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Schottky contact on a ZnO (0001) single crystal with conducting polymer

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High quality Schottky junctions were fabricated on a ZnO (0001) bulk single crystal by spin coating a commercial conducting polymer, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS), as the metal electrodes. The junctions exhibited excellent rectifying behavior with a typical ideality factor of 1.2. Such parameters as Schottky barrier height (ϕ_b) and built-in potential (V_{bi}) show negligible variation among junctions. The electron affinity of ZnO derived from ϕ_b and qV_{bi} values show a slight deviation ($\sim$0.2 eV), suggesting the existence of spontaneously formed interfacial dipole layer between ZnO (0001) polar surface and anionic PSS molecules. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2789697]

A wide-gap semiconductor zinc oxide (ZnO), for which *p*-*n* junction light emitting diode and quantum Hall effect have been already demonstrated,[1–3] is one of the promising compounds for realizing transparent oxide electronics.[4–7] For developing various electronic devices using ZnO, high quality electric contacts on ZnO, both Ohmic and Schottky contacts, have to be formed with desired properties. Metal/semiconductor Schottky junction is very useful for evaluating the electronic states of a semiconductor.[8] From the current and capacitance measurements, such electronic properties of the semiconductor as the ionized dopant concentration, depletion layer width, and band line-up parameters can be evaluated. Also, capacitance measurement can be used to probe carrier distribution and energy band discontinuity in semiconductor heterostructures.[9] Moreover, high-quality Schottky junction can be used for such applications as metal-semiconductor field-effect transistors and photodetectors.[10–12]

In order to form Schottky contact on an *n*-type ZnO, various noble metals with large work function such as Au, Ag, Pt, and Pd have been employed.[13–15] However, the junction properties were often found to be sensitive to the preparation methods of the metal deposition and/or the surface treatment condition, resulting in irreproducible properties if these processes were not well optimized. On the other hand, *p*-type conducting polymer, poly(pyrrole), was demonstrated to serve as a high quality Schottky contact on *n*-type inorganic compound semiconductors such as InP.[16,17] Solution based soft fabrication process may avoid the formation of interfacial trap states possibly due to small physical and/or chemical stresses at the interface, giving rise to better junction properties.

Here, we report on the realization of high quality Schottky junctions by simply spin coating a commercially available *p*-type conducting polymer on a ZnO (0001) single crystal.

ZnO single crystal substrate (Tokyo Denpa) was chemically etched with a diluted HCl solution, followed by ultrasonication in organic solvents and UV-ozone exposure for eliminating surface contaminants. The Zn-polar surface was then spin coated with poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) aqueous solution (H. C. Starck, Baytron PH500) and dried in a vacuum oven at 200 °C for 30 min in a glove box with Ar atmosphere. PEDOT:PSS coated glass substrates were also prepared through the same procedure for electrical measurements of the PEDOT:PSS thin films. The work function and the resistivity of PEDOT:PSS films were measured in air by photoelectron yield spectroscopy (Riken Keiki, AC-2) and a four point contact probe, respectively.

Figure 1(a) shows the chemical structures of PEDOT (left) and PSS (right). Polythiophene backbone of PEDOT forms the pathway for hole transport (π-conjugated system, dotted line), and PSS acts as an acceptor. Figure 1(b) shows photoelectron yield spectrum of a PEDOT:PSS film on glass substrate. From the linear fit to (Photoelectron yield)$^{1/2}$

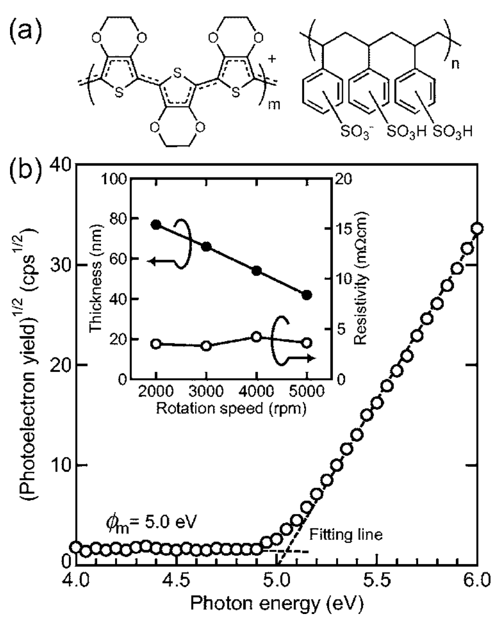

FIG. 1. (a) Chemical structures of PEDOT (left) and PSS (right). (b) Photoelectron yield spectrum of a PEDOT:PSS film coated on glass substrate. Broken straight lines denote the fitting lines to evaluate the work function (ϕ_m). The inset shows the film thickness and the electrical resistivity of PEDOT:PSS films formed on glass substrates as a function of the rotation speed during spin coating.

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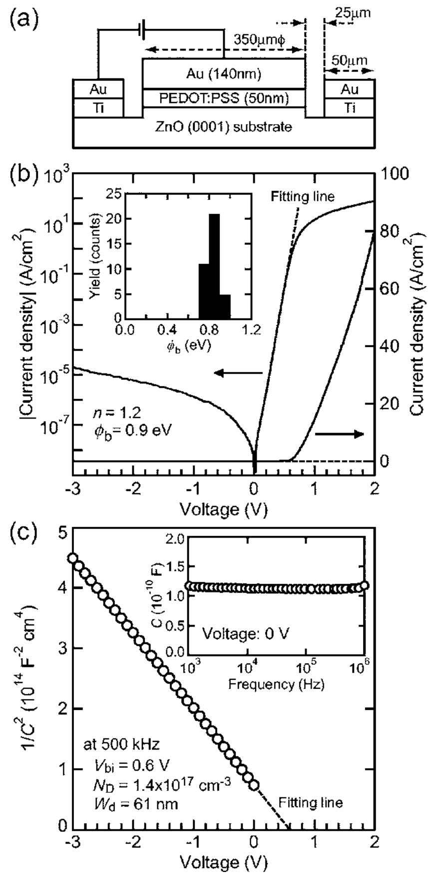

FIG. 2. (a) The schematic cross section of the PEDOT:PSS/ZnO Schottky junction. (b) The current density–voltage (J-V) characteristics for the PEDOT:PSS/ZnO Schottky junction. The ideality factor (n) and the Schottky barrier height (ϕ_b) are also shown. The histogram of ϕ_b among 37 junctions on a ZnO substrate is shown in the inset. (c) The capacitance-voltage (C-V) characteristics for the PEDOT:PSS/ZnO Schottky junction measured at 500 kHz. The built-in potential (V_{bi}), ionized donor concentration (N_D), and the depletion layer width (W_d) at $V=0$ V are also indicated. The frequency dependence of the junction capacitance at $V=0$ V is shown in the inset.

$\propto (h\nu - \phi_m)$ ($h\nu$ is photon energy), the work function (ϕ_m) of PEDOT:PSS was evaluated to be 5.0 eV, which is similar to the value reported in literatures.[18–20] The film thickness of PEDOT:PSS was controlled by the rotation speed of spin-coating ranging from 40 to 80 nm with no significant change in the resistivity as low as ~ 1 m Ω cm, as shown in the inset of Fig. 1(b). In the present study, the rotation speed was set at 4000 rpm and the thickness of PEDOT:PSS film was about 50 nm. It is worth noting that the optical transmittance of a 50 nm thick PEDOT:PSS film showed excellent internal transmittance of $>90\%$ for a wide region of wavelength from 250 to 1000 nm (not shown), which is suitable for optical application such as Schottky photodetectors.

Figure 2(a) shows the schematic structure of the PEDOT:PSS/ZnO Schottky junction. Au contact electrode was deposited on the PEDOT:PSS/ZnO by thermal evaporation. Circular mesa structures with a diameter of 350 μm and ring-shaped Ohmic electrodes (Ti/Au) were formed on the ZnO substrate by Ar ion milling and electron-beam evaporation through photolithography technique, where the junction area was 9.6×10^{-4} cm^2. The junction properties were examined by current density–voltage (J-V) and capacitance-voltage (C-V) measurements at room temperature in air under dark condition, using semiconductor parameter analyzer (Agilent Technologies, 4155C) and LCR meter (Agilent Technologies, 4284A), respectively. The forward bias (positive V) corresponds to the current flow from PEDOT:PSS to ZnO. Figure 2(b) shows a typical J-V characteristics in linear (right) and log (left) scales. The junction shows a good rectifying behavior: the rectification ratio $|J(2\text{ V})|/|J(-2\text{ V})|$ is as high as $\sim 10^7$. From the thermionic emission model,[8] a Schottky junction under forward bias has the J-V relation of

$$J = J_0 \exp\left(\frac{qV}{nk_BT}\right) \quad (V \gg 3k_BT/q), \tag{1}$$

where J_0 is the saturation current density, q is the elementary charge, V is the applied voltage, n is the ideality factor, k_B is Boltzmann's constant, and T is the absolute temperature. J_0 is expressed as

$$J_0 = A^* T^2 \exp\left(-\frac{\phi_b}{k_BT}\right), \tag{2}$$

where A^* is the effective Richardson constant with $A^* = 36$ A cm^{-2} K^{-2} for ZnO ($m_e^* = 0.3m_0$),[21] and ϕ_b is the Schottky barrier height. The slope and the J intercept from the linear fit to the semilog plot for $V=0.4-0.5$ V yield in $n=1.2$ and $\phi_b=0.9$ eV, respectively. The n value close to unity indicates the high quality of the junction. The resultant rectification ratio and n are comparable to the best value using Pt and Ag electrode in recent reports,[12,22,23] in spite of the simple spin-coating process in this study. The inset of Fig. 2(b) shows the histogram of ϕ_b variation among different 37 junctions on a ZnO substrate, indicating the considerably small deviation in their properties.

Figure 2(c) shows the $1/C^2$-V characteristics of the same device measured at 500 kHz. The $1/C^2$-V characteristics show good linearity in the measured voltage range, reflecting the small leakage current (observed tangent δ was as low as 0.01). Also, the linearity suggests the uniform distribution of the ionized donors in the ZnO substrate and the voltage independent relative permittivity (ε_s) of ZnO. The Schottky junction under reverse bias has a C-V relation of

$$\frac{1}{C^2} = \frac{2(V_{bi} - V)}{q\varepsilon_s\varepsilon_0 N_D}, \tag{3}$$

where C is the capacitance in unit area, V_{bi} is the built-in potential, ε_0 is the vacuum permittivity, and N_D is the ionized donor concentration in the depletion layer. The depletion layer width ($W_d = \varepsilon_s\varepsilon_0/C$) is expressed as

$$W_d = \sqrt{\frac{2\varepsilon_s\varepsilon_0}{qN_D}(V_{bi} - V)}. \tag{4}$$

From Eq. (3), the V intercept and the slope from the linear fit in Fig. 2(c) for $V=-3-0$ V yield in $V_{bi}=0.6$ V and $N_D = 1.4 \times 10^{17}$ cm^{-3}, assuming $\varepsilon_s = 8$.[21] The value of N_D is consistent with the value of the electron concentration in ZnO substrate obtained from Hall measurement with van der Pauw method, implying that the depletion layer is formed not in the PEDOT:PSS layer but in the ZnO layer. From Eq. (4), the depletion layer width spans from $W_d=61$ nm at 0 V to 150 nm at -3.0 V. The inset of Fig. 2(c) shows the frequency dependence of the junction capacitance at $V=0$ V. The almost frequency independent behavior may suggest the small effect of interfacial trap states in the junction. All the different 37 junctions show negligible variation in V_{bi} as well as ϕ_b (not shown).

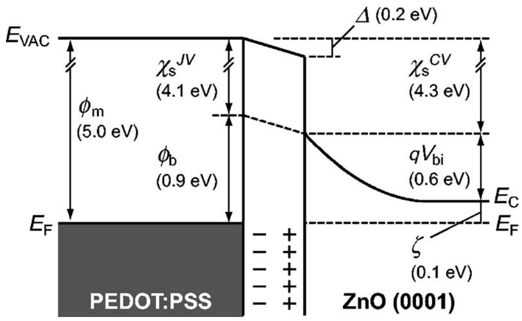

FIG. 3. The schematic energy band diagram of the PEDOT:PSS/ZnO Schottky junction. The evaluated junction parameters are also shown. E_{VAC}, E_F, and E_C are the vacuum level, the Fermi energy, and the bottom of the conduction band, respectively. ζ is the energy difference between E_C and E_F. χ_s^{JV} and χ_s^{CV} are the electron affinity from *J-V* and *C-V* measurements, respectively. Δ is the vacuum level shift. The positive and negative symbols represent the electric dipole layer spontaneously formed at the interface.

In a metal/*n*-type semiconductor Schottky junction, the electron affinity (χ_s) of the semiconductor can be determined from the *J-V* measurement using a simple relation of $\chi_s^{JV} = \phi_m - \phi_b$. In the present case, $\phi_m = 5.0$ eV and $\phi_b = 0.9$ eV lead to $\chi_s^{JV} = 4.1$ eV. While χ_s can also be deduced from *C-V* characteristics using a relation of $\chi_s^{CV} = \phi_m - (qV_{bi} + \zeta)$, where ζ is the energy difference between the bottom of the conduction band and the Fermi energy $(E_C - E_F)$, expressed as $\zeta = k_B T \ln(N_C/N_D)$, where N_C stands for the effective density of states at the conduction band bottom in ZnO. N_C is deduced to be 4×10^{18} cm^{-3} at room temperature from $N_C = 2(2\pi m^* k_B T/h^2)^{3/2}$, and then ζ yields in 0.1 eV. From $\phi_m = 5.0$ eV and $qV_{bi} = 0.6$ eV, χ_s^{CV} is evaluated to be 4.3 eV. The obtained values of χ_s^{JV} and χ_s^{CV} are within the range of reported values of 4.1–4.4 eV.[24–26] Note that χ_s^{JV} is smaller than χ_s^{CV} representing opposite tendency to the conventional Schottky junctions.

Figure 3 shows the resultant energy band diagram of the PEDOT:PSS/ZnO Schottky junction. The obtained junction parameters are also shown. The discrepancy of χ_s obtained from *J-V* or *C-V* measurements could be attributed to a dipole layer existing at PEDOT:PSS/ZnO (0001) interface, that is caused by static Coulomb interaction between the ZnO (0001) polar surface and the anionic PSS molecules in PEDOT:PSS. The importance of such a large spontaneous polarization along the *c* axis[27–29] was already pointed out in our quantum Hall effect experiments[3] and other experiments.[23] It is well-known that such interfacial dipole causes the vacuum level shift (Δ) for organic/metal and organic/organic interfaces.[30] This sort of dipole will shift the Schottky barrier height, giving rise to the difference between χ_s^{JV} and χ_s^{CV}, as shown in Fig. 3. Range of Δ for all the junction is 0.1–0.2 eV depending on the variation in ϕ_b and V_{bi}, where Δ increases linearly with the decreasing *n*. It should be mentioned that the magnitude of $\Delta \sim 0.2$ eV is in the same order with the vacuum level shift observed at the interface between PEDOT:PSS and organic molecules.[18]

In summary, high quality Schottky junctions were formed on a ZnO (0001) single crystal by employing a simple technique of spin-coating PEDOT:PSS as the metal electrode. The high rectification ratio and small *n* value near unity were reproducibly realized. The discrepancy in χ_s values obtained from *J-V* and *C-V* measurements suggest the existence of the interfacial dipole layer.

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