THE MEASUREMENTS OF SHEET CONDUCTANCE OF METALLIZED SILICON SURFACE BY TWO POINT TUNNELING PROBE

A Thesis in
Physics

by
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Abstract

We made measurements of the sheet conductance of the Si(111) 7 × 7 reconstructed surface and its metallization with Ag-overlayers. The experiment employs a STM-tip point tunneling probe coupled to a second spring-contact electrode to evaluate charge-carrier injection and transport via surface states prepared in-situ in UHV. The electron transport can be controlled by different bias voltage using our method. The measurements distinguish a surface-state contribution, a Schottky diode contribution, and a metallic-overlayers dependence on thickness, ranging from submonolayer coverage to 10 monolayers. The thin film conductance shows a strong dependence on the interface conductance of the semiconductor. It is important that the conductance is affected by scatterings in the thin film and tip spacing, and the tip and the semiconductor generate a tip-induced Schottky barrier when measurements are done on a M-S system which has a poor metallic surface.
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Chapter 1

Introduction

The mechanism of electrical conduction and the magnitude of the sheet conductance of semiconductor surfaces and interfaces are an important topic for the efficient operation of electronic devices [6]. As devices shrink to the nanoscale, the increasing surface/volume ratio emphasizes conduction of the surface.

The term sheet conductance is a function of the bulk conductivity of a thin metallic film, and is defined by $G_s = \sigma t$ where $\sigma$ is the bulk conductivity of a metal and $t$ is a metallic film thickness. A first attempt using a Scanning Tunneling Microscope (STM), measuring sheet conductance in relation to surface structure and the surface conductivity via surface states on reconstructed Si(111) $7 \times 7$, was reported by Hasegawa, Lyo and Avouris [7]. The single nanoscale point-contact resulted in conductance values $10^{-6} \, \Omega^{-1}$. Conductance into the bulk semiconductor (n-type, 1 $\Omega$cm) was estimated to be less than $10^{-12} \, \Omega^{-1}$. The implication was that as the length scale approaches that of a nano-scale point-contact, conductance via the surface begins to exceed that through the Schottky diode interface by orders of magnitude.

One problem with conductance values derived using this single point-probe method
is to isolate the contribution of the conductance to be solely due to surface conductivity via surface states [8]. As later established by Shiraki and coworkers [9], the measured current will, in general, flow through 3 channels - via surface states in the topmost ordered atomic layer; via bulk states in the space-charge layer beneath the surface; and via bulk states in the semiconductor. Similar measurements using nano-structured metallic pads in a 2-electrode configuration [10] create contact and spreading-resistance contributions.

To circumvent these problems, efforts have been made to perform measurements in-situ in Ultra-High Vacuum (UHV) using 4-point probe electrodes making contact with the surface at points separated by microscopic lengths. Using such a tool with a probe spacing of the order of tens of microns, Petersen et al. [11] observed that the sheet conductance of the Si(111) 7 × 7 surface changed by several orders of magnitude ($10^{-9} \, \Omega^{-1}$ to $8.0 \times 10^{-4} \, \Omega^{-1}$) when converted to the Si(111)-$\sqrt{3} \times \sqrt{3}$-Ag metallized and reconstructed surface. This huge difference in surface sheet conductance is due to the difference in the electronic transport through the different surface states on the two reconstructed surfaces [7, 8, 11, 12].

Since most of established techniques are based on the probe touch method, they have an intrinsic problem, namely that currents tend to flow through not only the surface channel but the other two channels, the depletion region and the bulk semiconductor channels. The most current flows through the bulk depletion region in this case. In order to make currents pass only through the metallic surface, the probe spacing should be comparable to the metallic film thickness. However, it is very dif-
Figure 1.1: Current trajectory for four point probe. (a) In case of macroscopic probe, the most current flows through bulk silicon. (b) In contrast, currents flow through the metallic surface and the depletion region for the microscopic probe.
ficult to make such a microscopic probe when the film thickness is a few monolayers. Hence the measurements by the established methods include errors because current paths are not well defined. A new method, which can control current paths, is needed for measuring the conductivity of a ultra-thin metallic surface with an extremely high accuracy.

1.1 Established techniques for measuring the surface conductivity

There are several methods to measure the conductivity of a silicon surface or thin film on the silicon. Most of them are based on the probe touch on the surface. These instruments normally consist of either two probes or four probes. Three representative techniques will be introduced.

The FPP method has been widely used for measuring the surface resistivity of Metal-Semiconductor (M-S) system or a prepared semiconductor surface. Two point probe (TPP), which is called Spreading Resistance Probe (SRP), is usually used to investigate the depth profile of a semiconductor. SRP has an intrinsic problem, where there is contact resistance between the tip and a sample. FPP does not have this problem because a voltmeter connected with two inner probes, which measures the potential drop between two probes, has much higher resistance than the contact resistance.
Figure 1.2: Three techniques for the measurements of the resistivity of a semiconductor. (a) Two Point Probe; the DC power is applied to both ends of a substrate. Two probes touch on a sample surface to measure the resistance difference between them. (b) Four Point Probe; four probes touch a semiconductor surface. The inner two probes measure voltage drop between them. A known current flows through between two outer probes. (c) Spreading Resistance Probe; applying voltage to between two probes, currents are measured between them. It thus measures spreading resistance.
1.1.1 Four Point Probe

FPP consists of two current carrying probes which are first and fourth probe, and two inner probes to measure voltage drop between these probes. The differential resistance measured by FPP may be written as

$$dR = \rho \frac{dx}{A}, \quad (1.1)$$

where $\rho$ is the resistivity, and $A$ is the area covered by currents. In thin film case, $A = 2\pi xt$, equation 1.1 then takes the form

$$R = \int_{x_1}^{x_2} \frac{\rho}{2\pi xt} dx \quad (1.2)$$

which can be rewritten as

$$R_s = \frac{\rho}{t} = \frac{\pi}{\ln 2} \frac{V}{I} \quad (1.3)$$

where $V/I$ is a measured resistance, $R_s$ is the sheet resistance, and $t$ is the film thickness.

1.1.2 Spreading Resistance Probe

SRP, which is composed of two probes, is a useful technique used to obtain the dopant profile of a semiconductor sample. A voltage difference is measured between two probes where a known current flows. Because two probes of SRP touch a sample surface, a divergent current flows between the probes. I-V curves by SRP then directly result in the spreading resistance (SR) which is proportional to the resistivity of a semiconductor.
By using Ohms law, the spreading resistance for SRP is given by [13]

\[ R_S = \frac{\rho}{4a} \]  

(1.4)

where \( a \) is the diameter of the probe. Figure 1.2 shows a typical SRP. By angle lapping the sample, a series of spreading resistance measurements are performed along the beveled area. A correction factor is used to convert spreading resistance into carrier concentration levels.
2.1 Scanning Tunneling Microscopy

STM was invented by Gerd Binnig and Heinrich Rohrer [14] of IBM’s Zurich Lab in Zurich, Switzerland in 1981. STM provides a topographical image of the atomic structure on the nanometer-scale. It consists of the scanner made of a piezoelectric tube (PZT), which provides a very sharp tip which is mounted on the scanner and a feedback loop (figure 2.1). A feedback loop is used to approach the tip to the sample as close as possible, which is usually around 10 Å, and to keep the gap between the tip and the sample a constant. The basic physical effect in the STM device is Quantum Tunneling Effect, by which a particle may penetrate the potential barrier, which is approximately the average work-function of a sample and the STM tip, whose energy is higher than the kinetic energy of the particle.

The STM scanner is made of PZT. Some materials have piezoelectricity property which generate voltage under a mechanical stress (see subsection 2.6.4. This phenomenon was discovered in 1880 in naturally-occurring single crystals. As voltage is
Figure 2.1: Schematic of STM measurement configuration. It consists of three piezoelectricity tubes. The distance between the STM tip and a sample can be controlled by a feed-back loop.
applied across the PZT material, it is mechanically stretched. Using this property, the scanner can be controlled at the atomic level.

Piezo-electronic plates are used for approaching the sample to the tip coarsely. This is sometimes called a coarse PZT. Before tuning on the feed-back loop, the sample should be as close as possible to the sample. Otherwise, it will take a very long time for the tip to approach close to the sample.

The feedback loop compares a tunneling current to a reference current. If the measured current is lower than the reference current, the tip moves toward the sample by one step, then it compares two currents again. It repeats this process until the measured current and the reference current are the same. Using this mechanism, the tip can approach close to the sample by several angstroms and keep a constant gap.

STM provides two different modes, the constant current mode and the constant height mode. In the constant current mode, the feedback loop compares the reference current with the measured current. If there is a difference between them, the tip is moving until the measured current equals the reference current. Collecting height information from the tip, a two-dimensional topographical image of a sample is obtained. On the other hand, the height of the tip is fixed in the constant height mode; the tip does not move along the z-direction (figure 2.1). The tip measures the tunneling current change sweeping the surface. The scanning speed is faster than that of the constant current mode because the feed back loop is turned off during measurement. This mode, however, has a problem. The tip may crash to the sample surface during scanning.
Mechanical vibration can make the STM image worse, therefore it is important for STM to be isolated from mechanical vibration. The mechanical vibration noise should be less than 0.1 Å to obtain good resolution images.

2.1.1 Scanning Tunneling Spectroscopy

Scanning Tunneling Spectroscopy (STS) technique provides information about the local density of states by performing a first derivative of the I-V curve $dI/dV$ (see text in section 2.1.1). The tunneling current is exponentially proportional to the gap between the tip and the sample [15].

$$I \propto e^{-2kd}$$  \hspace{1cm} (2.1)

where $k$ is a wave vector and $d$ is the tip spacing. An I-V curve is obtained by measuring the tunneling current ramping bias voltage. The typical I-V curve describes the resistance information. If the feedback loop is on, the tunneling current will be always a constant, which makes the I-V curve linear. The theory of STS has been developed by Tersoff and Hamann [16]. The tunneling current, which is a function of bias voltage, may be written as

$$I(V) \propto \int_{E_F}^{E_F+eV} \rho(\vec{r}, E) dE \rho(\vec{r}', E) = \sum_i |\psi_i(\vec{r})|^2 \delta(E - E_i)$$  \hspace{1cm} (2.2)

where $\rho(\vec{r}, E)$ is the local density of states (LDOS), and $E_F$ is the Fermi energy. Thus, STS provides LDOS information of the sample and the tip.

The tunneling current apparently depends on the geometry and electronic states of both the tip and the sample. In case of a metal-semiconductor interface, the DOS of
the metal is much higher than that of the semiconductor, which means the properties of the semiconductor are determined by the tunneling current.

The main obstacles to acquire accurate STS data are the condition of the tip, the condition of the sample and any noises. STS data are very sensitive to the condition of the STM tip and the position of the tip-sample. If the tip is extremely sharp, while taking data, the spectroscopy data may lose its consistency because the tunneling across the vacuum may be changed easily. This problem can be resolved by making the tip blunt. Carriers at the blunt tip will tunnel evenly toward the sample such that consistency is achieved. If data acquisition time is long, it may also generate some problems. The most serious problem is that the tip condition may be varied during measurement. Therefore it is important to make the scanning time as short as possible.

Another consideration is the noise from the stray capacitance formed between the STM head and the other component. The current due to the stray capacitance is typically several nano-amps, which is not negligible compared to the tunneling current. The noise current due to the capacitance is given by

$$I = \sum_{i} C_i \frac{dV_i}{dt},$$  \hspace{1cm} (2.3)

where $C_i$ is the stray capacitance. There are two methods to decrease this noise. The first method is to decrease the capacitance itself, and the second one is to decrease the slew rate related to the voltage ramping time. However, if the slew rate is decreased, it will create another problem in that the scanning time is increased. In order to
decrease the stray capacitance, first, all component should be away from the STM head as far as possible. Second, the wire connecting the tip and the op-amp should be as short as possible.

2.1.2 Ultra High Vacuum

All experiments were performed in the Ultra High Vacuum (UHV) system that is below $10^{-9}$ torr. There are several reasons a UHV system is required. First, a sample surface in the atmosphere is polluted easily and quickly by some environmental materials in air. Second, an electron needs enough mean free path in a chamber to perform some experiments such as Low Electron Energy Diffraction (LEED). Last, as a material is deposited onto a substrate, some contaminants may be mixed with the evaporating material while it evaporates.

It is important to know how long the clean surface can be kept at specific vacuum level. It depends on the incident flux on a surface and the vacuum level. The Hertz-Knudsen formula [17] provides the incident flux given by

$$F = \frac{P(T)a}{\pi L^{2} \sqrt{2 \pi m k T}}$$  \hspace{1cm} (2.4)

where $L$ is the distance from the substrate, $m$ is the mass of the effusing species, $T$ is the temperature, and $P(T)$ is the pressure which is a function of temperature. Equation 2.4 denotes that the flux is directly proportional to the pressure, which means a lower pressure keeps the surface clean longer.

The sticking coefficient, $S$, is a fraction of the incident flux, which can have a 0 to
1 value. A convenient description of the sticking coefficient for activated adsorption can be written as
\[ S(\theta) = \sigma f(\theta) \exp(-\frac{E_{\text{act}}}{kT}), \] (2.5)
where \( \sigma \) is the condensation coefficient which describes the effect of molecular orientation, and \( f(\theta) \) is the occupation factor which provides the probability of finding an adsorption site. The surface coverage of an adsorbed species is described as the number of adsorbed species per unit area of surface molecules.

### 2.1.3 Sample preparation

Double side polished n-doped silicon(111) wafers, with resistivity of 1-10 Ωcm and thickness is around 400 µm, was used for our experiments. This wafers are terminated by hydrogen atoms, so that the sample can be clean by removing hydrogen atom by heating.

After cleaned, the sample is mounted on the sample holder. At this moment, if an iron tweezers or a similar one are used for assembling, the sample surface may be polluted by a very small amount of nickel on the tool. Once it is polluted by nickel, we could see a \( \sqrt{19} \times \sqrt{19} \) LEED pattern (see figure 2.2) by heating the sample. The polluted substrate surface by nickel may be removed by high temperature, namely more than 1200 °C. However, in this case, the surface may be oxidized due to high temperature. A nickel free tweezers thus is required to keep the surface clean. The sample holder is made of molybdenum because it is a nickel-free material.

After installed on the sample holder, the sample needs to be cleaned by direct
heating under UHV to remove any materials on the surface, polluting by exposure to air. The base pressure should not be over $5 \times 10^{-9}$ torr, during cleaning the sample, so that this does not break the UHV condition, which is also important when the filament of LEED or an evaporator is degassed.

There are two main metallic surfaces used for our experiments, which are Si(111) $7 \times 7$ and Si(111) $\sqrt{3} \times \sqrt{3}$-Ag. These reconstructed surfaces are discussed in detail in section 4.1.
2.1.4 STM tip

In UHV system, the tungsten tip is widely used for a STM system because of its solid property. However, since tungsten is easily oxidized in air, other materials, which are not oxidized in air such as Pt-Ir or Au, are used for the STM tip in air. The diameter of the tungsten wire used is 0.02 inches. The tungsten tip can be etched by potassium hydroxide (KOH) solution to make it sharp.

The tantalum loop wire with diameter of 5 mm, is submerged in KOH solution to make a drop of KOH within the loop (figure 2.3). A voltage is then applied between the tip and the loop. The magnitude of applied voltage depends on the geometry of the loop and the amount of the KOH solution inside the loop. The sharpness of the tip is roughly checked by a micrometer. The tip is oxidized in several hours even if it is under UHV environment.

The STM tip may pick up impurity atoms, during scanning, on a sample surface. In case manganese deposited on a semiconductor, the tip can be easily polluted by manganese atoms during measurement. Four tips were prepared, and were kept at a STM tip slot installed in the UHV chamber.

There are two representative scanner types, a tube and a tripod one. The tripod PZT is controlled by three orthogonal piezo tubes. On the other hand, the inside and outside of the tube scanner is covered by a metal. The metal covering outside is consists of four pieces. The Z-direction movement is achieved by supplying voltage between inner electrode and outer electrode. The movement to X-Y direction can be
Figure 2.3: Electrochemical etching of the tungsten tip. Voltage is applied between the KOH solution which is within the wire loop and the tip.
achieved by applying voltage between two opposite electrode on the outside of the tube scanner.

2.1.5 Op-amp

The STM tip is directly connected to an op-amp which amplifies the weak tunneling current. A 100 $M\Omega$ resistor is mounted between pin 2 and pin 6 so that it turns the tunneling current into voltage (figure 2.4(a)). The output via this I-V converter is given by

$$V_{out} = I \times R + \text{applied bias voltage} \quad (2.6)$$

where $V_{out}$ is output voltage, $I$ is a current on the tip, and $R$ is 100 $M\Omega$. Table 2.1 shows the characteristics of OPA111 we used.

An op-amp is powered by a two-polarity voltage in the range of 5 V to 18 V. The I-V curve was taken with ramping operating voltage to examine the linearity of the op-amps. Figure 2.4(b) shows that the I-V curve has the linearity from -5.3 V to + 3.8 V, which means the data within this range are reliable. The I-V curve starts saturation out of the linear range. The linear range can be expanded by applying higher operating power.

2.2 Metal-Vacuum-Metal system

A metallic surface on Si(111) and the STM tip form a Metal-Vacuum-Metal (MVM) system [18].
Figure 2.4: (a) Circuit diagram for op-amp to convert the tunneling current to voltage. The tip is connected to op-amp directly. (b) op-amp test to make sure the output linearity
Figure 2.5: Energy diagram for Metal Vacuum Metal system. The diagram corresponds to the STM tip - vacuum - metallic surface
<table>
<thead>
<tr>
<th>Features</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low noise : 8nV √Hz max(10 kHz)</td>
<td>Precision instrumentation</td>
</tr>
<tr>
<td>Low bias current 1pA max</td>
<td>Data acquisition</td>
</tr>
<tr>
<td>Low offset : 250 µV max</td>
<td>test equipment</td>
</tr>
<tr>
<td>High open-loop gain : 120 dB min</td>
<td>Optoelectronics</td>
</tr>
<tr>
<td>High common-mode rejection : 100 dB min</td>
<td>Medical equipment</td>
</tr>
<tr>
<td>Low drift : 1 µV / °C</td>
<td>Radiation hard equipment</td>
</tr>
</tbody>
</table>

Table 2.1: Features of OPA111

Figure 2.5 displays the energy diagram for a MVM system. The tunneling current for this system is expressed by

$$j = \int_{0}^{\infty} dE_Z D(E_Z) N(E_Z),$$

(2.7)

where $N(E_Z)$ is the normal component of the energy distribution function, and $D(E_Z)$ is the normal component of the tunneling transmission probability. They each are given by

$$N(E_Z) = \frac{eK_BT}{2\pi^2\hbar^3} \ln \left( \frac{1 + \frac{\exp(E_F - E_Z)}{k_BT}}{1 + \frac{\exp(E_F - E_Z - eV)}{k_BT}} \right)$$

(2.8)

$$D(E_Z) \approx \exp\left[-\frac{2m}{\hbar^2} (\phi + E_F - \frac{eV}{2} - E_Z)\right]$$

(2.9)
where $\phi$ is the average work-function of the two metals. From equation 2.9, the tunneling transmission probability is proportional to $D \sim \exp\left(-\frac{2\sqrt{2m\phi}}{\hbar}s\right)$. The tunneling current decays exponentially as the tip spacing increases, or bias voltage decreases. The I-V characteristics thus show Ohmic behavior at low voltage and exponential behavior at high voltage.

2.3 Metal-Semiconductor interface

2.3.1 Schottky barrier

The Schottky barrier (SB) [19] is an energy barrier formed at the metal-semiconductor junction, and is important because of its rectifying property. In an ideal case, the barrier is expressed as equation 2.10. By assuming a metal and a semiconductor are in equilibrium, so that there is no charge transfer between them, the ideal Schottky barrier is given by

$$\phi_B = \phi_M - \chi_S \quad (2.10)$$

where $\phi_M$ is the work function of a metal, and $\chi_S$ is the electron affinity of a semiconductor. This equation 2.10 is called Schottky-Mott rule. In case the metal work function is greater than that of the semiconductor, when the metal is brought into contact the semiconductor, the Fermi level becomes a constant throughout the device. Then electrons in the semiconductor flow into lower metal states. This rearrangement occurs near the interface, and is localized, which makes the dipole layer (figure 2.6(a)). This generates the space charge region in the semiconductor, which result in band
bending due to the change of the potential in this region. The length of band bending is typically about 500 - 5000 Å. The experimental data reflect that $E_f$ is pinned, which is discrepancy with Schottky theory. This result is independent of evaporant source.

Bardeen suggested that the surface states are important to determine the SBH of a M-S system [20]. The periodicity of a semiconductor is terminated at the surface so that the wave function is an imaginary $k = iq$ [21]. However there is still a significant amplitude over a few layers from the surface.

The dispersion curve, $E(q)$, fills the energy gap within the band gap, and indicates the range of theoretically possible states. The surface states thus can be formed, and it is continuously distributed within the forbidden gap. With the interface states, the neutrality relation may be given by

$$Q_m + Q_{is} + Q_s = 0 \quad (2.11)$$

where $Q_m$ is the charge in the metal, $Q_{is}$ is the charge on the interface, and $Q_s$ is the charge in a semiconductor. So the Schottky barrier may be written as [22]

$$ (E_g - e\phi_0) = \frac{1}{eD_{it}} \sqrt{2e\epsilon_S N_D (\phi_{Bn} - \phi_n)} - \frac{e_1}{eD_{it} \delta} [\phi_m - \chi + \phi_{Bn}] \quad (2.12)$$

where $D_{it}$ is the density of surface state and $N_D$ is the semiconductor doping. A neutral level, $\phi_0$, characterizes the surface state, so that if the surface states are occupied up to $\phi_0$, and are empty above $\phi_0$, the surface is electrically neutral. The surface stats below $\phi_0$ are donor-like, and above $\phi_0$ are acceptor-like. In case of $\phi_0 < E_f$, the net
The Schottky Barrier Height: \( \Phi_B \)
Work Function of a Metal: \( \Phi_M \)
Electron Affinity: \( \chi_s \)
Energy Band Gap: \( E_g \)
Dipole Moment: \( \Delta \)
Surface Band Bending: \( eV_s \)
Fermi Energy Level: \( E_F \)

**Figure 2.6:** (a) Energy band diagram of a metal-semiconductor junction. There is band bending due to charge transfer from metal to silicon in case of a n-type semiconductor. (b) The change of the potential barrier due to image force.
charge of the surface states is positive. In contrast, if the net charge of it is negative, then $\phi_0 > E_f$. This implies the surface states make a role of negative feedback, which keeps the deviation of $\phi_0$ from $E_f$.

Another important factor to change SB is an image potential. As an electron, in a metal, approaches to a semiconductor, this electron feels the attractive potential due to its positive image charge with respect to the interface, which results in a Coulomb-like potential. The electric field due to the image charge may be written as

$$E(x) = \frac{-e^2}{16\pi \varepsilon \varepsilon_0 x}$$

where $\varepsilon_0$ is the dielectric constant in vacuum and $\varepsilon_i$ is the dielectric constant of the interfacial layer. This distort the potential barrier, and lowers the SBH approximately (see figure 2.6(b)),

$$\Delta \phi = e^6 N_D (\phi_B - V_N - k_B T) / 8\pi^2 (\varepsilon S \varepsilon_0)^{3/4}$$

The SBH maxima also shifts a little bit toward a semiconductor from the interface [23] [24] by (see figure 2.6(b))

$$\Delta x = \frac{1}{4} (e^2 / [2\pi^2 \varepsilon S \varepsilon_0 N_D (\phi_B - V_N - k_B T)])^{1/4}$$

Other important factors, to change the SBH, are sample temperature, the surface of the clean and etc.,
2.3.2 Interface states

In an ideal case, the charge neutrality relationship is given by

\[ Q_{SC} + Q_m = 0 \]  \hspace{1cm} (2.16)

where \( Q_{SC} \) is the charge in a semiconductor, and \( Q_m \) is the charge in a metal. Some charges at a semiconductor surface are transferred to a metal so that the depletion region is generated in the semiconductor, which causes band bending. Goldstein [25] calculated the band bending by solving Poisson equation, which leads to

\[ Q_{sc} = \sqrt{2\epsilon_s\epsilon_0 N_d e_0 |V_s|} \]  \hspace{1cm} (2.17)

where \( e_0 V_s \) is the SBH.

The SBH is affected by the interface states, which was studied by Cowley and Sze [26] with two assumptions. First, the density of states of the interface states is a constant. Second, the interface states are continuum. The charge density in the interfaces then may be written as

\[ Q_{is} = -e_0 D_m [(W_{ci} - W_{0i}) - \phi_B] \]  \hspace{1cm} (2.18)

where the subscript i indicates interface properties. In equation 2.11, \( Q_m \) and \( Q_{is} \) exist at both sides of the interface, and these charges generate the dipole layer with thickness of less than 10 Å. The dipole energy barrier is given by

\[ \Delta = \phi_m - \chi_s - \phi_B \]  \hspace{1cm} (2.19)

(see figure 2.6).
Ideally, the layers are parallel, and have different sign. In order to calculate the charge density in metal, we need to use the Gauss law of electro-static mechanics. We then have that

$$Q_m = -\frac{\varepsilon_0 \varepsilon_i \Delta}{e \delta_i}$$  \hspace{1cm} (2.20)$$

where $\delta_i$ is the interface gap. Equation 2.20 then may be rewritten as

$$\Delta = -e \frac{Q_m}{\varepsilon_0 \varepsilon_i} \delta_i$$  \hspace{1cm} (2.21)$$

Combining equations 2.19, 2.20 and 2.21, we have [1]

$$\phi_m - \chi_s - \phi_B = -e \frac{\delta_i}{\varepsilon_0 \varepsilon_i} (-Q_{sc} - Q_{is})$$  \hspace{1cm} (2.22)$$

$$= \left[ \frac{2e^2 \varepsilon_s N \delta_i^2}{\varepsilon_i^2 \varepsilon_0} (\phi_B - W_n) \right]^{1/2} - \frac{e^2 D_{is} \delta_i}{\varepsilon_i \varepsilon_0} [(W_{ci} - W_{oi}) - \phi_n]$$  \hspace{1cm} (2.23)$$

Since the first term of the RHS of this equation is negligibly small, the SBH may be written as

$$\phi_B = S_\phi (\phi_m - \chi_s) + (1 - S_\phi) \phi_B$$  \hspace{1cm} (2.24)$$

where $S_\phi$ is the slope parameter expressed by $S_\phi = \frac{1}{1 + \frac{e^2 D_{is} \delta_i}{\varepsilon_i \varepsilon_0}}$. If the top of the metal conduction band overlaps the energy gap of the semiconductor, a continuum state is formed within the gap states.

Heine [21] pointed out that the metal wave function decays into the semiconductor’s forbidden region, and the tail of the wave function makes surface states where Bardeen suggested, which is called MIGS(Metal Induced Gap States). The MIGS are Bloch states that have a complex wave vector of a bulk semiconductor. The neutrality
relationship, equation 2.11, then leads to

\[ Q_m + Q_{MIGS} + Q_s = 0 \] (2.25)

Although Bardeen suggests the concept of surface states, his theory does not properly interpret experimental data. According to the data, a continuum of interface states is not able to determine the SBH.

The example in figure 2.7 shows a chemical trend. Although no model can account for this trend, the linear relation between the barrier heights of various gold-semiconductor contacts and their indirect band gaps, where the minimum energy of the conduction band is at a different value of momentum relative to the maximum value of the valence band, is observed, which implies the conduction band minima at the boundary of a 1st Brillouin zone is important to determine the SBH.

### 2.4 Two Dimensional Physics

As the noble metals, namely gold and silver, are absorbed onto Si(111), a thin metallic film may form 2-D metallic surface. Electrons in this surface can travel along x and y directions, and are confined in z direction. The conduction band of the metallic surface is located at the \( \Gamma \) point of the surface Brillouin zone, and its shape is parabolic (further discussion is in section 2.4). The energy of 2-D metallic surface is given by [27]

\[ E = E_0 + \frac{\hbar^2 (k_x^2 + k_y^2)}{2m^*} \] (2.26)
Figure 2.7: Barrier heights of gold-semiconductor contacts plotted against the width of the indirect band gap of the semiconductor [1]
where $m^*$ is the effective mass, and where $E_0$ is the ground state energy. The Bloch wave function is given by

$$\psi = e^{ik_xx + ik_yy} \cdot \phi(x, y) \cdot f(z)$$

(2.27)

where $f(z)$ is a confined wave function, and $\phi(x, y)$ is the propagating wave function. The energy levels along the $z$ direction are quantized due to confinement, and are dependent on the thickness of the film. Figure 2.8 shows the energy levels and the correspond density of states of a 2-D metallic surface.

The density of states of 2-D metallic surface, as shown in figure 2.8, are a constant. Two-dimensional electron density states per unit energy and unit area are given by

$$D(E) = 2g_n \frac{1}{(2\pi)^2} \frac{d\vec{k}}{dE}$$

(2.28)

where $g_n$ is a valley degeneracy factor and 2 is from spin degeneracy. The density of state then is

$$D(E) = \frac{g_n m}{\pi \hbar^2}, E > E_0$$

$$= 0, E < E_0$$

(2.29) (2.30)

This equation means that there is no density of state when $E$ is less than $E_0$, and it does not depend on the energy.

## 2.5 Low Energy Electron Diffraction

Davisson and Germer found electrons, whose energy is between 15 eV to 200 eV, reflected on a nickel sample made a diffraction pattern [28] in 1927. Low Energy
Figure 2.8: 2-D free electron system. The film thickness are around (a)/(b) 0.5 nm and (c)/(d) 10 nm. (a) and (c) show the wave functions. (b) and (d) density of states [2].
Electron Diffraction (LEED) becomes a main technique to check the surface structures. Incident electrons, which have well-defined energy, are diffracted at a sample which is grounded to conduct away electrons. The sample should have well-defined surface in order to observe a LEED pattern.

Diffraction from a three-Dimensional (3D) lattice are typically satisfied with the Laue conditions given by

$$a_1 \cdot \Delta k = 2\pi h$$  \hspace{1cm} (2.31)

$$a_2 \cdot \Delta k = 2\pi k$$  \hspace{1cm} (2.32)

and

$$a_3 \cdot \Delta k = 2\pi l$$  \hspace{1cm} (2.33)

These equations can be solved when it is as

$$\Delta k = 2\pi (ha_1^* + ka_2^* + la_3^*)$$  \hspace{1cm} (2.34)

Equation 2.34 may substitute into equations 2.31, 2.32 and 2.33 to verify. This means a LEED pattern is correspondent with the reciprocal lattice structure of a sample surface. A LEED pattern, therefore, provides two information: First, the pattern gives the information of the parallel and rotational sample alignment, i.e, the surface structures of a sample in the reciprocal space. Second, the intensity of the pattern may offer the correct atomic position by I-V.

LEED can qualitatively provide the spacing between atom to atom by measuring the spacing between the electron gun and the LEED spot (See figure 2.9). Braggs
law is given by

$$n\lambda = ds\sin\theta$$  \hspace{1cm} (2.35)

where \(n = 0, 1, 2, \ldots\), and \(d\) is the spacing between atoms. De Broglie wave is described by

$$\lambda = \frac{h}{mv} = \frac{h}{2meV_0}$$  \hspace{1cm} (2.36)

where \(m\) is the mass of an electron, and \(e\) is \(1.602 \times 10^{-19}\) C. Equation 2.36 may be rewritten as

$$\lambda = \frac{1.227}{\sqrt{V_0}}\text{ nm}$$  \hspace{1cm} (2.37)

From figure 2.9, \(\sin\theta\) is correspondent to \(\frac{x}{r}\). By inserting equation 2.37 and equation 2.36 into equation 2.35, the spacing \(d\) can be calculated numerically as

$$d = \frac{1.227}{\sqrt{V_0\left(\frac{x}{r}\right)}}\text{ nm}$$  \hspace{1cm} (2.38)

We used AEP 8011 model which has four grids. LEED consists of a gun, a screen, the Wehmect cylinder and retard meshes (figure 2.9). The filament of a gun is made of two percent thoriated tungsten wire. The thoriated tungsten lowers the Fermi energy level, which can produce an electron beam at lower temperature. The typical filament temperature to produce an electron beam is around 1000 °C. Electrons radiated at the gun are accelerated by applying voltage to them when they pass through the Wehmect cylinder. The accelerated electrons strike the sample, and are reflected at the sample surface. The typical current produced by the electron beam on the sample is on the order of micro-amps. Before the reflected electrons reach the phosphorescent screen applied by high voltage, they penetrate four grids (figure 2.9).
Figure 2.9: Schematic for LEED. Electrons are ejected from the filament, and accelerate through Wehmect cylinder. Electrons hit the sample, and are reflected. The meshes filter out the inelastic scattered electrons.
The first grid is grounded so that electrons travel along the linear trajectory in no-field space. The second grid is applied by voltage which lower than a bit incident energy to remove the electron beam whose energy is much lower than the incident energy, that is, it removes inelastically scattered electrons. The second grid is connected to the third grid to improve the electron selection property. The fourth grid is grounded again to isolate the phosphorescent screen from the potential due to second and third grids. LEED, typically, has two grid. The advantage of the the four grids LEED is that it gives more accurate energy selection, which can make a very sharp pattern.

High voltage is applied to the phosphorus screen, which is coated by phosphorescent material to make a bright point when electrons strike the specific spot on the screen, to accelerate the selected electrons. The screen also should be made of a metallic material, so that electrons conduct away.

2.6  Evaporation

There are three major sputter deposition methods, which are E-Beam evaporation, thermal evaporation and sputter deposition. These methods are referred to as Physical Vapor Deposition (PVD). In E-Beam system, electrons strike the material to be evaporated. Thermal evaporation uses a direct heat method to evaporate a material which is inserted into a filament. While a direct current flows through the filament, the material is evaporated. This is a useful tool for the material which has a low evaporating temperature. The sputter deposition uses a plasma discharge which strike a
sputtering target to eject atoms from the target. This method is proper way for the material which has high melting temperature.

### 2.6.1 Evaporation rate

The physical model of an evaporation was studied by Hertz and Knudsen [17]. By experiments, Hertz found the evaporation rate is proportional to the difference between the equilibrium pressure and the hydrostatic pressure which is acting on the evaporant source. This rate is given by

$$\Phi = \frac{\alpha_e N A (P_e - P_h)}{(2\pi MRT)^{1/2}}$$

where $\Phi$ is the evaporation flux in number of atoms or molecules per unit time, $A$ is the absorbed area, $\alpha_e$ the coefficient of evaporation, $P_e$ is the equilibrium pressure, and the $P_h$ is the hydrostatic pressure. The coefficient of evaporation can have a value from 0 to 1. In case the hydrostatic pressure is 0, the evaporation rate is maximum.

### 2.6.2 Growth modes

Figure 2.10(d) shows the surface free energy of a semiconductor, $F_s$, the free energy of the interface between the metal and the substrate, $F_i$, and the free energy of the metallic surface, $F_f$. Bauer [29] suggested the film growth mode is determined by the difference of these free energies.

If $F_f + F_i - F_s \leq 0$, the adatom will be bound to the substrate more strongly than to each other. Thus, the film by adatom extends over the substrate to minimize the
Figure 2.10: Three representative film growth modes. (a) Frank-Van der Merwe growth mode. (b) Stranski-Krastinov growth mode. (c) Volmer-Weber growth mode. (d) The free energies for the boundaries in M-S system.
total energy. On the other hand, if $F_f + F_i - F_s > 0$, the adatom will be bound to each other strongly more than to the surface of the substrate. Therefore, the adatom will form 3-D islands in order to minimize the total energy.

There are typically three different film growth modes (figure 2.10). First is the Frank-Van der Merwe mode [30]. If the substrate affinity to the deposited material is stronger, the nucleation density is high. Islands then grow around nuclei in a two-dimensional fashion until one monolayer is completed (figure 2.10(a)). If the substrate affinity to the deposited material is weaker, islands will grow three-dimensionally in order to minimize the interaction between the deposited material and the substrate. Second is three-dimensional island growth mode, which is referred to as Volmer-Weber growth mode [31]. Metal growth on a oxide layer usually occurs in this growth mode. Third, an intermediate mode, called Stranski-Krastanov mode [32], occurs when the substrate-particle affinity is initially strong. A lattice mismatch between a film and a substrate introduces a strain into the growing film. After a few mono-layers cover the substrate, the film growth reverts to three-dimensional island formation in order to minimize the strain energy.

### 2.6.3 Evaporator

The evaporator of our main system, which includes a STM unit, is home-made unit. The design of the evaporator is by a direct heating method. Currents, flowing the tungsten filament, conduct away to the body of the evaporator which is grounded. When the filament is heated, the energy is transferred to an evaporant source. If the
sample temperature is higher enough to remove atoms from the material, it will start to evaporate. In our experiments, silver and gold are main materials. Because the nobel materials have low melting point, direct heating method is good for evaporation. The evaporator used consists of two independent evaporators, which may evaporate two materials at the same time. The two evaporators are covered by a cylindrical plate not to pollute other instruments in the main chamber. The evaporation rate is monitored by Quartz Crystal Monitor.

It has a shutter to block the evaporated atoms from the evaporator. There is a rectangular aperture at the center of the shutter with size of 5 mm × 5 mm because the substrate is very close to the shutter. The size of the deposited materials on a sample thus will be very close to the aperture size. A quartz crystal is installed in the entrance of the cylindrical cover, and is fixed to the rotational feed-through.

This evaporator is built on the $2\frac{3}{4}$" flange, and contains rotational feed-through to control the shutter and the quartz crystal. The evaporator also has electrical feed-through for flowing a current through the filaments, and for getting the signal from the Quartz Crystal. Table 2.2 shows the important features of evaporant materials.

### 2.6.4 Quartz crystal

Quartz crystal has a piezoelectricity property. A ceramic material has this piezoelectricity that can generate voltage(electrically charged) as mechanical stress is applied to the ceramic. Reversibly, when voltage is applied to a crystal, the quartz crystal will be stressed. Using this property, the evaporation rate can be measured.
<table>
<thead>
<tr>
<th>Name</th>
<th>Atomic number</th>
<th>Melting point (K)</th>
<th>Boiling Point (K)</th>
<th>Heat of vaporization (kJ mol⁻¹)</th>
<th>Heat capacity (J·mol⁻¹·K⁻¹(25))</th>
</tr>
</thead>
<tbody>
<tr>
<td>silver(Ag)</td>
<td>47</td>
<td>1,234.93</td>
<td>2,435</td>
<td>258</td>
<td>25.350</td>
</tr>
<tr>
<td>Gold</td>
<td>79</td>
<td>1,337.33</td>
<td>3,129</td>
<td>324</td>
<td>25.418</td>
</tr>
<tr>
<td>Titanium</td>
<td>22</td>
<td>1941</td>
<td>3,560</td>
<td>425</td>
<td>25.060</td>
</tr>
<tr>
<td>Indium</td>
<td>49</td>
<td>429.75</td>
<td>2,345</td>
<td>231.8</td>
<td>26.74</td>
</tr>
</tbody>
</table>

Table 2.2: Some features of elements

When a material is absorbed onto the quartz crystal, the resonance frequency of the quartz crystal is changed. The amount of the change depends on the properties of the material. The resonance frequency turns into electric signal by electrical circuit. The evaporation rate can be calculated by the change of resonance frequency.

### 2.7 Software

Omicron STM has its own software to control the STM unit and to record data. Since its original file input-output system is an old fashion, it is hard to transfer the data to another system. For that reason, new software has been programmed with Labview 7.1. Most of instruments, which are used for my experiments, have a GPIB port to communicate with the computer that has GPIB controller. These Instruments can be controlled by the software programmed by Labview 7.1, fifth generation graphical language by National Instruments Corp.
The taken data are analyzed by softwares such as Mathematica and Matlab. Especially Mathematica is very useful tool for fitting a plot.

Other softwares used are the Pspice 9.1, which is a circuit simulation software, by Orcad. Before setup the op-amps near the STM tip, the simulation were performed for determining what kind of op-amp fits best for our system. Even if the simulated data do not match perfectly with real data, it practically gives reasonable results.
Chapter 3

Characteristics of Current-Voltage Curves using Two Point Tunneling Probe

As discussed in chapter 1, the main current path of FPP system is the bulk crystal region, which generates an measurement error. Besides, it has some intrinsic problems. First, the macroscopic probe system, with probe spacing in the millimeter order, affects the sheet conductance because electrons scatter to the steps and the defects on the surface (see chapter 5). Because the number of scattering event is dependent on the the probe spacing, a microscopic probe system has been exploited in several ways. FPP also may generate the thermal drift electron, which leads voltage drop between two probes. This thermal effect depends on the geometry and the probe spacing. Second, while the metal probe touches a semiconductor sample, the probe and the semiconductor form a metal-semiconductor junction, which gives non linear effects. Third, the geometry of the probe at the contact point is not well defined. Last, the probe may damage the sample surface when it touches the surface. Non contact technique can be a solution for resolving these problems.
We suggest a new technique based on non contact in order for a current to flow only through the metallic surface, and resolve the above problems. Non contact plays an important role in the measurement of the surface conductance. In this chapter, the principle of the technique, Two Point Tunneling Probe (TP), and the electron transport mechanism in the M-S system are discussed in detail.

3.1 Basic configuration of Two Point Tunneling Probe

TP consists of two electrodes, which are the STM tip and the fixed grounded electrode (figure 3.1(a)). The STM tip maintains a gap, during measurement, in order for the electric field at the tip to be screened by the metallic surface. The latter is a Au-coated tungsten wire which touches the surface of the specimen. This electronic setup applies bias voltage between the tip and the electrode, but the substrate is floated (see section 3.6).

I-V curves obtained by TP may be divided into three regions which are Ohmic, tunneling dominant and non-linear region. The behavior of the curves in each region is determined by different transport mechanisms. We emphasize again all of these characteristics come from the non-contact design (figure 3.1).

Figure 3.1(b) displays the equivalent electric circuit diagram for TP, which contains five resistors. A metal-semiconductor system consists of three channels and we may consider these channels as three independent resistors connected in parallel, which are surface resistor $R_S$, depletion resistor $R_D$, and bulk resistor $R_B$. The vacuum gap between the tip and the metallic surface is correspondent to a variable
Figure 3.1: (a) TP configuration consisting of the tip which grounds the surface and adjustable tunneling gap coupled to a wire clip (b) Equivalent circuit diagram.
resistor $R_T$, where the resistance is a function of bias voltage and the tip spacing (see section 3.4). The vacuum barrier height for a clean metal surface is about 4 eV above the Fermi energy. Since the tunneling current is increased, as the vacuum gap is decreased or the electron energy is increased, the tunneling resistance could be negligible when the vacuum gap is very small, compared with the metallic surface resistance. Contact resistance $R_C$ is generated when the electrode touches an ultra-thin metal-semiconductor system.

Because M-S system has an asymmetrical property, the different current direction, which depends on the sign of bias voltage, gives different transport phenomena. One is Ohmic transport at negative bias voltage, and the other is ballistic (non-linear) one at positive bias voltage. Whichever the current direction is chosen, electrons undergo tunneling process across vacuum gap. Thus I-V curve can be divided into three region, the Ohmic region (I), the tunneling dominant region (II) and the non-linear region (III) (figure 3.3). The electron transports for three regions are discussed below in the rest sections of this chapter.

### 3.2 Typical STM and Two Point Tunneling Probe

TP is made of modifying a typical STM unit. The original sample holder has two clamps touching the front and back side of a sample surface. These clamps are to hold a sample to the sample holder. The electrode is connected to the back of the sample holder, where it is also connected directly to the sample surfaces (figure 3.2(a)). In this design, since currents flow through via several trajectories (arrows in figure 3.2(a)),
it is very hard to control current paths.

We put the four ceramics between the sample and the clamps to isolate the sample from the sample holder, that is, the sample is floated. And then, the electrode is moved from the back of the sample holder to the sample surface to make sure that a current flow only between two probes (figure 3.2(b)).

3.3 Ohmic transport

TP permits measuring the surface conductance. At negative bias voltage, electrons are injected via the electrode, and move towards the tip (region I in figure 3.3). The metallized surface screens the electric field so that no electric field penetrate the metallic surface, which means there is no electric field in silicon. Since an electron moves along the electric field, and there is no electric filed in silicon at negative bias, the electron would move only through the metallic surface. Furthermore, because the resistance of the surface channel is much lower than that of silicon channel, and there is contact resistance at the contact, most of charge carrier selects the metallic surface channel. The I-V curves in negative bias voltage region then will be linear (region I in figure 3.3, i.e Ohmic). The slope of the I-V curve, in this linear region, gives directly the conductance of a metallic surface.

The electrical conductivity of a thin metallic surface is affected by impurities, collisions with phonons, and defects in a metal, where electrons undergo scattering with these defects. However, when a current flows through an ultra-thin metallic film, electrons also suffer from the scattering at both boundaries(figure 3.4). Considering
Figure 3.2: STM structure for (a) imaging (b) surface conductance. The electrode is connected at both sides of the sample in (a). In contrast, it touches front side only in (b)
Figure 3.3: A typical I-V characteristics for TP. It can be divided into three regions, Ohmic, tunneling dominant and non linear region. Below diagram shows the current paths for each case.
the scattering at boundaries is important to get the exact surface resistivity of an ultra thin film. As the film thickness increases, the scattering at the thin film surface is decreased, and its conductivity is close to that of three-dimensional metal. If the film thickness is of the order of MFP of an electron, the resistivity will be greater than that of a 3-D metal (see chapter 5).

3.4 Tunneling

Whichever the sign of bias voltage is applied, electrons undergo the tunneling process across the vacuum barrier. The tunneling process is negligible at high bias voltage because the tunneling resistance is much smaller than the metallic surface resistance or the silicon bulk resistance (equation 3.2). The tunneling process however is dominant in the low voltage region (shaded region in figure 3.3) because its resistance is higher.

**Figure 3.4:** Electron scattering at the boundaries
than the surface resistance. The tunneling current may be expressed by

\[
I = \frac{4\pi e}{\eta} \int_{0}^{eV} \rho_s(E_F - eV + \varepsilon) |M|^2 \rho_t(E_F + \varepsilon) d\varepsilon
\]  

(3.1)

where \(\rho_s\) is the local density of the sample, \(\rho_t\) is the local density of the tip, and \(M\) is the tunneling matrix element. If the shape of a potential barrier is non-square and it is not a constant, the Wentzel-Kramers-Brillouin (WKB) method should be used.

The transition probability is given by

\[
T(E) \propto \exp\left[-\frac{2}{\eta} \int_{0}^{S} \sqrt{2m\phi(z)} - Edz\right]
\]  

(3.2)

The tunneling current, which is dependent on the barrier geometry, is expressed by

\[
I \propto \exp\left[-\frac{2d\sqrt{2m}}{\phi - E \eta}\right]
\]  

(3.3)

where \(m\) is the electron mass, \(d\) is the width of the barrier, and \(\phi\) is the barrier height. Equation 3.3 does not take into account the image potential and the tilt of the potential barrier due to the work-function difference between the tip and the sample. The tilt of a barrier is negligibly small, but it is not small at high bias voltage. If the tip is closer, the force between real and image charges become stronger.

The vacuum barrier height (VBH) can be measured by TP as STS is capable of doing. VBH is determined not only the work-functions of the tip and the sample but the tip position. The closer the tip is, the lower the VBH is (see figure 3.5).

Figure 3.5 shows that the I-V curve exponentially increases, and it starts showing the linear behavior at specific bias voltage in the negative bias region. By measuring the
tunneling current, the vacuum barrier width and the barrier height can be determined by equation 3.3.

Figure 3.5(a) shows the fitting of the I-V curves to get the fit parameter, the vacuum barrier height. The fitting was achieved by Mathematica with the fitting function

\[ I \propto \exp\left[\frac{2d\sqrt{2m(\phi - E)}}{\hbar}\right] \]  

where \( d \) is the tip spacing, \( \phi \) is the work function of the metal surface, and \( E \) is the electron energy. Equation 3.4 offers the relationship between the tip spacing and the vacuum barrier height. Figure 3.5(b) shows clearly the VBH is proportional to tip spacing.

3.5 Ballistic transport

As discussed in sections 3.3 and 3.6, I-V curves in negative bias voltage region show Ohmic behavior. I-V characteristics in positive bias voltage region show non-linear behavior due to ballistic electron transport (region III in figure 3.3). By applying positive bias voltage, electrons tunnel across the vacuum gap between the tip and the electrode as hot electrons. Since hot electrons may cross over SB, they provide a component conductance in the subsurface depletion region and/or bulk silicon. Injected electrons pick up increasing forward momentum with increasing voltage, and penetrate through the surface into the space-charge region, which is depleted of carriers. However, some of hot electrons move along the metallic surface because
Figure 3.5: (a) Fitting the I-V curve (b) Vacuum barrier height vs tip spacings, varying film thickness.
these electrons do not have enough energy to cross SB due to scattering inelastically in metallic film. Therefore, region III in figure 3.3, the I-V curve offers the information of the conductance of a metallic surface and silicon (figure 3.1(b)).

The direction and amount of current in an electronic circuit at specific voltage are determined by the distribution and the magnitude of the resistors in the circuit, that is, a circuit follows Ohm’s law. However, when electrons are injected ballistically into a metal-semiconductor system, currents do not follow Ohm’s law because the electric field between the tip and the metallic surface force electrons to inject into M-S system. The current thus may flow through the bulk silicon more than the metal film, although the resistance of metal film is much lower than that of silicon.

The I-V curve now exhibits increasing non-linear behavior. If a film is thicker than MFP of an electron in the metal, since the electron is not able to penetrate the metallic surface, the most current will move through the metallic surface, whichever the sign of bias voltage is applied. The I-V curves for such a thick film, therefore, have y-axis symmetry, as shown in figure 4.12. We carried out experiments to obtain an I-V curve for a titanium metal at room temperature in air. The I-V curve (figure 3.6) shows the y-axis symmetry, as expected.

The STM tip was used as a hot electron injector. Electrons are injected from the STM tip to a metal-semiconductor system. In this case, charge carriers may undergo four stages: First, currents tunnel across vacuum gap from the tip to the metallic film. Second, once electrons reach the metal, they can be either elastically or scattered inelastically while penetrating in the metal. In inelastic scattering case,
Figure 3.6: I-V curve for a titanium metal in air. It has the y-axis symmetry
some of the energy of incident electrons are transferred to other electrons in a metal. Inelastic scattering may generate a secondary electron which also may cross over the SB, if the energy of the secondary electron is higher than the barrier. In case of elastic scattering in the metal, the energy of incident electrons is conserved, but their momentum is changed. Third stage is the reflection at the interface. Last, after crossing the interface, electrons can generate impact ionization, exciting electron-hole pair. Undergoing these process, electrons will face to the electrode which is touching the metallic surface.

3.5.1 Free electron model

The behavior of valence electrons, in the most outer shell of an atom, can be explained by the free electron model, where the electron is free from its ion. The Drude model, a free electron model, is expressed by

\[ \sigma = ne\mu \]  \hspace{1cm} (3.5)

where \( \sigma \) is the conductivity in a three-dimensional system or it become the sheet resistance in a two-dimensional system, \( n \) is a carrier concentration, \( e \) is the magnitude of an electric charge, and \( \mu \) is the carrier mobility which is called the average drift velocity.

An equation can be set using Newton’s second law in the presence of the electric
field. We have that

\[ F = m^* a = eE \]  

\[ = m^* \frac{dv}{dt} = eE \]  

where \( E \) is the electric field, \( m^* \) is the effective mass of an electron in a semiconductor, and \( v \) is the velocity of an electron due to the electric field. By assuming the electric field and the effective mass are a constant, and the initial velocity of an electron is zero, the velocity of an electron then may be written as

\[ v = \frac{etE}{m^*} \]  

Electrons undergo collisions in this system, and move along the electric field. This is called the net drift velocity.

### 3.5.2 Tunneling from the tip to the metallic metal

The first stage of the electron transport through a metal-semiconductor junction is the tunneling process which occurs at the vacuum gap between the tip to and the metal. Although it depends on the geometry of the tip and the sample, it is possible to understand this phenomenon approximately by simplifying the situation.

If the STM tip has nearly planar, planar tunneling theory can be applied \[33\] by Wentzel-Kramers-Brillouin(WKB) methods. This can be solved by Schrödinger equation for one dimensional potential barrier, and is given by approximately

\[ I_T \propto e^{-2kd} \]  

(3.9)
where \( d \) is the vacuum gap, and \( k = \sqrt{W - (2E - k_\text{F}^2)} \) (\( W \) is the work function of a metal, and \( E \) is an electron energy). The tunneling current shows exponential behavior.

### 3.5.3 Transport through the thin metal film

In a metal, electrons could scatter from electrons, phonon and impurities. Inelastic scattering causes the energy loss of electrons, and may generate secondary electrons. In contrast, elastic scattering give a more isotropic angular distribution at the interface without losing its energy.

In case of phonon scattering event, the energy of phonon is just a few meV. We thus can consider it as a quasi-elastic scattering. This scattering causes the emission or the absorption of acoustic phonons. If a metal has more than one electron per primitive cell, the energy of the emission and the absorption of optical phonons can be over 50 meV. If the energy is 10 eV above the Fermi level, the major process is electron-electron scattering, and electrons will lose half of its energy [34]. By assuming the density of state of the electron is a constant, the final state of an electron will be proportional to electron energy \( E \). During e-e scattering, secondary electron may be generated, and the number of secondary electrons is dependent on the energy loss of an electron. The distribution of secondary electrons, whose energy should be below \( eV_T \) [35], follows the square law, and is given by

\[
D(E) = (eV_T - E)^2
\]

(3.10)
The total scattering probability is proportional to $E^2$. Crowell [36] has calculated the inelastic mean-free path.

$$\lambda_i \propto \frac{(E - E_0)}{E^2} \quad (3.11)$$

Thus the attenuation could be expressed as

$$\exp[-d/\lambda(E)] \equiv \exp[-\eta E^2/(E - E_0)], \quad (3.12)$$

where $\eta$ is the strength of inelastic scattering, which is proportional to the film thickness. The mean free path in equation 3.12 may be rewritten as

$$\lambda(E) = \frac{d(E - E_0)}{\eta E^2} \quad (3.13)$$

Electrons also may have elastic scattering events by imperfections, which makes the momentum distribution broaden.

There are two limited circumstances. First, if the inelastic mean free path $\lambda_i$ is comparable to the elastic mean free path, $\lambda_e$, electrons will suffer from multiple scattering events, and lose their energy such that they are not able to cross over the Schottky barrier. Second, if $\lambda_e \ll \lambda_i$, it will undergo the multiple elastic scattering before inelastic scattering occurs, which means the transport is diffusive. The initial momentum distribution in the metal is independent of the momentum distribution at the interface.

3.5.4 Transmission at the M-S interface

When the energy of incident electrons is less than the SBH, they are scattered back into the metal. In case the electron energy is higher than the SBH, quantum mechan-
ical reflection occurs. The other one, to be considered, is whether the metal grows up epitaxially. If it is a epitaxial system, the transverse momentum is conserved. By assuming the density of state of a metal and the STM tip are a constant and the electron distribution is an isotropic cone toward the surface of the metal film, the critical angle may be expressed by

\[
\sin^2(\theta_{\text{crit}}) = \frac{m^* eV - eV_b}{m_0 eV + E_f}
\]

(3.14)

where \(eV_b\) is the Schottky barrier height, \(E_f\) is the Fermi level, \(m^*\) is the effective mass of an electron in a semiconductor, and \(m\) is the electron mass. Only electrons, where an incident angle is less than the critical angle, can cross the interface.

### 3.5.5 Transport in the semiconductor

After crossing the interface of a M-S system, electrons undergo several processes, which are scattering with phonons, impact-ionization and back scattering into metal. Among these events, the impact ionization is prominent. When the energy of incident electrons is sufficiently high, higher than the gap energy of a semiconductor, the impact ionization may be occurred: electron-hole pairs can be generated. These electron-hole pairs can be separated by the electric field due to the depletion region. The impact ionization rate, then, is given by [37].

\[
\frac{1}{\tau_I} \propto (E - E_F - V_0 - E_{\text{th}})^2
\]

(3.15)

where \(E_{\text{th}}\) is the ionization threshold energy which is of the order of the energy gap of a semiconductor. The MFP of impact ionization can be deduced by multiplying
the impact ionization by the electron velocity.

\[ \lambda_I = v \cdot \tau_I \quad (3.16) \]

Since \( v \propto \sqrt{E - E_F - V_0} \) [38], the MFP of impact ionization may be rewritten as

\[ \lambda_I = \lambda_I^0 \frac{\sqrt{E - E_F - V_0}}{E - E_F - V_0 - E_{th}^2} \quad (3.17) \]

The probability for excitation of a secondary electron is given by [38]

\[ P_I = 1 - \exp \left[ -\frac{W}{\lambda_I(E)} \right] \quad (3.18) \]

\[ = 1 - \exp \left[ -\frac{W}{\lambda_I^0} \frac{E - E_F - V_0 - E_{th}^2}{\sqrt{E - E_F - V_0}} \right] \quad (3.19) \]

where the optical-phonon scattering and the electric field due to the depletion region are neglected, \( W \) is a width of the depletion region, and \( S_I = \frac{\lambda_I}{\lambda_I^0} \) is a fit parameter.

By assuming a free-electron-like semiconductor, and the conservation of momentum is taken into account, the threshold \( E_{th} = \frac{3}{2} E_G \) [39], where \( E_G \) is the band gap of a semiconductor. If the real band structure is considered, the threshold energy is lower than \( 3/2 E_G \) [40].

### 3.6 Energy diagram for electron transport in Two Point Tunneling Probe

In TP system, the silicon substrate is floated, so that the whole M-S system has the same Fermi level. We may describe the energy diagram for electron transport of TP as shown in figure 3.7. There are two metal films at both sides, which are connected each other because they actually are the same metallic surface. When the system is
applied by positive bias voltage, the Fermi level of the STM tip will be higher than that of the M-S system. Currents, then, flow from the tip to the electrode, and suffer from five different current sources, as discussed above subsections (figure 3.7(a)).

In contrast, by applying negative bias voltage, currents flow from the electrode to the STM tip (the solid line in figure 3.7(b)). In this case, most of currents flow along the metallic surface, because the Fermi level of the M-S system is not affected by bias voltage, it is a constant throughout the M-S system. However, since the Fermi level of the metallic surface is higher than that of the STM tip, currents flow through the metallic surface to the STM tip (the solid line in figure 3.7(b)). This is a very important characteristic in that it provides a method to measure the surface resistivity.

From the energy diagram (figure 3.7), we have three conclusions: (a) I-V curves will be affected by the Schottky barrier in the region where bias voltage is less than the SBH, but we can neglect this Schottky barrier effect out of this region. (b) an electron suffers from the Schottky barrier only if the positive bias voltage is applied. In the negative bias region, currents flow only through the metallic surface. (c) we thus can see the SB effect in the positive bias region because currents crosses the SB (see section 4.4).
Figure 3.7: (a) At positive bias voltage, free electrons undergo various scatterings passing through the M-S system. There are five current sources (b) At negative bias voltage, most of electrons flow through the metallic surface.
Chapter 4

Sheet Conductance of Thin Metallic Film

Experiments were carried out using TP to investigate the characteristics of well-established metallic surfaces, Si(111) $7 \times 7$, Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag, and silver layers on reconstructed surfaces. From taken data, we show that the sheet conductance increases linearly as the film thickness increases, and is sensitive to semiconductor interfaces.

4.1 Two Dimensional metallic surfaces

The surface states of a ultra-thin metallized surface on a semiconductor are the equivalent of two-dimensional gas, and the electron density of a 2-D gas is proportional to Fermi wave vector.

The relationship between the shape of Fermi surface and the band dispersion determines the property of a 2-D metallic surface. Since $k_F \propto \sqrt{n}$, where $n$ is electron density in 2-D system, the electron density of the metallized silicon surface can be tunable. Table 4.1 shows the information of 2-D metallic surfaces [41], and figure 4.1 shows 2-D Fermi surfaces for several 2-D metallic surfaces.
<table>
<thead>
<tr>
<th>Surfaces</th>
<th>Fermi wave vector $k_F$ (Å$^{-1}$)</th>
<th>Electron density $n_{2D}$ (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Si(111)7 \times 7$</td>
<td>0.01</td>
<td>$1.5 \times 10^{11}$</td>
</tr>
<tr>
<td>$Si(111)\sqrt{3} \times \sqrt{3} - Ag$</td>
<td>0.08</td>
<td>$1 \times 10^{13}$</td>
</tr>
<tr>
<td>$Si(111)\sqrt{3} \times \sqrt{3} - Au$</td>
<td>.15</td>
<td></td>
</tr>
<tr>
<td>$Si(111)\sqrt{21} \times \sqrt{21} - (Ag + Au)$</td>
<td>.26</td>
<td>$4 \times 10^{14}$</td>
</tr>
<tr>
<td>$Si(111)\sqrt{7} \times \sqrt{3} - In$</td>
<td>1.5</td>
<td>$3.6 \times 10^{15}$</td>
</tr>
</tbody>
</table>

**Table 4.1: 2D metallic surface**

We designed to measure the conductance of the ultra-thin epitaxial Ag-films as a function of thickness (1-10 monolayers) for both reconstructed surfaces. 99.999 % -Ag was evaporated from the heated W-filament, and monitored by QCM. The deposition rate of silver onto the silicon substrate was 1 ML per minute. All experiments were performed at room temperature.

We have used TP to first reproduce earlier results for reconstructed Si(111) 7 $\times$ 7 and Ag on the surface. The 7 $\times$ 7 silicon surface has the low density of dangling bond surface states ($n \leq 10^9$cm$^{-2}$ compared with Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag surface $n \sim 10^{13}$cm$^{-2}$ [41]). This is reflected in a difference in the surface differential sheet-resistance of two orders of magnitude, 30 k$\Omega$ falling to 0.3 k$\Omega$ [11, 12].
Figure 4.1: Fermi surfaces for several 2D metallic systems
4.1.1 Si(111) 7 × 7

Each atom of silicon bulk crystal forms four covalent bonds, which are broken at the surface and form dangling bonds. The great number of dangling bonds produce higher surface free energy. In order to change the surface structure, it is needed to transfer energy to the substrate. Si(111) 7 × 7, which was discovered in 1959 [42], is a famous example. This surface has twelve maxima arising twelve adatoms in a unit cell [43]. Takayanagi et al. [44] suggested the dimer-adatom-stacking-fault (DAS) model which is now widely accepted. According to this model, Si(111) 7 × 7 consists of sub-surface dimers, twelve adatoms and a stacking fault in half of a unit cell.

There are some surface bands in this reconstructed surface (see figure 4.2(a)). Among these bands, the $S_1$ band is a little below of the Fermi energy level, and is nearly flat, which means the effective mass is very large, that is, the group velocity is very small. Therefore Si(111) 7 × 7 surface has a poor metallic surface.

The Si(111) 7 × 7 surface was reconstructed on a n-type Si(111) wafer, 10 Ωcm, by passing a direct current through the crystal. Typically, the crystal was heated to 1250 °C for 10 seconds followed by annealing at 860 °C to expand the size of Si(111) 7 × 7 domains. The temperature was then reduced slowly to room temperature over 2 minutes.
Figure 4.2: (a) Si(111) 7 × 7 band diagram [2] (b) Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag band diagram [3]. Both diagram obtained by angle-resolved photoemission spectroscopy
4.1.2 Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag or Au

The structure of Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag and Si(111) $\sqrt{3} \times \sqrt{3}$ - Au is the same. The difference between them is the electronic density. The recipe for Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag and Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag are also the same. The $\sqrt{3} \times \sqrt{3}$-Ag surface can be formed by evaporating 1 monolayer (ML) ($7.8 \times 10^{14}$ atoms/cm$^2$) of Ag onto the Si(111) $7 \times 7$ surface and baking the surface at 500 °C for 1 minute.

The $\sqrt{3} \times \sqrt{3}$ structure is less stable than the Si(111) $7 \times 7$ structure at high temperature. However it keeps its clean surface for a long time at room temperature under UHV condition. Inserting the silver slug in the tungsten filament of the evaporator, the filament is heated for evaporating silver (see section 2.6). The rate of evaporation is 1 ML per a minute, which is monitored by QCM.

Many groups have been researching to model the Si(111) $\sqrt{3} \times \sqrt{3}$ surface structure. Takahashi in 1988 suggested Honeycomb chain Trimer model [4] (figure 4.3 which is widely accepted.

During annealing of Si(111), the adatoms of the Si(111) $7 \times 7$ are removed, and silicon atoms form the trimer structure. The atoms forming trimer structure have the covalent bond, which splits into anti-bonding and bonding, with silver atoms. Theoretically, the anti-bonding will become the surface conduction band which is denoted by $S_1$, and would overlap with the bulk conduction band. On the other hand, the bonding will become the surface valence band which is denoted by $S_2, S_3$, and would overlap with the bulk valence band. It was revealed, by angle-resolved ultraviolet
Figure 4.3: HCT model for Si(111) $\sqrt{3} \times \sqrt{3}$ system (a) top view (c) side view of Honeycomb chain Trimer (HCT) model [4] (b) is the structure of Si(111)- $7 \times 7$
photoelectron spectroscopy experiments, that the surface conduction band is below the Fermi level, and overlap with the bulk valence band. The surface conduction band is around $\Gamma$ and narrow (see figure 4.2(b)). The shape of $S_1$ is a parabolic, and extend over the bulk conduction band, which means the Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag has a good metallic surface. The electron density of the Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag is about 100 times higher than that of the Si(111) 7 × 7. Excess electrons are transferred to the this 2-D surface band, and it makes Si(111)- $\sqrt{3} \times \sqrt{3}$ a very good conductor.

4.1.3 Si(111) $\sqrt{21} \times \sqrt{21}$-(Ag+Au)

The mixed the Si(111) $\sqrt{21} \times \sqrt{21}$-(Ag+Au) surface is obtained by depositing 0.2 MLs Au at room temperature onto the Si(111) $\sqrt{3} \times \sqrt{3}$-Ag surface. This structure has a much larger Fermi surface due to extra electrons which come from deposited Au.

4.1.4 Si(111) $\sqrt{7} \times \sqrt{3}$ -In

Si(111) $\sqrt{7} \times \sqrt{3}$ - In was discovered by Rotenberg et al. [45]. This surface is a nearly free electron metal in two-dimensions. We can make this surface by depositing indium onto the Si(111) 7 × 7 followed by annealing to 500 - 600 K to remove the excess indium. The contributions of the 2-D metal of Si(111) $\sqrt{7} \times \sqrt{3}$ - In are from silicon dangling bonds as well as indium atoms. As discussed in section 4.1, since this metallic surface has very high electron density, we can consider this as a nearly free electron.
4.2 LEED patterns

Reconstructed surface structures are checked by LEED before the sample is transferred to the sample holder in the STM unit. The sharpness of LEED patterns depend on the cleaning method of the sample and surface status. For example, in case of Si(111) $7 \times 7$, after flashing at 1250 °C, the Si(111) is annealed at 860 °C to increase the size of Si(111) $7 \times 7$ domains. Then, the LEED pattern for Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag become very clear when it is baked at 500 °C for more than 10 minutes. The LEED patterns of other surfaces [46] were also observed.

Figure 4.4 (a) shows a Si(111) $7 \times 7$ pattern (see section 4.1.1), and figure 4.4 (b) shows a Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag pattern (see section 4.1.2).

4.3 I-V measurements on Si(111)$7 \times 7$ and Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag by Two Point Tunneling Probe

Using TP, first, experiments were performed on the Si(111)$7 \times 7$ and the Si(111) $\sqrt{3} \times \sqrt{3}$-Ag reconstructed surfaces which are well studied. The reasons, we chose these surfaces, are that they are well established surfaces, and the conductance difference between two surfaces is very large.

Since the surface conductance of the Si(111) $\sqrt{3} \times \sqrt{3}$-Ag is much greater than that of the Si(111) $7 \times 7$, the electron transport on the surfaces shows different behavior. In case of the Si(111) $7 \times 7$, because it has a very small surface conductivity, the metallized surface is not able to screen the electric field, which results in the field
Figure 4.4: Leed Patterns for (a) Si(111) $7 \times 7$ (b) Si(111) $\sqrt{3} \times \sqrt{3}$
penetration into the silicon bulk. Most of carriers thus flows through the bulk silicon channel, applied by whichever sign of bias voltage (figure 4.5(a) and (c)).

In contrast, the Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag metallized surface screens the electric field at the surface, and prevents field penetration into the silicon at negative bias voltage, so that there is no electric field in silicon (figure 4.5(b)), resulting in no current in the bulk silicon (section 3.3). Increasing tip spacing causes less tunneling current (1 nA decreasing to 0.1 nA), which is reflected in the I-V curves in Ohmic region being displaced but remaining parallel and linear (i.e. Ohmic). We can directly obtain the conductance of the surface by taking the slope in the Ohmic region.

When positive bias voltage is applied, electrons are injected into the silicon substrate ballistically (figure 4.5(d)). In this case, although the resistance of the bulk silicon is much larger than that of the metallic surface, most of currents may flow the bulk channel because of their ballistic behavior.

The I-V curves in figure 4.6(b) were obtained with varying tunneling-gap spacings. Although the shape of the I-V curves look similar with the I-V spectroscopy of a typical STM system [47], I-V curves, obtained by a typical STS, are not able to offer the surface conductance because current paths are not well defined.

It is not possible to get the sheet resistance of the Si(111) $7 \times 7$ surface using TP because it has a poor metallic surface, which is not able to screen the electric field at the tip. In order to measure the surface conductance of the Si(111) $7 \times 7$ surface, we used the method performed by Hasegawa et al., taking the slope of the I-V curves [7] by a typical STS. They claimed charge carriers would flow through the
Figure 4.5: Current diagram at negative bias voltage for (a) Si(111) 7 × 7 surface, which is not able to screen the electric field at the tip, (b) Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag, which can screen the electric field because the metallic surface has high conductivity, and at positive bias voltage for (c) Si(111) 7 × 7 (d) Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag
Figure 4.6: I-V curves of silver deposited metal surface. (a) and (c) are for the Si(111) 7 × 7. (b) is for the Si(111) $\sqrt{3} \times \sqrt{3}$-Ag. Since Si(111) $\sqrt{3} \times \sqrt{3}$-Ag has high conductivity, the linearity is observed at negative bias voltage region. In contrast, Si(111) 7 × 7 has the poor metallic surface, so it is not able to screen the electric field between the tip and the sample. This makes electrons move into the sample.
surface at zero voltage. Using this method, the conductance on Si(111) 7 × 7 surface, they obtained, is $10^{-6} \, \Omega^{-1}$ which does not match with the published data by Heike et al. [8]. Heike et al. designed a kind of Scanning Tunneling Potentiometer to measure the sheet resistance on the Si(111) 7 × 7 surface. The sheet resistance they earned is approximately $3.5 \times 10^{-9} \, \Omega^{-1}$. They suggests that the discrepancy between their data and Hasegawa’s data is due to currents flowing through the space charge layer and bulk silicon as well as the metallized surface in Hasegawa experiments.

In our experiment, the conductance around zero voltage does not depend on, and is approximately $3.0 \times 10^{-9} \, \Omega^{-1}$, which is in good agreement with the value Heike has obtained [8], because TP is an effective device to flow currents through the metallic surface.

### 4.4 Schottky barrier of Si(111) 7 × 7 and $\sqrt{3} \times \sqrt{3}$ - Ag

In order to see the SB in I-V curves, we need to apply positive bias voltage, as discussed in section 3.6. Since the Si(111) 7 × 7 has a poor metallic surface (see section 4.1.1), it is very hard to observe the Schottky barrier. However, as the tip approaches to the surface, the SB shows up clearly at around 0.7 volts because the SB can be induced not by the Si(111) 7 × 7 metallic surface but by the STM tip. Figure 4.8 displays how I-V curves change, while the tip spacing is decreased from 9 Å to 1 Å. When the tip is closer than 5 Å, the curves start turning down (arrow at positive bias voltage region in figure), which shows the SB. This SB thus is from the M-S system, which is formed by the STM tip and the metallic surface.
Figure 4.7: I-V curves for $\sqrt{3} \times \sqrt{3}$ of changing the polarity of the probes
The Schokky barrier is found around 0.7 eV, which is close to the known experimental value, 0.67 eV for tungsten-silicon system.

If a metallic surface has high conductance, when carriers move through the metal, they may not have enough energy to cross over the SB due to inelastic scattering, where the carrier flows through the metallic surface. Hence, there are two current sources: first source is a current via the metallic surface (Ohmic behavior), and second one is a current via the bulk silicon after crossing the SB (non-linear behavior). Since the collected current, at the electron which touches the surface, contains these two different sources, and the amount of each current is comparable, the Schottky barrier is not clearly shown up in the I-V curves for $\sqrt{3} \times \sqrt{3} - \text{Ag}$.

### 4.5 Two dimensional resistance

The analytical solution for the resistance of a 2-D metallic surface researched by Mahan [48]. I describe, in this section, how he derives it. Conformal transformation is used for the solution. A mapping described in [49] is first used.

Figure 4.9(c) is a diagram in z space, which shows the geometry of two probe separated by $L = (x_1 + x_2)/2$. The point (A, B, ..., F) in z-space is correspondent with the map points (A', B', ..., F'). The big circle has a unit circle, and the small one can be expressed by $(x_1 - x_2)/2$. The conformal map of the diagram of figure 4.9(c) is
Figure 4.8: I-V curves while the tip approaches toward the surface. The Schottky barrier appears when the tip spacing is less than 5 Å.
the shaded region in figure 4.9(d). The map then is given by

\[
w = \frac{z - a}{a z - 1}
\]

(4.1)

\[
a = \frac{1 + x_1 x_2 + \sqrt{(x_1^2 - 1)(x_2^2 - 1)}}{x_1 + x_2}
\]

(4.2)

\[
R_0 = \frac{x_1 x_2 - 1 - \sqrt{(x_1^2 - 1)(x_2^2 - 1)}}{x_1 - x_2}
\]

(4.3)

The solution of Laplace’s equation in \( w = u + i v \) is

\[
\phi(\rho) = A + B \ln(\rho)
\]

(4.4)

where \( \rho \) is a radius vector. The constants \( A \) and \( B \) can be determined by boundary conditions, \( \phi(\rho = 1) = \phi_1 = a \) and \( \phi(\rho = R_0) = \phi_2 \), and are given by

\[
A = \phi_1, \quad B = \frac{\phi_2 - \phi_1}{\ln(R_0)}
\]

(4.5)

The current density then is

\[
\vec{J} = -\sigma \vec{\nabla} \phi(\rho)
\]

(4.6)

The total current is

\[
I = 2\pi \rho (\hat{\rho} \cdot \vec{J}) = -2\pi \sigma B
\]

(4.7)

\[
= \frac{2\pi \sigma}{|\ln(R_0)|} \nabla \phi
\]

(4.8)

From this, the resistance is given by

\[
R = \frac{\ln(R_0)}{2\pi \sigma} = \frac{\phi_1 - \phi_2}{I}
\]

(4.9)

By making \( z \) to \( \frac{z}{a_1} \), scale is done to change this into real distance.

\[
x_1 = \frac{L + a_2}{a_1}, \quad x_2 = \frac{L - a_2}{a_1}
\]

(4.10)
From equation 4.10, we can derive

\[ R = \frac{4a_1a_2}{\left[ \sqrt{L^2 - (a_1 - a_2)^2} + \sqrt{L^2 - (a_1 + a_2)^2} \right]^2} \]  

(4.11)

4.6 Estimation of the sheet conductance

The sheet resistance of the Si(111) \( \sqrt{3} \times \sqrt{3} \)-Ag surface from the geometry of the experiment, as shown in figure 4.9, can be estimated. When estimating the sheet resistance of 4-point probe, they assume a current has circular distribution. However, we assume charge carriers move linearly to the other electrode to make the calculation easier. Hence the calculation might contain an error. The estimation of the sheet resistance of this experiment should be further studied.

The STM tip has a projected area on the metallized surface. The electrode is made of a gold coated tungsten wire which has 0.1 mm diameter. The separation between the tip and the electrode is around 1 mm. With these geometry information, the differential resistance is given by

\[ \text{d}R = \rho \frac{\text{d}x}{A} = \rho \frac{\text{d}x}{2tx\tan \theta} \]  

(4.12)

where \( t \) is the effective thickness of the metallic \( \sqrt{3} \times \sqrt{3} \)-Ag surface, \( A \) is the effective cross section area, and \( \rho \) is the resistivity. From the figure 4.9, \( \tan \theta = \frac{D - d}{2t} \). By carrying out the integration over the area of collected current (figure 4.9(d)), we have

\[ R = \frac{\rho}{t} \int_{D - d}^{D + d} \frac{\text{d}x}{x} \]  

(4.13)
Figure 4.9: (a), (b) geometry of two point tunneling probe configuration $\sim 1$ mm, $d \sim 10\text{Å}, D \sim 0.1$ mm (d) conformal map for figure (c)
Using the given geometry in figure 4.9 and equations 4.11, 4.9, and by assuming the film thickness is 1 ML of silver, we can estimate the metallized $\sqrt{3} \times \sqrt{3}$-Ag surface to have the sheet conductance

$$G_s = \sigma t \sim 3.4 \times 10^{-4} \, \Omega^{-1}$$

where $\sigma$ is the conductivity. This value is higher than the published value [50], which was measured by macroscopic FPP, $\sigma_s \approx 1.2 \times 10^{-4} \, \Omega^{-1}$. Because TP is an effective technique to measure the sheet resistance, as discussed in chapter 3, our sheet resistance is more correct.

We do not consider the scattering effects at the interfaces when we estimate the sheet resistance. Hence the real surface conductance must be lower than the estimation (see chapter 5).

4.7 Silver layers on Si(111) 7 × 7 and Si(111) $\sqrt{3} \times \sqrt{3}$-Ag

Hasegawa performed experiments at room temperature by FPP [51] to investigate the features of the Ag layer on the Si(111) $\sqrt{3} \times \sqrt{3}$ and the Si(111) 7 × 7. According to their results, first, in case of the Si(111) 7 × 7, the conductance jumps as soon as the shutter opens. However, the resistance does not change significantly until 3 MLs are deposited. After 3 MLs, the resistance drops dramatically. Finally, when the shutter is closed, the resistance is raised slightly. They found that the conductance changes during deposition Ag atoms onto two different metallic surfaces. This experiment is different from my experiment, in that they measured the conductance
during deposition while we measured after deposition.

Fig 4.10 shows the RHEED oscillation for the Si(111) $7 \times 7$ and Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag surface, where silver layers are deposited at room temperature and 160 K. The RHEED oscillation is observed during silver growing on both surfaces at 160 K. However, the oscillation does not appear while silver is absorbed onto the Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag. In contrast, the oscillation shows up as the thickness of silver layer on the Si(111) $7 \times 7$ increases. Since the Si(111) $7 \times 7$ has high surface energy due to the dangling bond, the first layer of the surface is evenly covered by silver. And then the Ag layer on the Si(111) $7 \times 7$ is grown by quasi layer-by-layer mode up to several MLs. The Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag surface has low surface energy because the dangling bonds does not exist. Silver layer on the surface therefore forms islands from the very beginning.

Figure 4.11 shows the various phases of silver on the Si(111) $7 \times 7$ [52, 53], which are formed by baking. At high temperature region, all of silver atoms is desorbed, which means the absorbed silver atoms does not react with a substrate. The largest area of figure 4.11 is $\sqrt{3} \times \sqrt{3}$-Ag area, which means it is easy to form $\sqrt{3} \times \sqrt{3}$-Ag pattern.

In our experiments, silver is absorbed onto two different reconstructed surfaces, $\sqrt{3} \times \sqrt{3}$-Ag and $7 \times 7$. Because the absorbed silver layer may be separated from the Si(111) $7 \times 7$ surface [53], where the silver layer is not bound with the Si(111) $7 \times 7$, the most electrons move along the absorbed Ag layer. Few electrons will flow through the Si(111) $7 \times 7$ channel because of its low conductivity. In case of $\sqrt{3} \times \sqrt{3}$-Ag, on
Figure 4.10: RHEED intensity during Ag disposition. Ag the on Si(111) $7 \times 7$ (a) at RT and (b) 160 K. The RHEED oscillation is observed in (a) and (b). However, it is clearer at low temperature. Ag on the Si(111) $\sqrt{3} \times \sqrt{3}$ (c) at RT and (d) at 160 K. No oscillation is observed in (c) and (d).
Figure 4.11: Change of surface structure varying substrate temperature and coverage of Silver atoms
the other hand, the carrier will move along two different channels, $\sqrt{3} \times \sqrt{3}$-Ag and deposited silver layer.

Figure 4.12 shows the I-V curves with several silver thicknesses on the Si(111) $7 \times 7$. The characteristics of the I-V curves are similar with that of Si(111) $\sqrt{3} \times \sqrt{3}$-Ag because they have high surface conductance. Again, we stress Ohmic behavior is observed at negative bias voltage region, which is the key characteristic of our experiments.

Equation 4.14 suggests that the sheet conductance changes linearly against film thickness. This is obtainable as long as silver film on the Si(111) $7 \times 7$ and the Si(111) $\sqrt{3} \times \sqrt{3}$-Ag substrates is ultra-thin. The linearity is observed for both substrates, but with different slopes suggesting different film resistivities. This linearity can be simply described by

$$R = \sigma \frac{A}{l} \quad (4.15)$$

$$= \sigma \frac{t \cdot w}{l} \quad (4.16)$$

where $\sigma$ is the conductivity, $t$ is the thickness of cross section, $w$ is the width of cross section of the material, and the $l$ is the length of the material (see figure 4.13(a)). The width and the length are a constant, but the thickness apparently is changed. Hence the conductance of the silver thin films is changed by only the film thickness. By assuming the conductivity of ultra-thin film, we can explain figure 4.14, where the film conductance is proportional to the film thickness.

Although we assume the conductivity of ultra-thin silver film is a constant, the
Figure 4.12: I-V curves of silver absorbed Si(111) 7 ×7 surface for (a) 2 MLs (b) 4 MLs (c) 10 MLs. The linearities are observed to all figure in region 1.
Figure 4.13: (a) Diagram for the resistivity calculation. (b) Resistivity vs film thickness. The resistivity of the thin film case varies with film thickness [5].
Figure 4.14: Change in the conductance (relative to that of the Si(111) $7 \times 7$ surface) with increasing thickness of silver monolayers (MLs). Data shown for the Si(111) $\sqrt{3} \times \sqrt{3}$ - Ag substrate (♦) and the Si(111) 7 × 7 (■) substrate.

The conductance of a thin metal film on a semiconductor may be varied with increasing film thickness [54, 55, 5]. Figure 4.13(b) shows the resistivity varies with the copper film thickness.

Another important result of figure 4.14 is two slopes are not the same. We will discuss this in chapter 5.

4.8 Conductance change by charge transfer

The conductance of the silver layer on two different reconstructed surfaces in section 4.7 may be affected by some phenomena such as the charge transfer and the
scattering at thin film interfaces. The basic assumption is that the structural defects such as imperfection and impurities give very small effect to the film resistance. In this section, we show how the charge transfer changes the film conductance. In chapter 5, we discuss how the scattering affects the film conductance.

The conductance of Ag films on the Si(111) 7 × 7 has a linear relationship to the film thickness, as discussed in chapter 4, which implies the change of the film resistance depends on the film thickness. This plot may be shifted by charge transfer, which affects also the y-intercept of the plot. The linear curve will meet the zero point if it shifts downward until the curve meets it. This means when Ag atoms are absorbed onto the substrate surface, some electrons in the Ag layers may transfer to the substrate, which lowers the film conductance, that is, the slope is shifted.

The Si(111) 7 × 7 reconstructed surface has three surface states, namely $S_1$, $S_2$, and $S_3$ (see figure 4.2). While silver is adsorbed onto the substrate, the binding energy of the core level shifts to a relatively lower value, and the $S_1$ state disappears around 0.2 MLs, and the $S_2$ and $S_3$ states are partially filled [56]. On the other hand, the conductance of the space charge layer does not change significantly [11, 57], which means the surface states due to dangling bonds are filled not by the electron in space charge layer but by the electrons of the silver atom. While silver grows up on the substrate, the electrons of Ag atoms move to the empty states of dangling bonds of the Si(111) 7 × 7, so that the conductance of Ag film is lowered. Hence, as soon as Ag deposited onto the metallic surface, some of the very beginning atom fill the dangling bonds of the Si(111) 7 × 7. We need to remind the silver layer on the Si(111) 7 × 7
is not bound with the Si(111) 7 × 7 [53].

The other linear curve, silver layer on $\sqrt{3} \times \sqrt{3}$ in figure 4.14, also does not pass zero point. However, it is closer the zero point because $\sqrt{3} \times \sqrt{3}$ has much higher conductance than that of the Si(111) 7 × 7, the electron transport to the metallic states is negligible. Hence, y-intercept is closer to zero point than that of Ag film on the Si(111) 7 × 7.
In this chapter, we discuss qualitatively the scattering effects at the boundaries, and how this affects the sheet conductance. When electrons pass through ultra-thin metal film, they will suffer from scattering at the interfaces, which affects significantly the film conductance.

If the film thickness is greater than mean free path of an electron in a metal, the scattering at thin film interfaces will be negligible. The film thickness, in our experiments, is several monolayers, which is much thinner than the MFP of an electron. The scattering at the interfaces, therefore, is important to figure out the sheet resistance of the ultra-thin silver layer.

5.1 Fuchs and Sondheimer model

Fuch and Sondheimer (F-S) suggest a model to account for the sheet resistance with scattering at film interfaces for a continuous single crystalline film. According to the
F-S model, the conductivity is associated with MFP of an electron and the metal thickness.

\[
\frac{\rho_d}{\rho_\infty} = \frac{1}{1 - D(l, p)}
\]  

(5.1)

where \(D(l, p) = \frac{3}{2} l_\infty (1 - p) \int_{l_\infty}^1 \frac{1 - \exp(-\frac{d}{l_\infty} t)}{1 - p \exp(-\frac{d}{l_\infty} t)} \, dt\), \(d\) is the film thickness, \(\rho_\infty\) is conductivity of infinity thickness, \(l_\infty\) is mean free path of infinity thickness, and \(p\) is the peculiarity coefficient. \(P\) demonstrates an electron scattering at the interface, which can have 0 to 1. In case of perfect metal surface, \(p\) is equal to 0, assuming electrons at the surface is totally scattered diffusively. When electrons at the surface are totally reflected, \(p\) is equal to 1. However in case of silver layer on the Si(111) \(7 \times 7\), since the data are not properly fitted by F-S model [54]. Despite of this limitation, this model can provide a theoretical basis in many cases.

F-S model needs to be modified if there is grain boundary, which is called Mayadas-Shatzkes model [58].

### 5.2 Conductance change by scattering at the boundaries

The boundaries of the Si(111) \(\sqrt{3} \times \sqrt{3}\) and the Si(111) \(7 \times 7\) have different interface structure and conductivity, because the property of the boundary between vacuum and Ag film is a quite different from the boundary between the silicon surface and the Ag film, which comes from the different conductance and interface structures.

There are three different interfaces in these metallic surfaces. One interface is between Si(111) \(\sqrt{3} \times \sqrt{3}\) - Ag and Si(111), another one is between the vacuum and
In these surfaces, electrons are reflected, scattered diffusively, or transmitted at the three different boundaries. Undergoing these events, electrons may pass through two channels, silver layer channel and the metallic surface channel. Figure 5.1 shows charge carriers flowing and scattering through two channels.

In order to explain qualitatively why the slopes of two plots of figure 4.14 are not parallel, we introduce an electronic circuit model, so that the two metallic films and film interfaces are denoted by independent resistors. There are three resistors in the metallic surface: Two resistors are for two metallic films, the Ag layer and the Si(111) $\sqrt{3} \times \sqrt{3}$ (or $7 \times 7$) surface. Three interfaces may be considered as one...
variable resistor because the difference interface gives different scattering effect. The total resistance then can be written as

$$\frac{1}{R_T} = \frac{1}{R_{Ag}(t)} + \frac{1}{R_s} + \frac{1}{R_i} \quad (5.2)$$

where $R_i$ is the resistance of the interfaces, $R_{Ag}(t)$ is the resistance of the silver layer, and $R_s$ is the resistance of the reconstructed surface. The interface resistance, which is related to the scattering, should be the functions of bias voltage and the film resistance, while the film resistances are a constant at specific film thickness. We thus can rewrite equation 4.13 as

$$R_s' = \frac{\rho}{t} \Omega f(R_T) \quad (5.3)$$

where $\Omega = \frac{1}{D-d} \int_{\frac{1}{2}}^{1} \frac{dx}{x}$ which is a constant, and $f(R_T)$ denotes the scattering effect which is a function of the total resistance. Equation 5.3 can be rewritten in terms of the conductance as

$$G \propto f'(R_T)t \quad (5.4)$$

where $G$ is the surface conductance. This equation shows that the slope of the graph, where the conductance plotted against the film thickness, is determined by $f'(R_T)$ which is dependent of interface properties.

5.3 Scattering of various Si(111) $\sqrt{3} \times \sqrt{3}$ structures

We were performed experiments to measure the surface conductivities of three different superstructures, the Si(111) $\sqrt{3} \times \sqrt{3}$ -Ag, Si(111) $\sqrt{3} \times \sqrt{3}$ - Au, and Si(111) $\sqrt{21} \times \sqrt{21}$ - (Ag + Au). From the graph, where the conductance is plotted against
their Fermi wave vectors (figure 5.2), the conductance of reconstructed surfaces is proportional to the Fermi wave vector.

It first is easy to derive the sheet conductance in terms of mean free path using Drude model. In equation 3.5, the electron concentration, which is denoted by \( n \), is given by

\[
n = \frac{2}{(2\pi)^2} \int_0^{k_F} d \vec{k} = \frac{k_F^2}{2\pi}
\]  

(5.5)

The integration is performed over the Fermi disk. The \( \mu \) in equation 3.5 is expressed as

\[
\mu = \frac{e}{m^*} < \tau >
\]  

(5.6)

where \( m^* \) is the effective mass, and \( < \tau > \) is the average momentum relaxation time.

By inserting equation 5.5 and 5.6 into equation 3.5, equation 3.5 can be rewritten as

\[
\sigma = \frac{e^2}{h} l k_F
\]  

(5.7)

where \( l \) is the mean free path. Hence the sheet conductance is proportional to the mean free path and the Fermi energy.

\[
\sigma \propto l k_F
\]  

(5.8)

where \( k_F \) is Fermi wave vector. This equation means that the mean free path in those reconstructed surfaces is a constant. We may conclude then that the MFP, in ultra-thin films which have the same structure, is nearly the same. However, Drude model is to explain the electron transport for an ideal case. Drude model therefore should be modified to include the scattering effect.
Equation 5.8 may be modified as

$$\sigma \propto l k_F f(p) \quad (5.9)$$

where $p$ is the scattering coefficient that is a fraction of electrons at both surfaces. $f(p)$ is the function of the scattering at the boundaries.

The data on thin metallic surfaces, which are the Si(111) $\sqrt{3} \times \sqrt{3}$ and Si(111) $\sqrt{21} \times \sqrt{21}$ - Ag+Au, are based on $\sqrt{3} \times \sqrt{3}$, reflect the mean free path of these surfaces is independent of the conductance of metallic surfaces. However, since the MFP is proportional to the Fermi wave vector, it is not possible the MFP is independent of the Fermi wave vector to maintain a constant slope. Thus, the $f(p)$ should decrease as the fermi wave vector increases.

As a result, the scattering effect at the boundary for three different superstructures is not the same because the conductance depends on the conductance at the interface and the interface structure. This result supports our simple model in section 5.2.
Chapter 6

Discussion

Most of established probe methods based on the contact generates problems such as a contact resistance and a surface damage. A non-contact technique can provide advantages. We have developed TP based on a partial non-contact technique, and measured the conductance of thin metallic films measured.

Our technique provides a method which makes currents flow only through the metallic surface so as to measure the conductance with high accuracy. This technique can be applied for all kinds of metallic surface on a semiconductor. It is also capable of measuring the resistivity of a semiconductor surface. However, in this case, since one electrode touches the semiconductor surface, it generates a contact resistance. It therefore is needed to introduce a correct factor to resolve this issue.

The data measured by TP reflect the conductance of metallic films is linearly increased as Ag film grew up on the reconstructed surfaces in the ultra-thin domain. It is also important that the conductivity of a metallic surface is affected by the probe spacing. Figure 4.14 shows that the conductance of a thin metal film is sensitive of a reconstructed surface state, which is due to the scattering at the interfaces.
We suggest a simple electronic circuit model to analyze the behavior of electrons in our system. I-V curves shown in this thesis can be divided into three regions, Ohmic region, tunneling dominant region and non-linear region. Among these regions, Ohmic region, which is the most important part, offers a method to measure directly the resistance of a metallic surface. When the tip is close to a M-S system which has a poor metallic surface, the tip and the semiconductor generate a tip induced Schottky barrier. We could observe this SB at non-linear region.

The measurements clearly distinguish the bias-voltage dependent current paths, and provide insight into current injection and transport mechanisms. Even if the conductivity calculation we showed in section 4.6 does not provide the exact numerical sheet resistance, it could give a meaningful value. We need to improve our method to obtain the exact value.

In summary, there are three key conclusions to emerge from the measurements using TP.

1. The I-V curves distinguish different current injection and surface current conduction mechanisms.
2. Surface sheet resistance values vary greatly with mode of current injection.
3. Ultrathin film sheet resistance values of metallic contacts are a sensitive function of the sheet conductance of the interfaces.

One future experiment using TP would be to investigate the behavior of spin polarized electrons on a thin-magnetic surface. Spin polarized electrons can be generated by a magnetized Ni(100)tip. A full non-contact technique also could be made
of extending two-point tunneling probe. This technique would be useful to measure a metallic surface without surface damage.
Bibliography


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