Transparent polymer Schottky contact for a high performance visible-blind ultraviolet photodiode based on ZnO

M. Nakano,[1,a)] T. Makino,[2] A. Tsukazaki,[1] K. Ueno,[2] A. Ohtomo,[1] T. Fukumura,[1] H. Yuji,[3] S. Akasaka,[3] K. Tamura,[3] K. Nakahara,[3] T. Tanabe,[3] A. Kamisawa,[3] and M. Kawasaki[1,2,4]

[1]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[2]*WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[3]*Advanced Compound Semiconductors R&D Center, ROHM Co., Ltd., Kyoto 615-8585, Japan*
[4]*CREST, Japan Science and Technology Agency, Tokyo 102-0075, Japan*

(Received 3 July 2008; accepted 1 September 2008; published online 24 September 2008)

We report on a high performance visible-blind Schottky ultraviolet photodiode composed of a ZnO (0001) bulk single crystal and a transparent conducting polymer, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), fabricated with a simple spin-coating process at room temperature in air. The quantum efficiency as high as unity in ultraviolet region and a visible rejection ratio of about 10^3 were achieved in the spectral response of the photodiode under zero-bias condition. The normalized detectivity of the photodiode was evaluated to be 3.6×10^{14} cm Hz$^{1/2}$/W at 370 nm. [DOI: 10.1063/1.2989125]

Optoelectronic device application using wide-gap semiconductors is one of the important research fields in transparent semiconductor technology. Zinc oxide (ZnO), which has a direct band gap of 3.37 eV, is one of the promising compounds for transparent oxide electronics. By exploiting its unique optical and electrical functionalities, the demonstrations have been reported on ZnO-based semiconductor devices such as *p-n* junction ultraviolet (UV)-blue light-emitting diodes and transparent thin film transistors.[1–4] In addition, the observation of quantum Hall effect in ZnO/$Mg_xZn_{1-x}O$ heterostructures has opened an exotic field in device physics based on complex oxide heterostructures.[5,6] On the other hand, ZnO-based photodetectors have been left behind in development compared to those based on GaN and related materials despite their great importance for UV light detection.

There are various types of UV photodetectors: a simple photoconductor, a *p-n* photodiode, a Schottky photodiode, a metal/semiconductor/metal photodiode, and so on.[7,8] Among them, a Schottky photodiode has many advantages compared to other photodetectors in the aspects of simplicity in fabrication, high quantum efficiency, high response speed, low dark current, high UV/visible contrast, and possible zero-bias operation.[7–9] Although several attempts have been made at fabricating a Schottky UV photodiode based on ZnO (Refs. 10–13), high performance was difficult to be achieved probably due to a difficulty in fabricating a good Schottky contact with low leakage current on ZnO surface.[14–17]

We recently developed a high-quality Schottky contact both on Zn- and O-polar ZnO surfaces by using a conducting polymer, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), as a metal electrode.[18,19] Because PEDOT:PSS thin film has an internal transmittance of nearly 100% in a wide wavelength range from 250 to 800 nm, in addition to a resistivity of as low as 10^{-3} Ω cm and a large work function of 5.0 eV (Ref. 18), we can use this polymer as a transparent Schottky contact on ZnO. Here, we report on a high performance ZnO-based UV photodiode using PEDOT:PSS transparent Schottky contact.

A schematic device structure is shown in the inset of Fig. 1. PEDOT:PSS aqueous solution (H. C. Starck, Baytron PH500) was spin coated on top of a hydrothermally grown Zn-polar ZnO (0001) single crystal substrate (Tokyo Denpa) with a rotation speed of 4000 rpm, yielding in 50-nm-thick transparent thin film. After baking of PEDOT:PSS thin film at 200 °C for 30 min, 100-nm-thick Au contact pads (350 μm ϕ in diameter) were formed by thermal evaporation through a shadow mask, followed by device isolation into 500×500 μm^2 pieces. Ti/Au Ohmic contact was formed at the backside of the substrate by electron-beam evaporation. Current-voltage (*I-V*) and capacitance-voltage (*C-V*) characteristics were measured with a semiconductor parameter analyzer (Agilent Technologies, 4155C) and a LCR meter (Agilent Technologies, 4284A), respectively.

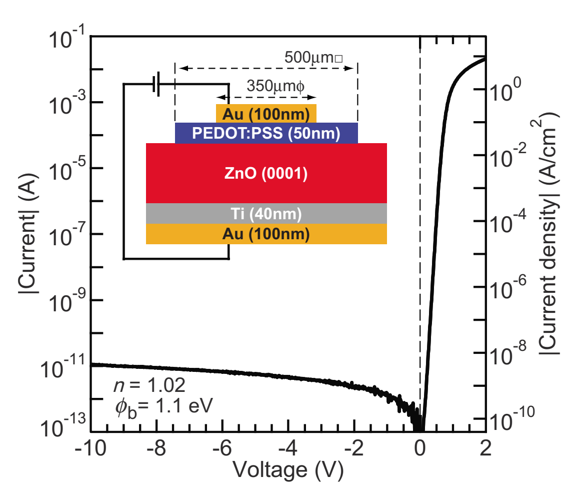

FIG. 1. (Color online) A typical current-voltage (*I-V*) characteristic of the PEDOT:PSS/ZnO Schottky photodiode under dark condition. The ideality factor (n) and the Schottky barrier height (ϕ_b) are also shown. The inset shows a schematic cross section of the PEDOT:PSS/ZnO Schottky photodiode. The active device areas for measurements under dark and illuminated conditions are 2.5×10^{-3} and 1.5×10^{-3} cm^2, respectively.

[a)]Electronic mail: nakano@imr.tohoku.ac.jp.

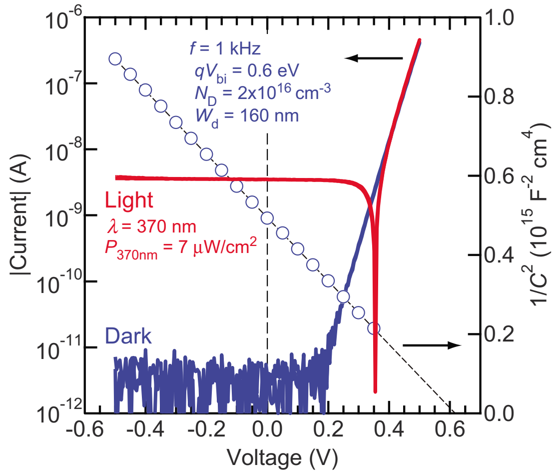

FIG. 2. (Color online) The *I-V* (blue curve) and the $1/C^2$-V (blue open circles) characteristics under dark condition and the *I-V* characteristic (red curve) under illuminated condition (λ=370 nm, $P_{370\ nm}$=7 μW/cm^2) of the particular device for which photodiode characteristics were examined. The measurement frequency (f) for C is 1 kHz. The dashed line denotes a fitting to the $1/C^2$-V curve for evaluating the built-in potential (V_{bi}), the ionized donor concentration (N_D), and the depletion layer width (W_d) at V=0 V.

Spectral response was examined using a monochromatized Xe lamp as light source. Incident light power (P_λ) was calibrated by a conventional UV-enhanced Si *p-i-n* photodiode (Hamamatsu S2281) and a UV power meter (Hamamatsu C6080–03). As seen in the inset of Fig. 1, the active junction area was 2.5×10^{-3} cm^2 (A_{dark}) for measurements under dark condition. Meanwhile, the active junction area was reduced to 1.5×10^{-3} cm^2 (A_{opt}) for measurements of the photodiode characteristics under illuminated condition due to the presence of the opaque Au contact pad. These two areal parameters were used properly for analysis described below. All the measurements were performed at room temperature in air.

Figure 1 shows a typical *I-V* characteristic under dark condition in a semilogarithmic scale. The corresponding current density (J) normalized by A_{dark} is also shown in a right axis. The junction showed excellent rectifying behavior with a current rectification ratio of 10^{10} at ±2 V and a leakage current as low as 10 pA up to -10 V. The ideality factor (n) and the Schottky barrier height (ϕ_b) were evaluated within a framework of the thermionic emission model by using the equation of $J=J_0\exp(qV/nk_BT)$, where q, k_B, T, and V are the elementary charge, Boltzmann's constant, the absolute temperature, and the applied voltage, respectively, while $J_0=A^*T^2\exp(-\phi_b/k_BT)$ is the saturation current density and A^* is the effective Richardson constant with A^*=36 A cm^{-2} K^{-2} for ZnO (m_e^*=0.3 m_0, m_e^* being the effective electron mass). The obtained low n value of 1.02 and the high ϕ_b value of 1.1 eV imply a formation of a defect-free abrupt metal/semiconductor interface. Those values are comparable to the best value recently reported in ZnO-based Schottky junctions with silver oxide contact.[20,21]

Figure 2 shows an effect of UV irradiation on the *I-V* characteristics. The blue and the red curves are the *I-V* characteristics measured under dark and illuminated conditions, respectively. A relatively larger background noise current ($\sim10^{-11}$ A) was observed in the dark *I-V* curve than the one ($<10^{-12}$ A) in Fig. 1 because the former was measured with an electromagnetically unshielded measurement system while the latter was obtained in a shielded prober system. Upon irradiating UV light with a wavelength (λ) of 370 nm and a light power ($P_{370\ nm}$) of 7 μW/cm^2, an apparent photodiode operation with a photovoltaic effect was observed as a significant short-circuit current $|I_{SC}|=3.5\times10^{-9}$ A at V=0 V and an open-circuit voltage V_{OC}=0.36 V at I=0 A. The obtained V_{OC} was smaller than the built-in potential (V_{bi}=0.6 V), which was estimated from the *C-V* measurement as explained below, because of the small incident light power as the measurement condition for Fig. 2. After the turn-off of UV light, the *I-V* curve immediately returned to the identical one under dark (not shown), suggesting the negligible contribution of a persistent photoconductivity from the bulk region of ZnO (Ref. 22).

The blue open circles in Fig. 2 show the $1/C^2$-V characteristics measured with the frequency (f) of 1 kHz under dark condition. The obtained data show an ideal relationship expressed as $1/C^2=2(V_{bi}-V)/q\varepsilon_s\varepsilon_0N_D$, where C is the capacitance normalized by A_{dark}, ε_s is the relative permittivity, ε_0 is the vacuum permittivity, and N_D is the ionized donor concentration in the depletion layer. By using ε_s=8 for ZnO, V_{bi}=0.6 V and $N_D=2\times10^{16}$ cm^{-3} were obtained. The depletion layer width, $W_d=\varepsilon_s\varepsilon_0/C$, was evaluated to be W_d=160 nm at V=0 V. If we assume an absorption coefficient of ZnO as 2×10^5 cm^{-1} and a consequent penetration depth of light as 50 nm in UV region,[23] almost all of incident photons were absorbed within the depletion layer.

P_λ dependence of the $|I_{SC}|$ at λ=370 nm is shown in the inset of Fig. 3(a). The dashed straight line of η=1 is also indicated, where η is the quantum efficiency, that is, the number of carriers generated per incident photon calculated by the equation of $\eta=(|I_{SC}|/qA_{opt})/(P_\lambda/h\nu)$ at V=0 V (Ref. 7), where h is Plank's constant and ν is the frequency of light. Around a low power region, a good linearity was observed with the high η of about unity, while higher power irradiation resulted in a slight deviation toward saturation, possibly due to a contribution of a persistent photoconductivity from bulk ZnO region as observed in GaN-based photodetectors.[22,24] In the evaluation of the spectral response described below, the P_λ was kept within a low power region to eliminate this undesirable effect.

The main panel of Fig. 3(a) shows the spectral response of the photodiode; the zero-bias responsivity (R_λ), expressed as $R_\lambda=|I_{SC}|/A_{opt}P_\lambda=\eta q/h\nu$ (Ref. 7), is plotted against a wavelength of an incident light. The line of η=1 and the R_λ of the Si *p-i-n* photodiode used in this study are also indicated for comparison. The device attained a high R_λ and consequently high η of about 0.3 A/W and unity at λ=370 nm, respectively, with an excellent UV/visible rejection ratio of about 10^3. It is worth noting that the $|I_{SC}|$ in visible region was of the order of 10^{-11} A, which is comparable to the current detection limit of our photodiode characterization system (see the dark *I-V* curve in Fig. 2). Therefore, the given UV/visible rejection ratio is the lower bound of the true value.

Figure 3(b) shows the transmission spectra of a sapphire, a 50-nm-thick PEDOT:PSS thin film on a sapphire, and a ZnO single crystal substrate, respectively. A PEDOT:PSS has an internal transmittance of nearly 100% in a wide range from 250 to 800 nm. In shorter wavelength than 250 nm, however, a decrease in the transmittance was observed due to

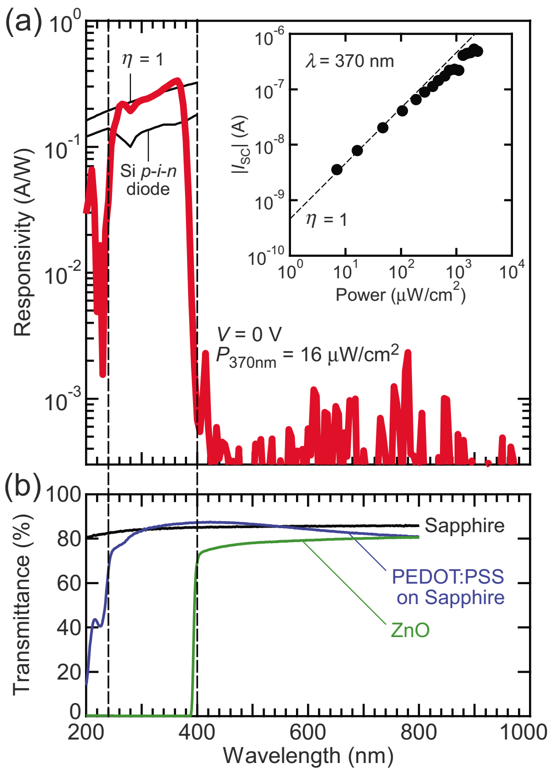

FIG. 3. (Color online) (a) The spectral response of the PEDOT:PSS/ZnO Schottky photodiode at $V=0$ V and $P_{370\ \mathrm{nm}}=16\ \mu\mathrm{W/cm}^2$. That of the Si *p-i-n* photodiode and a spectrum corresponding to a quantum efficiency (η) of unity are also indicated for comparison. The inset shows the incident light power (P_λ) dependence of the short-circuit current (I_{SC}) at $\lambda=370$ nm with the dashed line representing $\eta=1$. (b) Transmission spectra of a sapphire, a 50-nm-thick PEDOT:PSS thin film on a sapphire, and a ZnO single crystal substrate.

an optical transition in PEDOT:PSS thin film. A large decrease in the transmittance for ZnO below 400 nm is attributed to a band-to-band transition, leading to the generation of photocarriers. Consequently, almost all of incident photons in UV region from 250 to 400 nm can pass through a PEDOT:PSS layer with ignorable absorption and be absorbed within the depletion layer of ZnO, leading to the high η. The shape of the spectral response depicted in Fig. 3(a) shows an excellent correspondence with the transmission spectra of the constituent layers.

As a final remark, the normalized detectivity (D^*_λ), which is a figure of merit commonly used for various types of photodetectors, is evaluated by using the equation of $D^*_\lambda = R_\lambda(R_0A_{\mathrm{dark}}/4k_BT)^{1/2}$, where R_0A_{dark} is a resistance area product under dark condition expressed as $R_0A_{\mathrm{dark}} = (k_B/qA^*T)\exp(\phi_b/k_BT)$ for a Schottky photodiode within the thermionic emission model.[8,9] By adopting the values of $R_{370\ \mathrm{nm}}=0.3$ A/W and $\phi_b=1.1$ eV of the present photodiode, the R_0A_{dark} and the D^*_λ at $\lambda=370$ nm ($D^*_{370\ \mathrm{nm}}$) were evaluated to be $2.4\times10^{10}\ \Omega\ \mathrm{cm}^2$ and 3.6×10^{14} cm $\mathrm{Hz}^{1/2}/\mathrm{W}$, respectively. The obtained $D^*_{370\ \mathrm{nm}}$ is relatively high among those of conventional UV photodetectors,[7] reflecting the high $R_{370\ \mathrm{nm}}$ and the high R_0A_{dark}. Furthermore, the $D^*_{280\ \mathrm{nm}}$ of 2.4×10^{14} cm $\mathrm{Hz}^{1/2}/\mathrm{W}$, calculated using the values of $R_{280\ \mathrm{nm}}=0.2$ A/W, is comparable to the best value reported in a recent AlGaN-based *p-i-n* UV photodiode.[25]

In summary, we realized a high performance visible-blind UV photodiode by employing a PEDOT:PSS/ZnO Schottky junction. The excellent performance has become possible due to a high transparency of PEDOT:PSS in UV region and nearly ideal Schottky characteristics with negligible leakage current. Because of the low-cost materials and easy-to-make processes, the present device is promising for the applications of highly sensitive UV light detection.

M.N. is supported by Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. The work is partly supported by Asahi Glass Foundation.

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