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Energy-level alignment and electrical properties of Al/p-type Si Schottky diodes with sorbitol-doped PEDOT:PSS as an organic interlayer

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ABSTRACT

The current–voltage (*I–V*) characteristics of Al/p-type Si Schottky diodes with pristine and 5 wt.% sorbitol-doped organic PEDOT:PSS interlayers have been investigated. It was found that the barrier heights of the diodes with pristine and sorbitol-doped PEDOT:PSS are higher than those of a conventional Al/p-type Si Schottky diode because of the modification of the effective barrier height by the organic interlayer. It is noted that the Al/p-type Si Schottky diode with sorbitol-doped PEDOT:PSS interlayer exhibits higher barrier height and lower series resistance, as compared to Al/p-type Si Schottky diodes with pristine PEDOT:PSS interlayer. In addition, UPS measurements indicate that the position of the HOMO level is closer to the Fermi level for pristine PEDOT:PSS than for sorbitol-doped PEDOT:PSS. As a result, the hole injection barrier height is 0.15 eV lower in the pristine PEDOT:PSS structure than in the sorbitol-doped PEDOT:PSS. This value closely matches the difference in barrier heights (0.12 eV) seen in the *I–V* measurements. An energy-level alignment diagram is also presented and discussed for the structures studied. The Poole–Frenkel mechanism is found to dominate the reverse leakage current in both structures, indicating the presence of structural defects and trap levels in the organic film.

1. Introduction

High-quality metal-semiconductor diodes with low ideality factors using thin interfacial films are crucial for the electronic devices. To achieve such diodes, polymeric or non-polymeric organic compounds can be used as contacts to inorganic semiconductors such as Si, GaAs, and InP to continuously control the barrier height at particular semiconductor interfaces [1–3]. Such organic materials have attracted significant attention because of their ease of device processing, low cost, suitability for large-area devices, and wide range of applications in electronic and optoelectronic devices [4,5], and numerous studies have been performed to investigate the electronic properties of various organic thin films on semiconductors [6,7]. However, most inorganic materials have higher electron mobilities than organic materials. Therefore, attempts have been made to fabricate high-performance electronic devices that take advantage of both organic and inorganic semiconductors. The growth of organic thin films on inorganic semiconductor substrates can modify the electronic properties of the metal/semiconductor MS contacts, since the Schottky barrier heights of metal-semiconductor contacts are changed by the formation of a dipole layer between the semiconductor and the organic film [8]. For instance, the insertion of a copper phthalocyanine (CuPc) interlayer in between a Pt film and a Ge substrate changes the Schottky barrier height of this interface [9].

In recent years, conducting polymers have received much attention because of their wide range of device applications. Among organic materials, poly (3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) has become very attractive because of its good environmental stability, low band gap, low redox potential, and high optical transparency in its electrically conductive state. These advantages make PEDOT:PSS an excellent candidate for use in electronic or optoelectronic devices [10,11]. In our previous work, an attempt was made to investigate the effect of PEDOT:PSS on the electrical properties of the Pt/n-Ge Schottky contact as interlayer [12]. The PEDOT:PSS interlayer effectively modified the interfacial potential barrier of the

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Pt/n-Ge Schottky contact resulting in an increased barrier height. PEDOT:PSS is a good p-type semiconducting polymer, and therefore it has been proposed for use as a hole injection layer or as an electrode for organic solar cells and light-emitting diodes [13,14]. However, its relatively low conductivity is still a major road block to the wide spread device applications. Recently, several approaches have been developed to improve the conductivity of PEDOT:PSS, including thermal treatment; secondary doping of inert solvents such as glycerol, sorbitol, dimethyl sulfoxide, *N*,*N*′-dimethyl formamide (DMF), and tetrahydrofuran (THF); and doping of polymers such as poly (vinylpyrrolidone) and polyethylene oxide or conducting nanomaterials such as carbon nanotubes [13,15,16]. These additives have been reported to improve the hole extraction from polymer solar cells [17]. The enhanced conductivity observed when sorbitol-doping is performed is believed to be related to the interaction between the sorbitol and the PEDOT:PSS. In this paper, an attempt has been made to investigate the electrical characteristics of Al/p-type Si Schottky contacts with pristine PEDOT:PSS or sorbitol-doped PEDOT:PSS as an organic interlayer. The effect of sorbitol doping on the work function of the PEDOT:PSS and pristine PEDOT:PSS have been determined using the ultraviolet photoelectron spectroscopy (UPS) measurements. Despite the difficulty in measuring the work function using UPS, the work function values determined from the UPS spectrum are in good agreement with the previously published values, mentioned in the discussion that follows later. Furthermore, the barrier heights determined from the UPS measurements are in reliable agreement with the barrier height values obtained from the current–voltage (*I*–*V*) characteristics. The reverse leakage conduction mechanisms of the fabricated structures have also been investigated.

2. Experimental details

P-type Si (100) (boron-doped) wafers with a doping concentration of 5×10^{15} cm^{-3} were used in this study. The native oxide on the front surface of the Si was removed by immersion in HF:H_2O (1:10) solution and subsequent rinsing in deionized (DI) water, followed by drying in high-purity nitrogen. The pristine PEDOT:PSS and 5 wt.% sorbitol-doped PEDOT:PSS organic polymer films were spin-coated on p-type Si for 30 s at 2000 rpm and then annealed for 20 min at 120 °C. Then, 30-nm-thick Al electrodes were fabricated on the PEDOT:PSS (with and without sorbitol doping) thin films by thermal evaporation through a metal shadow mask with the area of 100 μm × 100 μm. The current–voltage (*I*–*V*) characteristics of the Al/PEDOT:PSS (with and without sorbitol doping)/p-type Si Schottky structures were measured using a precision semiconductor parameter analyzer (Agilent 4156C). Ultraviolet photoelectron spectroscopy (UPS) (AXIS-NOVA, Kratos Inc.) with a excitation energy of He I (21.2 eV) was employed to characterize the electronic structure of the Al/PEDOT:PSS (with and without sorbitol doping)/p-type Si Schottky structures. An energy resolution in UPS of 0.05 eV was determined from the slope of the Fermi edge of a cleaned Au surface. UPS spectra were collected with a hemispherical electron energy analyzer, and with the sample-biased at −10.0 V to clear the surface vacuum level.

3. Results and discussion

Fig. 1 shows the *I*–*V* characteristics of the Al/p-type Si Schottky diodes with pristine PEDOT:PSS or sorbitol-doped PEDOT:PSS as an organic interlayer measured at room temperature. As can be seen from Fig. 1, Al/p-type Si Schottky diodes with and without interlayer exhibited rectifying behavior, with the current levels being decreased on insertion of the interlayer. The current shows an exponential increase in the forward bias and a weaker voltage dependence in the reverse bias. Therefore, thermionic emission theory can be used to analyze the electrical properties of the devices. When a Schottky device with a series resistance and an interface layer is considered (with respect to forward bias voltages of $V > 3kT/q$), it is assumed that the net current of the device is due to the thermionic emission, and thus it can be expressed as [18]:

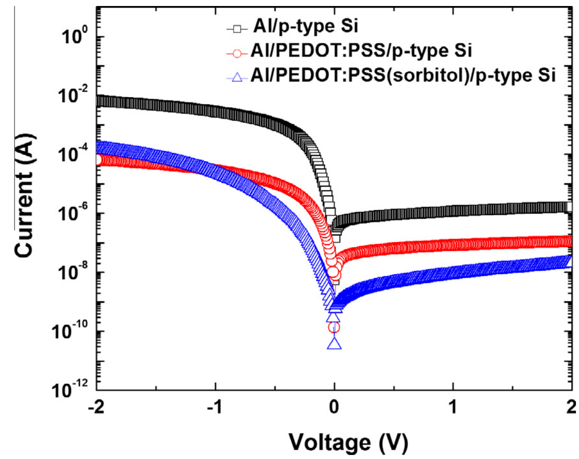

Fig. 1. *I*–*V* characteristics of Al/p-type Si Schottky diodes with and without pristine and sorbitol-doped PEDOT:PSS interlayers.

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

where I_0 is the saturation current given by:

$$I_0 = AA^{**}T^2 \exp\left(-\frac{q\Phi_{b0}}{kT}\right) \quad (2)$$

q is the electron charge, V is the applied voltage, k is the Boltzmann constant, n is the ideality factor, A^{**} is the Richardson constant (32 A cm^{-2} K^{-2}), T is the temperature, and Φ_{b0} is the barrier height. The saturation current I_0 is obtained as the intercept at $V = 0$ V and ideality factor from the slope of linear fitting the straight line portion of the plot of ln(I) versus V. The linear fitting equation is given as $\ln(I) = \ln(I_0) + (q/nkT)V$ obtained from Eq. (1) from which the saturation current I_0 and the ideality factor are determined. Once I_0 is determined, the barrier height (Φ_{b0}) can be evaluated as:

$$\Phi_{b0} = \frac{kT}{q} \ln\left(\frac{AA^{**}T^2}{I_0}\right) \quad (3)$$

As previously mentioned, the ideality factor can be determined from the slope of the linear region of the plot of ln(I) versus V as:

$$n = \frac{q}{kT}\left(\frac{dV}{d(\ln I)}\right) \quad (4)$$

The barrier height and ideality factor are found to be 0.58 eV and 1.05 for the Al/p-type Si Schottky diode, respectively. On the other hand, our measurements showed that the barrier height and ideality factor of the Al/PEDOT:PSS/p-type Si Schottky diode are 0.61 eV and 1.06, respectively, and those of the sorbitol-doped PEDOT:PSS Schottky diode are 0.73 eV and 1.26, respectively. Thus, the barrier heights of the Al/p-type Si Schottky contacts with pristine and sorbitol-doped PEDOT:PSS interlayers are higher than that of the conventional Al/p-type Si Schottky contact. This is attributed to the modification of the effective barrier height due to the organic interlayer, which influences the space charge region of the inorganic substrate [19]. Namely, the organic film forms a physical barrier between the metal and the Si substrate, preventing the metal from directly contacting the Si surface [19–21]. Therefore, the PEDOT:PSS interlayer produces a substantial shift in the work function of the metal and in the electron affinity of the semiconductor, and this in turn increases the barrier height. Moreover, it is observed that the barrier height increases further for the sorbitol-doped PEDOT:PSS Schottky structure. A detailed description of this phenomenon is presented below.