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Polymer Schottky contact on O-polar ZnO with silane coupling agent as surface protective layer

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We report on a Schottky junction fabricated on O-polar ZnO surfaces with a silane-coupling agent as a protective layer, and a conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as a deep work function metal electrode, simply by using wet processes. The silane-coupling agent prevented the O-polar ZnO surface from an etching reaction in contact with the acidic PEDOT:PSS solution, resulting in a good rectification with a current rectification ratio of 10^7 at ± 1 V. The junction characteristics were systematically controlled in accord with the electron density in ZnO ranging from 8×10^{14} to 4×10^{16} cm^{-3}. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2956419]

A metal/semiconductor Schottky junction is one of the most fundamental devices that can be used to evaluate various semiconductor parameters including carrier density and Schottky barrier height as well as carrier density profile and band gap discontinuity.[1,2] ZnO is one of the oxide semiconductors possessing a wide direct band gap of 3.37 eV and a large electron affinity (χ_s) of 4.1–4.4 eV.[3] Recent advances in ZnO epitaxial growth techniques led to the demonstrations of light-emitting *p-n* homojunction diode and quantum Hall effect at $Mg_xZn_{1-x}O/ZnO$ heterointerfaces.[4–6] Fabrication of a good Schottky contact to the ZnO surface will further promote an understanding of the device physics and practical applications such as photodiodes. However, it has been difficult to reproduce high performance Schottky junctions on ZnO with noble metals such as Au, Pt, and Ag,[7–10] despite the high *S*-index due to the strong ionicity[11] and a number of proposed surface treatment methods. To account for an intrinsic nature of ZnO surface lying under this issue, a model of the Fermi level pinning due to the oxygen vacancies near the surfaces has been proposed.[12]

Recently, we proposed a conducting polymer, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS), as a good candidate for Schottky contact electrode on the Zn-polar surface.[13] PEDOT:PSS is composed of π-conjugated PEDOT and *p*-type dopant of PSS and has been widely used as hole injection electrodes in organic electronic devices. Electrical conductivity and work function (ϕ_m) of the PEDOT:PSS used in our experiments are about 300 S cm^{-1} and 5.0 eV, respectively. This polymer electrode is expected to avoid a surface damage because of the moderate fabrication processes at room temperature.

It is well known that Zn- and O-polar surfaces have quite different chemical reactivities.[14] Usually, epitaxial film surfaces are terminated by the O-polar surface; hence it is desired to form good Schottky contact on the O-polar surface with use of PEDOT:PSS. However, the O-polar surface is easily degraded by acidic PEDOT:PSS as described below. This study aims at developing a robust Schottky contact on the O-polar surface with PEDOT:PSS by using a silane-coupling agent as a protective layer. Indeed, good Schottky junctions were fabricated on ZnO single-crystalline substrates having a wide range of electron density.

A silane-coupling agent, 3-aminopropyltriethoxysilane (APS), was chosen for the surface protective layer, since aminopropylsilanes were demonstrated to prevent a surface reaction with acids.[15] The APS layer was formed on the hydrothermally grown O-polar ZnO substrates (Tokyo Denpa) with different electron densities n_{Hall} (see Table I). Each substrate (5×5 mm^2) was dipped for 1 min into a diluted 0.1 mol/l APS water solution with 10 vol % isopropyl alcohol. The thickness of the APS layer was determined to be several monolayers thick by x-ray reflectivity measurements

TABLE I. The Schottky junction parameters obtained from *J-V* and *C-V* measurements for the O-polar ZnO substrates with different n_{Hall} (samples A–D) and a Zn-polar ZnO substrate. The parameters from Zn-polar ZnO are after Ref. 13.

Sample	n_{Hall} (cm^{-3})	n	ϕ_b (eV)	N_D-N_A (cm^{-3})	qV_{bi} (eV)
A	3.7×10^{16}	1.3	1.03	7.6×10^{16}	0.29
B	5.0×10^{15}	1.3	0.94	1.1×10^{16}	0.14
C	3.4×10^{15}	1.4	0.88	9.3×10^{15}	0.13
D	7.8×10^{14}	1.6	1.02	2.8×10^{15}	0.14
Zn-polar ZnO (Ref. 13)	1.0×10^{17}	1.2	0.9	1.4×10^{17}	0.6

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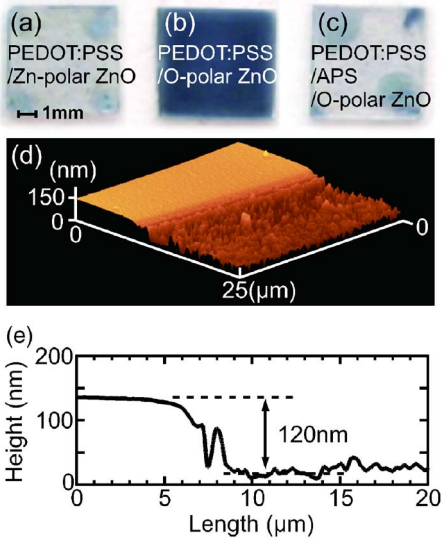


FIG. 1. (Color online) Top view photographs of (a) PEDOT:PSS/Zn-polar ZnO substrate, (b) PEDOT:PSS/O-polar ZnO substrate, and (c) PEDOT:PSS/APS/O-polar ZnO substrate. Size of the substrates is 5×5 mm^2. (d) Atomic force microscope image (25×25 μm^2) of an O-polar ZnO surface after the removal of PEDOT:PSS layer, where the flat area was protected by a photoresist before the spin coating of PEDOT:PSS solution. (e)Cross-sectional profile averaged along the boundary between the rough and flat surfaces in (d).

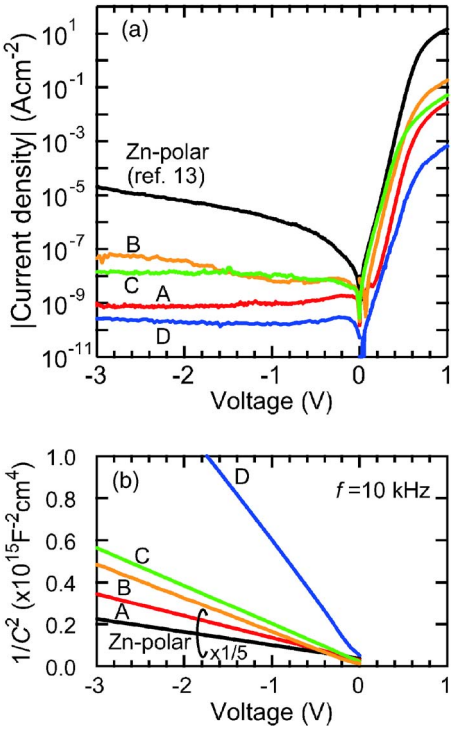


FIG. 2. (Color online) Voltage dependence of (a)current density and (b) $1/C^2$ of PEDOT:PSS/APS/O-polar ZnO junctions on different n_{Hall} substrates (samples A–D) and PEDOT:PSS/Zn-polar ZnO junction [black curve (Ref. 13)]. Note that $1/C^2$ values in (b) for sample A and Zn-polar ZnO are multiplied by 1/5.

for the layer grown on a sapphire substrate (10×10 mm^2) as a reference. On the APS layers formed on the O-polar ZnO surfaces, PEDOT:PSS layers were formed under the same spin-coating condition as reported previously.[13] As references, PEDOT:PSS layers were directly formed on Zn- and O-polar ZnO substrates. For electrical measurements, circular-shaped mesa structures were fabricated as reported previously.[13] Conventional photolithography and Ar ion milling were used to form circular-shaped Schottky contacts (350 μm in diameter) and ring-shaped Ohmic contacts with the separation gap of 25 μm, where the former contacts were Au electrode deposited on PEDOT:PSS by thermal evaporation and the latter contacts were Ti/Au electrodes deposited on ZnO substrate by electron beam evaporation. The Ti/Au Ohmic contacts were confirmed by current-voltage characteristics between two adjacent ring-shaped outer electrodes.[7] Hall effect measurement was performed to evaluate n_{Hall} in the ZnO substrates (5×5 mm^2) with Van der Pauw geometry under a magnetic field scan of ±1 T. Current density-voltage (J-V) and capacitance-voltage (C-V) measurements were carried out at room temperature by using a semiconductor parameter analyzer (Agilent Technologies, 4155C) and an *LCR* meter (Agilent Technologies, 4284A), respectively.

Figure 1(a) shows a top view of the PEDOT:PSS directly formed on Zn-polar substrate (PEDOT:PSS/Zn-polar ZnO). The thickness of the PEDOT:PSS is about 50 nm and the sample is sufficiently transparent. However, the PEDOT:PSS directly formed on O-polar ZnO (PEDOT:PSS/O-polar ZnO) becomes thicker than 1500 nm, yielding in a blackish opaque appearance, as shown in Fig. 1(b). The striking difference arises from high reactivity for the latter as described below. Figure 1(d) shows an atomic force microscopy image of an O-polar ZnO substrate after the removal of PEDOT:PSS, where the half was directly coated with the PEDOT:PSS and another half was protected with a photoresist beforehand. The former region shows a rough surface morphology, while the latter surface shows a very flat morphology. Figure 1(e) shows a cross-sectional profile averaged along the boundary between the rough and flat surfaces in Fig. 1(d), which represents dissolution of ZnO with nearly 120 nm in depth. Such dissolution of ZnO in PEDOT:PSS solution was also confirmed by electron probe microanalysis of the removed PEDOT:PSS layer that contains considerable concentrations of Zn (~1 at. %). Such inevitable degradation of O-polar surface with PEDOT:PSS solution prohibits high performance PEDOT:PSS/O-polar ZnO Schottky junction, in contrast with the PEDOT:PSS/Zn-polar ZnO junction. Figure 1(c) shows a top view of the PEDOT:PSS formed on O-polar substrate coated by APS (PEDOT:PSS/APS/O-polar ZnO). The thickness of the PEDOT:PSS is typically about 50 nm keeping its transparency, representing that APS can effectively suppress the surface reaction. The use of APS layer enables us to obtain high performance Schottky junctions reproducibly as described hereafter.

Figure 2(a) shows the typical J-V curves of the junctions on the four O-polar substrates having different n_{Hall} in addition to reference data for that on the Zn-polar substrate[13] listed in Table I. All the junctions exhibit a good rectification behavior with the rectification ratio as high as 10^7 at bias voltage of ±1 V, representing the formation of good Schottky contact on the O-polar surface of ZnO via APS protective layer. The current density at high forward bias voltage is mainly limited by the sheet resistance of the ZnO substrates, roughly scaled as $1/n_{\mathrm{Hall}}$. The APS layer apparently contributes to the additional resistance, since the slope of J-V curves at 1 V does not exactly correspond to the difference in n_{Hall}. Indeed, the current density both for the forward and reverse biases is two or more decades lower than that of Zn-polar junction.[13]

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The ideality factor (n) and the Schottky barrier height (ϕ_b) for all the junctions were evaluated with thermionic emission model using the following equation: $J=J_0\exp(qV/nk_BT)$, where q is the elementary charge, V is the applied voltage, k_B is Boltzmann's constant, and T is the absolute temperature. J_0 is the saturation current density expressed as $J_0=A^*T^2\exp(-\phi_b/k_BT)$, where $A^*=36$ A cm^{-2} K^{-2} is the effective Richardson constant with $m^*=0.3m_0$, m^* is the electron effective mass, and m_0 is the free electron mass.[1] The obtained values of n and ϕ_b are also listed in Table I. The values of n and ϕ_b ranged 1.3–1.6 and 0.88–1.03 eV, respectively. The latter values are relatively higher than the reported values of 0.6–0.8 eV for Schottky junctions with noble metal electrodes,[10] although the contribution of APS layer is not taken into account in this analysis.

Figure 2(b) shows $1/C^2$-V curves at a voltage frequency (f) of 10 kHz for the same junctions. The dissipation factor for all the samples was as low as 0.01. The C did not depend on f from 1 kHz to 1 MHz at $V=0$ V. The $1/C^2$-V curve under reverse bias shows an ideal relationship expressed as $1/C^2=2(V_{bi}-V)/q\varepsilon_S\varepsilon_0(N_D-N_A)$, where V_{bi} is the built-in potential, ε_S is the dielectric constant of ZnO, ε_0 is the vacuum permittivity, and $N_{D(A)}$ is the ionized donor (acceptor) concentration in the depletion layer.[1] The effective donor concentration (N_D-N_A) and V_{bi} deduced from the fit to the experimental data by using the above equation are listed in Table I. The linearity of $1/C^2$-V plots indicates uniform N_D-N_A distribution through depletion layers in the substrates. The slope inversely proportional to N_D-N_A systematically decreases with increasing n_{Hall} for the junctions A–D and the Zn-polar junction. On the other hand, the V_{bi} of O-polar junctions are much smaller than that of Zn-polar junction. This smaller V_{bi} can be attributed to the interface dipole or the vacuum level shift,[13,16] and/or the surface polarity dependence observed in silver oxide/ZnO Schottky junctions.[17] For better understanding, precise control of thickness and molecular orientation of the APS layer is required. Despite such uncertainty, these J-V and C-V characteristics clearly indicate that PEDOT:PSS serves as a Schottky contact electrode on the O-polar ZnO substrates with the use of APS protective layer.

Finally, we address the relationship between n_{Hall} and N_D-N_A, as shown in Fig. 3. It is consistent that n_{Hall} increases roughly proportional to N_D-N_A. The value of n_{Hall} for all the junctions, however, tends to be smaller than N_D-N_A. This tendency implies that unintentional impurities and defects acting as donor and/or accepter have larger activation energy than thermal energy at room temperature (~25 meV) in the hydrothermally grown ZnO single crystal substrate.[18,19]

In summary, high quality Schottky junctions were fabricated in a PEDOT:PSS/APS/O-polar ZnO structure via simple wet processes. The results pave a pathway to apply PEDOT:PSS for the Schottky contact not only on ZnO single crystals but also on standard ZnO thin films and heterostructures with O-polar surface termination.

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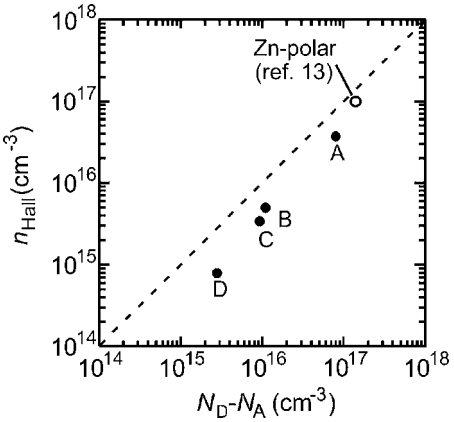


FIG. 3. The relationship between n_{Hall} and N_D-N_A, where the former and the latter were evaluated from Hall effect and C-V measurements, respectively. The closed and open circles correspond to the values of O-polar (samples A–D) and Zn-polar ZnO (Ref. 13) substrates, respectively. The broken line represents the n_{Hall} is equal to N_D-N_A.

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