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# Capacitance–voltage and current–voltage characteristics of Au Schottky contact on n-type Si with a conducting polymer

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**Abstract**

Capacitance–voltage and current–voltage characteristics of Au/n-type Si (n-Si) and Au/poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT : PSS)/n-Si Schottky diodes were investigated in this study. The interfacial phenomenon was explained in terms of the generation of an interfacial dipole subsequently affecting the electron-injection barrier. The authors found that inserting a PEDOT : PSS layer at the Au/n-Si interface may result in the formation of an interfacial dipole, increase the upward band bending in Si near the interface and reduce the reverse-bias leakage current. In this study, higher quality Schottky junctions were formed on n-Si using a simple technique of spin-coating PEDOT : PSS as the metal electrode.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The metal–semiconductor (MS) contact is one of the most widely used rectifying contacts in the electronics industry [1]. Due to the technological importance of Schottky diodes which are among the most simple of the MS contact devices, a full understanding of the nature of their electrical characteristics is of great interest [1]. It is well known that there are a vast number of reports on the experimental studies of Schottky diodes, metal–insulator–semiconductor devices and solar cells, for which the current–voltage characteristics are still intensively studied [1–7]. In addition, the MS Schottky junction is very useful for evaluating the electronic states of a semiconductor. There are a significant number of theoretical studies on these MS contacts [8–10]. Regarding Schottky contacts, recent investigations have described the barrier heights of Au [8, 11–13], Al-TiW-$Pd_2Si$ [14], Cr [15], Mg [15], Al [15, 16], Ni [16, 17], PtSi [18], NiSi [18], Pt/$HfO_2$ [19] and Pt [5] on n-type Si (n-Si). However, the junction properties were often found to be sensitive to the preparation methods of the metal deposition and the surface treatment condition [16–18, 20, 21], resulting in irreproducible properties if these processes were not well optimized [16]. On the other hand, because of its several advantages (such as high work function, high conductivity, high stability in the oxidized state and the ability to incorporate water-soluble polyelectrolyte dopants), poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT : PSS) has become one of the most widely studied conducting polymers in both academia and industry. PEDOT : PSS is a potential p-type semiconductor material for use in electronic and optoelectronic devices. It serves to enhance the efficiency of the polymer light-emitting diodes and is sometimes regarded as a polymer electrode. On the other hand, p-type conducting polymer has been demonstrated to serve as a high-quality Schottky contact on n-type inorganic semiconductors such as InP and ZnO [22–26]. The solution based soft fabrication process may avoid the formation of the interfacial trap states possibly due to small physical and chemical stresses at the interface giving rise to better junction properties [24]. In this paper, we reported the capacitance–voltage ($C$–$V$) and current density–voltage ($J$–$V$) characteristics of Au Schottky contact on n-Si with and without a conducting polymer. In this study, higher quality Schottky junctions were formed on n-Si using a simple technique of spin-coating PEDOT : PSS as the metal electrode. This information was very helpful for fabricating Si-based Schottky diodes.

## 2. Experimental details

Four-inch Si(1 0 0) wafers of n-type purchased from the Guv Yeam International Co., Ltd were used in the experiment. The n-type wafers were doped with phosphorus to about $2 \times 10^{15}\,\mathrm{cm}^{-3}$. The n-Si samples were cleaned in chemical clean solutions of acetone and methanol. Then the n-Si sample was chemically etched with a diluted HF solution for 1 min, rinsed with DI water and blown dry with $N_2$. Au (40 nm) Schottky contacts with square patterns ($0.16\,\mathrm{cm}^2$) were deposited onto the n-Si surface and In (40 nm) ohmic contacts were deposited onto the n-Si surface by sputter coater, which were referred to as Au/n-Si Schottky diodes. Figure 1($a$) shows the schematic structure of the Au/n-Si Schottky junction. In addition, the n-Si surface was spin coated with a PEDOT : PSS aqueous solution. Next, the PEDOT : PSS films were baked at 150 °C for 30 min in air. The PEDOT : PSS film thicknesses were about 30 nm. Then Au (40 nm) contacts with square patterns ($0.16\,\mathrm{cm}^2$) were deposited onto the PEDOT : PSS films and In (40 nm) ohmic contacts were deposited onto the n-Si surface by sputter coater, which were referred to as Au/PEDOT : PSS/n-Si Schottky diodes. Figure 1($b$) shows the schematic structure of the Au/PEDOT : PSS/n-Si Schottky junction. Planar-type metal contacts were formed by sputter coater. The Au/n-Si and Au/PEDOT : PSS/n-Si Schottky diodes were characterized by $C$–$V$ and $J$–$V$ measurements. The $C$–$V$ characteristics of the Schottky diodes were measured using a Keithley 590 CV analyzer. The $J$–$V$ characteristics of Schottky diodes were measured using a Keithley Model-4200 semiconductor characterization system. We found that the repeatability of the findings was satisfactory. To identify the band bending in n-Si near the PEDOT : PSS/n-Si interface, x-ray photoelectron spectroscopy (XPS) was used to examine the barrier height at the interface. We used a monochromatic Al K$\alpha$ source for XPS analysis. The binding-energy scale was calibrated using the position of the Au 4f peak, measured on a clean gold foil in electrical contact with the substrate. The position ($E_v$) of the valence-band maximum (VBM) is determined by extrapolating two solid lines from the background and straight cutoff in the spectra [27–30].

## 3. Results and discussions

The measured $S^2/C^2$ ($S$ is the Schottky contact area) as a function of applied voltage $V$ at 1 MHz for Au/n-Si or Au/PEDOT : PSS/n-Si Schottky diodes is shown in figure 2. According to the $C$–$V$ relationship of $S^2/C^2 = (2/\varepsilon_s q N_d)(V_i - V)$ for a Schottky diode [31], from

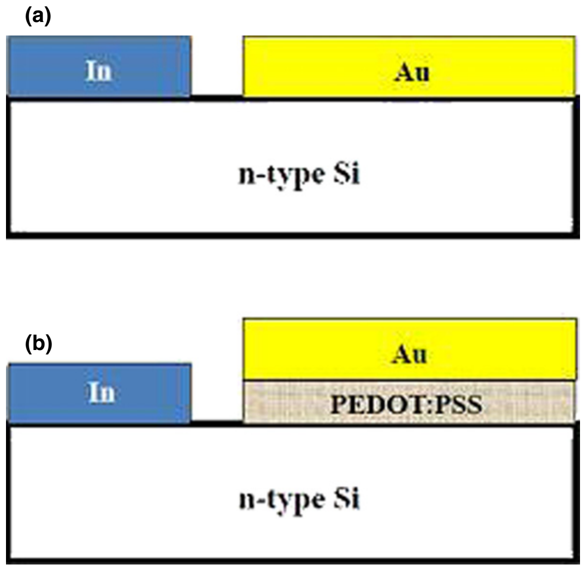


**Figure 1.** The schematic cross section of the ($a$) Au/n-Si and ($b$) Au/PEDOT : PSS/n-Si Schottky junction.

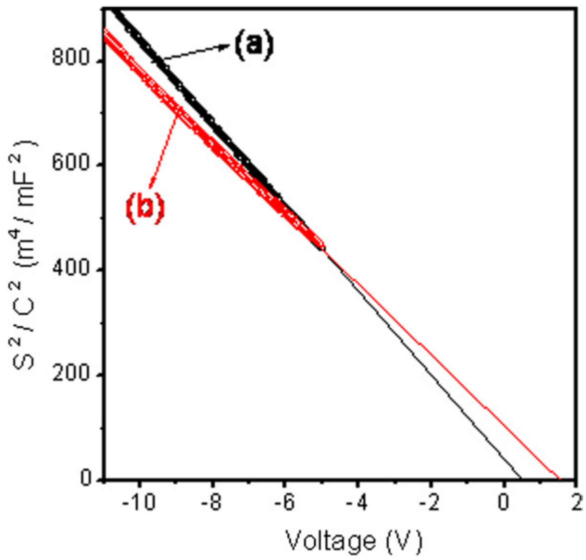


**Figure 2.** $S^2/C^2$–$V$ curves of (a) Au/n-Si and (b) Au/PEDOT : PSS/n-Si Schottky diodes at room temperature.

the slope of figure 2, $N_d$ of $1.56 \times 10^{15}$ and $2.53 \times 10^{15}\,\mathrm{cm}^{-3}$ for Au/n-Si and Au/PEDOT : PSS/n-Si Schottky diodes were calculated, respectively. $q$ is the electron charge, $\varepsilon_s = 11.7\varepsilon_0$ for Si [32], $\varepsilon_0$ is the permittivity in vacuum, $N_d$ is the carrier concentration and $V_i$ is the $x$ intercept at $S^2/C^2 = 0$. These values are similar to those obtained from the Hall measurement with the Van der Pauw method, implying that the depletion layer is formed not in the PEDOT : PSS layer but in the n-Si layer. In addition, the Au/PEDOT : PSS junction is almost ohmic, because the work function of PEDOT : PSS is similar to Au. The Schottky barrier height ($q\phi_{CV}$) is related to $V_i$ by the relationship of $q\phi_{CV} = qV_i + kT + q\xi$, where $q\xi$ is equal to $(E_C - E_F) = kT[\ln(N_c/N_d)]$ and $E_C$ is the energy of the conduction band edge, $E_F$ is the energy of the Fermi level, $N_c$ ($N_c = 2.8 \times 10^{19}\,\mathrm{cm}^{-3}$) [32] is the effective

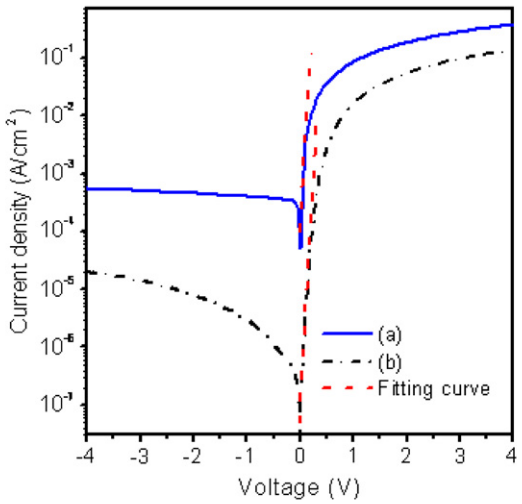


**Figure 3.** $J$–$V$ curves of (a) Au/n-Si and (b) Au/PEDOT : PSS/n-Si Schottky diodes at room temperature and the fitting curve to the forward biased $J$–$V$ characteristics in the TE regime.

**Table 1.** The experimentally obtained characteristic parameters of the Au/n-Si and Au/PEDOT : PSS/n-Si Schottky diodes.

| | $q\phi_{CV}$ (eV) | $q\phi_{JV}$ (eV) | $n$ |
|---|---|---|---|
| Au/n-Si | 0.78 | 0.64 | 1.22 |
| Au/PEDOT : PSS/n-Si | 1.79 | 0.84 | 1.08 |

density of states in the conduction band of n-Si, $T$ is the measurement temperature and $k$ is the Boltzmann constant. $q\phi_{CV}$ for Au/n-Si and Au/PEDOT : PSS/n-Si Schottky diodes is 0.78 and 1.79 eV, respectively. The difference in $q\phi_{CV}$ between the Au/n-Si and the Au/PEDOT : PSS/n-Si Schottky diodes and the higher $q\phi_{CV}$ ($q\phi_{CV} = 1.79$ eV) for the Au/PEDOT : PSS/n-Si Schottky diodes than the Schottky limit may be attributed to enhancing the upward band bending in Si near the PEDOT : PSS/n-Si interface. An explanation for this will be given later.

To further confirm whether the calculated $q\phi_{CV}$ for Au/n-Si or Au/PEDOT : PSS/n-Si Schottky diodes is reasonable, $J$–$V$ measurements were performed. Figure 3 shows the $J$–$V$ characteristics of the Au/n-Si and Au/PEDOT : PSS/n-Si Schottky diodes. The fitting curve of the forward biased $J$–$V$ characteristics in the thermionic emission (TE) regime is also shown in figure 3. The barrier heights ($q\phi_{JV}$) and ideality factors ($n$) were obtained from the forward $J$–$V$ characteristics, according to the equation $J = A^{**}T^2 \exp(-q\phi_{JV}/kT)[\exp(qV/nkT) - 1]$ [16, 33]. $A^{**}$ is the effective Richardson constant (114 A cm$^{-2}$ K$^{-2}$ for n-Si) [32]. By fitting a linear curve to the $J$–$V$ characteristics in figure 3, $q\phi_{JV}$ and $n$ can be calculated. $q\phi_{JV}$ for Au/n-Si and Au/PEDOT : PSS/n-Si Schottky diodes is 0.64 and 0.84 eV, respectively; while $n$ for Au/n-Si and Au/PEDOT : PSS/n-Si Schottky diodes is 1.22 and 1.08, respectively. The experimentally obtained characteristic parameters of the Au/n-Si and Au/PEDOT : PSS/n-Si Schottky diodes from $C$–$V$ and $J$–$V$ measurements are given in table 1.

For Au/PEDOT : PSS/n-Si Schottky diodes, the presence of $n \approx 1$ revealed that the dominant current transport mechanism has TE. Reduced leakage current by one order of magnitude was noted for Schottky diodes with PEDOT : PSS layers compared with Schottky diodes without PEDOT : PSS layers. As well as suppressing reverse-bias leakage, the presence of PEDOT : PSS was found to substantially improve $n$ of the modified surface diodes compared with the unmodified surface diodes, suggesting that such a PEDOT : PSS modification process could be useful for various Si-based Schottky diodes. For the Au/n-Si Schottky diodes, we find that $q\phi_{CV}$ ($q\phi_{CV} = 0.78$ eV) is higher than $q\phi_{JV}$ ($q\phi_{JV} = 0.64$ eV), because the presence of the induced tunnelling component by Au-induced gap states and defects existing in Si near the Au/n-Si interface and the image-force lowering are not considered for the barrier-height calculation according to the TE model. This results in an underestimated barrier height calculated from the TE model (due to the formation of the larger $n$ ($n = 1.22$) than 1). In addition, we find that $q\phi_{JV}$ (the reverse-bias leakage current density) for Au/PEDOT : PSS/n-Si Schottky diodes is higher (lower) than $q\phi_{JV}$ (the reverse-bias leakage current density) for Au/n-Si Schottky diodes, because of the presence of the induced tunnelling component by Au-induced gap states and defects existing in Si near the Au/n-Si interface. Although the reactivity of Au with Si is very small, Au silicide formation is known when Au is evaporated onto the Si surface at room temperature [8, 34]. Photoemission spectroscopy study of the room-temperature-grown Au/Si interface revealed the process of Au–Si alloy formation [11]. For Au/PEDOT : PSS/n-Si Schottky diodes, the $n$ value close to unity and the decrease in the reverse-bias leakage current pointed to the high quality of the junction and the discrepancy (the neglect of the image-force lowering) in barrier-height values obtained from $C$–$V$ and $J$–$V$ measurements, suggesting the existence of the interfacial dipole layer [25]. Among the $C$–$V$ methods, the barrier height is most commonly calculated from the intercept voltage, determined by an extrapolation of the $1/C^2$ versus $V$ curve to $1/C^2 = 0$. The barrier height so determined is $q\phi_{CV}$ for sufficient forward bias to cause flatband conditions in the semiconductor, meaning that $q\phi_{CV}$ is unrelated to the interfacial dipole ($\Delta$) and $q\phi_{CV}$ is deeply related to the band bending in the semiconductor. As a result, we deduce that $q\phi_{JV}$ may be close to $q\phi_{CV}$ based on the absence of $\Delta$ and the neglect of the image-force lowering. If $\Delta$ is found, the difference between $q\phi_{JV}$ and $q\phi_{CV}$ will be equal to $\Delta$ based on the neglect of the image-force lowering. It is reported that $\Delta$ is formed between organic and organic, inorganic and organic, due to various origins such as charge transfer across the interface, redistribution of electron cloud, interfacial chemical reaction and other types of rearrangement of electronic charge [35, 36]. The equation $q\phi_{JV} = q\phi_{\rm m} - \chi + \Delta$ was previously employed by Ishii *et al* [35] and Agrawal and Ghosh [37] for calculating the barrier heights of electron injection [25]. $q\phi_{\rm m}$ is the work function of the electrode and $\chi$ is the electron affinity of the solid before the electrode fabrication. This explains why $q\phi_{CV}$ is higher than $q\phi_{JV}$ for Au/PEDOT : PSS/n-Si Schottky diodes. Thus, we deduce that $\Delta$ ($\Delta = -0.95$ eV) at the PEDOT : PSS/n-Si interface equals the difference between

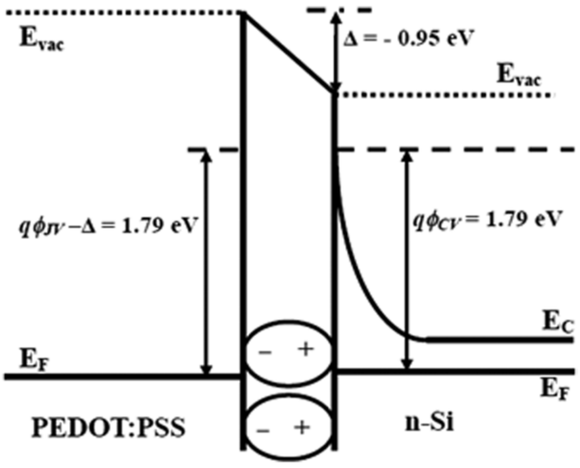


**Figure 4.** Schematic band diagrams of the PEDOT : PSS/n-Si Schottky junction.

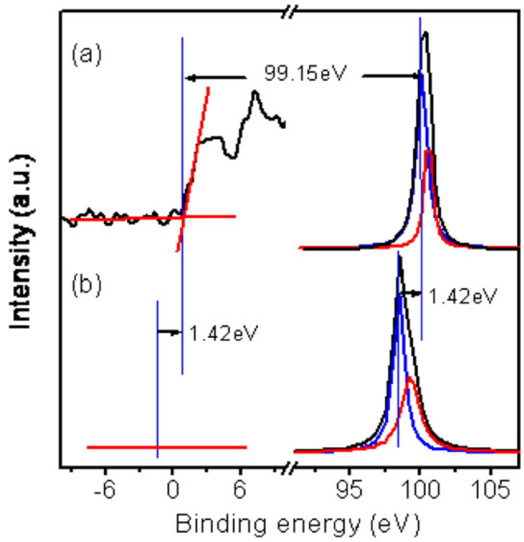


**Figure 5.** (a) The left-hand figure presents the spectrum of the valence-band region and the right-hand spectrum shows the Si 2p core-level spectra on the n-Si surfaces. (b) Si 2p core-level spectra at the PEDOT : PSS/n-Si interfaces.

$q\phi_{JV}$ and $q\phi_{CV}$ for Au/PEDOT : PSS/n-Si Schottky diodes [25]. The presence of $\Delta < 0$ at the PEDOT : PSS/n-Si interface may lead to decreased barrier height for electrons and increased electron-injection efficiency, lowering the effect of the strong band bending in Si near the interface on the electrical property of the Au/PEDOT : PSS/n-Si Schottky diode. Recently, a systematic study showed that $\Delta$ of up to 1 eV can exist in interfaces between PEDOT : PSS and pentacene [38]. The energy band diagram of the PEDOT : PSS/n-Si Schottky junction is shown in figure 4. Koch *et al* [39] suggested that the formation of $\Delta$ is most likely related to this change in the difference in vacuum levels ($E_{vac}$) between organic semiconductors.

To confirm the band bending in n-Si near the PEDOT : PSS/n-Si interface and the barrier height at the PEDOT : PSS/n-Si interface, XPS was employed to determine $E_v$ of n-Si samples and the position ($E_{Si2p3/2}$) of the Si $2p_{3/2}$ core-level peak at the n-Si surfaces before or after the PEDOT : PSS coating. The PEDOT : PSS film thicknesses, as estimated from atomic force microscopy, were about 10 nm. Electron spectroscopy is an increasingly important technique for measuring abrupt semiconductor interface potentials using a direct contactless nondestructive method [40]. Figure 5 shows an example of the Si 2p core level and the valence-band spectrum collected on a n-Si sample without a PEDOT : PSS overlayer. The Si 2p spectra are deconvoluted for Si $2p_{3/2}$ and Si $2p_{1/2}$ [41]. $E_v$ was measured to be 0.79 eV and $E_{Si2p3/2}$ was observed at 99.94 eV, implying that the binding-energy difference between $E_{Si2p3/2}$ and $E_v$ equals 99.15 eV, agreeing with the previously reported value of 99.10 eV [41]. Figure 5 also shows the Si 2p core-level XPS spectra at the PEDOT : PSS/n-Si interface. We find that $E_{Si2p3/2}$ at the PEDOT : PSS/n-Si interface is located at 98.52 eV. Based on the results shown in figure 5 and the band gap energy ($E_g = 1.12$ eV) [28] of n-Si, the upward band bending formed in Si near the PEDOT : PSS/n-Si interface was estimated to be 1.5 eV and the barrier height at the interface was calculated to be about 1.75 eV, which is similar to the result obtained from the $C$–$V$ measurements.

## 4. Conclusions

In summary, the electrical properties of the Au/n-Si and Au/PEDOT : PSS/n-Si Schottky diodes have been explored. We found that the presence of PEDOT : PSS for n-Si Schottky diodes could lead to increased band bending in n-Si near the PEDOT : PSS/n-Si interface determined from $C$–$V$ and XPS measurements and the formation of $\Delta$ determined from $C$–$V$ and $J$–$V$ measurements. For Au/n-Si Schottky diodes, the formation of the larger $n$ than 1 and the discrepancy in barrier-height values obtained from $C$–$V$ and $J$–$V$ measurements suggest the existence of the interface states associated with Au-induced gap states, resulting in the formation of the tunnelling component of the current through the barrier and increased reverse-bias leakage current density. In this study, higher quality Schottky junctions were formed on n-Si using a simple technique of spin-coating PEDOT : PSS as the metal electrode.

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