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Schottky ultraviolet photodiode using a ZnO hydrothermally grown single crystal substrate

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A Schottky ultraviolet photodiode using a (0001) ZnO single crystal grown by the hydrothermal growth method is reported. The photodiode consisted of a semitransparent Pt film for the Schottky electrode and an Al thin film for the Ohmic electrode. The photodiode had polarity dependences on current-voltage characteristics and on responsivity. In the case of the Schottky electrode on the zinc surface, the responsivity was 0.185 A/W at a wavelength of 365 nm. On the other hand, the responsivity was 0.09 A/W for an oxygen surface. The results are attributed to the polarity dependences of surface chemical reactivity and the surface state density on ZnO surfaces. [DOI: 10.1063/1.2715100]

ZnO is a promising metal oxide semiconductor with a band gap of 3.2 eV and a large exciton binding energy of 60 meV.[1] A blue light-emitting diode using ZnO (Ref. 2) has been attracting much interest recently. On the other hand, ZnO has been studied for its application not only to a light-emitting device but also to a photodetecting device. Ultraviolet (UV) photodetectors using ZnO thin film[3–5] were investigated in photoconduction and Schottky diode types. Liang *et al.* reported ZnO Schottky UV photodetectors of metal-semiconductor-metal structure using a ZnO thin film deposited on a sapphire substrate.[4] In all of the studies described above, ZnO thin films deposited on various substrates such as sapphire were used because of the similar lattice structure.

In 2004, a large bulk ZnO crystal was grown by the hydrothermal growth method.[6] We previously reported a photoconductive UV detector using the ZnO bulk substrate.[7] Although the photoconductive UV detector had a high sensitivity, the time response was slow (>1 s). On the other hand, it has been difficult to make good Schottky barrier contacts on a ZnO bulk substrate because of surface reaction and contamination. Therefore, various surface treatments for Schottky barrier contacts have been investigated. Allen *et al.* reported a Schottky barrier diode using a ZnO bulk substrate grown by the pressurized melt-growth technique and cleaned with organic solvents.[8] A high performance with an ideality factor of 1.1 was obtained using a Ag electrode. In addition, several properties such as polarity effect for electrode materials have been revealed. However, as for optical properties, there has been no report on a Schottky diode type photodetector using a ZnO bulk substrate.

In this letter, we report a Schottky UV photodiode using a ZnO bulk substrate grown by the hydrothermal growth method. The spectral responsivity and polarity dependences of a Schottky UV photodiode are investigated.

In the experiments, n-type (0001) ZnO single crystal substrates (Tokyo Denpa Co., Ltd., $10\times10\times0.3$ mm^3) were used. Each substrate was grown by the hydrothermal growth method.[6] The hydrothermally grown ZnO bulk substrate has good properties such as high purity, high crystallinity, and mass productivity. Using the van der Pauw method (Toyo; Resi-Test 8300), resistivity and Hall mobility of the ZnO substrate were measured at room temperature to be 1×10^2 Ω cm and 2×10^2 cm^2 V^{-1} s^{-1}, respectively. We fabricated Schottky barrier photodiodes both on the Zn surface (Zn-polar sample) and on the O surface (O-polar sample).

Before fabrication of the diodes, a cleaning method for the ZnO bulk substrate was examined using acetone, ethanol, isopropyl alcohol, tetramethyl ammonium hydroxide (TMAH), and HCl water solutions. Isopropyl alcohol was finally used with an ultrasonic cleaner since reverse saturation current in the Schottky barrier diodes was small.

A positive resist was spin coated on the ZnO substrate. After UV exposure, the positive resist was developed by TMAH (2.38 wt %) water solution and then rinsed with pure

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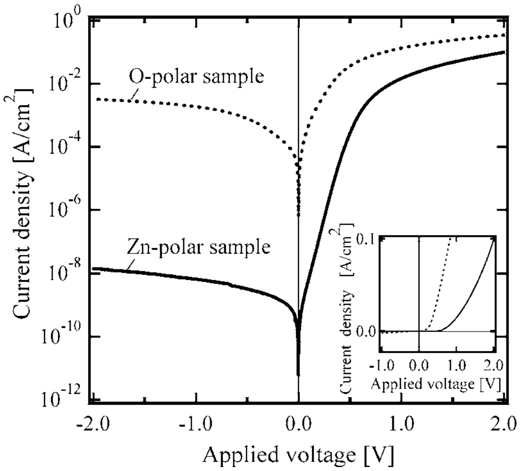

FIG. 1. Current-voltage characteristics of the Schottky photodiode with a Pt Schottky semitransparent electrode on the Zn surface (Zn-polar) and O surface (O-polar).

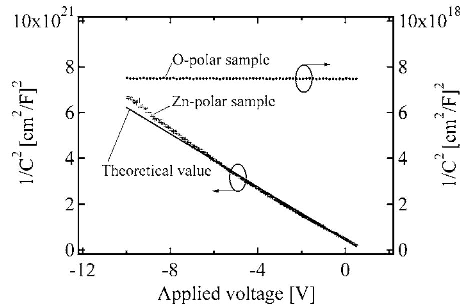

FIG. 2. Measured value of $1/C^2$ as a function of applied voltage at 1 kHz. The solid line shows the theoretical values with $N_D=10^{14}$ cm^{-3} and $V_{bi}=0.8$ V at $T=300$ K.

water. A semitransparent 3-nm-thick Pt film was patterned to be a square as a Schottky electrode on the surface of the ZnO substrate using a lift-off process by an oblique incidence magnetron sputter system (ULVAC; MPS-3000), which was able to deposit the Pt film without damaging the ZnO substrates. The square window for UV detection was 820 μm wide. A 100-nm-thick Pt film was deposited on the semitransparent Pt film by a lift-off process to fabricate a circular electrode with a diameter of 200 μm for wiring. A 60-nm-thick SiO_2 film was deposited on the Pt semitransparent film for antireflection coating in the UV region. Finally, a 150-nm-thick Al-doped ZnO film and a 150-nm-thick Al film were deposited on opposite surfaces of the ZnO substrate for an Ohmic electrode. A diced 1.0 mm^2 chip was bonded to the TO-18 stem using Ag paste. A Au wire was bonded to the Schottky electrode. A 0.3-mm-thick quartz plate window was glued on the cap.

Figure 1 shows the typical current-voltage (*I*-*V*) characteristics of the Schottky photodiode measured with a semiconductor measurement system (Keithley; SCS-4200) after placing in a dark condition for 2 min at room temperature. The *I*-*V* characteristics plotted linearly are shown in the inset of Fig. 1. The current increases at 0.8 V with increase in the voltage when the voltage is applied to the Zn-polar sample. On the other hand, in the case of the O-polar sample, the forward biased current increases at 0.4 V, which is smaller than that of the Zn-polar sample. Under the condition of reverse bias voltage of -10 mV, it was found that the dark current density of the Zn-polar sample is 1.3×10^{-10} A/cm^2. On the other hand, the dark current density of the O-polar sample is 1.6×10^{-5} A/cm^2, which was larger by five orders of magnitude than that of the Zn-polar sample. A significant difference was also found in the breakdown voltage V_b between the Zn- and O-polar samples. V_b for the Zn-polar sample was approximately 70 V, while V_b for the O-polar sample was approximately 7 V. The current density J of the photodiode is given by the following equation on the basis of thermionic emission theory:[9]

$$J = J_S\left[\exp\left(\frac{qV}{nkT}\right) - 1\right],$$

$$J_S = A^* T^2 \exp\left(-\frac{q\phi_{B0}}{kT}\right), \quad (1)$$

where J_s is the saturation current, q is the electron charge, V is the applied voltage, n is the ideality factor, k is the Boltzmann constant, T is the absolute temperature, A^* is the effective Richardson constant ($\sim$32 A/cm^2 k^2 for m^* equal to $0.27m_0$, where m_0 is the electron mass), and ϕ_{B0} is the zero-biased Schottky barrier height. The Schottky barrier height, the ideality factor of the diode, and the saturation current density were calculated by fitting Eq. (1) to the measured values in Fig. 1 to be 0.96 eV, 1.1, and 3.0×10^{-10} A/cm^2 for the Zn-polar sample and 0.6 eV, 3.1, and 2.0×10^{-5} A/cm^2 for the O-polar sample, respectively. Under the abrupt approximation, the relationship between the capacitance of the depletion layer and the voltage is given by [9]

$$\frac{1}{C^2} = \frac{2(V_{bi} - V - kT/q)}{q\varepsilon_s N_D}, \quad (2)$$

where V_{bi} is the built-in potential, ε_s is the semiconductor permittivity, and N_D is the donor impurity density. If N_D is constant throughout the depletion layer, a straight line is obtained by plotting the value of $1/C^2$ as a function of V. Figure 2 shows the measured values of $1/C^2$ as a function of V. The value of $1/C^2$ for the Zn-polar sample is explained well, as shown in Fig. 2, by Eq. (2). However, for the O-polar sample, the value of $1/C^2$ is nearly constant, which does not agree with Eq. (2). This fact shows that the Schottky barrier junction on a Zn-polar surface seems to be much better than on an O-polar surface.

The spectral responsivity of the fabricated photodiodes was measured in the wavelength region from 250 to 850 nm using a *I*-*V* transfer amplifier (Keithley; 428-PROG), a Xe arc lamp, and a calibrated monochromator (JASCO; IUV-25). The spectral responses of both samples are shown in Fig. 3. The responsivity and external quantum efficiency for the Zn-polar sample are 0.185 A/W and 62.8%, respectively, at a wavelength of 365 nm, and those for the O-polar sample are 0.09 A/W and 31.0%, respectively. From those measurements, it was found that the responsivity for the Schottky barrier of the Zn surface is two times higher than that for the O surface. The polarity dependence in the Schottky photodiode was attributed to the difference in surface reactivity and/or the defect density in the ZnO substrate surface. We investigated the surface defects on the surfaces of ZnO substrates using the etch pit method. Figures 4(a) and 4(b) show optical micrographs of the Zn-polar and O-polar surfaces of

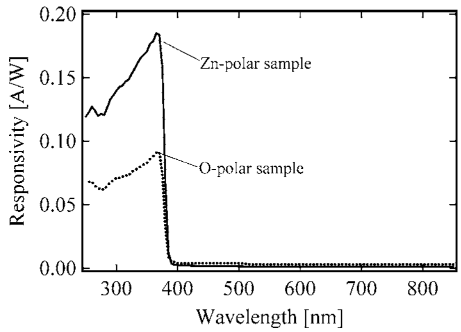

FIG. 3. Spectral responsivity of the photodiodes for the Zn-polar and O-polar samples.

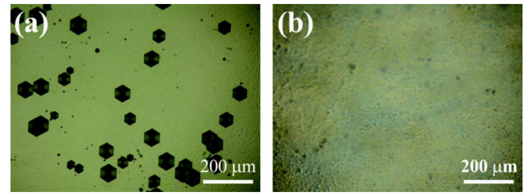

FIG. 4. Optical micrographs of (a) Zn-polar and (b) O-polar surfaces of ZnO substrates after etching in HCl (0.7 vol %) solution for 1 min at 60 °C.

the ZnO substrate after etching in HCl (0.7 vol %) solution for 1 min at 60 °C. The etch pit density on the Zn-polar surface is on the order of 10^3 cm^{-2}. On the other hand, the etch pit density on the O-polar surface is larger than that on the Zn-polar surface on the order of 10^5 cm^{-2}. This result suggests that the polarity dependence of the photocurrent may be attributed to the surface chemical reactivity and/or the surface state density on ZnO surfaces. Since the Schottky barrier height is pinned lower by a large number of surface states on the O-polar surface, the lowered barrier height increases the saturation current. In addition, a large number of surface states on the O-polar surface trap the photocarriers generated by UV light irradiation and thus the photocarriers recombine in the surface states. On the other hand, the surface state density on the Zn-polar surface is low and thus the Schottky barrier on the Zn-polar surface by the Pt/ZnO contact was good rectification property. Photocarriers generated in the depletion layer of the substrate surface can reach the electrode efficiently due to low trapping probability. Therefore, a photodiode with a high responsivity can be achieved using the Zn-polar surface.

In summary, a Pt/ZnO Schottky barrier photodiode for an UV detector has been fabricated from a single crystal ZnO substrate grown by the hydrothermal growth method. The responsivity of the fabricated photodiode was 0.185 A/W. The high responsivity was achieved by the Schottky contact on the Zn-polar surface, which was two times higher than that on the O-polar surface. The fabricated photodiode can be operated as a visible-blind UV sensor since the responsivity in the wavelength region larger than 380 nm is smaller by three orders of magnitude than that in the UV region.

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