Stability of liquid metal Schottky contacts

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All evolutionary aspects of Schottky barriers e.g. the factors contributing to the band alignment at metal-semiconductor interfaces, are still not well understood. Liquid metal-semiconductor interfaces provide an opportunity to probe them since their formation process eliminates or minimizes many influencing factors e.g. formation of oxide layer, changes in surface morphology due to impact of deposited metal atoms etc. when compared to the formation of solid metal semiconductor interfaces. However, the liquid state of metal possessing higher equilibrium thermodynamic energy, may induce instability at interfaces by inducing interfacial reactions ultimately showing up in ageing effect. The liquid metals namely Hg and Ga on p-type silicon show no such effect and hence can be fruitfully exploited for probing evolutionary aspects of metal-semiconductor interfaces through liquid metal route.

Keywords: Schottky barrier, Saturation current, Barrier height, Ideality factor
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1 Introduction

Metal-semiconductor contacts, both of ohmic and rectifying nature have been viewed as an interesting field for research and development primarily because of their wide range of applicability. Rectifying metal-semiconductor contacts have drawn much interest in recent years with an aim to improve the understanding of the role of various physical processes occurring at the interfaces and may be expected to provide significant inputs for controlling the ultimate terminal behaviour of the devices. Most of the rectifying metal-semiconductor contacts, fabricated and investigated are formed by depositing a metallic overlayer by techniques like vacuum evaporation using thermal or electron-beam source, sputtering etc. overprepared (cleaved or chemically etched or cleaned) semiconductor surfaces. It has been found that the evolution and growth of metallic overlayers in such contacts are influenced by the crystallographic and chemical nature of the semiconductor surfaces, defects, local morphology and flaws, dangling bonds etc., which decide the electronic nature of the surfaces. In usual preparation techniques of such contacts, the above surface conditions can further get modified (a) by specific cleaning and etching sequences followed during surface preparation and (b) by specifics of the metallic overlayer preparation technique followed during the Schottky contact preparation. However, in case of reactive semiconductor surfaces e.g. silicon, the condition of surfaces obtained after following a specific cleaning and etching sequence can again get modified by exposure to the ambient. Moreover, the deposition techniques, as already outlined, involve bombardment and equilibration of high energy/velocity ions, atoms or molecules onto the so prepared surfaces and thus there is a great probability of further alteration in the surface conditions and properties of the semiconductor substrates depending on the chosen deposition technique.

It is known that these initial surface conditions are responsible for the development of further interface layers and its properties and therefore the evolution of barriers during the first few monolayers of such a contact is likely to be crucial in the alignment of Fermi levels at the metal-semiconductor interface. In this context, the work of Stanford and other groups have been revealing. Based on these results, two kinds of barrier height values i.e. thin overlayer and thick overlayer values have been observed. While the first one is observed to be sensitive to the substrate overlayer and other conditions, the latter one is relatively stabilised value. All these show the importance of local states/situations on the barrier formation.

In the field of semiconductor surface and interface research, efforts have continuously been made to improve, design, and develop more appropriate experimental techniques, which could provide better insight into the band alignment and their controlling
factors at such interfaces. Notable among these are photo-electron spectroscopy, use of synchrotron radiation sources and free electron laser techniques etc. These have helped in looking into the role of local states in the background of bulk states. However, in case of Schottky contacts formed in usual manner, the revealed information in various experiments and discussion following them may not be necessarily free from ambiguity due to modifications caused in local interface conditions by impingement of high velocity ions and atoms or species of the metallic overlayers.

Hence, it is proposed that liquid metal Schottky contacts may provide an attractive and novel opportunity to look into various aspects of the evolution of Schottky interfaces in relatively beneficial manner. The noteworthy advantages of liquid metal Schottky contacts vis-a-vis the solid metal contacts formed by usual manner with techniques like vacuum evaporation/e-beam evaporation/sputtering etc. are following:

(a) The simple and quick formation of the contact with semiconducting substrate surfaces reduces the possibility of their contamination (oxidation by adsorption of chemical species from the atmosphere etc.) specially in case of reactive semiconducting surfaces.

(b) The possibility of damage to the morphology, defect structure etc. of the semiconductor substrate surfaces is almost eliminated as for forming the liquid metal overlayers, high velocity atoms, ions or species are not required to be bombarded, adsorbed and thermally equilibrated at the surfaces.

(c) Liquid metal contacts provide additional flexibility to monitor changes in the Schottky interface behaviour with addition and slow dissolution of other metallic species in a particular host liquid metal Schottky contact, e.g. alloying another metal in a host liquid metal in which it can easily dissolve.

More explicit physical information requires stable and reliable behaviour from the prepared liquid metal Schottky interfaces. This becomes more significant in view of the general fact that liquid state of the matter is comparatively a higher thermodynamical energy state with relatively more mobile constituent species, compared to the solid state and these might lead to time dependent changes in the interfacial conditions. Thus investigation of stability and ageing of such contacts becomes important. In view of this, we present here our results about the stability of mercury and gallium liquid metal Schottky interfaces on $p$-silicon which have been investigated for their Schottky behaviour by Wittmer$^{9,10}$.

2 Experimental Details

The Schottky contacts were made on (100) surfaces of $p$-type silicon crystal having doping density of around $10^{15}$ cm$^{-3}$. The ohmic back contact was made on unpolished side by depositing a thick film (3000Å) of aluminium and sintering it for around half an hour at 500°C. The front polished surface was mildly etched in a mixture of electronic grade nitric acid, hydrofluoric acid and acetic acid and was then washed with deionised water and quickly dried$^{11}$. This crystal was then immediately placed on the metal base plate of the sample holder system$^{12}$ and the suitable capillary arrangement of the system was lowered to the proper place for making the contact. Pure liquid metals, mercury$^{12}$ and gallium$^{13}$ were put into the capillary using a disposable syringe. The $V$–$I$ characteristic data were acquired using a microprocessor controlled digital millivolt source and measuring the resulting current through Keithly electrometer model 614.

3 Results and Discussion

The nature of $V$–$I$ characteristics obtained for Hg-Si($p$) and Ga-Si($p$) diodes and shown in Fig. 1 seem to correspond to a good rectifying behaviour. However, the equivalent circuit of a practical Schottky diode (Fig. 2) additionally includes a series
resistance $R_s$ (arising on account of material outside the junction and the contact resistances at the two terminals) and a shunt resistance $R_{sh}$ (arising from characteristics of the material within the barrier including insulating interfacial layer).

Therefore, for getting more realistic $V-I$ characteristics, the obtained $V-I$ data need to be corrected for their presence as they do start affecting the specific parts of $V-I$ characteristic as marked in Fig. 3. In presence of the two resistances, the thermionic emission current through a Schottky diode can be expressed as\cite{14},

\[ I = I_d + I_p \]  \hspace{1cm} \ldots (1)

\[ = I_o \exp\left\{ q(V-IR_s)/nkT \right\} - 1 \]  \hspace{1cm} \ldots (2)

where $I_d$ is the diode current, $I_p$ the shunt current, $G_p(=1/R_{sh})$ the shunt conductance and $I_o$ is the saturation current and is given as,

\[ I_o = A^* A T^2 \exp\left( -\frac{q \Phi_b}{kT} \right) \]  \hspace{1cm} \ldots (3)

where, $A$ is area of in interface, $A^*$ Richardson constant, $T$ the temperature in Kelvin, $\Phi_b$ the barrier height and $n$ is the ideality factor.

At large reverse biases and assuming $R_{sh} >> R_s$, (as is always the case with good diodes) Eq. (1) reduces to:

\[ I = I_o + G_p V \]  \hspace{1cm} \ldots (3)

Thus, $G_p$ can be evaluated using it. The values of $G_p$ as determined for Hg-Si($p$) and Ga-Si($p$) diodes fabricated and investigated over here are 5.37 and 10 micro mho respectively. Under the assumption

$$(V-IR_s) >> kT \text{ and } R_{sh} >> R_s,$$ Eq. (1) for forward current can be expressed as:

\[ I = I_o \left[ \exp\left( \frac{q}{nkT} (V-IR_s) \right) - 1 \right] \]  \hspace{1cm} \ldots (4)

Defining conductance $G=dI/dV$, the Eq. (4) can be rearranged as\cite{14}:

\[ \frac{G}{I_d} = \frac{q}{nkT} (1-GR_s) \]  \hspace{1cm} \ldots (5)

Thus, a plot of $G/I_d$ with $G$ is expected to be a straight line whose slope and intercept can be used to estimate the values of $R_s$. The values of $R_s$ estimated for the two fabricated diodes in this way are found to be 110 and 100 ohm for Hg-Si($p$) and Ga-Si($p$) diodes respectively. The impact of these corrections on $V-I$ characteristics of these two liquid metal diodes is shown in Fig. 4, where $V-I$ curves before correction are also shown.

There are many factors e.g. presence of an interfacial layer, the image force lowering of the barrier due to penetration of the wave functions of the metal electrons into the semiconductor etc. which make the barrier height of a Schottky diode bias dependent. If linear bias dependence is assumed, the thermionic emission current through a Schottky diode can be expressed as:

\[ I = I_o \exp\left( \frac{q V}{nkT} \right) \left[ 1 - \exp\left( -\frac{q V}{kT} \right) \right] \]  \hspace{1cm} \ldots (6)

So a plot of $\ln \left[ I/\left\{ 1-\exp(-qV/kT) \right\} \right]$ against $V$ can lead to evaluation of $I_o$ and this can then be used to

![Fig. 2—Equivalent circuit of a practical Schottky diode with series and shunt resistances](image_url)

![Fig. 3—Current-voltage characteristics of a practical Schottky diode](image_url)
evaluate the barrier height and ideality factor. Apart from considering bias dependence of barriers, this kind of plot also uses substantial amount of \( V-I \) data under reverse bias to fall on a straight line and thus facilitates a better evaluation of the saturation current and the ideality factor\(^{15}\). This kind of analysis has been carried out for corrected \( V-I \) data of both diodes and the values of the barrier height and the ideality factor have been evaluated as a function of time (100 and 200 hours after preparation for Hg-Si\((p)\) and Ga-Si\((p)\) Schottky diodes respectively) to look into the stability aspect of the diodes. These are given in Table 1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Hg-Si((p)) Time (hr)</th>
<th>( \phi_{b(I-V)} ) (eV)</th>
<th>( n )</th>
<th>Ga-Si((p)) Time (hr)</th>
<th>( \phi_{b(I-V)} ) (eV)</th>
<th>( n )</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>00</td>
<td>0.70</td>
<td>1.02</td>
<td>00</td>
<td>0.81</td>
<td>1.07</td>
</tr>
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<td>22</td>
<td>0.70</td>
<td>1.02</td>
<td>24</td>
<td>0.81</td>
<td>1.07</td>
</tr>
<tr>
<td>3</td>
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<td>0.69</td>
<td>1.02</td>
<td>48</td>
<td>0.81</td>
<td>1.07</td>
</tr>
<tr>
<td>4</td>
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<td>0.69</td>
<td>1.02</td>
<td>72</td>
<td>0.85</td>
<td>1.05</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>0.69</td>
<td>1.03</td>
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<td>0.82</td>
<td>1.07</td>
</tr>
<tr>
<td>6</td>
<td>200</td>
<td>--</td>
<td>--</td>
<td>192</td>
<td>0.84</td>
<td>1.07</td>
</tr>
</tbody>
</table>

The stabilities in many Schottky diodes known as ageing effects and are exhibited in the form of changes in the values of barrier height etc. due to various reasons. Some of these may be time dependent reaction and formation of some third phase at the interface, adsorption of reactive molecules from the atmosphere or deliberately created environments\(^{16}\), intrinsic relaxation at the interface etc\(^{17}\). It is evident from Table 1 that there is no significant change in the values of barrier heights and ideality factors of investigated Hg-Si\((p)\) and Ga-Si\((p)\) diodes with time.

### 4 Conclusion

Thus it can be concluded that these liquid metal Schottky diodes show no significant ageing effect. Although mercury and gallium are known to be non-reactive with silicon\(^{18}\), even other ageing mechanisms are insignificant. Therefore, these liquid metal Schottky contacts can form suitable configurations to look more closely into various evolutionary aspects of such interfaces.

### References