confidence in the validity of the applied approximations in the previous derivation. If the fitting was limited to a much smaller range of 0.04 V below the barrier height, i.e., 0.852 – 0.856 V , the extracted subthreshold swing would be 66.9 mV/decade . This is expected, considering that the

approximations in the previous derivation are better when the tip bias is much lower than the barrier height.

Figure 4.1 (a) A simulated BEEM spectrum based on Equation (4.1) plotted in both linear and logarithmic-linear scale. The linear fit of $\log_{10}(I_{\text{BEEM}}) \sim V$ (black solid line) in the logarithmic-linear curve gave a subthreshold swing of 61.2 mV/decade. (b) A simulated BEEM spectrum based on Equation (4.2) plotted in both linear and logarithmic-linear scale. The linear fit of $\log_{10}(I_{\text{BEEM}}) \sim V$ (black solid line) in the logarithmic-linear curve gave a subthreshold swing of 64.4 mV/decade.

Figure 4.1 (b) is another simulated BEEM spectrum for a Au/n-Si system plotted in both linear and logarithmic-linear scale based on the constant current BEES described by Equation (4.2). All the parameters used were the same as those used in Figure 4.1 (a). The black solid line in the range of 0.356 V–0.856 V in the logarithmic-linear scale curve is a linear fit of $\log_{10}(I_{\text{BEEM}}) \sim V$. The fitting gave a subthreshold swing of 64.4 mV/decade. If the fitting was limited to the range of 0.04 V below the barrier height, i.e., 0.816–0.856 V, the extracted subthreshold swing would be 69.8 mV/decade. This verifies that the normalization by the tunneling current in Equation (4.2) does not change the overall exponential behavior of BEEM spectra in the subthreshold region; however, it slightly changes the subthreshold swing.

4.3 Subthreshold Characteristics-Experimental Verification

4.3.1 Experimental Details

To test the preceding simulation results, we carried out an experiment on a Au/n-Si(111) sample. The n-Si(111) substrate was first etched with a buffered hydrofluoric acid and then loaded into an ultra-high vacuum (UHV) preparation chamber with a base pressure of 3×10^{-10} mbar. A gold film of 5 nm thick and 0.5 mm in diameter was then deposited by thermal evaporation onto the silicon substrate without any other prior treatment. After the deposition, the sample was transferred *in-situ* into the RHK UHV STM chamber for the BEEM measurements. A chemically etched W tip that was cleaned by electron-bombardment in UHV was used for the measurements. All the BEEM results presented in this chapter were acquired at room temperature with a negative tip bias.

4.3.2 Verification of the Subthreshold Characteristics

In order to verify the subthreshold characteristics described by both Equations (4.1) and (4.2), we acquired BEES at both constant tunneling gap and constant tunneling current conditions.

Figure 4.2 (a) is the zoomed-in view of the subthreshold region of a typical spectrum (an average of a few spectra at the same location) taken at a constant gap condition (i.e., the feedback loop was off). The setpoint was at a tip bias, $V_{\text{Tip}} = -0.1$ V and the tunneling current, $I_t = 1$ nA. The acquisition of the BEEM spectra at constant gap at room temperature is much more difficult than acquiring at constant current condition, largely due to the drift issue. The spectra presented here were carefully checked to ensure that the forward and backward sweeps were nearly identical, i.e., the drift is minimized. Figure 4.2 (b) is the full spectrum with the fit. The fit (black solid line) was carried out using Equation (4.1) with the R factor and the barrier height as two adjusting parameters and with all other parameters [8, 9] the same as those used in the simulation in Figure 4.1. The fitting range was limited to 0.2 eV self-consistently above every barrier height being evaluated. The extracted barrier height was 0.856 eV and the corresponding tip bias is indicated by the vertical blue dashed line. The vertical green line corresponds to the value of 60 mV below the extracted barrier height. It can be seen that the fitting with the constant gap Bell-Kaiser model was reasonably good in both the region above the threshold and in the subthreshold region. The enlarged view of the subthreshold region in Figure 4.2 (a) shows that the BEEM current in the subthreshold region exponentially decreases at a rate of about 60–70 mV/decade.

Figure 4.2 (a) A zoomed-in view of the subthreshold region of an experimental BEEM spectrum (red circles, average of a few spectra) at constant gap condition ($V_{\text{Tip}} = -0.1$ V, $I_t = 1$ nA) on a 5-nm Au/n-Si(111) sample. The black solid line is the fit with Equation (4.1), with the fitting range limited to 0.2 eV self-consistently above every barrier height being evaluated. The green solid line is the extrapolation based on the fitting. (b) The full spectrum of (a). (c) A linear fit (black solid lines in both linear and logarithmic-linear scale) of the subthreshold region of experimental data (red and black circles) with $\log_{10}(I_{\text{BEEM}}) \sim V$ gave a subthreshold swing of 68.3 mV/decade. The thinner black dashed lines are the extrapolations of the model based on the fit.

To have a more direct and quantitative test of the simulation results, a linear fit of $\log_{10}(I_{\text{BEEM}}) \sim V$ was performed for the experimental data in the range of 0.816–0.856 V (40 mV below the extracted barrier height.), as shown in Figure 4.2 (c). The extracted subthreshold swing was 68.3 mV/decade, which is very close to the one extracted in Figure 4.1 (a) in the same fitting range.

Figure 4.3 (a) is a close-up view of the subthreshold region of a typical spectrum (an average of a few spectra) taken at a tunneling current condition of $I_t = 5$ nA, while Figure 4.3 (b) shows the full spectrum. The fitting (black solid line) was carried out in the same way as the spectrum in Figure 4.2 (a), except that this fitting used Equation (4.2), i.e., the Bell-Kaiser model for constant tunneling current. The extracted barrier height was 0.834 eV and the corresponding tip bias is indicated by the vertical blue dotted line. The vertical green line corresponds to the value of 60 mV below the extracted barrier height. It can be seen that the fitting with the Bell-Kaiser model works reasonably well both in the region above the threshold and in the subthreshold region, as pointed out by other researchers [2, 10]. The enlarged view of the subthreshold region shows that the BEEM current in the subthreshold region exponentially decreases at a rate of about 60–70 mV/decade.

Figure 4.3 (a) A zoom-in view of the subthreshold region of an experimental BEEM spectrum (red circles, average of a few spectra) at $I_t = 5$ nA on a 5-nm Au/n-Si(111) sample. The black solid line is the fit using Equation (4.2) and the fitting range was limited to 0.2 eV self-consistently above every barrier height being evaluated. The green solid line is the extrapolation based on the fitting. (b) The full spectrum of (a). (c) A linear fitting (black solid lines in both linear and logarithmic-linear scale) of the subthreshold region of experimental data (red and black circles) with $\log_{10}(I_{\text{BEEM}}) \sim V$ giving a subthreshold swing of 72.0 mV/decade. The thinner black dashed lines are the extrapolations of the model based on the fit.

A linear fit of $\log_{10}(I_{\text{BEEM}}) \sim V$ to the experimental data in the range of 0.795–0.835 V (40 mV below the extracted barrier height.) shown in Figure 4.3 (c), gave a subthreshold swing of 72.0 mV/decade. This is slightly larger than the one extracted from constant gap BEES in Figure 4.2 (c). This is expected, as discussed in the subthreshold characteristics section. The extracted subthreshold swing depends weakly on the fitting range and varies slightly between 60–75 mV/decade from spectrum to spectrum.

One important application of the subthreshold Equation (4.7) is to estimate the actual tip temperature. For the experiment where the sample is being directly cooled down, but the tip is not, one can estimate the actual tip temperature by fitting the subthreshold region of the BEEM spectra [5].

4.4 A New Model that Includes Subthreshold Characteristics

4.4.1 Comparison on the Goodness-of-fit in the Subthreshold Region

Before we proceed to propose a new model, we will first demonstrate that the square ($n = 2$) model fits poorly in the near-threshold region, as it does not consider the subthreshold characteristics.

Figure 4.4 (a) A zoomed-in view of the near threshold region of a representative BEEM spectrum (red circles, average of a few spectra) taken at constant gap condition ($V_{\text{Tip}} = -0.1$ V, $I_t = 1$ nA) from a 5-nm Au/n-Si(111) sample. The black, green, and blue solid lines are the fits with the $n = 2$ model, our proposed model and the Bell-Kaiser model (Equation (4.1)), respectively and the fitting range was all limited to 0.2 eV self-consistently above every barrier height being evaluated. The barrier heights extracted from these fittings are indicated by the respective vertical dashed lines. (b) The full spectrum of (a). (c) The square of residual at each tip bias for the fittings in (b). The green and blue curves are shifted up by 5 and 10 pA^2 , respectively for clarity.

Figure 4.4 (a) is a close-up view of the same BEEM spectrum as Figure 4.2 (a) (red circles, average of a few spectra) acquired at a constant gap condition, with the full spectrum shown in Figure 4.4 (b). The black and blue solid lines are the respective fits with the $n = 2$ model and the Bell-Kaiser model at the constant gap (Equation (4.1)) respectively, and the fitting range was both limited to 0.2 eV self-consistently above every barrier height being evaluated. The barrier heights extracted from the two fits are 0.822 and 0.856 eV, respectively. The barrier height from the $n = 2$ model is about 0.03–0.04 eV less than that from the Bell-Kaiser model. The close-up view shows that the Bell-Kaiser model fitted reasonably well in the near threshold region, while significant deviations from the experimental spectrum in this region can be observed for the $n = 2$ model. This is further confirmed by the square of residuals at each tip bias shown in Figure 4.4 (c), where the dotted vertical lines are the respective barrier heights extracted.

4.4.2 Proposed Model

The $n = 2$ model is widely used to extract the barrier height from BEEM spectra. However, in the previous section we have demonstrated that this model does not fit the subthreshold region and gives a barrier usually smaller than the one extracted from the full Bell-Kaiser model. Similar problems also occur for other simple models [11, 12]. In order to take the subthreshold BEEM current into account in the fit, we propose the following simple model:

$$I_{BEEM} = \begin{cases} R(kT)^2 \exp\left(\frac{eV - \Phi_{BH}}{kT}\right), & \text{for } eV \leq \Phi_{BH} \\ R(kT)^2 \left[1 + \left(\frac{eV - \Phi_{BH}}{kT}\right) + \frac{\left(\frac{eV - \Phi_{BH}}{kT}\right)^2}{2!} \right], & \text{for } eV > \Phi_{BH} \end{cases} \quad (4.8)$$

where R is a constant to be determined from fitting, I_{BEEM} is the BEEM current. For $eV \leq \Phi_{BH}$, this model uses Equation (4.7) to describe the subthreshold behavior. For $eV - \Phi_{BH}$ much larger than kT , the proposed model approaches the $n = 2$ model. For eV that is slightly larger (about a few kT or less) than Φ_{BH} , we still adopt the subthreshold equation. As an approximation, however, the exponential term are expanded into power series and only the low order terms (up to second order) are used. In this way, the proposed model approaches the $n = 2$ model when $eV - \Phi_{BH}$ is much larger than kT and it retains the continuity at $eV = \Phi_{BH}$. Compared to the $n = 2$ model, this simple model includes the subthreshold characteristics and is temperature dependent.

The green solid line in Figure 4.4 (a) is the fit with the proposed model. The inset of Figure 4.4 (a) shows that this model is almost the same as the $n = 2$ model in the high bias range. Figure 4.4 (a) also shows that the proposed model significantly improves the fitting of near threshold region compared to the $n = 2$ model. This is even clearer by looking at the square of the residuals in Figure 4.4 (c). Furthermore, the extracted barrier height from the proposed model is 0.862 eV, which is very close to the value from the Bell-Kaiser model.

For the bias a little bit above the threshold (e.g., above 0.92 V), Figure 4.4 (c) shows that there are certain deviations, even for the Bell-Kaiser model. However, most of

these deviations appeared to be common for all three models. A closer look at the original spectra often indicates that this is due to some random small jumps in the spectra, which therefore cannot be attributed to the fitting models.

4.4.3 Estimation of the Subthreshold BEEM Current

From Equation (4.8) of the proposed model, we can see that the BEEM current is equal to $I_{\Phi_{BH}} = R(kT)^2$ when $V = \Phi_{BH} / e$. When $eV - \Phi_{BH} = -\ln(10)kT \approx -60 \text{ meV}$ at room temperature, the BEEM current will be about $I_{\Phi_{BH} - \ln(10)kT} = I_{\Phi_{BH}} / 10$, and when $eV - \Phi_{BH} = 10kT \approx 0.26 \text{ eV}$, the BEEM current will be $I_{\Phi_{BH} + 10kT} \approx 60I_{\Phi_{BH}}$.

To further verify the preceding prediction, the constant gap BEES from Figure 4.2 (a) is plotted in Figure 4.5 (a) again. Figure 4.5 (b) is a zoom-in of the near threshold region. The three vertical dashed lines correspond to the extracted barrier height, 60 mV below the barrier height, and 0.26 V above the barrier height. The BEEM current at 0.26 V above the barrier is about 98 pA. From the proposed model, we would expect the BEEM current at the barrier height to be around $98/60 \approx 1.63 \text{ pA}$, while the zoomed-in spectrum in Figure 4.5 (b) shows that the actual BEEM current is about 2.1 pA. In the subthreshold region, we would expect the BEEM current to be around $1.63/10 \approx 0.16 \text{ pA}$, while Figure 4.5 (b) shows the actual BEEM current is about 0.3 pA. The actual BEEM currents for both of these predictions are within 50% of error [13].

Figure 4.5 (a) A representative constant gap ($V_{\text{Tip}} = -0.1$ V, $I_t = 1$ nA) BEES together with the fitting using the proposed model. (b) An enlarged view of Figure 4.5(a). According to the proposed model the BEEM current at $10kT$ (k is Boltzmann constant, and T is the temperature) above the barrier is about 60 times of the BEEM current at the barrier height, while the BEEM current at $\ln(10)kT$ below the barrier is about 1/10 times of the BEEM current at the barrier height.

Given that the proposed model does not fit the subthreshold region as well as the Bell-Kaiser model does, the prediction with the proposed model will not be so accurate. However, as an analytical model and as an approximation, it provides a reasonably good estimation on the subthreshold BEEM current by looking at the BEEM current at 0.26 eV above the barrier for the spectra acquired at room temperature. By comparing the estimated BEEM current and the noise level in the spectrum, one can easily determine if this subthreshold BEEM current can be observed in the experiment. Note that the value of $10kT$ is chosen such that it is not far from the barrier so that the fitting does not deviate much from the experimental data at that bias, and it is also not too close to the barrier so that the BEEM current is reasonably high.

Finally, we can see from Equation (4.8) that the ratios between the BEEM currents at the three biases do not depend on the material (either metal or semiconductor) used. However, the three tip biases will shift accordingly if a diode with a different barrier height is used.

4.4.4 Application to Constant Current BEES

The BEEM spectra shown above were mostly taken at constant gap. However, in practice, BEEM spectroscopy is usually performed in constant current condition due to the difficulty in acquiring the constant gap BEES. In this section, we will compare the fittings of BEES acquired at a constant current condition with the three models.

Figure 4.6 (a) A zoomed-in view of the near threshold region of a representative BEEM spectrum (red circles, average of a few spectra) taken at $I_t = 5$ nA from a 5-nm Au/n-Si(111) sample. The black, green, and blue solid lines are the fittings with $n = 2$, the proposed model and the Bell-Kaiser model (Equation (4.2)), respectively and the fitting range was all was limited to 0.2 eV self-consistently above every barrier height being evaluated. The barrier heights extracted from these fittings are indicated by the respective vertical dashed lines. (b) The full spectrum of (a). (c) The square of residual at each tip bias for the fitting in Figure 4.6 (a). The green and blue curves are shifted up by 0.1 and 0.2 pA^2 , respectively for clarity.

Figure 4.6 (a) is a zoomed-in view of a typical BEEM spectrum (red circles, an average of a few spectra) acquired at $I_t = 5$ nA, with the full spectrum shown in Figure 4.6 (b). The black, green, and blue solid lines are the fittings with the $n = 2$ model, the proposed model and the Bell-Kaiser model (Equation (4.2)), respectively and the fitting range was limited to 0.2 eV self-consistently above every barrier height being evaluated. The barrier heights extracted from the three fittings are 0.801, 0.831 and 0.835 eV, respectively. The barrier height from the $n = 2$ model is again about 0.03–0.04 eV less than that from the Bell-Kaiser model. Figure 4.6 (b) illustrates that the Bell-Kaiser model can predict closer to the experimental data in the higher bias range. This is because it has considered the tunneling gap change during the constant current spectrum. The zoomed-in view shows that the Bell-Kaiser model fits very well in the near-threshold region, while significant deviations from experimental spectrum in this region can be observed for the $n = 2$ model. The proposed model does not fit as well as the Bell-Kaiser model does; however, it has significant improvement in the near-threshold region compared to the $n = 2$ model. This is further confirmed by the square of residual at each tip bias shown in Figure 4.6 (c), where the dotted vertical lines are the extracted barrier heights. The fitting range can be higher than 0.2 eV, however, we note that a zoomed-in view of the near-threshold region often shows that the deviation becomes larger when the fitting range increases.

4.5 Comparison of BEES Fitting with Various Models

4.5.1 Introduction

As discussed in Chapter 3, there have been many simplified BEEM models for BEES fitting: $n=5/2$, $n = 2$ and “ $n = 2$ divided by eV ”, i.e.,

$$I_{BEEM} = \begin{cases} 0, & \text{for } eV \leq \Phi_{BH} \\ R(eV - \Phi_{BH})^n, & n = 5/2 \text{ or } 2, \text{ for } eV > \Phi_{BH} \end{cases} \quad (4.9)$$

$$I_{BEEM} = \begin{cases} 0, & \text{for } eV \leq \Phi_{BH} \\ R \frac{(eV - \Phi_{BH})^2}{eV}, & \text{for } eV > \Phi_{BH} \end{cases} \quad (4.10)$$

In the previous section we also proposed a new simplified model, which considers the subthreshold characteristics. In this section, we will give a comprehensive comparison on the goodness-of-fit for all these models and also on the extracted barrier heights.

4.5.2 Comparison of Goodness-of-fit

Figure 4.7 (a) is a zoomed-in view of a typical BEEM spectrum (red circles, an average of a few spectra) acquired at $I_t = 5$ nA, with the full spectrum shown in Figure 4.7 (b). The green, magenta, cyan and blue solid lines are the fittings with the $n = 5/2$, $n = 2$, the “ $n = 2$ divided by eV ”, the proposed and the Bell-Kaiser models (Equation (4.2)), respectively and the fitting range was all limited to 0.2 eV self-consistently above every barrier height being evaluated. The barrier heights extracted from the five models are 0.771, 0.801, 0.809, 0.831 and 0.835 eV, respectively. We will discuss more on the extracted barrier difference in the next section.

Figure 4.7 (a) A zoomed-in view of the near threshold region of a representative BEEM spectrum (red circles, average of a few spectra) taken at $I_t = 5$ nA from a 5-nm Au/n-Si(111) sample. The solid lines are the fittings with various models. The fitting range was all was limited to 0.2 eV self-consistently above every barrier height being evaluated. The barrier heights extracted from these fittings are indicated by the respective vertical dashed lines. (b) The full spectrum of (a). (c) The square of residual at each tip bias for the fitting in (b). The green, magenta, cyan and blue curves are shifted up by 0.15, 0.30, 0.45 and 0.60 pA^2 , respectively, for clarity.

Figure 4.7 (b) illustrates that the “ $n = 2$ divided by eV” model and the Bell-Kaiser model can predict closer to the experimental data in the higher bias range. This is because they have considered the tunneling gap change during the constant current spectrum. The zoomed-in view shows that the Bell-Kaiser model fits very well in the near-threshold region, while significant deviations from experimental spectrum in this region can be observed for the $n = 5/2$, the $n = 2$, and the “ $n = 2$ divided by eV” models. The proposed model does not fit as well as the Bell-Kaiser model does; however, it has significant improvement in the near-threshold region compared to all other simplified models. This is further confirmed by the square of residual at each tip bias shown in Figure 4.7 (c), where the dotted vertical lines are the extracted barrier heights. The fitting range can be higher than 0.2 eV; however, we note that a zoomed-in view of the near-threshold region often shows that the deviation becomes larger when the fitting range increases. This will be illustrated and discussed later in the next section.

4.5.3 Comparison on Extracted Barrier Height

In this section we will have a full view of the differences of barrier height extracted from different models. Figure 4.8 shows the extracted barrier height from different models with different fitting ranges of 0.2, 0.3, and 0.4 eV. A few findings can be made from this figure: (a) for different models with the same fitting range, there is a general trend of increasing barrier height. The extracted barrier height from the $n = 5/2$ model is systematically 0.03–0.05 eV less than that from the $n = 2$ model, which is well documented in the literature [15, 16]. The barrier height from the $n = 2$ model is similar to that from the “ $n = 2$ divided by eV” model. It is slightly less, especially at higher

fitting range. The barrier height from the $n = 2$ model is consistently 0.03–0.04 eV less than that from the Bell-Kaiser model (Equation (4.2)). The barrier height from the proposed model are in good agreement with the one from the Bell-Kaiser (BK) model, but starts to deviate more at higher fitting ranges. (b) For different fitting ranges with the same model, there is also a trend of decreasing barrier height when increasing the fitting range.

Figure 4.8 Extracted barrier heights from various fitting models with different fitting ranges: 0.2 (red circle), 0.3 (black triangles) and 0.4 eV (green stars).

Figure 4.9 Comparison of fittings with different fitting ranges using the constant-current Bell-Kaiser model. (a), (c), and (e) are with fitting range of 0.2 eV. (b), (d), and (f) are with fitting range of 0.4 eV. (a) and (b) show the full spectra, while (c) and (d) are the zoom-in views of (a) and (b), respectively. (e) and (f) are the square of residuals. The blue vertical lines correspond to the extracted barrier height.

As shown in Figure 4.8, the fitting ranges affect the extracted barrier height. Now we will have a detailed comparison on the fittings with different fitting ranges. Figures 4.9 (a) and (b) show the same experimental spectrum, together with fittings with the Bell-Kaiser model (constant current equation) at fitting ranges of 0.2 eV and 0.4 eV. The zoomed-in views in Figures 4.9 (c) and (d) show that the fitting is much better for the fitting range of 0.2 eV than that of 0.4 eV. This is also supported by the square of residuals in Figures 4.9 (e) and (f). This comparison suggests that a relatively small fitting range should be generally used when fitting with the BEEM spectra. However, we would also like to point out that this may not be true for spectra with very small signal-to-noise ratios. In fact, we found that for spectra with very small signal-to-noise ratios (especially for oxide based samples), a larger fitting range is usually preferred. This intuitively makes sense, because the signal-to-noise ratio could be even less 1 if the fitting range is limited to say 0.2 eV. With a relatively larger fitting range, the signal-to-noise ratio will be high enough and overall square law trend still maintains.

4.6 Error Estimation

As shown in the preceding section, the barrier height extracted from the same fitting model may still be different using different fitting ranges. In practice, it is not clear what the “best” fitting range is. Thus, it is necessary to estimate the error of the extracted barrier height. In this section, we will discuss the error estimation of the barrier height extracted from one single spectrum.

Figure 4.10 is the coefficients of determination calculated when the constant-current Bell-Kaiser model fit the spectrum in Figure 4.7 (b) the best for each testing

barrier height. The ultimate “best” barrier height corresponds to the one that gave the largest coefficient of determination, i.e., 0.835 eV. One way to estimate the error or uncertainty from the fitting is to specify a minimum coefficient of determination. For instance, if the minimum acceptable coefficient of determination is set to 0.998, the acceptable barrier height could range from 0.820 to 0.850 eV. In this case, the extracted barrier height would be 0.835 ± 0.015 eV. However, the setting of the minimum acceptable coefficient of determination differs from one spectrum to another and is thus a little arbitrary.

Figure 4.10 Coefficient of determination at different barrier height values.

Another method to estimate the error of the barrier height from the fitting is to fit a spectrum using the same model with a few different fitting ranges. For instance, fitting the spectrum in Figure 4.7 (b) using the constant-current Bell-Kaiser model with the

fitting range of 0.2, 0.3, and 0.4 eV gave the barrier height of 0.835, 0.830, and 0.824 eV, respectively. This means that the barrier height could vary from 0.824 to 0.835 eV.

For most spectra from the metal/semiconductor devices, the error of the extracted barrier height is estimated to be not larger than ± 0.02 eV. For spectra from the metal/dielectric/semiconductor devices, the error of the extracted barrier height is typically around ± 0.1 eV. This estimated uncertainty is close to what Cai *et al.* estimated [17].

4.7 Conclusion

A simple analytical equation describing the subthreshold behavior is derived from the Bell-Kaiser model, revealing that the BEEM current exponentially decreases with a rate of ~ 60 mV/decade at room temperature. This is further supported by both the constant-gap spectra and constant-current spectra from a Au/n-Si(111) sample. While the complete Bell-Kaiser model fits the experimental data nicely, great deviations could occur when fitting with simplified square model. We therefore propose a more accurate, yet still simple, analytical model for the BEEM spectra fitting. We showed that this model significantly improves the fitting in the near-threshold region and gives a barrier height value close to the one extracted from the complete Bell-Kaiser model. More importantly, it provides a quick method to estimate of the subthreshold BEEM current based on the BEEM current above the barrier: the BEEM current at the barrier height is about 1/60 times of that at $10kT$ above the barrier, while the BEEM current at $\ln(10)kT$ below the barrier is about 1/10 times that at the barrier height. Finally, we made a comprehensive comparison of the extracted barrier heights for a few different models at

different fitting ranges. Systematic differences in the extracted barrier heights were found for models of $n = 5/2$, $n = 2$ and the Bell-Kaiser models.

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Chapter 5 Comparison of BEEM Studies in the High Bias Range for Au/Dielectric Samples with *In-situ* and *Ex-situ* Deposited Au

5.1 Introduction

As mentioned in Chapter 2, most BEEM measurements of metal/oxide/semiconductor devices reported in the literature were performed with *in-situ* metal deposition. There are only a few exceptions. Zheng *et al.* [1, 2] reported BEEM studies on Au/HfO₂/SiO₂/Si under a high-vacuum condition and with *ex-situ* Au deposition. However, they pointed out that no BEEM signal was observed at most locations of the sample. This is not the case for BEEM studies under the UHV condition with *in-situ* metal deposition. Lee [3] from Pelz's group at the Ohio State University also documented studies on Pd/SiO₂/Si samples with *ex-situ* Pd deposition in a Ph.D. thesis. However, Lee did not observe the expected barrier height of ~4 eV for the Pd/SiO₂ interface; instead, they observed a barrier height much higher than ~4 eV. They concluded that the lift-off processing altered the metal/oxide interface properties or contaminated the interface. Kaczer *et al.* [4] also reported one BEEM measurement with *ex-situ* deposited Pd and obtained reasonably good results. However, after transferring their sample into the UHV system, they degassed the sample at 350–400 °C for 10 min, which might have produced a cleaner Pd surface.

Before setting up the UHV STM/BEEM system with *in-situ* metal deposition, we spent about one and a half years using a BEEM system with a high vacuum of 6×10^{-8}

mbar and *ex-situ* metal deposition. After using this high-vacuum system on the SiO₂ samples (and various other oxide samples) for some time, we realized that we could not even obtain the BEEM spectra showing a correct barrier height for Au/SiO₂. We tried to resolve this problem, but without proper data from a working system that could be used for careful comparison, it was never clear what the main cause of the problem was and how it could be avoided. Nevertheless, by studying the literature thoroughly, we found critical points that provided a better understanding of the issue. This also motivated us to set up the UHV system. Firstly, we could carry out BEEM measurements of low-barrier devices (e.g., Au/n-Si) regularly and consistently, here we limited the tip bias to the low bias range, e.g., -0.3 to -1.5 V). There was only a problem when we carried out measurements of devices with a high electron barrier height. Secondly, the two groups (Pelz's group at the Ohio State University and Ludeke's group at IBM) who routinely studied metal/oxide samples always performed the BEEM measurement under a UHV condition and mostly with *in-situ* metal deposition. Thirdly, BEEM measurements of metal/n-type semiconductor devices showed that the BEEM current increased all the way up to a high tip bias of -8 V or even further [5–8]. These measurements were all carried out under the UHV condition and the devices were prepared with *in-situ* metal deposition in a UHV (although we note that Refs 5, 6, and 8 do not mention this explicitly). However, when we measured the Au/n-Si device with the high-vacuum BEEM system and *ex-situ* Au deposition, we did not observe the similar behavior in the high tip bias range. We almost always found that the BEEM current increased up to about -3 V and then started to decrease quickly. This further hinted that there was something very different for the BEEM measurements in the high bias range for devices prepared with

ex-situ and *in-situ* metal deposition. To be exact, after we set up the UHV STM/BEEM system, we successfully carried out the BEEM measurements up to a high tip bias for the Au/n-Si device with *in-situ* Au deposition and found that the BEEM current increased with the tip bias up to -10 V. This is similar to what others found on metal/n-type semiconductor devices with *in-situ* metal deposition. In addition, we realized that the change in the tip height during our experiment over a wide bias range (e.g., -0.3 to -10 eV) was always significantly larger than what was reported by Kaczer *et al.* [9]. Lastly, we occasionally obtained spectra showing a correct barrier for Au/SiO₂ samples; however, we found that more often than not, the area being probed was severely modified. In addition, this modification usually occurred when the BEEM spectrum was ramped in one direction from high to low (e.g., -6.5 to -0.3 V) at a setpoint of a low tip bias but high tunneling current (e.g., -0.3 V, 5 nA). Once the tip bias reached -0.3 V, it quickly returned to -6.5 V and the recording of another spectrum commenced. The modification seldom occurred if the tip bias ramped back to -6.5 V slowly. Of course, if the tunneling current was very high but the feedback parameters were not properly adjusted, the modification could easily occur. This, together with various other reasons, motivated us to set up the UHV system with *in-situ* metal deposition.

In general, we see from the literature that *in-situ* metal deposition provides a superior condition for the BEEM measurement of high-barrier devices. We wish to point out that there is no difficulty at all in the BEEM measurement of low-barrier devices (e.g., Au/n-Si) with *ex-situ* metal deposition [10]. In fact, BEEM studies on low-barrier devices (e.g., Au/n-Si or Au/n-GaAs and other related devices) with inert metal bases and PtIr tips have been performed regularly with BEEM systems working in air [10, 11]. We

therefore ask two questions. What causes this difference in the BEEM measurement between high biases and low biases? Which plays a more critical role, the interface or surface?

In this chapter, we address these questions by carrying out a controlled comparison. We first compare the BEES results on the Au/5 nm SiO₂/n-Si sample with *in-situ* and *ex-situ* deposited Au. We then investigate the effect of metal/dielectric interface and metal surface to address what causes the BEES differences.

5.2 Experimental Details

Three sets of samples were used in this study. All BEEM spectra presented in this and the remaining chapters were acquired in constant tunneling current mode.

The first sample measured was 5-nm SiO₂ on phosphorous-doped (doping concentration: $\sim 1 \times 10^{15} \text{ cm}^{-3}$) n-Si(100) substrate prepared with thermal oxidation in a furnace. The backside was heavily doped and annealed to make good ohmic contact. The sample was cut into a 6 mm $\times$ 3 mm piece and then cleaned with acetone and IPA. After the sample was loaded into the UHV preparation chamber with a base pressure of 3×10^{-10} mbar, it was degassed at 350 °C for ~ 10 min. The pressure during degassing was in the middle 10^{-9} mbar range. After cooling to room temperature, the sample was further cooled to around -151 °C with liquid nitrogen and Au dots having thickness of ~ 5 nm and diameter of 0.5 mm were thermally evaporated onto the sample. After warming to room temperature, the sample was transferred to the adjacent UHV STM chamber for the *in-situ* BEEM measurement at room temperature.

After the *in-situ* BEEM measurement, the same sample was taken out and left in air ($\sim 25^\circ\text{C}$) for about 4 hours. It was then transferred back to the UHV STM chamber for further BEEM measurements. This experiment is referred to as the *ex-situ* BEEM measurement here.

Another sample was prepared in a similar way to the sample in the *in-situ* experiment. However, this sample was not degassed before Au deposition. The Au was deposited at room temperature. This sample was not taken out of the UHV after Au deposition. We note that deposition of Au with the sample being cooled by liquid nitrogen does not produce any obvious difference in the BEEM measurements. The only difference is that the Au morphology slightly differs. This experiment is referred to as *in-situ* BEEM measurement without degassing. With this experiment, we studied the effect of metal/dielectric interface contamination.

5.3 Comparison of BEES

Figures 5.1 (a) and (c) show typical spectra obtained in the *in-situ* and *ex-situ* BEEM experiments, respectively. Spectra (b) and (d) are the zoom-in views of spectra (a) and (c), respectively. Each spectrum is an average of four to six spectra acquired at the same location. The spectrum in Figure 5.1 (a) was fitted with the constant-current Bell-Kaiser model and the fitting range was limited to 0.5 V self-consistently above each barrier being evaluated. The fitting gave a barrier height of ~ 4.1 eV, which is consistent with the results of BEEM studies on an Au/SiO₂ sample reported by others [12].

Figure 5.1 (a) A typical BEEM spectrum (red dots) from the Au (*in-situ*)/5-nm SiO₂/n-Si with $I_t = 8$ nA. The fitting (black solid line) was carried out with the constant-current Bell-Kaiser model with a fitting range of 0.5 V self-consistently above each barrier being evaluated. The fitting gave a barrier height of 4.1 eV as indicated by the vertical blue line. (b) The zoom-in view of (a). (c) A typical BEEM spectrum from the the Au (*ex-situ*)/5 nm SiO₂/n-Si with $I_t = 5$ nA. The barrier height appeared to be much higher than 4.1 eV. The fitting (black solid line) shown was using the proposed BEEM model in Chapter 4 and gave a barrier height of ~6.5 eV. (d) The zoom-in view of (c).

In the *ex-situ* BEEM measurement (Figure 5.1 (c)), the spectrum appeared to be quite different. The threshold appeared to be around 6 eV, which is much higher than 4.1 eV. The barrier is too high to fit with the Bell-Kaiser model. Thus, we used our proposed simplified model for the fitting instead. The fitting range was chosen to be 1.5 eV self-consistently above the barrier height being evaluated owing to the small signal-to-noise ratio. The fitting gave a barrier height of ~6.0 eV, which is much higher than that obtained from the *in-situ* BEEM measurement. The magnified view of the spectrum (Figure 5.1 (d)) shows that the noise level in the tip bias range of -3 to -6 V was significantly higher than that below -3 V. However, the noise level for the *in-situ* measurement was almost constant below the threshold. As discussed later, this is likely related to the relatively large change in tip height during the *ex-situ* measurement.

STM and corresponding BEEM images ($V_{\text{Tip}} = -6.5$ V, $I_t = 1$ nA) obtained from the *in-situ* BEEM measurements are shown in Figures 5.2 (a) and (b), respectively. The Au was deposited at low temperature (about -151 °C), and the surface roughness of the Au was thus less than that when Au was deposited at room temperature. In addition, there are valleys where the Au appeared to be much lower than in the surrounding areas. The BEEM image is non-uniform and has no clear correlation with the STM topography. This is similar to what was found for Pt/SiO₂ samples by Cai *et al.* [13]. The variations in the BEEM current could be due to variations in metal thickness, variations in SiO₂ thickness, and Au/SiO₂ interface inhomogeneity. Both the STM and BEEM images can be reproduced all over the sample and also from sample to sample. Additionally, the STM and BEEM images do not obviously change even after scanning of the same area for a number of hours.

Figures 5.2 (c) and (d) show the STM and corresponding BEEM images ($V_{\text{Tip}} = -6.5$ V, $I_t = 1$ nA) obtained from *ex-situ* BEEM measurements respectively. The STM topography is not as clear and it appears to differ from that acquired for the *in-situ* prepared sample. The BEEM image is also very different from the one obtained for the *in-situ* prepared sample. Overall, the BEEM currents are strongly suppressed. Figures 5.2 (c) and (d) show one of the best images obtained for the *ex-situ* prepared sample. In general, it is much more difficult to scan the *ex-situ* prepared sample at a high bias, since the scanning is more unstable and the STM images are usually fuzzy. The BEEM images usually show extremely small BEEM current and cannot be reproduced when scanning the same area again.

In contrast, scanning on the *ex-situ* prepared sample at a low bias is stable and gives clear images. Figures 5.2 (e) and (f) are examples of STM and BEEM images acquired at $V_{\text{Tip}} = -0.1$ V and $I_t = 0.5$ nA. The BEEM image is just background noise, since the tip bias is much lower than the barrier height. In addition, the STM image is similar to Figure 5.2 (a), which was obtained at high bias for the sample before air exposure (*in-situ* prepared sample). This demonstrates that exposure to air does not affect the Au morphology. It also suggests that scanning the *ex-situ* prepared sample at high bias is somehow affected by the exposure to air.

(a)

(b)

(c)

(d)

(continued on next page)

(e)

(f)

Figure 5.2 (a) and (b) are STM (color scale from dark to bright: 0–4 nm) and BEEM (color scale from dark to bright: 0–13 pA) images acquired at $V_{\text{Tip}} = -6.5$ V, $I_t = 1$ nA from the *in-situ* BEEM measurement. (c) and (d) are STM (color scale: 0–4.8 nm) and BEEM (color scale: 0–5 pA) images taken at $V_{\text{Tip}} = -6.5$ V, $I_t = 1$ nA from the *ex-situ* BEEM measurement. (e) and (f) are STM (color scale: 0–5.5 nm) and BEEM (color scale: –0.7 to 0.7 pA) images taken at $V_{\text{Tip}} = -0.1$ V, $I_t = 0.5$ nA from the *ex-situ* BEEM measurement.

5.4 Effects of the Interface and Surface

The previous section showed that exposing the *in-situ* prepared sample to air for ~4 hours affected the BEEM measurement in the high bias range, not only in terms of BEEM spectroscopy but also in terms of imaging. By exposing the sample to air, there may be contaminations such as water vapor and/or organic materials on the Au surface. On the other hand, the exposure to air may also slightly contaminate the metal/dielectric

interface. The obvious question is: which plays the more significant role? We address the roles of interface contamination and metal surface contamination in this section.

5.4.1 Au/Dielectric Interface

This section addresses the role of interface contamination. When performing BEEM measurement on metal/oxide samples, pioneering groups [14, 15] usually degassed the samples in UHV to remove water vapor and organic contamination from the oxide surface before depositing the thin metal film. Cai *et al.*[16] also mentioned that degassing was necessary to observe BEEM current for the Pt/Sc₂O₃ sample. Here we present the BEEM results for the sample without degassing before Au deposition.

Figure 5.3 A representative BEEM spectrum (red circles) taken at $I_t = 5$ nA. The fitting (black solid line) was performed with constant-current Bell-Kaiser model and the fitting range was 0.5 eV self-consistently above every barrier height being evaluated. Extracted Barrier is 4.1 eV, which is indicated by the vertical blue line.

Figure 5.3 is an average (red circles) of four BEEM spectra obtained at the same location and $I_t = 5$ nA. The fitting (black solid line) with the constant-current Bell-Kaiser model gave a barrier height of 4.1 eV, where the fitting range was limited to 0.5 eV self-consistently above each barrier height being evaluated. The extracted barrier height is the same as that (Figure 5.1 (a)) for the *in-situ* prepared sample with degassing.

Examples of typical STM and BEEM images acquired at $V_{\text{Tip}} = -6.5$ V and $I_t = 5$ nA are shown in Figures 5.4 (a) and (b), respectively. The STM topography differs from that (Figure 5.2 (a)) obtained for the *in-situ* prepared sample, as the Au was evaporated at room temperature in this case, while it was evaporated at low temperature (about -151 °C) for the sample in Figure 5.2 (a). The BEEM image, however, is very similar to Figure 5.2 (b), with clear contrast and variation of ~ 13 pA in the image.

To obtain more information from the BEEM image, we plot the BEEM image histograms of Figures 5.2 (b) and 5.4 (b) together in Figure 5.4 (c). The two histograms show similar behavior: a small portion of the locations have very high BEEM currents from ~ 2 pA to almost 13 pA, which correspond to the very bright areas in the BEEM images. The majority of locations have very small BEEM currents of about 0.4–0.5 pA, which correspond to the darker areas in the BEEM images.

(a)

(b)

(c)

Figure 5.4 Typical (a) STM (color scale from dark to bright: 3 nm) and (b) BEEM (color scale from dark to bright: 0–13 pA) images acquired at $V_{\text{Tip}} = -6.5$ V, $I_t = 1$ nA from the *in-situ* prepared sample but without degassing before Au deposition. (c) The histograms of the BEEM images of Figure 5.2 (b) and Figure 5.4 (b).

In summary, we see that degassing did not have any significant effect on either spectroscopy or imaging in the high bias range. This suggests that the possible contamination of the metal/dielectric interface during air exposure does not have any significant effect on the BEEM measurements in the *ex-situ* experiment. Hence, it is likely that Au surface contamination plays the more important role.

5.4.2 Au Surface

Air exposure contaminates the Au surface and possibly the Au/SiO₂ interface. However, as demonstrated in the previous section, the interface contamination does not have any significant effect in the high bias range in terms of either spectroscopy or imaging. In this section, we closely examine the difference in the Au surface during spectroscopy between the *in-situ* and *ex-situ* experiments. The results for the *in-situ* experiment are not those for the Au/SiO₂/n-Si sample, but from those for an Au/HfO₂/n-GaAs sample. However, the Au thickness and deposition process are the same as for the *in-situ* SiO₂ sample. Since we are only looking at the changes of the Au surface between the *in-situ* and *ex-situ* experiments, the underlying oxide does not affect the Au surface changes during spectroscopy.

To thoroughly examine the difference in spectroscopy between *in-situ* and *ex-situ* deposited Au surfaces, we took a few BEEM spectra over a wide range of tip bias at the same location continuously. (Note that the tip bias changed at the same rate for the forward and backward spectra in this study.) The corresponding changes in tip height were observed and recorded simultaneously during the BEEM spectroscopy. The STM

and BEEM images of the same area were acquired before and after the BEEM spectra for comparison.

In the *in-situ* experiment, spectra were obtained by ramping from -9.9 V to -0.3 V and then ramping back at the same rate to -9.9 V (setpoint: $V_{\text{Tip}} = -9.9$ V, $I_t = 4$ nA). Figures 5.5 (a) and (b) are STM images obtained at $V_{\text{Tip}} = -6.5$ V, and $I_t = 1$ nA before and after taking 20 BEEM spectra at the location indicated by the red arrow. All spectra in the forward direction are shown in Figure 5.5 (c). We see that Figures 5.5 (a) and (b) are identical, except for a bump in Figure 5.5 (b) at the location where the spectra were acquired. The bump was about 10–15 nm in size and 2–3 nm in height. It appeared to be material transfer from the tip to the metal thin film. The mechanism of material transfer between the tip and sample has been discussed by others [17, 18] and is beyond the scope of this study. A close look at the corresponding change in tip height shows that the overall tip height increases with the number of spectra recorded. The total increase after all spectra were recorded was about 3–4 nm, which is consistent with the changes in the STM images. Furthermore, the total change in tip height was much more for the first few spectra but less for the later spectra. Additionally, we notice that the change in the tip height for a single spectrum was usually no more than 1 nm. It will soon be shown that the change in tip height is much larger for the *ex-situ* prepared sample.

Figure 5.5 STM images acquired at $V_{\text{Tip}} = -6.5$ V, $I_t = 1$ nA (a) before (color scale: 5.5 nm) and (b) after (color scale: 5.5 nm) 20 BEEM spectra taken at the location as indicated by the red arrow. (c) The BEEM spectra taken at the location as indicated by the red arrow in Figure 5.5 (a). The spectra were acquired by ramping the tip bias from -9.9 V to -0.3 V and then ramping back at the same rate (setpoint: $V_{\text{Tip}} = -9.9$ V, $I_t = 4$ nA). Only spectra in forward direction are shown for clarity.

Theoretically and ideally, the tip heights should all overlap, which is found to be true if the spectra were only acquired in the low tip bias range, e.g., -0.1 to -1.5 V. In addition, the degree of Au surface modification depends on the tip bias range and the tunneling current: the higher either factor is, the more severe the modification is. In general, the BEEM current decreases as the number of spectra increases, especially when the modification is more obvious. For this reason, we usually limited the tip bias to about -6.5 or -5.5 V during normal spectroscopy, so that the change in BEEM current was not significant.

We now have a look at what happens for the *ex-situ* prepared sample. The investigation was carried out for the same 5-nm Au/5-nm SiO₂/n-Si sample after it was exposed to air for ~ 4 hours. The same procedure as previously described was carried out. However, since the imaging quality was much better at low bias, the images were acquired at $V_{\text{Tip}} = -0.1$ V, $I_t = 0.5$ nA. The spectra were obtained by ramping from -0.1 V to -10 V and then ramping back at the same rate to -0.1 V (setpoint: $V_{\text{Tip}} = -0.1$ V, $I_t = 5$ nA). The STM images before and after 10 spectra are shown in Figures 5.6 (a) and (b), respectively. A large bump formed at the location where the spectra were acquired, as indicated by the red arrow. The bump was about 40–50 nm in size and ~ 10 nm in height. The total height of the bump is consistent with the changes in the tip height during the spectra, which are shown in Figure 5.6 (c).

Figure 5.6 STM images acquired at $V_{\text{Tip}} = -0.1$ V, $I_t = 0.5$ nA (a) before (color scale: 12 nm) and (b) after (color scale: 12 nm) 10 BEEM spectra taken at the location as indicated by the red arrow. (c) The BEEM spectra taken at the location as indicated by the red arrow in Figure 5.6 (a). The spectra were acquired by ramping the tip bias from -0.1 V to -10 V and then ramping back at the same rate (setpoint: $V_{\text{Tip}} = -0.1$ V, $I_t = 5$ nA). Spectra of both forward and backward directions are shown. The bump at the center of Figure (a) was also created in the same way before this experiment.

Compared with the results for the *in-situ* prepared sample, there are a couple of significant differences. The bump is much bigger in both size and height. The change in tip height for each single spectrum was generally about 3–4 nm, which is much larger than that for the *in-situ* prepared sample. The tunneling between the tip and Au film was in a UHV environment in both cases, and the only change was that the *ex-situ* prepared sample was exposed to air for ~4 hours. Therefore, we conclude that the Au surface contamination due to exposure to air is responsible for the difference in bump height. This contamination greatly accelerated material transfer between the tip and Au film. This might also be the reason why the noise level increased significantly, as the material transfer started earlier and was more violent. On the other hand, the metal base thickness increased far more rapidly for the *ex-situ* prepared sample. As a result, the injected electrons had to transport through a much thicker metal film. All these factors led to the BEEM measurement of the “contaminated” sample being much more difficult and very unreliable.

Finally, we point out that Quattropani *et al.* [12] mentioned that short exposure to air did not affect the results. However, our finding suggests the opposite. One possible reason for the disagreement is that we purposely exposed the sample to air for ~4 hours, which might have been much longer than the time that Quattropani *et al.* exposed their sample.

5.5 Conclusion

We found that there can be significant difference between BEEM measurements in the high bias range for the *in-situ* and *ex-situ* prepared samples. While the BEEM

measurement in the UHV for metal/dielectric/semiconductor samples with *in-situ* metal deposition was reliable and consistent, the corresponding measurement for the *ex-situ* prepared sample did not give a proper barrier height. We further showed that Au/SiO₂ interface contamination does not significantly affect the BEEM measurement. Instead, we found a great difference in terms of the change in tip height during BEEM spectroscopy. The change in tip height during spectroscopy in the range of –0.3 to –10 V for the *ex-situ* deposited Au was several times greater than that from the *in-situ* deposited Au. All these differences were shown to be due to contamination of the Au surface during exposure to air.

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Chapter 6 Electronic Properties of Ultrathin Dielectrics

Determined from Ballistic Electron Emission Spectroscopy

6.1 Introduction

With the continued scaling of metal-oxide-semiconductor field effect transistors, SiO₂ or SiON (silicon oxy-nitride) is now reaching its thickness limit as an effective gate dielectric mainly owing to gate leakage issue [1]. Alternative approaches, such as metal gate/high- κ dielectrics, have already been successfully demonstrated [1]. It is expected that high- κ dielectrics will also reach a scaling limit like SiO₂ after a few technology nodes. Therefore, it is crucial to clarify this limitation by studying the intrinsic properties of these ultrathin dielectrics. In this chapter, we investigate the electronic properties of ultrathin dielectrics, including native silicon oxide (grown for different durations) and high- κ dielectrics of CeO₂ and La₂O₃.

6.1.1 Ultrathin (1 nm or less) Dielectrics

To date, there have been few studies on ultrathin SiO₂ and other dielectrics thinner than 1 nm. Tang *et al.* [2] and Muller *et al.* [3] evaluated the minimum thickness for an ideal SiO₂ gate oxide to be around 0.7 nm. A few first-principles calculations indicated that the band edges at the SiO₂/Si interface change gradually instead of abruptly and the bandgap of SiO₂ decreases on the SiO₂ side near the interface [4–7]. In BEEM studies, Ludeke *et al.* [8] and Quattropani *et al.* [9] observed a much smaller threshold than the expected metal/SiO₂ barrier in some areas of very thin SiO₂ samples, but not for

thick samples. LaBella *et al.* [10, 11] and Sumiya *et al.* [12] both found rather low electron barrier heights for ultrathin calcium fluoride (CaF_2) samples compared with thicker CaF_2 films in the same structures. However, it is still unclear what electronic properties the dielectric has when its thickness lies in the crossover regime of losing its bulk-like properties.

6.1.2 Native Oxide on Si Grown in Air

Native oxide grown in air at room temperature on hydrofluoric acid (HF) etched Si has been studied by several groups [13-16] using a variety of techniques, such as ellipsometry, X-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy, and transmission electron microscopy (TEM). Here we briefly review the major findings so far.

Morita *et al.* [13–15] reported a layer-by-layer growth of native oxide on Si in air at room temperature. They showed that native oxide grown in this way had thickness of about 5.6 and 6.7 Å after 4 days and 1 week, respectively. Grundner *et al.* [16] investigated the native oxide grown in air spanning from a few hours to one year. They found that the native oxide was only about one monolayer after 3 hours and about 9 Å after 2 weeks, and reached a limiting thickness of ~1.4 nm after 1 year. TEM studies by Carim *et al.* [17] showed, however, that the native oxide of the diluted-HF etched Si after 3 hours exposure to air had thickness ranging from 0.5 to 1.5 nm and had average thickness of 1.0 nm. This seems to contradict the results of previous studies by other groups. For a review on the early years of work on native oxide, one can refer to Carim [18]. The growth of native silicon oxide also depends on substrate doping type and

doping concentration. As shown by Morita *et al.* [13–14], native oxide on p⁺-Si (doping concentration: 10²⁰ cm⁻³) grows slightly faster than the one on the n-Si (doping concentration: 10¹⁵ cm⁻³) in the early stage and it grows much faster on n⁺-Si (doping concentration: 10²⁰ cm⁻³). The surface oxidation of n⁺-Si could be enhanced by the field-assisted mechanism [13]. In our studies, n-type Si substrates with a low doping concentration ($\sim 3 \times 10^{15}$ cm⁻³) were used.

6.2 Experimental Details

The native oxide samples were mainly prepared on n-type Si(100) ($\sim 3 \times 10^{15}$ cm⁻³ phosphorous doped) substrate. The substrates were first cleaned with acetone and isopropanol and then etched with buffered hydrofluoric (BHF) acid. The substrates were then dipped in deionized water for 2 s and finally blown with dry N₂. After these cleaning procedures, the substrates were left in air (temperature: ~ 24.5 °C, relative humidity: 55%) for different durations: ~ 10 min (fresh sample), 3 days and 1 week. Another native oxide sample was prepared on n-type Si(111) substrate (3×10^{15} cm⁻³ phosphorous-doped) in the same way as the other samples and left in air for about 26 months.

BEEM measurements of the native oxide samples were all performed after the setup of the UHV STM/BEEM system. For the fresh, 3-day, and 1-week samples, the BEEM measurements were performed with *ex-situ* Au deposition. An Au film with thickness of 7 nm and diameter of 0.5 mm was first thermally evaporated onto these samples. The samples were then transferred through air into the UHV STM/BEEM system. BEEM measurements of the sample after 26 months were performed with *in-situ* Au deposition so that the possibly high barrier of Au/SiO₂ could be probed. This sample

was degassed in the UHV preparation chamber at $\sim 355^\circ\text{C}$ for about 20 min. A 7-nm layer of Au was then deposited at room temperature. The BEEM measurements with the UHV STM/BEEM system were all carried out with a W tip at room temperature.

The high- κ dielectric samples were prepared by our collaborators at the Tokyo Institute of Technology, Japan. N-type Si(100) ($3 \times 10^{15}\text{ cm}^{-3}$ phosphorous-doped) substrates were first cleaned with a solution of H_2SO_4 and H_2O_2 (ratio of 3:1) at 110°C for 10 min and then dipped into a 1% HF solution to form a hydrogen-terminated surface. After cleaning, CeO_2 (0.3 nm and 1.3 nm) or La_2O_3 (0.5 nm) was deposited by electron-beam evaporation at pressure of $\sim 10^{-6}\text{ Pa}$ and a rate of 0.1 nm/min with the substrate temperature held at 300°C . After oxide deposition, only the 1.3-nm CeO_2 sample was annealed at 500°C for 30 min in N_2/H_2 (97:3) ambient. These oxide thicknesses were calibrated against ellipsometry and transmission electron microscopy measurements of a relatively thick oxide sample prepared in the same way as the 1.3-nm CeO_2 sample. A 50-nm layer of aluminum was deposited on the back of all samples by thermal evaporation in order to make a good ohmic contact. Using thermal evaporation, a 9-nm layer of Au was evaporated onto the top of each sample through a shadow mask to form 0.5-mm-diameter dots. Finally, the samples were transferred *ex-situ* into a modified RHK STM for BEEM measurements. These measurements were carried out at base pressure of $8 \times 10^{-8}\text{ mbar}$, using a mechanically cut PtIr tip except for the 1.3-nm CeO_2 sample. The *in-situ* BEEM measurement of the 1.3-nm CeO_2 sample was performed with the UHV STM/BEEM system. The sample was first loaded into the UHV preparation chamber and degassed at 310°C for 4 hours 30 min. Then 5 nm of Au was thermally evaporated at

room temperature. BEEM measurements of this sample were carried out with a W tip at room temperature.

6.3 Native Oxide on Si

6.3.1 Ultrathin Native Oxide

Figure 6.1 shows representative spectra of the three Au/native oxide/n-Si(100) samples left in air for different durations: the freshly etched, 3-days, and 1-week samples. The fittings of these three spectra with the constant-current Bell-Kaiser model gave almost the same barrier heights (0.84, 0.84, and 0.83 eV, respectively). This means that the high barrier of Au/SiO₂ had not yet formed, suggesting that no significantly thick native oxide layer had yet formed. On the other hand, the BEEM current for the sample left in air for 3 days decreased to only 50% of that of the fresh Au/n-Si sample, and the decrease in the BEEM current for the sample left in air for 1 week was much greater, about 90%.

According to the work of Morita *et al.* [13–15] and Grundner *et al.* [16], the thickness of the native oxide layer of the lightly doped Si(100) left in air for 3 days was likely to be about 3–5 Å and that for the one left in air for 1 week about 6–8 Å. The barrier heights for the two samples were the same as that of Au/n-Si. Our results show that the oxides in this thickness range (6–8 Å or less) did not have the same electronic barrier as the bulk SiO₂. One possible reason to account for the detection of the lower barrier height is the quantum tunneling of ballistic electrons below the conduction band minimum of the bulk SiO₂. These native oxide films are extremely thin, likely no thicker than 6–8 Å. The effective barrier within the oxide, if it forms already, is expected to be

ultra narrow. Therefore, significant tunneling through the oxide is expected, and the BEEM current would start to increase at an energy corresponding to the conduction band minimum of the silicon substrate, giving the barrier height of Au/n-Si. An alternative explanation is the induced gap states resulting from the exponential decay of the silicon conduction band wavefunctions into the oxide, as described by Muller *et al.* [19] and Neaton *et al.* [20]. These gap states induced by the silicon substrate effectively reduced the oxide thickness.

Figure 6.1 Typical BEEM spectra from Au/native oxide/n-Si(100) samples grown for different durations: freshly etched (red), 3 days (blue), and 1 week (magenta). All the spectra were all normalized to a tunneling current of $I_t = 1$ nA. The fittings (black solid lines) with the constant current Bell-Kaiser model gave the barrier heights of 0.84, 0.84, and 0.83 eV, respectively.

To have a better overview of the three samples, the histograms of the BEEM images (note that each pixel in an image represents the BEEM current at that pixel under the scanning condition, and thus, each histogram is basically the distribution of the BEEM current in each image) taken at $V_{\text{Tip}} = -1.5$ V, $I_t = 1$ nA for all the samples are plotted in Figure 6.2. All these distributions have a small percentage of pixels peaking around zero with no or extremely small BEEM current. This is also true for the freshly etched Si sample. It is very unlikely this was due to the local formation of thick native oxide. In fact, if so, the percentage of these areas should increase with the oxidation time, which is not the case. For the majority of locations, the three distributions peak around 18, 11, and 4–5 pA, respectively, for the three increasing oxidation times. The spectra shown in Figure 6.1 were just examples taken at these locations. Spectra acquired randomly at these locations gave almost the same barrier height, while the BEEM currents varied within these distributions. The overall decrease in the BEEM current with increasing oxidation time is an indication that the native oxide was growing, even though the thickness was not thick enough to produce a bulk-like barrier.

Figure 6.2 The histograms of the BEEM images taken at $V_{\text{Tip}} = -1.5$ V, $I_t = 1$ nA from the Au/native oxide/n-Si(100) samples grown for different durations: freshly etched (red), 3 days (blue), and 1 week (magenta).

6.3.2 Thicker Native Oxide

In the previous section, we showed that a layer of native oxide of 6–8 Å or less does not exhibit a bulk-like barrier. As one would expect, as the oxidation increases, the native oxide eventually becomes thick enough to provide a bulk-like barrier. In this section, we study the 7-nm Au/native oxide/n-Si(111) sample. This sample was left in air for ~26 months for the native oxide to grow after the BHF etch.

Figure 6.3 Typical STM (color scale: 3.5 nm) and corresponding BEEM (color scale: 0–30 pA) images from the Au/native oxide (26 months)/n-Si sample. The images were taken at $V_{\text{Tip}} = -6.5$ V, $I_t = 1$ nA. The red arrows indicate the areas with some relatively high BEEM current, which will be used as the markers in the discussion later.

Imaging this sample at $V_{\text{Tip}} = -1.5$ V and $I_t = 1$ nA (imaging at a very high tunneling current like 5 nA or even 3 nA was almost never stable and the tip crashed easily for some reason) did not reveal any obvious BEEM current. This indicates that the native oxide is much thicker than those on the samples discussed in the previous section. Therefore, we chose to scan at a much higher tip bias. Typical STM and BEEM images acquired at $V_{\text{Tip}} = -6.5$ V and $I_t = 1$ nA are shown in Figure 6.3. Overall, the BEEM current is higher than that of the 5-nm SiO_2 sample. Clear contrast is also present in the BEEM image, with some bright (high BEEM current) areas as indicated by red arrows.

The clear contrast in the BEEM images, however, does not necessarily mean that the interface barrier heights are different. Further spectroscopy studies in the respective locations are needed to clarify this point. In addition, the sizes of these bright areas are larger than the spatial resolution of BEEM, which gives the potential to detect the possible barrier height differences.

Several types of BEEM spectra were observed for this sample, as shown in Figure 6.4. Figure 6.4 (a) is a spectrum taken at $I_t = 2$ nA in the bright areas as indicated by the red arrows in Figure 6.3 (b). Two thresholds of around 0.8 and 4 eV appear in this spectrum. The BEEM current between these two thresholds seems to be roughly linear. Similar spectra were observed on a Pt/2.7-nm SiO₂/n-Si(100) sample by Ludeke *et al.* [8] and a 10-nm Au/1-nm SiO₂/n-Si(100) sample by Quattropani *et al.* [9]. Ludeke *et al.* [8] excluded the possibility of direct Pt/n-Si contact because of the relatively small BEEM current that they observed; however, they mentioned the possibility of either thinner oxide underneath or impurities embedded in the oxide. In addition, their lower threshold was about 1.1 eV, which is higher than what we observed (as shown later). Quattropani *et al.* [9] did not give the value of the lower threshold for the spectra with linear BEEM current below the high threshold, but they argued that electron tunneling through the oxide barrier was unlikely since they observed a linear increase in the BEEM current instead of the exponential increase. They did sometimes, but very rarely, observe some spectra showing a low threshold of ~0.9 eV (without showing the spectrum to a high bias) and they attributed such observations to the local absence of the oxide layer.

To clarify the observed behavior, BEEM spectra were acquired at a much higher tunneling current. Figure 6.4 (b) shows an average of six BEEM spectra taken at $I_t = 10$

nA at the same location as for Figure 6.4 (a). Fitting with the constant-current Bell-Kaiser model gave a barrier height of 0.83 eV, which is the same as that of Au/n-Si and also that of those native oxide samples left in air for 3 days and 1 week. This again means that the oxide layer at these locations is still not thick enough. On the other hand, the considerably smaller BEEM current compared with that of the Au/n-Si device and even those of the native oxide samples discussed earlier indicates that the oxide layer in these areas is very likely thicker than the layers oxidized for 3 days and 1 week. In other words, it is very unlikely that these areas are in direct Au/n-Si contact; instead, it is likely that the oxide layer is thicker than 6–8 Å, but thinner than 1.4 nm.

A typical BEEM spectrum (an average of six spectra taken at $I_t = 4$ nA) in the darker areas in Figure 6.3 (b) is shown in Figure 6.4 (c). The fitting of this spectrum gave a barrier height of ~4.1 eV, which is the same as that of Au/5-nm SiO₂/n-Si. This suggests that the oxide layer in these areas is already thick enough to have the bulk-like electronic barrier. The native oxides in these areas had probably reached the limiting thickness of ~1.4 nm [16].

Reverse BEEM spectra taken at the same locations gave a very weak current with a threshold of ~1.1 eV, which is close to the bandgap of silicon at room temperature. As will be discussed in more detail later in this chapter for the thicker CeO₂ sample and for the oxidized GaAs sample in Chapter 7, this signal is very likely the STM-PC signal instead of a ballistic electron signal. This means that the BEEM spectra at negative bias should also have the STM-PC component. However, the signal was much smaller than the real ballistic electron signal. Figure 6.4 (c) shows a very weak current below the barrier of ~4.1 eV. This is very likely also the STM-PC signal.

In summary, we found two types of areas with barrier heights of ~ 0.83 and ~ 4.1 eV for the native oxide sample oxidized in air for 26 months. The areas with barrier heights of ~ 4.1 eV are likely to have a native oxide layer of ~ 1.4 nm, while the areas with barrier heights of ~ 0.83 eV are likely to have a native oxide thickness slightly greater than $6\text{--}8$ Å but less than 1.4 nm. Our results also show that the native oxide growth is not uniform on the nanoscale, even though the overall native oxide thickness increases with oxidation time. Our results further suggest that the thickness inferred by other studies is the average thickness on a large spatial scale [13–16]. This demonstrates the unique advantage of the BEEM technique, i.e., high spatial resolution. Kaczer *et al.* [21] studied the variations in oxide thickness employing the BEEM technique and found no obvious variations related to the oxide film in terms of BEEM current magnitude. Here, however, we show that variations in the BEEM current with the oxide thickness can sometimes be distinguished for some particular devices: if the oxide thickness is near the cross-over regime and the oxides provide different barrier heights, there are significantly different BEEM current magnitudes.

Figure 6.4 Three types of BEEM spectra from Au/native oxide (26 months)/n-Si: (a) one spectrum taken at $I_t = 2$ nA from the areas with high BEEM current like the ones indicated by the red arrows in Figure 6.3 (b), (b) one taken at $I_t = 10$ nA from the same areas as those mentioned in (a), (c) one taken at $I_t = 4$ nA from the areas with relatively low BEEM current. The fitting (black solid line) of the spectrum (b) with the constant current Bell-Kaiser model gave a barrier height of ~ 0.83 eV. The fitting (black solid line) of the spectrum (c) with the proposed model gave a barrier height of ~ 4.1 eV.

6.4 High- κ Dielectric on Si

To further verify that dielectrics thinner than a critical value do not have bulk-like electronic properties, we performed similar BEEM measurements for the high- κ dielectrics on Si: 0.3-nm CeO_2 and 0.5-nm La_2O_3 . We also compared the results with those for a dielectric of 1.3-nm CeO_2 .

6.4.1 Ultrathin Dielectric

Typical BEEM spectra (I_{BEEM}/I_t vs. tip bias) with the respective theoretical fittings for three different samples are outlined in Figure 6.5 (a): Au/n-Si(100) (blue plus), Au/0.3-nm CeO₂/n-Si(100) (red dots), and Au/0.5-nm La₂O₃/n-Si(100) (magenta triangles). Each spectrum was fitted with the “ $n = 2$ divided by eV” model as described in Chapter 4, with the tunneling current set to the setpoint current and the fitting range limited to 0.4 eV above the best-fit barrier height. The spectra for the 0.3 nm CeO₂ and 0.5 nm La₂O₃ samples gave almost the same barrier height as the spectrum obtained for the Au/n-Si(100) sample (~ 0.81 eV). However, the BEEM currents for these two oxide samples were significantly attenuated compared with that for the Au/n-Si sample. To obtain statistical information from the BEES analysis of these samples, the dual parameter Φ_{BH} vs. R factor distributions are plotted in Figure 6.5 (b), with each data point representing the fitting results with the “ $n = 2$ divided by eV” model for a single spectrum randomly taken across each sample. Figure 6.5 (b) shows that the majority of the spectra for these three samples gave a similar barrier height of ~ 0.8 eV. However, for the 0.3-nm CeO₂ and 0.5-nm La₂O₃ samples, larger barrier height spreads and smaller R values (and hence lower electron transmissions) were obtained.

Figure 6.5 (a) Representative BEES spectra (I_{BEEM}/I_t vs. Tip Bias) with corresponding theoretical fittings for three samples: 9 nm Au/n-Si(100), 9 nm Au/0.3 nm CeO₂/n-Si(100) and 9 nm Au/0.5 nm La₂O₃/n-Si(100). (b) R factor versus barrier height distributions from the three samples in (a).

In particular, for the La₂O₃ sample, there are three different regions: two regions around 0.8 eV with R factor values peaking $\sim 9 \times 10^{-3} \text{ (eV)}^{-1}$ and $\sim 2 \times 10^{-3} \text{ (eV)}^{-1}$; and

the third region with a barrier height of 1.0–1.1 eV and an R factor value of $\sim 2 \times 10^{-3} \text{ (eV)}^{-1}$.

To better understand the R factor versus barrier height distributions, we show an example of the STM topography and the corresponding BEEM image for the La_2O_3 sample in Figure 6.6. The images were taken at $V_{\text{Tip}} = -1.5 \text{ V}$ and $I_t = 1 \text{ nA}$. The BEEM image has bright and dark patches that show no clear correlation with the corresponding STM topography, indicating that the contrast was not due to the Au morphology. Instead the contrast likely stems from the non-uniformity of the oxide film, with the dark areas having thicker oxide film. To better understand the non-uniformity of the oxide, three representative BEES spectra (Figure 6.7) were taken in the bright and dark areas, corresponding to the three different regions in the R factor vs. barrier height distribution; each spectrum is an average of a few spectra. Spectra (1) and (2) gave the same barrier height of 0.81 eV; however, the R value ($1.8 \times 10^{-3} \text{ (eV)}^{-1}$) of spectrum (2) is almost one order of magnitude smaller than the R value ($1.1 \times 10^{-2} \text{ (eV)}^{-1}$) of spectrum (1), suggesting that spectrum (2) is for an area with a thicker oxide layer. In contrast, the barrier (1.00 eV) of spectrum (3) is higher than those of the other two spectra. This higher barrier for spectrum (3) could arise from the STM-PC effect; the actual barrier might be even higher (see a later discussion on the results for the thicker CeO_2 sample). However, as spectrum (3) did not have a barrier as small as those in spectra taken for other regions, it is suggested that the probed area had an even thicker oxide layer.

(a)

(b)

Figure 6.6 (a) STM topography (color scale: 0–4 nm) of Au film, and (b) the corresponding BEEM image (color scale: 0–13 pA) from the 0.5 nm La_2O_3 sample taken at $V_{\text{Tip}} = -1.5$ V, $I_t = 1.0$ nA.

For Au/oxide/n-Si samples, the barrier height extracted from BEES typically represents the offset between the Fermi level of Au and the conduction band minimum of the oxide, without considering the charge trapping. Others have reported that the electron barrier height of Au/ CeO_2 is in the range of 0.9–1.5 eV [22–24], and ~3.1 eV or even higher for the Au/ La_2O_3 interface according to Refs. 25 and 26. However, our BEEM measurements give the barrier heights for both Au/0.3-nm CeO_2 /n-Si and Au/0.5-nm La_2O_3 /n-Si of ~0.8 eV, similar to the Au/n-Si barrier height. Like most high- κ dielectrics grown on silicon [25, 27], there could be an interfacial silicon oxide layer. However, we detected a barrier height of 0.8 eV, and this suggests that the barrier of the interfacial silicon oxide layer was not yet (or not fully) formed.

Figure 6.7 Three different types of BEES spectra (each is average of a few spectra) with respective fittings (black solid lines) from the 0.5 nm La_2O_3 sample. The three types of spectra represent the three different regions in the R factor vs. barrier height distribution. Spectra (2) and (3) are magnified by 4 times ($\times 4$) and shifted vertically for a clearer view. Fittings of the three spectra (1)–(3) give the barrier heights of 0.81 eV, 0.81 eV and 1.00 eV, and R factor values of $1.1 \times 10^{-2} (\text{eV})^{-1}$, $1.8 \times 10^{-3} (\text{eV})^{-1}$, and $1.9 \times 10^{-3} (\text{eV})^{-1}$, respectively.

As discussed for the ultrathin native oxide samples, one possible reason for the detection of the lower barrier height is quantum tunneling of the ballistic electrons below the conduction band minimum of the dielectric. The dielectric films in our samples are extremely thin, nominally 1–2 monolayers. The effective barrier within the oxide, if it exists, is expected to be ultra narrow. Therefore, significant tunneling through the oxide

is expected, and the BEEM current would start to increase at an energy corresponding to the conduction band minimum of the silicon substrate, giving the barrier height of Au/n-Si. Another possibility is the induced gap states resulting from the exponential decay of the silicon conduction band wavefunctions into the oxide, as described by Muller *et al.* [19] and Neaton *et al.* [20].

6.4.2 Thicker Dielectric

To understand the transition from ultrathin (less than 1 nm) to bulk-like oxide, we studied a slightly thicker oxide film.

We first studied the sample before the setup of the UHV STM/BEEM system. Figure 6.8 (a) shows a representative BEES spectrum (negative tip bias) of the 9-nm Au/1.3-nm CeO₂/n-Si(100) sample. Fitting this spectrum with the “ $n = 2$ divided by eV” model gave a barrier height of 1.06 eV and an R factor of $5.7 \times 10^{-4} \text{ (eV)}^{-1}$. The extracted barrier is significantly larger than that of Au/n-Si, and possibly that of Au/CeO₂ [22–24]. However, it is too close to the silicon bandgap at room temperature, which implies that the signal could be STM-PC. To establish the contribution of STM-PC, we performed reverse-bias BEES (RBEES) on the same sample. A representative spectrum is shown in Fig. 6.8 (a) for the positive-tip-bias side. Fitting of this spectrum gave a barrier height of 1.11 eV and an R factor of $7.5 \times 10^{-4} \text{ (eV)}^{-1}$, both of which are very close to values obtained from the BEES spectrum. In addition, the polarity of the signal is in the same direction as that of BEES. Further confirming that the BEES and the RBEES spectra are independent of the tip bias polarity is the almost identical statistical R factor vs. barrier height distribution shown in Fig. 6.8 (b). As discussed by Heller *et al.* [28] and Li *et al.*

[29], all these features suggest that the detected signal actually arose from STM-PC for the 1.3-nm CeO₂ sample. The STM-PC signal was also observed for an even thicker ~1.8 nm CeO₂ sample.

Apart from the STM-PC threshold, we did not observe any obvious threshold up to -2.5 V. However, BEEM spectra up to the high bias range showed another threshold around 6.0–6.5 eV. As shown and discussed in Chapter 5, BEEM measurements in the high bias range for *ex-situ* prepared samples can be very unreliable and usually give a much higher barrier height of 6.0–6.5 eV, compared with the actual barrier of ~4.1 eV for the Au/SiO₂/n-Si sample.

To avoid this issue, we performed BEEM measurements again for a sample with similar CeO₂ thickness of 1.3–1.4 nm. This measurement was performed under ultra-high vacuum conditions using an etched W tip at room temperature. A typical spectrum is shown in Figure 6.8 (c). The fitting of this spectrum gave a barrier height of 3.9 eV. Previously when we used a different fitting algorithm, the barrier height was extracted as ~3.6 eV, and this difference is likely due to the relatively high level of noise in the spectrum. This is much higher than the interface barrier of Au/CeO₂ reported by others [22–24], but is close to the interface barrier of Au/SiO₂ (~4.1 eV). This likely indicates that a significant layer of silicon oxide formed between CeO₂ and the silicon substrate. The existence of the interfacial silicon oxide layer blocks electrons with energies less than the Au/SiO₂ barrier. This also explains why we detected the ~1.1 eV threshold of STM-PC in the BEEM measurements of the *ex-situ* prepared sample. One may wonder why we did not detect the STM-PC signal in the *in-situ* BEEM measurement. We did not explore this in depth; however, we do have some evidence showing that the STM-PC

signal strength decreases somehow for the *in-situ* BEEM measurement. Further studies are needed to confirm this.

Figure 6.8 (a) Representative BEES and RBEES spectra (I_{BEEM}/I_t vs. Tip Bias) with corresponding theoretical fittings for the 1.3-nm CeO_2 sample. (b) R factor versus barrier height distributions extracted from BEES and RBEES all from the 1.3-nm CeO_2 sample. (c) A representative spectrum (an average of 14 spectra) up to high tip bias for the 1.3-nm CeO_2 sample with *in-situ* BEEM measurements.

6.5 Influence of Quantum Tunneling

As discussed previously, the observed smaller barrier height from the ultrathin dielectric samples compared to that from their bulk ones can possibly be attributed to the electron tunneling through the bulk barrier. To have a quantitative understanding, further calculation is carried out using native silicon oxide devices as an example.

The aim of this calculation is to compute the BEEM spectrum for an Au/oxide/n-Si device with a given oxide thickness based on the experimental BEEM spectrum from an Au/n-Si device. To simplify the calculation, it is assumed that the electron energy distribution in the tip is very narrow, i.e., all the electrons have the energies close to the Fermi energy. The transmission coefficient (TC1, Figure 6.9 (a)) at the Au/n-Si interface is calculated using the approximation of a step potential [30] with a barrier height of 0.84 eV. The transmission coefficient (TC2, Figure 6.9 (b)) at the Au/SiO₂ interface is calculated using the Wentzel–Kramers–Brillouin (WKB) approximation [31] assuming the SiO₂ thickness is 3 Å and the Au/SiO₂ interface barrier is 4.1 eV. The BEEM current from the Au/SiO₂ device at a given tip bias is approximately the BEEM current from the Au/n-Si device at the same tip bias divided by TC1 and multiplied by TC2. Figure 6.9 (d) shows the resulted spectrum together with other experimental spectra and Figure 6.9 (e) is its zoomed-in view. As shown, the BEEM current for a 3 Å SiO₂ device is significantly smaller than what was observed on even the 1-week native oxide device, which was expected to have a native oxide layer of 6–8 Å. Therefore, the influence of the electron tunneling through the oxide barrier is negligible and it is very unlikely that the observed smaller barrier height from the ultrathin dielectric samples compared to that from their bulk ones was due to the electrons tunneling through the bulk barrier.

Figure 6.9 (a) Calculated transmission coefficient (TC) for electrons to transmit through the Au/n-Si interface. (b) Calculated transmission coefficient (TC) for electrons to transmit through the Au/SiO₂ (3 Å) interface. (c) Experimental BEEM spectra from Au/n-Si, 3-day, and 1-week native oxide samples, together with a calculated BEEM spectrum from an Au/0.3 nm SiO₂/Si sample. (d) Zoomed-in view of (c). Electron energies are referenced to the Au Fermi level.

6.6 Conclusion

A systematic study of native oxide at different oxidations stages was performed employing ballistic electron emission spectroscopy. We found that native oxide with a thickness of 6–8 Å or less does not have bulk-like electronic properties, while native

oxide with a thickness of ~ 1.4 nm is thick enough to have the same electron barrier height as thicker SiO_2 . On the other hand, even though it does not have a high barrier, the ultrathin (6–8 Å or less) native oxide still strongly suppresses ballistic electron transport. In addition, we found that native oxide on silicon grows non-uniformly on the nanoscale. Even after more than two years, native oxides in some local (nanoscale) areas are still not thick enough to exhibit the same bulk-like electron barrier as the thicker SiO_2 . BEEM measurements of the ultrathin CeO_2 and La_2O_3 samples also show that dielectrics below a critical thickness do not have a bulk-like electron barrier height. Similarly they also strongly affect ballistic electron transport. Combining the BEEM image and BEEM spectra, we showed that it is possible to distinguish dielectric thickness difference on the nanoscale.

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Chapter 7 Characterization of Metal/Dielectric/n-GaAs Devices using BEEM

7.1 Introduction

High- κ dielectrics on GaAs have been actively studied in the search for material systems with enhanced electrical performance over silicon-based metal-oxide-semiconductor devices [1–2]. However, there is usually a strong Fermi-level pinning effect at metal/dielectric interfaces. Understanding the Fermi-level pinning strongly depends on accurate measurement of the interface barrier height of the metal/dielectric interface [2, 3]. Barrier heights of metal/dielectric interfaces have usually been deduced from internal photoemission [3, 4]. Internal photoemission spectra on metal/oxide/semiconductor structures usually have a strong subthreshold component and it may involve both electron and hole transport and other optical transitions [5]. Thus, it is necessary to establish a more straightforward and reliable method to determine the barrier height of a metal/dielectric structure. This motivates us to employ BEEM to determine the barrier height.

High- κ dielectrics deposited on GaAs substrate usually have an interfacial GaAs oxide layer. The GaAs oxide interfacial layer can result in a high density of interface traps and Fermi-level pinning [6]. A detailed understanding of how the GaAs oxide interfacial layer affects electron transport is therefore also critical to the advancement of high- κ GaAs devices. Although the effects of the interfacial GaAs oxide on the growth and performance of high- κ dielectrics grown on GaAs have been explored [7], there has been a lack of detailed work reporting the energy barriers of the oxidized GaAs [5,8].

In this study, the electron barrier height of oxidized GaAs is first determined using STM-based BEES. The samples were also characterized by energy-dispersive X-ray spectroscopy (EDX) in a TEM, and XPS to examine the composition of the oxide layer. Our results indicate the existence of two thresholds in the BEES spectra. This is similar to what was observed for ultrathin SiO₂-based samples [9, 10], where the origin of the first threshold was thought to be related to impurities embedded in the oxide layer or a thinner oxide layer underneath the probed area. Here, however, we show that this first threshold is related to STM photocurrent. With the origin of the first threshold identified, we extracted the second threshold associated with the electron barrier height of the Au/oxidized GaAs interface.

After determining the barrier height of the interface of Au/oxidized GaAs, we determine the barrier heights of Au/high-k dielectric (Al₂O₃, HfO₂)/ interfaces.

7.2 Experimental Details

7.2.1 Au/Oxidized GaAs/n-GaAs

The GaAs oxide layer was formed by oxidizing an n-type GaAs(100) ($\sim 2 \times 10^{16} \text{ cm}^{-3}$) substrate at 500 °C in a mixture of N₂/O₂ ambient. A backside ohmic contact was made by electron-beam evaporation of a composite layer consisting of Ni(5 nm)/Ge(25 nm)/Au(100 nm)/Ni(20 nm)/Au(200 nm), followed by annealing in N₂ ambient at 450 °C.

TEM measurements were taken on cross-sections of a sample using an FEI Titan system, operated at 200 kV. EDX spectra were acquired in scanning TEM (STEM) mode, using an electron probe with a diameter of $\sim 0.2 \text{ nm}$. EDX measurements were taken at

center of the thin oxide films to assure that the spectrum was only measured from the oxide layer.

XPS measurements were performed in a separate UHV VG ESCALAB 220i-XL system equipped with a monochromatic Al K α source (1486.6 eV) and a concentric hemispherical energy analyzer. The background pressure in the analysis chamber was in the 10^{-10} mbar range. A Shirley background subtraction was used for curve fitting of the XPS results followed by a least-square-error fit with a mixture of Gaussian and Lorentzian line shapes.

For the BEEM measurement, the sample was first transferred into the UHV (3×10^{-10} mbar) preparation chamber and degassed at 350–360 °C for 80 minutes. After cooling to room temperature, the sample was further cooled with liquid nitrogen to –147 °C. A Au dot of 0.5 mm diameter and ~5 nm thickness was deposited *in-situ* by thermal evaporation to form the top Au film. After warming up to room temperature, the sample was transferred *in-situ* to the adjacent UHV (3×10^{-10} mbar) STM/BEEM chamber and a gold wire with a diameter of 75 microns was used to gently touch the Au film for grounding. All the BEEM measurements were performed at room temperature.

7.2.2 Au/High-k Dielectric/n-GaAs

N-type GaAs(100) ($\sim 2 \times 10^{16} \text{ cm}^{-3}$) substrate was first etched with a 1:1 HCl solution followed by a 10:1 NH₄OH solution. The surface was then passivated with sulfur by soaking into a (NH₄)₂S solution and blown with dry N₂. After these pretreatments, the samples were immediately loaded into an atomic layer deposition (ALD) system. A layer of Al₂O₃ (or HfO₂) dielectric of 5 nm was grown at 300 °C (or 250 °C) using

trimethylaluminum (TMA, or hafnium) and H_2O as precursors. The Al_2O_3 sample was finally annealed at $500\text{ }^\circ\text{C}$ in N_2 for ~ 30 seconds. The backside contact was made using the same method as the oxidized GaAs sample.

For the BEEM measurements, the Al_2O_3 (or HfO_2) sample was first degassed at $360\text{ }^\circ\text{C}$ (or $300\text{ }^\circ\text{C}$) in UHV for ~ 10 min. Then a layer of 5-nm Au was deposited at room temperature (about $-151\text{ }^\circ\text{C}$ for HfO_2 sample). The sample was then transferred *in-situ* into the adjacent UHV STM/BEEM chamber for BEEM measurements at room temperature.

7.3 Barrier Height of Au/Oxidized GaAs/n-GaAs

7.3.1 Characterization with EDX and XPS

Figure 7.1 (a) shows the TEM micrograph of the oxidized GaAs layer on the GaAs substrate. From Figure 7.1, we estimated the oxidized GaAs layer was around 3 nm thick. It can also be seen that there is a relatively large variation in the thickness of the oxide.

EDX spectra in Figure 7.1 (b) were taken from the substrate and the oxide layer. Comparing the two spectra, we find that the oxide layer contains primarily the elements of Ga and O, and a small amount of As. Using standardless, thickness-corrected EDX analysis, we find that the Ga to As ratio in the oxide layer is about 4.6.

Figure 7.1 (a) TEM micrograph of the stack of oxidized GaAs/n-GaAs (note that the top SiO₂ layer was a capping layer for the TEM specimen preparation), and (b) EDX spectra taken from the substrate (red) and the oxide layer (black), respectively.

Figure 7.2 XPS spectra of (a) Ga 3d and (b) As 3d of the oxidized GaAs. The Ga 3d spectra show the oxide layer mainly contains Ga^{+3} , Ga^{+2} and Ga^{+1} oxidation states. The As 3d spectra show that the oxide layer has As^{+5} and As^{+3} oxidations states.

To further investigate the chemical bonding states of Ga and As in the oxide layer, XPS characterization was performed. Figures 7.2 (a) and (b) show the Ga 3d and As 3d core level spectra, respectively. It can be seen in Figure 7.2 (a) that the observed broad spectrum consists of a mixture of peaks in addition to the substrate peak, i.e., Ga^0 located at ~ 19.6 eV [7]. After curve fitting using parameters taken from the work by Kim *et al.* [7], it is concluded that a significant amount of Ga suboxides are present. The As 3d

spectrum in Figure 7.2 (b), on the other hand, shows two clear oxidation states, As^{+3} and As^{+5} . This is consistent with other XPS results reported [7]. A detailed analysis shows that the Ga to As ratio in the oxide is about 4.8. This is consistent with the earlier EDX results shown in Figure 7.1 (b).

7.3.2 Characterization with BEES

In Figure 7.3 (a), the blue dotted graph is an averaged spectrum of three BEES spectra taken at various virgin (unmodified) locations on the sample at a tunneling current of $I_t = 2.0$ nA. Figure 7.3 (b) shows the complete spectrum over the full range of -10 to -0.3 V. Two thresholds exist in the range of -5.0 to -0.3 V. In order to extract the threshold voltage, we used the square model as following [11]:

$$I_{BEEM} = R \times (eV - \Phi_{BH})^2, \quad (7.1)$$

where I_{BEEM} is the BEEM current, e is the elemental charge, Φ_{BH} is the interface barrier height and R is an attenuation factor. Fitting of the lower threshold (black solid line) with Equation (7.1) gave a barrier of $\sim 1.4 \pm 0.1$ eV with a fitting range limited to ~ 2.9 eV. We would like to point out that this fitting would not have been reliable if the fitting range was limited to a smaller interval (say 1.8 eV), due to the extremely small signal-to-noise ratio in such a situation. In order to get the second threshold from the BEES spectrum, the I_{BEEM} component associated with the first threshold was subtracted from the original spectra. The resulting spectrum is shown as a red dotted spectrum with a fitting curve shown as a green solid line also in Figure 7.3 (a). The fitting result gave a barrier height of $\sim 3.55 \pm 0.05$ eV with the fitting range limited to ~ 4.6 eV. In this case, increasing or decreasing the fitting range by ~ 0.4 eV does not change the barrier by more than 0.05 eV.

Figure 7.3 (a) BEES in the near-threshold regions with the fitting of a two-threshold model: 1) original BEES (blue dotted), 2) fitting of the first threshold (black solid line) giving rise to a barrier of ~ 1.4 eV, 3) BEES after subtracting the component from the first threshold (red dotted line) with the respective fitting (green solid line), giving rise to a barrier of ~ 3.55 eV. Note the curves are shifted downwards for clarity, and 4) the fitting of the original spectrum with the components from both thresholds (red solid line); (b) The original averaged spectrum at $I_t = 2.0$ nA. (c) Averaged BEES and RBEES with respective fittings at $I_t = 8.0$ nA. Both fittings give thresholds of $\sim 1.4 \pm 0.1$ eV; (d) The average of a few RBEES up to 10 V at $I_t = 4.0$ nA.

Bell *et al.* [11] observed three thresholds on Au/n-GaAs devices: 0.89, 1.18, and 1.36 eV. The threshold of 1.4 eV we observed is close to the highest of the three. It was difficult to tell based on our preliminary results where this threshold comes from. To further identify the source of the first threshold, we have conducted a more in-depth study on the first threshold by taking both BEES and RBEES at a much higher tunneling current in order to have a better signal-to-noise ratio. Figure 7.3 (c) shows the average of 20 BEES and six RBEES taken from the same sample at a tunneling current of 8 nA. A few important observations can be made. First, the current flow directions (indicated by the sign of I_{BEEM}) are the same for both of these spectra. In addition, the fittings of the two spectra both resulted in barrier heights of 1.4 ± 0.1 eV (with a fitting range of ~ 1 eV above the threshold), a value approximately the same as the bandgap of the GaAs substrate at room temperature. The R factors from the fittings were $0.8 \times 10^{-13} \text{ A} \cdot (\text{eV})^{-2}$ and $1 \times 10^{-13} \text{ A} \cdot (\text{eV})^{-2}$ for BEES and RBEES, respectively, which means that the current magnitude near the thresholds is very similar for the two types of spectra. As discussed in Chapter 5, these features suggest that the signal associated with the first threshold arose from STM-PC instead of a real ballistic electron signal. The extracted threshold is also consistent to what Li *et al.* observed on Au/octanedithiol/n-GaAs device [12]. To get an idea of the contribution from STM-PC compared to the contribution from the real ballistic electron signal in the BEES after the second threshold, we measured the RBEES spectrum up to 10 V, as displayed in the inset of Figure 7.3 (d). This plot shows that the maximum current magnitude is only ~ 0.2 pA or less at $I_t = 4$ nA, which is much less than the observed current in the BEES after the second threshold. This illustrates that the

current observed after the second threshold is contributed by the actual ballistic electron signal and the STM-PC component is negligible.

Based on the above findings, the first threshold of ~ 1.4 eV corresponds to the bandgap of the GaAs substrate, while the second threshold of ~ 3.55 eV is associated with the barrier height of the Au/oxidized GaAs interface.

Pruniaux *et al.* [13] and Hasegawa *et al.* [14] reported that the extracted barrier height of a Au/oxidized GaAs interface showed a barrier height slightly higher or lower than that of Au/n-GaAs. The extracted barrier height from our BEES study is much higher. The reason remains unclear. However, as shown and mentioned in Ref. 14, the current-voltage characteristics of Au on GaAs oxide oxidized at 400 °C and 500 °C are deteriorated and could be quite different from the diodes of Au on oxidized GaAs prepared with other methods. The barrier height extraction from these current-voltage characteristics based on the Schottky model may therefore be unreliable.

7.4 Barrier Height of Au/High-k Dielectric/n-GaAs

In this section, we mainly determine the barrier heights of Au/Al₂O₃ and Au/HfO₂. A typical BEEM spectrum acquired at $I_t = 10$ nA from the 5-nm Au/5-nm Al₂O₃/n-GaAs sample is shown in Figure 7.4. The fitting was performed with the constant-current Bell-Kaiser model and a fitting range of 0.5 eV self-consistently above each barrier being evaluated. The fitting gave a barrier of ~ 4.2 eV. The barrier height of a metal/multi-layer/semiconductor device probed by BEEM is the barrier between the metal and the layer that has the highest barrier. The barrier we extracted here is higher than the barrier we determined earlier for the Au/oxidized GaAs layer. Even though is a significant

interfacial GaAs oxide layer, this barrier height should not be affected. Therefore, the Au/Al₂O₃ interface barrier height is about 4.2 eV. This is close to what was found using another method [15].

Figure 7.4 A typical BEEM spectrum (average of three spectra) acquired at $I_t = 10$ nA on a 5-nm Au/5-nm Al₂O₃/n-GaAs sample. Fitting (black solid line) with the constant current Bell-Kaiser model with a fitting range of 0.5 eV gave a barrier height of 4.2 eV, which is indicated by the blue vertical line.

Figure 7.5 is a typical spectrum taken at $I_t = 2$ nA from the 5-nm Au/5-nm HfO₂/n-GaAs sample. Fitting with the proposed model discussed in Chapter 5 gave a barrier height of ~4.1 eV, which is higher than the barrier height of the Au/oxidized GaAs layer. Therefore, the interface barrier of Au/HfO₂ is about 4.1 eV. This extracted barrier height, however, is about 0.4 eV higher than what Afanas'ev *et al.* reported [3].

Figure 7.5 A typical BEEM spectrum (average of 40 spectra) acquired at $I_t = 2$ nA on a 5-nm Au/5-nm HfO₂/n-GaAs sample. Fitting (black solid line) with the proposed simplified model with a fitting range of 1.5 eV gave a barrier height of 4.1 eV, which is indicated by the blue vertical line.

7.5 Conclusion

We determined the barrier heights of Au/oxidized GaAs, Au/Al₂O₃, and Au/HfO₂ to be 3.55, 4.1, and 4.1 eV, respectively.

For Au/oxidized GaAs/n-GaAs, we found two thresholds in the BEES spectra. By studying the BEES and RBEES spectra in detail, we identified that the first threshold at ~1.4 eV originated from STM-PC. We used a two-step procedure to separate the two thresholds and determined that the second threshold corresponds to an electron barrier of ~3.55 eV for the Au/oxidized GaAs interface.

In Chapter 6, we also observed BEEM spectra with two thresholds for the thicker native oxide sample. We further showed that the lower of the two thresholds was due to ballistic electron transport. This, together with the results on the oxidized GaAs sample in this chapter, suggests that the two-threshold behavior in the BEES studies of metal/dielectric samples can arise from either STM-PC or ballistic electron signal.

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Chapter 8 Conclusion and Recommendations

In this work, we employed ballistic electron emission microscopy (BEEM) to investigate the electronic properties of dielectrics on both silicon and GaAs substrates. In terms of the BEEM technique, we studied the subthreshold characteristics of the ballistic electron emission spectra and proposed a new simplified analytical model for BEEM spectrum fitting.

8.1 Conclusion

In terms of the BEEM technique, the subthreshold characteristics of ballistic electron emission spectra were investigated. A simple analytical equation describing the subthreshold behavior of the BEEM spectra was derived. This equation shows that the BEEM current in the subthreshold region decreases at a rate of ~ 60 mV/decade. This was verified by both simulation and experiment. Applying the subthreshold equation, we next proposed a new simplified analytical model for the BEEM spectrum fitting. This model significantly improves the fitting near and below the threshold compared with using other simplified models. More importantly, the model provides a method to quickly estimate the BEEM current at and below the barrier height according to the BEEM current above the barrier.

It was shown that the BEEM measurement of samples with high barriers (~ 3.0 eV or above) cannot be performed properly if the metal base electrode is deposited *ex-situ*. However, there is no problem if the metal is deposited *in-situ* in a UHV. We further

showed that the main reason is that the contamination of the Au surface strongly affects tunneling between the tip and Au base, thus affecting the BEEM spectroscopy.

The electronic properties of ultrathin dielectrics with thickness of ~ 1 nm or less were investigated to clarify the scaling limit of the gate dielectrics. BEEM studies were performed for both native oxides on Si and high- κ dielectrics on Si. Both these studies show that a dielectric of less than a certain thickness (about 6–8 Å or so) in a metal/dielectric/semiconductor structure does not have the same electronic properties as its thicker bulk dielectric. However, these ultrathin dielectrics still strongly attenuate ballistic electron transport. In addition, we found that the native oxide on silicon does not grow uniformly on the nanoscale. This suggests that BEEM is capable of distinguishing the dielectric thickness on the nanoscale.

Finally, we determined the barrier height of a few important GaAs-based metal/oxide/semiconductor devices. For the Au/3-nm oxidized GaAs/n-GaAs device, the BEEM spectra had two thresholds of 1.4 and 3.55 eV, respectively. In an in-depth study, we showed that the first threshold arises from the STM photocurrent (STM-PC) signal, and thus determined the barrier height of Au/oxidized GaAs to be ~ 3.55 eV. We next determined the barrier heights of Au/Al₂O₃/n-GaAs and Au/HfO₂/n-GaAs. We hope these determined barrier heights can serve as a good reference for other studies.

In BEEM studies for Au/native oxide/n-Si and Au/3-nm oxidized GaAs/n-GaAs devices, we detected the spectra with two thresholds: one low and the other much higher. However, the origins of the first threshold differ for the two devices. For the Au/native oxide/n-Si sample, the first threshold is due to the local native oxide being too thin, while for the oxidized GaAs sample, the first threshold is identified as the STM-PC signal.

8.2 Recommendations

While STM is a surface characterization technique, BEEM is a STM-based technique used mainly to characterize the interfaces of materials (e.g., the interfaces of a metal/semiconductor Schottky diode and metal/insulator/semiconductor devices). Even though there are many restrictions and difficulties in using the BEEM technique (especially in the high bias range), there are promising research directions related to this technique.

8.2.1 Oxide Breakdown Studies on Specially Fabricated Devices

During the present work, we spent much time studying the degradation and breakdown of the oxide layer employing BEEM. Unfortunately, we did not obtain promising and convincing results. In the literature, there have been a few studies on oxide breakdown employing BEEM [1–5]; however, as pointed out by Ludeke *et al.*[1], Wen *et al.*[2], and Kaczer *et al.* [3, 4], the metal base was almost always found to be severely damaged, leaving a large crater at the location that was stressed. We observed a breakdown sequence similar to that reported by Zheng *et al.* [3] by July–August, 2008, which was before we set up the *in-situ* UHV STM/BEEM system. However, we found that these breakdown events were most frequent when the tip bias swept slowly from high (e.g., -6.5 V) to low (e.g., -0.3 V) and ramped back quickly to high bias (e.g., -6.5 V) to start the recording of another spectrum. In fact, by observing the BEEM current and tip height with an oscilloscope during the spectroscopy, we found that these breakdown events happened at the point of quickly ramping back to high bias. When the tip bias ramped back slowly (i.e., at the same rate as for the forward direction), the breakdown

almost never happened. This indicates that the breakdowns were very likely induced by tip or metal-base failure at high current. When the STM feedback cannot respond quickly enough, the tip and the metal base can be very close and sometimes even come into contact, thus causing an extremely high current and leading to the local damage/melting of tip and/or the metal base. We have also checked the STM topography many times after breakdown events. The Au topography was always found to show heavy damage, with there being a crater having a diameter of 30–50 nm. The modified area was sometimes even larger. While the oxides have probably broken down in these cases, it seems likely that the oxide breakdown was caused by metal failure or melting.

We also attempted to stress the metal-oxide-semiconductor (MOS) structure with conventional electrical stress prior to making the BEEM measurement. However, owing to the large capacitor area (0.5 mm in diameter) and the fact that the breakdown is local, it is almost impossible to find the breakdown location after the application of conventional stress. Even though we can increase the breakdown hardness and there may be multiple breakdown events, the early-breakdown locations eventually become large enough to prevent further breakdown events at other locations.

Nevertheless, we see great potential in investigating oxide breakdown by employing BEEM. To realize this technique in practice, a specially designed and fabricated device is necessary. If one can fabricate a MOS device with an area of 1–10 μm^2 or so and apply the conventional electrical stress, it will be much easier to find breakdown locations. This of course requires a scanning electron microscope (SEM) to locate the device and a manipulator to position the ground wire more precisely. There are a few eventualities. First, the Au film is still very thin. When breakdown occurs, there

may or may not be damage to the Au film. If there is (which is likely after a relatively hard breakdown) and we can locate it with an SEM, we can simply scan the area, take the BEEM spectra, and observe what has happened; if not, the problem is more challenging, as we may need to search over the whole device.

Another method is to fabricate a device with some patterning by etching or using some other methods. On this device, there will be a small area of $1\text{--}10\text{ }\mu\text{m}^2$ or even a few hundred square nanometers with a very thin oxide layer, perhaps $1\text{--}2\text{ nm}$ thick. This area will be surrounded by a thicker oxide layer of 3 nm or more. In this case, the metal base layer can be very large. The challenge is, however, that we need some kind of marker to be fabricated during the patterning of the oxide, so that we can locate the area with thinner oxide. This may still require the facilitation of an SEM depending on the how the marker is made.

8.2.2 Combining STM and BEEM Results

Another promising research direction is to combine BEEM and STM results for the oxide. Here we mean that the oxide sample is directly examined via STM, with there being no metal layer on the oxide. From STM scanning of the oxide directly, we may have an idea of the morphology of the oxide surface. In this way, we will know if any of the features of the oxide appear on the metal surface after metal deposition. If they do, it will be possible to correlate the BEEM results with the underlying oxide directly. In addition, it is possible to decouple the effects of metal thickness, oxide thickness, and possibly metal/oxide interface inhomogeneity.

8.2.3 Reverse BEEM and STM-PC

As mentioned in Chapter 2, there have been very limited studies on reverse-bias BEEM (RBEEM) measurement. RBEEM studies of metal/p-type semiconductor have been shown to be able to probe the hole barrier [6, 7]. However, there still seems to be insufficient understanding of RBEEM spectroscopy. It is now believed that the STM-PC component is almost always present in BEES and REBEES measurements of metal/n-type semiconductor devices [8]. The question is how great the contribution of STM-PC is to RBEEM spectra. After decoupling the STM-PC component from the ballistic electron signal, it may be easier to interpret the RBEEM results for metal/n-type semiconductor devices.

8.2.4 Tunneling in the High Bias Range

As we showed in Chapter 5, there is a significant difference in the tunneling for the *in-situ* and *ex-situ* deposited Au surfaces. In addition, we found that there is material deposition from the tip for both cases, even though it is much weaker in the *in-situ* case. The mechanism of the material transfer between the tip and sample has been discussed by others [9, 10]. However, most of the reported cases of material transfer between the tip and sample involved a pulse voltage, instead of a sweeping voltage under a constant-current condition. Therefore, it is worth investigating whether the mechanism of the material transfer is the same. On the other hand, it is also necessary and interesting to study why there is such a significant difference between the tunneling for *in-situ* and *ex-situ* deposited Au surfaces.

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