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The double Gaussian distribution of inhomogeneous barrier heights in the organic-on-inorganic Schottky devices

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We have fabricated an Au/perylene–monoimide (PMI)/n-Si organic-on-inorganic Schottky device by spin coating of PMI solution on an n-Si semiconductor wafer. Current–voltage (*I*–*V*) measurements on the device in the temperature range of 75–300 K were carried out. An abnormal decrease in the experimental barrier height Φ_B and an increase in the ideality factor n with a decrease in temperature have been observed. This behaviour has been explained on the basis of thermionic emission theory with a double Gaussian distribution of the barrier heights due to the barrier height inhomogeneities.

1 Introduction Nowadays, organic thin films and organic-based hybrid structures have gradually rising application areas in various electronic devices, such as diodes [1–3], dye sensitized solar cells (DSSCs) [4], organic light emitting diodes (OLEDs) [5, 6], RFID tags [7] and xerography [8]. Therefore, it would be quite important a better understanding of the metal–organic interface in the further development and improvement of organic and molecular electronics.

The most important feature characterizing a Schottky barrier is its barrier height Φ_B. Recently, considerable attention has been focused on the barrier height inhomogeneity in the Schottky devices [1–28]. Several methods and approximations have been proposed to explain the formation of barrier from different materials including inorganic and/or organic interfaces and also to specify the behaviour of barriers at different bias and environmental conditions. But, there is still a large necessity for new experiments and studies to provide more insight into the mechanisms occurring at the barrier and to determine Φ_B more accurately.

Barrier inhomogeneity at metal–semiconductor Schottky interfaces has been investigated as an important phenomenon in explaining the non-ideal behaviour of the Schottky diodes [9–16]. The Gaussian distribution model has been successfully used to understand the non-ideal behaviour of real Schottky contact, for example, the linear decrease of apparent barrier height Φ_B and an increase in the ideality factor n with the inverse of absolute temperature [9, 10]. The ballistic electron emission microscopy (BEEM) has also supported the existence of a Gaussian distribution of barrier heights in Schottky diodes [29, 30]. Chand and Kumar [13–15] applied a model to a Pd_2Si/n-Si Schottky diode and proved the existence of two Gaussian distributions of the barrier height [14].

The performance and reliability of organic based Schottky barrier diodes especially depends on the formation of organic interfacial layer at metal–semiconductor (MS) interface and also on inhomogeneities of the Schottky barrier formation at MS interface [17–28]. The existence of such an organic layer can have a strong influence on diode characteristics. Therefore, it is important to determine the interface and barrier properties of such an organic based Schottky device [17–28].

In the previous work, we have reported the effect of the use of an organic film on the modification of electrical properties of Si Schottky diode [31]. The experimental procedure is described there in detail [31]. The goal of this study is to analyse barrier height inhomogeneity in Au/perylene–monoimide (PMI)/n-Si Schotttky diodes. The temperature dependent barrier characteristics of diodes is discussed in frame of thermionic emission theory with a double Gaussian distribution of the barrier heights around a mean value due to the barrier height inhomogeneities prevailing at the organic–inorganic semiconductor interface.

2 Experimental In this study, we have used an n-type P-doped Si semiconductor wafer with (100) orientation, having 380 μm thickness and 0.1–20 Ω cm resistivity. Before making contacts, the wafer was chemically cleaned using the Radio Corporation of America (RCA) cleaning procedure. Immediately after surface cleaning, gold metal with a purity of 99.99% was thermally evaporated on the whole back surface of the wafer with a thickness of 1500 Å in a pressure of approximately 5×10^{-6} Torr. Then, a heat treatment was made at 500 °C for 3 min in vacuum to obtain a low resistivity ohmic contact. Next, a PMI organic film was formed by spin coating method with a Laurell Spin Coater. The chemical structure of PMI is given in Fig. 1a. The thickness of film was measured to be approximately 150 nm by a Discrete Wavelength Ellipsometer TT-30. After then, Schottky contacts were deposited on this organic film with a diameter of 2 mm by a metal shadow mask by evaporating 99.99% purity gold metal with a thickness of 1500 Å in a 5×10^{-6} Torr pressure. The schematic representation of the device is shown in Fig. 1b. The current–voltage measurements were performed by a Keithley 2410 SourceMeter in a wide temperature range between 75 and 300 K using an ARS Closed Cycle Cryostat Model DE202 AI and a Lake Shore model 331 temperature controller.

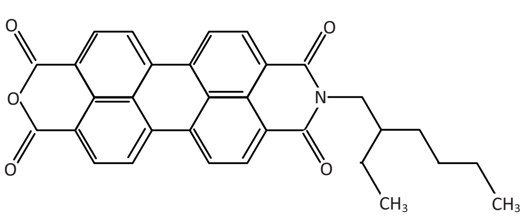
3 Results and discussion As is well known, the thermionic emission is the predominant mechanism of Schottky barrier diodes and the *I–V* characteristics of Schottky devices in the forward bias are given by the following relations [32]:

$$I = I_0\left[\exp\left(\frac{qV}{nkT}\right) - 1\right], \tag{1}$$

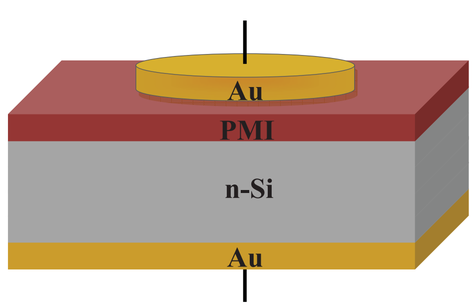
$$I_0 = AA_R T^2 \exp\left(-\frac{q\Phi_B}{kT}\right), \tag{2}$$

where q is the electronic charge, I_0 the saturation current, n the diode ideality (quality) factor, A the Schottky contact area, A_R the effective Richardson constant that is equal to $112\ \mathrm{A\,cm^{-2}\,K^{-2}}$ for n-type Si [32], T the absolute temperature in Kelvin, and Φ_B is the Schottky barrier height. Figure 2 represents the semilog *I–V* characteristics of the Au/PMI/n-Si Schottky diodes in the temperature range of 75–300 K. The values of the ideality factor n and the barrier height Φ_B were calculated from intercepts and slopes of the forward bias *I–V* characteristics at each temperature according to Eqs. (1) and (2), respectively and illustrated in Fig. 3.

Figure 3 shows the values of n (indicated by closed circles) and Φ_B (indicated by open triangles) as a function of temperature. The experimental value of n increased while the values of Φ_B decreased with a decrease in temperature, as can be seen in Fig. 3. The experimental values of n and Φ_B range from 5.08 and 0.675 eV (at 300 K) to 15.32 and 0.179 eV (at 75 K), respectively. A strong increase in the barrier height with measurement temperature cannot be



(a)



(b)

Figure 1 (online colour at: www.pss-a.com) (a) Chemical representation of PMI. (b) Cross-sectional view of Au/PMI/n-Si Schottky diode.

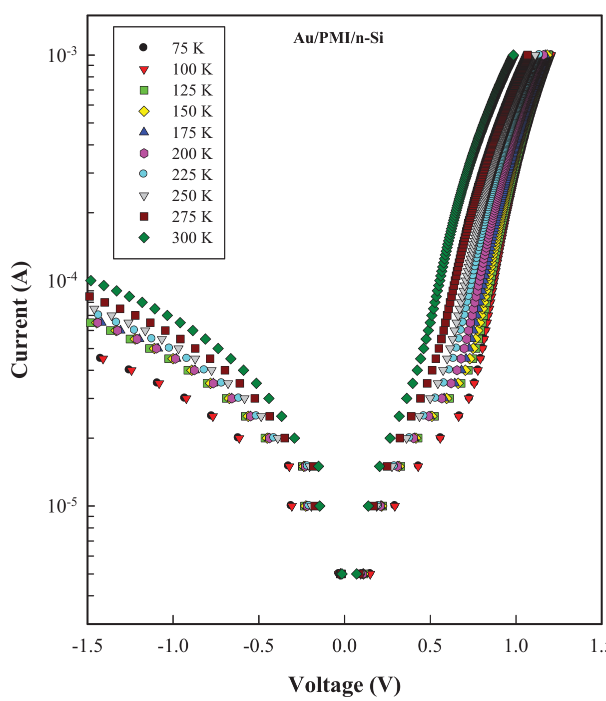


Figure 2 (online colour at: www.pss-a.com) Current–voltage characteristics of Au/PMI/n-Si Schottky devices at various temperatures.

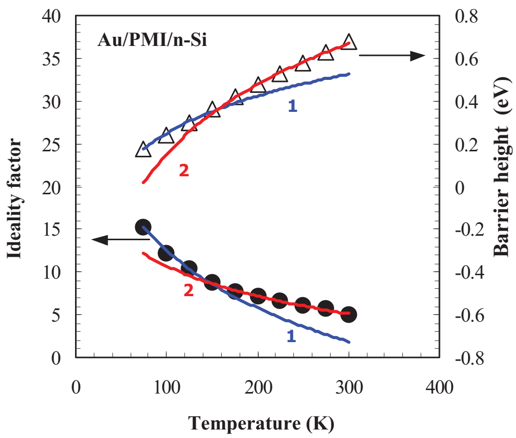


Figure 3 (online colour at: www.pss-a.com) Temperature dependence of the ideality factor (n) (closed circles) and the zero-bias barrier height (Φ_{b0}) (open triangles) for the Au/PMI/n-Si Schottky devices. The continuous curves related to the open triangles and the closed circles show estimated values of Φ_{ap} and n_{ap}.

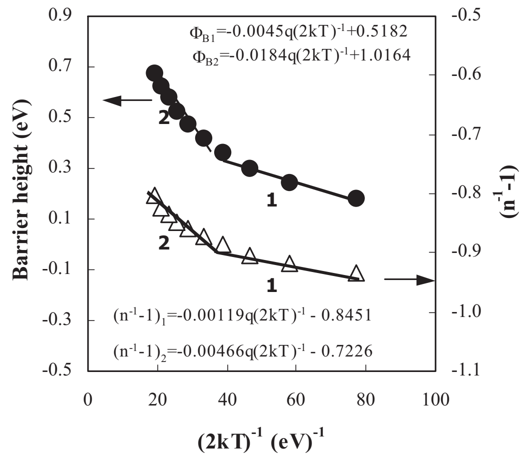


Figure 4 Zero-bias apparent barrier height (closed circles) and apparent ideality factor (open triangles) versus $(2kT)^{-1}$ plots of Au/PMI/n-Si Schottky devices according to a double Gaussian distributions of barrier heights.

explained theoretically. This is a commonly observed phenomenon in real Schottky diodes and attributed to the Schottky barrier height inhomogeneity [9–16]. The current at Schottky barrier diodes will preferentially flow through the lower barriers at low temperature. However, as the temperature increases, electrons gain sufficient thermal energy to surmount the higher barriers. Thus, the barrier heights obtained from I–V–T characteristics are generally in good agreement with the Schottky barrier height inhomogeneity model.

The Schottky barrier height inhomogeneity of the Au/PMI/n-Si Schottky diode was evaluated by Gaussian distribution of the barrier heights [9–16]. Figure 4 shows the experimental plot of Φ_{ap} (indicated by closed circles) and $(n_{ap}^{-1}-1)$ (indicated by open triangles) versus $(2kT)^{-1}$. Normally, for a homogeneous material, this type of plot is a single straight line for which the ordinate intercept determines the zero-bias mean barrier height $\overline{\Phi}_{b0}$ and the slope gives the zero-bias standard deviation σ_{s0}. However, in this case, the best fit of the experimental data for Au/PMI/n-Si Schottky device requires two straight lines corresponding to $i=1$, 2 for different temperature ranges (75–150 K and 175–300 K, respectively) with a transition temperature at ~175 K. This implies that the mean apparent barrier height and standard deviation at zero bias assume different values for the two different temperature intervals and Φ_{ap} and n_{ap} are given by the straight line equations [14]

$$\Phi_{ap}=\overline{\Phi}_{b0}^{(i)}(T=0)-\frac{q(\sigma_{s0}^{(i)})^2}{2kT}, \quad (3)$$

$$\left(\frac{1}{n_{ap}}-1\right)=\gamma^{(i)}-\frac{q\xi^{(i)}}{2kT}, \quad (4)$$

where $\gamma^{(i)}$ and $\xi^{(i)}$ quantify the voltage deformation of the barrier height distribution. The values for relevant parameters were obtained as $\overline{\Phi}_{b0}^{(1)}=0.518\,\text{eV}$, $\sigma_{s0}^{(1)}=0.067\,\text{eV}$, $\overline{\Phi}_{b0}^{(2)}=1.016\,\text{eV}$, and $\sigma_{s0}^{(2)}=0.135\,\text{eV}$. On the other hand, the values $\gamma^{(1)}=-0.845$, $\xi^{(1)}=0.0012$, $\gamma^{(2)}=-0.722$, and $\xi^{(2)}=0.0046$ were calculated. The results clearly demonstrate that two Gaussian distributions of the barrier height exist at the PMI/n-Si Schottky contact. Furthermore, as can be seen in Fig. 3, the continuous solid lines related to the closed circles show the data estimated with $\overline{\Phi}_{b0}^{(1)}$, $\sigma_{s0}^{(1)}$ and $\overline{\Phi}_{b0}^{(2)}$, $\sigma_{s0}^{(2)}$ parameters for the continuous curve 1 and 2 using Eq. (3) in the temperature range of 75–300 K, respectively. The continuous solid lines related to the open triangles depict the data estimated with $\gamma^{(1)}$, $\xi^{(1)}$ and $\gamma^{(2)}$, $\xi^{(2)}$ parameters for the continuous curve 1 and 2 using Eq. (4) in the temperature range of 75–300 K, respectively.

A conventional activation energy $\ln(I_0/T^2)$ versus $1000/T$ plot (indicated by closed circles) of the device is shown in Fig. 5 according to Eq. (2). The experimental data are seen to fit asymptotically to a straight line at higher temperatures only. The values for activation energy and Richardson constant A_R were determined from the slope and the intercept at ordinate of the linear region of the $\ln(I_0/T^2)$ versus 1000/T plot as 0.0586 eV and $4.2\times10^{-9}\,\text{A cm}^{-2}\,\text{K}^{-2}$, respectively. The A_R value is much lower than the theoretical value of $112\,\text{A cm}^{-2}\,\text{K}^{-2}$ for n-Si. This deviation in Richardson plots may be due to the inhomogeneous barrier and potential fluctuations at the metal/semiconductor interface; that is, the current through the contact will flow preferably through the lower barriers [9–16]. The $\ln(I_0/T^2)$ versus 1000/T plot has shown nonlinearity behaviour at low temperatures. Now, to explain these behaviours, the combination of Eqs. (2) and (3) can be rewritten as

$$\ln\left(\frac{I_0}{T^2}\right)-\frac{1}{2}\left(\frac{q\sigma_{s0}^{(i)}}{kT}\right)^2=\ln\left(AA_R^{(i)}\right)-\frac{q\overline{\Phi}_{b0}^{(i)}}{2kT}. \quad (5)$$

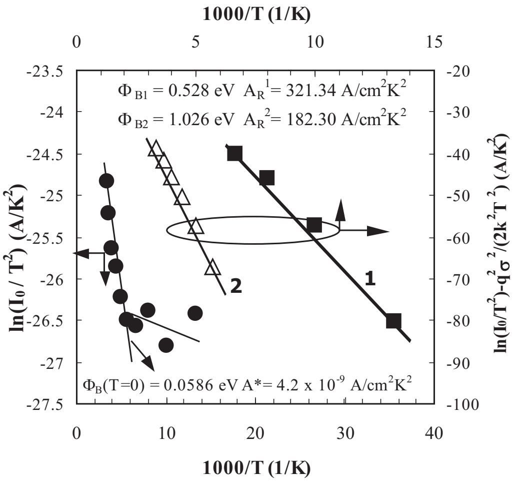


Figure 5 Conventional Richardson plot of the $\ln(I_0/T^2)$ versus $1000/T$ plot (indicated by closed circles) and modified Richardson $\ln(I_0/T^2) - (1/2)(q\sigma_{s0}^{(i)}/kT)^2$ versus $1000/T$ plots of Au/PMI/n-Si Schottky devices according to a double Gaussian distributions of barrier heights. Straight lines (1) and (2) indicate the best fitting of the experimental results in the temperature range 75–150 K and 175–300 K, respectively.

The open triangles and closed squares in Fig. 5 give the best linear fitting for the modified Richardson plots of $\ln(I_0/T^2) - (1/2)(q\sigma_{s0}^{(i)}/kT)^2$ versus $1000/T$ for both values of $\sigma_{s0}^{(i)}$ and zero-bias mean barrrier height $\overline{\Phi}_{b0}^{(i)}$ obtained as $\overline{\Phi}_{b0}^{(1)} = 0.518\,\text{eV}$ in 75–150 K and $\overline{\Phi}_{b0}^{(2)} = 1.026\,\text{eV}$ in 175–300 K, respectively. Richardson constant values of $A_R^{(1)} = 321.34\,\text{A cm}^{-2}\,\text{K}^{-2}$ for low (75–150 K) and $A_R^{(2)} = 182.30\,\text{A cm}^{-2}\,\text{K}^{-2}$ for high temperature range (175–300 K) were found from the ordinate intercept, respectively. Richardson constant value of $A_R^{(2)}$ is very close to the theoretical value ($112\,\text{A cm}^{-2}\,\text{K}^{-2}$) [32].

4 Conclusions In summary, an abnormal decrease in Schottky barrier and an increase in ideality factor with decreasing temperature have been observed. This behaviour has been attributed to the barrier inhomogeneities by assuming a Gassuian distribution of barrier heights at the organic–inorganic semiconductor interfaces. The above results reveal that the *I–V* characteristics of Au/PMI/n-Si Schottky device are satisfactorily interpreted on the basis of a Chand–Kumar model that shows the existence of two Gaussian distributions of the barrier height.

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