Chapter Three

Metal-Si(H) Junctions

Covalent attachment of molecules to the silicon surfaces by Si-C linkage needs Si-H surfaces to be produced. In the present work, Si-H surfaces are freshly prepared under clean conditions by etching silicon sample in diluted HF as discussed in Chapter Two. Here, a brief introduction to the stability of Si-H surfaces is given with a detailed study on their spectroscopic characterizations by X-ray Photoelectron Spectroscopy (XPS) and Surface Photovoltage (SPV) techniques. Electrical measurements by current-voltage, capacitance-voltage in dark and under illumination are done by forming mercury-Si(H) [Hg-Si(H)] junctions and the junction parameters are estimated by Mott-Schottky plots. Modifications in the junction parameters of metal-semiconductor junctions with change in the work function of the contacting metal is studied by evaporating Al and Au over Si-H surfaces to form Al-Si(H) and Au-Si(H) junctions and characterizing them electrically. Results obtained in this chapter are taken as reference for metal-molecules-semiconductor junction studies done by interfacing ethynylbenzene series of molecules between metal and silicon surfaces, which is discussed in Chapter Four.
3.1. Introduction to Si-H Surface

Silicon surfaces are the important starting materials in the fabrication of modern electronic devices [1-6] and the surface conditions play a major role in such device applications. Also at the same time, it is well known that silicon is prone to surface oxidation and there is always a thin layer of oxide present over its surface [7]. But, for the molecular attachment over silicon surfaces, the oxide layer has to be removed to produce Si-H bonds, which can be done by etching silicon surfaces with hydrofluoric acid (HF). HF etches the surface oxide layer without reacting with silicon, producing hydrated silicon (Si-H) surfaces that is favorable for attachment of organic molecules [8]. It is observed experimentally that such surfaces are stable for certain duration and there is almost negligible surface oxidation for a time scale of few minutes [9]. Uniform H-terminated surface (without any chemical contamination) has Si-H bonds protruding in space and form a good platform for attachment of unsaturated molecules by covalent bonding [7].

Spectroscopic studies of Si-H surfaces is done by different groups using X-ray photoelectron spectroscopy (XPS) [9], surface photovoltage (SPV) [10-12], ATR-FTIR spectroscopy, Raman spectroscopy [7,13] etc. Such studies reveal the composition of
different elements on the surfaces and give an account of surface contaminations and SPV measurements gives the measure of band bending [14] on the surface due to the surface contaminations. For Si-H surfaces prepared under clean conditions, we expect the presence of H and little or no contamination of other elements such as C, O, F. Si-H surface for small processing time scale, is taken as the reference for spectroscopic studies of the molecularly modified surfaces.

3.2. Spectroscopic Characterizations

3.2.1. X-ray Photoelectron Spectroscopy (XPS)

Much of the XPS studies are done on, before and after etching conditions of silicon surfaces [12]. Spectra of unetched or oxidized surfaces reveal the presence of Si 2p peak at 99.6 eV along with Si-O peak around 103 eV. The spectrum shows the signatures of oxide peak at 532 eV along with carbon contamination at 285.6 eV. XPS spectrum of Si-H shows Si (2p) peak at 99.6 eV with the suppression of Si-O and oxide peaks, having little or no traces of other carbon contaminations [10-12]. In the present context, XPS measurements of unetched silicon surface (oxidized silicon) and freshly etched surface (Si-H) surface are carried out at high vacuum of 10^{-11} torr, using Al-k(α) rays at a take-off angle 35° and the results are shown in Figure 3.1a and b.
Figure 3.1: XPS spectra recorded on (a) bare silicon surface (b) Si-H surface created by chemical etching.
Figure 3.1a is the spectra recorded for unetched silicon surface showing Si (2p) peak at 99.6 eV and Si-O peak at 103.3 eV. Figure 3.1b is for Si-H surface showing Si (2p) peak at 99.6 eV, there is a suppression of Si-O and O(1s) peaks at 103.3 and 532.2 eV, respectively. This shows that freshly etched silicon has almost negligible oxide, and hence the Si-H surface is favorable for covalent attachment of unsaturated organic molecules.

### 3.2.2. Surface Photovoltage (SPV)

SPV studies reveal the extent of band bending at semiconductor surface due to surface contamination. The simplest attachment over silicon surface is that of H-atoms, forming Si-H bonds and as Si-H bond is polar in nature, we expect surface band bending [15-17].

In the present SPV measurements, flux of incident light and the gap between sample's surface and the top electrode (ITO) are kept constant so that the observed SPV signal is proportional to the magnitude of surface band bending [18,10] and the signal of the sample is corrected with the background spectrum (SPV phenomenon and the measurement setup is discussed in Chapter Two). Figure 3.2 shows SPV spectra recorded on freshly prepared Si-H surface. The curve is an average of three sets of measurements. The onset of photo-signal for the curve occurs at 1.05 eV, which is close to the silicon band gap. Results of the
obtained spectrum is compared and discussed in detail with the spectrum for molecularly modified surfaces in *Chapter Four*.

Figure 3.2: Surface photovoltage curve recorded on H-terminated silicon surface as a function of energy of incident light.

3.3. Charge Transport in Hg-Si(H) Junction

3.3.1. Current-Voltage Characteristics

For the electrical characterizations of the reference junction, freshly prepared Si-H surface is loaded on our home made electrical conductivity setup described in *Chapter Two*. Si-H surface is placed in contact with mercury and the needle of the conductivity setup is lowered on the Al-coated back contact of the
sample. This constitutes Hg-Si(H) junction. Forward bias refers to bottom silicon contact being positive with respect to the top metal contact. Hg-Si(H) junction is subjected to current limit of ±10 μA and the

Figure 3.3: Current-voltage characteristics of Hg-Si(H) junction (a) linear plot (b) semi-logarithmic plot.
I-V data is recorded using Keithley meters. Figure 3.3a shows linear I-V characteristics of the reference Schottky junction, the curve reaches 10 µA at 0.26 V in the forward region. Figure 3.3b shows the semi-logarithmic plot of the same curve. Transport properties across junction can be understood by considering thermionic emission equation (1.6) for metal-semiconductor junction [19]

\[ J = A^* T^2 \exp \left( -\frac{q\Phi_b}{k_B T} \right) \exp \left( \frac{qV}{nk_B T} \right) \left[ 1 - \exp \left( -\frac{qV}{k_B T} \right) \right] \]

where \( J \) (Acm\(^{-2}\)) is the current density, \( A^* \) the Richardson constant (32 AK\(^{-2}\)cm\(^{-2}\) for p-type Si), \( k_B T \) the thermal energy, \( n \) the ideality factor and is equal to 1 if the charge transport is entirely by thermionic emission process, \( \Phi_b \) is the Schottky barrier between the metal and semiconductor.

Effective barrier height and ideality factor are obtained from the slope and intercept of \( \ln [J/(1 - \exp(-qV/k_B T))] \) versus \( V \) plot. Intercept \( J_s \) obtained from the graph is substituted in the expression for barrier height \( \phi_s = \frac{k_B T}{q} \ln \left( \frac{A^* T^2}{J_s} \right) \) to obtain \( \Phi_B \) and the slope calculated is substituted in \( n = \left( \frac{k_B T / q}{\text{slope}} \right) \), to get the ideality factor. The intercept (\( J_s \)) and the slope obtained from the graph equals 1.52x10\(^9\) and 25.14, respectively [19], the barrier
height and the ideality factor determined from these values is given in Table 3.1. Ideality factor being greater than 1, indicates that the transport mechanism across the junction is not entirely by thermionic emission, other factors like extra potential drop at the interfacial layer due surface states, potential drop due to series resistance and recombination in the space charge region can contribute to the charge transport [20-22]. The value of barrier height obtained for Hg-Si(H) junction is close to the reported value [23].

Table 3.1: Various charge transport Parameters estimated for Hg-Si(H) junction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Barrier height “eV” (I-V)</th>
<th>Ideality factor “n”</th>
<th>Barrier height “eV” (C-V)</th>
<th>Surface potential Vd0 “V”</th>
<th>Surface state density (x10^{11} eV^{-1} cm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-H</td>
<td>0.796</td>
<td>1.62</td>
<td>0.6</td>
<td>0.32</td>
<td>2.05</td>
</tr>
</tbody>
</table>

For photoconductive studies, the reference junction Hg-Si(H), is subjected to blue and white light illumination. It is known that the surface properties or surface modifications of silicon is best explored under blue illumination, as this light with wavelength around 467 nm (measured on commercial LED using Ocean Optics USB 2000+ miniature fiber optics spectrometer) penetrates only upto 0.3 µm into the silicon surface [19]. Hence using blue light,
the contributions to the junction properties due to only surface excitations can be studied. Bulk and surface excitations can be analyzed using white light illumination. I-V measurements are limited to 10 μA, in the forward region. Figure 3.4 shows I-V data of the reference sample under dark, blue and white lights. The increase in the photocurrent due to increase in the charge carriers caused by photoexcitation is clearly seen. Photocurrent for blue illumination show a slight increase with respect to dark current in the reverse bias, where as there is a large photocurrent recorded under white light. This aspect of photocurrent on the reference junction will be discussed in the next chapter, while discussing the photoeffect on different metal-molecules-Si junctions.

Figure 3.4: Current-voltage measurements of Si-H junction in dark and under illumination of blue and white lights.
3.3.2. Work Function Dependent Barrier Heights of Metal-Si(H) Junctions

Mott-Schottky relation between barrier height and metal work function of metal-semiconductor junction show that barrier heights vary according to the work function of contacting metals [19]. Extensive studies on metal-silicon junction has been done by Turner and Rhoderick and have shown that the barrier height depends on the method of preparation of silicon surfaces. For example, in case of etched silicon surfaces, barrier height depends on the choice of metal and for the cleaved surfaces in ultra high vacuum, it is independent of the metal. Variation of barrier heights for n and p-types of silicon is shown in Ref. [24]. For p-type metal-semiconductor junction, the barrier heights decreases with the increase in work function of metal. In this section, it is aimed to discuss the effect of depositing two different metals, namely Al (Φ\text{Al} = 4.2 \text{ eV}) and Au (Φ\text{Au} = 5.15 \text{ eV}) on p-type Si(H) surface and study the dependence of barrier height on the metal work function.

Freshly prepared Si(H) is placed in the vacuum chamber of the metal evaporator and evaporation of the contacting metals is done at 1 x 10^{-6} \text{ torr} vacuum is done using shadow mask. Al dots are evaporated immediately after gold. Dots of 1 mm diameter of both the types of metals are evaporated on Si-H
surfaces and electrical characterizations of Au-Si(H) and Al-Si(H) junctions are done. Along with the room temperature characterization, temperature dependent studies of these junctions is also carried out to understand the variations of junction parameters with temperature.

Figure 3.5 shows I-V plots for Al-Si(H) and Au-Si(H) junctions, showing Schottky and ohmic behavior, respectively. The difference in the I-V response for the two junctions can be explained with respect to the work function of the evaporated metals. Consider Al-Si(H) junctions, the work function of Al ($\Phi_{Al} = 4.2 \text{ eV}$) is less than the p-Si ($\Phi_{Si} = 4.95 \text{ eV}$), and it is necessary condition for the junction to be Schottky in nature. For Au-Si(H) junction, the work function of Au ($\Phi_{Au} = 5.15 \text{ eV}$) is close to the work function of p-Si ($\Phi_{Au} = 4.95 \text{ eV}$) and this condition gives rise to ohmic behavior.
Figure 3.5: Current-Voltage characteristics of (a) Al-Si(H) junction (b) Au-Si(H) junction, these junctions are constituted by thermal evaporation of metals.
Figure 3.6 shows energy band diagrams of Al-Si(H) and Au-Si(H) junctions with their respective parameters. From these band bendings it is clear that the resulting I-V curve for Al-Si(H) junction is Schottky and ohmic for Au-Si(H) junction. The parameters for Al-Si(H) junction can be calculated by thermionic emission equation (1.6).

For temperature dependent measurements, Au-Si(H) and Al-Si(H) junctions are heated in vacuum chamber and the plots
Figure 3.7: Temperature dependent current-voltage curves of
(a) Al-Si(H) junction (b) Au-Si(H) junction.
are shown in Figure 3.7. In the Figure 3.7a, I-V curves for Al-Si(H) junction become more conducting with the increase in temperature and the reverse leakage current also increases. This kind of behavior is expected for metal-semiconductor junction [19] without any interfacial layer. The dependence is due to the formation of the junction at the Al-Si(H) interface. For Au-Si(H) junctions there is no temperature dependence seen indicating the absence of space charge region. This weak dependence is due to negligible difference in the work functions of Au and p-Si.

3.3.3. Current-Voltage Measurements of Back-to-Back Junctions

For the back-to-back junction conductivity of two similar Hg-Si(H) junctions, the two-probe mercury set-up (Figure 2.14) discussed in the previous chapter is used. Freshly prepared Si-H sample is loaded on the two holed mercury probe and the brass plates are lowered over the sample followed by the tightening of nuts. Measurements are done between the voltages ranging from ± 2V. The proposed setup for back-to-back junction conductivity measurements using soft electrical contacts is described in the previous section. I-V curve of the reference junction for two-probe contacts is sigmoidal and symmetric on both sides of the voltage axis as shown in Figure 3.8.
Figure 3.8: Back-to-back junction current-voltage curve of Hg-Si(H) junction.

The current rises sharply in the beginning and starts saturating from 0.3 V. Maximum current of the two junctions in back-to-back configuration is 4.45 μA at 2V. Transport equation for such junctions is obtained by considering the equation for a metal-semiconductor junction and obtaining the equation for the junctions connected in back-to-back configuration. Consider equation (1.3) for metal-semiconductor junction in its simplest form

\[ J = J_0 \exp \left( \frac{qV}{nk_BT} \right) \]
where \( J_0 = AT^2 \exp\left(\frac{-q\Phi_b}{k_BT}\right) \) and other terms have their usual meaning. For the two Schottky junctions in back-to-back configuration the net current is given by [25, 26]

\[
J = J_0 \tanh\left(\frac{qV}{2nk_BT}\right)
\]

(3.1)

where \( J_0 \) is the amplitude or the saturation value of the current. The shape of the curve obtained is sigmoidal (S-shaped) and is a key feature of junctions in back-to-back configuration. This inherent shape of curve is decided by the factor \( (q/nk_BT) \). Derivative of equation (3.1) gives a symmetric peak function that is centered at zero voltage and twice of its width is equal to ideality factor ‘n’ of an individual junction [26]. This has been applied successfully in case of metal-organic semiconductor junctions in back-to-back configuration [26]. \( J_0 \) is directly read from saturated value of experimental curves (Figure 3.8) and the ideality factor is obtained by derivative of these curves. Barrier height (\( \phi_b \)) can be estimated from the directly obtained value of \( J_0 \). The values obtained are listed in Table 4.3 of the next chapter.

One of the advantage of two-probe junction to single probe is that here \( J_0 \) can be estimated directly from the saturation values and \( n \) from the derivative of I-V curve. In case of single junction, \( J_0 \) has to be estimated from limiting value of equation for metal-
semiconductor junction by extrapolating the experimental data, which is susceptible to certain degree of uncertainty.

The importance of the two-probe conductivity setup can be seen by concentrating on the time dependent stability of junctions created on etched silicon surface. It is very well known that, etched silicon surface is stable for some time on laboratory scale and then starts getting oxidized with respect to time. Unlike H-terminated surfaces, the surfaces chemically etched, using the mixture of nitric acid and hydrofluoric acid, gives high density of active surface atoms and are more prone to surface oxidation and contamination. Oxidation of such surfaces, with respect to time can be measured with our two-probe mercury setup. To test this, the p-type silicon sample with (100) orientation and 1 ohm-cm resistivity (supplied by Bharat Electronics Limited, Bangalore) is chosen. The sample is dipped in the solution of HNO$_3$ and HF (17:3 v%) for 3 minutes, which reduces the thickness of silicon by etching smoothly with moderate etching rate [27]. The sample is then thoroughly washed with copious amount of deionized water and immediately loaded for conductivity measurements. Time dependent conductivity curves are recorded over a period of 26 hrs and these results are shown in Figure 3.9. Figure shows that the I-V curves are highly conducting in the beginning and gradually become less conducting due to surface oxidation/contamination of
silicon. The shift in the I-V curves of the junction from a higher conducting state to the lower conducting state clearly shows that silicon surfaces etched with HNO$_3$ + HF are highly prone to surface oxidation with time. This clearly shows that our setup is quite sensitive to probe the changes in conductivity due to change in the surface conditions of the semiconductor.

Figure 3.9: Current-voltage curves of back-to-back junction formation on HNO$_3$+HF treated silicon surface. The curves become less conducting with the passage of time.
3.3.4. Capacitance-Voltage Characteristics of Hg-Si(H) Junction

Capacitance-voltage (C-V) measurements on Hg-Si(H) junction are carried out by superimposing sinusoidal ac signal of 25 mV on dc bias. According to theory, it is proved that capacitance measurements are extremely sensitive to interface states [28]. By measuring capacitance as a function of voltage and frequency, the bulk as well as the interfacial properties of the junctions can be understood. Apart from barrier height information, one can estimate dopant density, density of states etc. Traps located at the metal-semiconductor interface, respond differently at different frequencies. They follow ac signal at lower frequencies and respond well to these frequencies, hence a noticeable change in capacitance curves with respect to bias voltage at lower frequency can be seen. Capacitance at higher frequencies are constant as the traps do not respond to these frequencies [28]. From these responses of the junction, one can get a more useful information of the junction/interface parameters. Hence, in the present context, C-V measurements are done for the reference junction at different frequencies in dark and under illumination.

C-V measurements on Hg-Si(H) junction, are done at different frequencies ranging between 500 Hz and 1 MHz (in steps of 500 Hz, 1 kHz, 100 kHz, 500 kHz and 1 MHz), so as to scan the
Figure 3.10: C-V measurements of Hg-Si(H) junction for frequencies ranging from 500 Hz to 1 MHz.

Figure 3.11: $1/C^2$ vs $V_r$ plot for the reference junction.
capacitance response of the junction with respect to bias voltage for a wide range of frequencies. Capacitance as a function of voltage for different frequencies is plotted in the Figure 3.10. The typical Mott-Schottky relation between capacitance and voltage (equation 1.7) is used to estimate the required junction parameters [28, 29]. The equation is

\[
\frac{1}{C^2} = \frac{2(V_{d0} - V_r)}{qA \varepsilon_s \varepsilon_0 N_a}
\]

where \(V_{d0}\) is surface potential, \(V_r\) the applied reverse voltage, \(q\) is electron charge, \(A\) the area of contact between metal and silicon surface, \(\varepsilon_0\) the permittivity of free space, \(\varepsilon_s\) the dielectric constant of semiconductor and \(N_a\) the dopant concentration of semiconductor.

From the slope and intercept of Mott-Schottky plots \((1/C^2 \text{ versus } V_r)\) in Figure 3.11, under reverse bias, one can estimate the surface potential \(V_d\), barrier height \(\Phi_b\) and bulk doping density \(N_a\). Surface potential, \(V_d = V_{d0} - (V/n)\), \(V_{d0}\) is the surface potential at zero bias obtained from the \((1/C^2 \text{ vs } V)\) plot. Barrier height is calculated using the relation \([V_i + V_d + (kT/q)]\), \(V_i\) is the voltage intercept. Dopant density \(N_a\) calculated is within an experimental error, close to supplier's data \((2\sim3 \times 10^{15} \text{ cm}^{-3})\). The parameters calculated is given in Table 3.1.
The total capacitance of the junction at lower frequencies is the contribution from interface states and from the space charge region, as the interface states are known to respond only at these frequencies. But at higher frequencies these states do not respond and hence the contribution to the capacitance is only from the space charge region. Therefore to estimate the trap density or the interface density at the junction, one needs to measure the capacitance at low and high frequencies and the difference in the magnitude of capacitance at these frequencies is a direct measure of interface states density. Under this consideration, the interface density of states $D_{it}$ is given by equation 3.2 [30]

$$D_{it} = \sqrt{\frac{q\varepsilon_0\varepsilon_0 N_s}{2V_d}} \left[ \frac{(C_{LF} - C_{HF})}{qC_{LF}} \right]$$

(3.2)

where $C_{LF}$ and $C_{HF}$ are the capacitance at lower and higher frequencies at the applied bias $V$, $V_d$ is voltage dependent surface potential and other terms have their usual meaning. In the present case, $C_{LF}$ is 500 Hz and $C_{HF}$ is 1 MHz. Calculated value of interface density for the reference junction is given in Table-3.1.

Variation of $D_{it}$ as a function of energy difference between the surface fermi energy ($E_F^S$) and the top of valence band i.e., $D_{it}$ vs $(E_{SS} - E_V)$ is shown in Figure 3.12 for the reference junction.
Here, $E_{ss}$ is the position of energy of interface states from the top of valence band ($E_v$). There is an exponential increase in the density of surface states from midgap toward the top of the valence band. These values of $D_{it}$ are quite close to the reported values in the literature [31] on metal-molecules-semiconductor junctions.
3.3.5. Hg-p⁺Si(H) Junction

Junction characteristics for metal and highly doped p-silicon (p⁺-Si) samples are also studied by forming Hg-(p⁺-Si(H)) junction. This junction is the reference for all Hg-molecules-p⁺Si junctions, discussed in the next chapter. p⁺-Si samples are etched in HF as in case of p-type crystals, but unlike p-Si, p⁺- samples do not require back ohmic contact for electrical characterizations. p⁺-Si samples used have the resistivity of 0.001 ohm-cm. The etched samples are loaded on mercury conductivity setup Figure(2.13)

Figure 3.13 : Current-voltage characteristics of Hg-(p⁺-Si(H))

junction.

Hg-(p⁺-Si(H)) junction and the electrical characterization of the reference junction is carried out at room temperature. Figure 3.13
shows I-V plot for the reference junction and the curve is ohmic. Though there is a wide Fermi level difference between mercury and the p⁺-Si samples, the transport across the junction is tunneling, due to very small depletion width of the highly doped semiconductor. Hence the nature of the curve is linear and not Schottky.

3.4. Conclusions

This chapter gives a detailed spectroscopic characterization of the reference surface and electrical characterizations of reference junctions. XPS studies reveal Si(2p) peak and the absence of oxygen and Si-O peaks at 532.6 eV and 103 eV respectively. This shows that the hydrated surface is clean, with no other contaminations and favorable for the attachment of organic molecules. Meanwhile the SPV results showed a peaking curve demonstrating band bending caused due to the polar nature of the Si-H bond on the surface. Junction dependence on the work function is clearly observed, in case of Al-Si(H) and Au-Si(H) junctions. I-V behavior is Schottky for Al-Si(H) junction and ohmic with respect to Au contact. Capacitance curves obtained with respect to voltage showed frequency dependent behavior with well peaked curve at lower frequencies and constant curve at higher frequencies. The junction responded very little to blue radiations.
and showed large change for white illumination. Ohmic behavior of the reference junction for Hg-p⁺Si junction is explained due to narrow depletion width of the p⁺ samples.
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