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Characterization of ZnO metal–semiconductor–metal ultraviolet photodiodes with palladium contact electrodes

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Abstract
ZnO metal–semiconductor–metal (MSM) photodiodes with palladium (Pd) contact electrodes were fabricated. It was found that the barrier height at the Pd/ZnO interface was 0.701 eV. With an incident wavelength of 370 nm and 1 V applied bias, it was found that the maximum responsivity of the Pd/ZnO/Pd MSM photodiodes was 0.051 A/W, which corresponds to a quantum efficiency of 11.4%. For a given bandwidth of 100 Hz and 1 V applied bias, we found that the noise equivalent power and the corresponding detectivity D^* were 1.13×10^{-12} W and 6.25×10^{11} cmHz$^{0.5}$ W^{-1}, respectively.

1. Introduction

In recent years, much research has been focused on semiconductor-based ultraviolet (UV) photodiodes. Photodiodes operating in the short wavelength UV region are important devices that can be used in various commercial and military applications. For example, visible-blind UV photodiodes can be used in space communications, ozone layer monitoring and flame detection. Currently, light detection in the UV spectral range still uses Si-based optical photodiodes. Although these devices are sensitive to visible and infrared radiation, the responsivity in the UV region is low since the room temperature bandgap energy of Si is only 1.2 eV. With the advent of optoelectronic devices fabricated on wide direct band gap materials, it becomes possible to produce high-performance solid-state photodiodes that are sensitive in the UV region. For example, GaN-based UV photodiodes are already commercially available. ZnSe-based UV photodiodes have also been demonstrated.

For photodetector applications, operation speed is an important issue. Previously, it has been shown that electron mobility in AlGaN/GaN heterostructures is limited by the charged dislocation scattering, interface scattering and phase separation effects. These factors should also limit the operation speed of GaN-based photodetectors. ZnO is another wide direct bandgap material that is sensitive in the UV region [1, 2]. The large exciton binding energy of 60 meV and wide bandgap energy of 3.37 eV at room temperature make ZnO a promising photonic material for applications such as light emitting diodes, laser diodes and UV photodiodes. Indeed, ZnO has attracted much attention in recent years [3–5]. High quality ZnO epitaxial layers can be grown by metalorganic chemical vapour deposition [1], molecular beam epitaxy (MBE) [6] and pulsed laser deposition [7] on top of ZnO substrates [2], sapphire substrates [8] and epitaxial GaN layers [9]. Recently, it has been shown that it is possible to achieve ZnO epitaxial layers with high electron mobility by multi-step pulsed laser deposition (PLD) [7]. It has been reported that the saturation velocity of ZnO is higher than that of GaN [10]. Compared with GaN, it has also been found that ZnO is less susceptible to irradiation effects [10]. Thus, ZnO-based photodetectors are potentially useful for high-speed UV light sensing. ZnO Schottky diodes and metal–semiconductor–metal photodiodes detecting in the UV region have also been demonstrated [4]. MSM photodiodes consist of interdigitated Schottky contacts deposited on the top of an active layer. To achieve high-performance MSM UV photodiodes, it is important to achieve a large Schottky barrier height at metal–semiconductor interface. A large barrier height leads to small leakage current and high breakdown voltage which could result in improved responsivity and photocurrent-to-dark current contrast ratio. To achieve a large Schottky barrier height on ZnO, one can choose metals with high work functions [11]. However, many of the high work function metals are not stable at high temperatures. In other words, severe inter-diffusion might occur at metal–ZnO interface. Palladium (Pd) is an interesting metal that has recently been used as a stable Schottky contact of wide bandgap GaN [12–14]. Pd is a good conductor with superior thermal and chemical stabilities. GaN-based UV photodetectors and Schottky diodes with Pd contact electrodes have also been demonstrated [12–14]. Although the study of the ZnO Schottky diodes with Pd contact electrodes had been reported, yet neither the properties of ZnO-based MSM photodetectors with Pd contacts nor the detectivity of these devices could be found in the literature to our knowledge. In this work, we report the growth of ZnO epitaxial layers by MBE and the fabrication of ZnO-based MSM photodiodes with Pd electrodes. Noise behaviour of the fabricated photodiodes will also be discussed.

2. Experiments

Samples used in this study were grown by radio frequency (rf) plasma-assisted MBE (Omni Vac) on C-plane sapphire substrates. After degreased in trichloroethylene and acetone, sapphire substrates were etched in H_2SO_4:H_3PO_4 = 3:1 at 110 °C for 30 min followed by rinsing in de-ionized water. These sapphire substrates were then loaded into the growth chamber. The base pressure in the growth chamber was $\sim 1.4 \times 10^{-11}$ Pa. The source material of Zn was elemental Zn (6N) evaporated from a commercial Knudsen cell (Crea Tech). Oxygen radicals pregrowth treatment and surface nitridation were used to eliminate Zn-polar inversion domains and control the growth of a single-domain O-polar ZnO film [15]. We then grew a 1000 nm thick unintentionally doped ZnO epitaxial layer with conventional two-step growth method, i.e., a low temperature buffer layer growth at 400 °C and a high temperature growth at 650°C. We subsequently annealed the ZnO epitaxial layer *in situ* at 750 °C. At this moment, we observed a 3 × 3 reconstruction pattern which indicates O-polar of our ZnO films [16]. From room temperature Hall measurements, it was found that the carrier concentration and mobility of the as-grown ZnO films were 1.71×10^{16} cm^{-3} and 26.4 cm^2 V^{-1} s^{-1}, respectively. The low mobility observed from our ZnO epitaxial layers may be attributed to the large lattice mismatch between ZnO and the underneath sapphire substrates [17]. Due to the large lattice mismatch, dislocation scattering and scattering through defects may be considered as possible scattering mechanisms. Dislocation scattering is due to the fact that acceptor centres are introduced along the dislocation line, which capture electrons from the conduction band in the ZnO semiconductor. The dislocation lines become negatively charged and a space-charge region is formed around it, which scatters electrons travelling across the dislocations, thus reducing the mobility. The samples were then characterized by photoluminescence (PL) and x-ray diffraction (XRD).

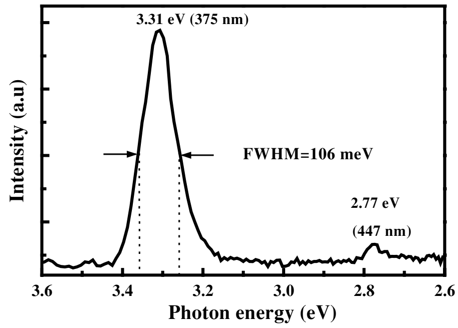

Figure 1. Room temperature PL spectrum of epitaxial ZnO films.

ZnO MSM photodiodes were then fabricated. Prior to the deposition of contact electrodes, wafers were dipped in acetone and methanol to clean the surface. A 100 nm thick Pd film was subsequently deposited onto the sample surface by electron beam evaporation to serve as metal contacts. Standard lithography and etching were then performed to define the interdigitated contact pattern. The fingers of the Pd contact electrodes were 13 μm wide and 146 μm long with 8 μm spacing. The active area of the whole device was 146 × 146 μm^2. Photocurrent and dark current of the fabricated photodiodes were then measured by an HP4145B semiconductor parameter analyser. Spectral responsivity measurements were also performed using a light source (Oriel Optical System) which employed a 250 W xenon arc lamp and a monochromator covering the range of 300–600 nm. Low frequency noise of the fabricated photodetectors was also measured in the frequency range of 1 Hz ∼ 100 kHz using a low noise current preamplifier and an HP35670A fast Fourier transform spectrum analyser.

3. Results and discussion

Figure 1 shows the room temperature PL spectrum of our ZnO epitaxial films. It was found that we observed a strong excitonic related PL peak at 375 nm (3.31 eV) and a very weak green band emission at around 450 nm. The green luminescence band is originated from oxygen vacancy related defects. It was also found that full-width-half-maximum (FWHM) of the excitonic-related PL peak was 106 meV [13]. Furthermore, it was found that the intensity ratio between excitonic band emission and green band emission was extremely large. These results all indicate good crystal quality of our ZnO epitaxial layers [8].

Figure 2 shows current–voltage (*I*–*V*) characteristics of the fabricated ZnO MSM photodiodes with Pd electrodes measured in dark and under illumination. During photocurrent measurements, the wavelength of the excitation light was 370 nm while the incident optical power was 100 mW. It was found that the dark *I*–*V* curve could be fitted well by the

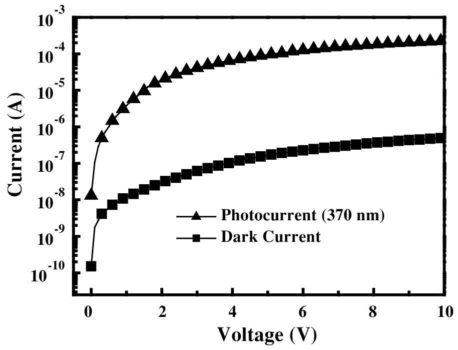

Figure 2. *I–V* characteristics of the fabricated Pd/ZnO/Pd MSM photodiodes measured in dark (dark current) and under 370 nm illumination (photocurrent).

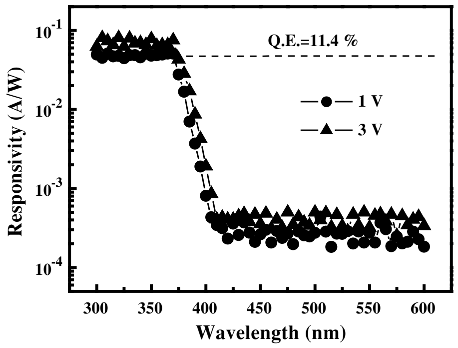

Figure 3. Measured spectral responsivities of the fabricated Pd/ZnO/Pd MSM photodiodes.

simple thermionic emission model [18] shown in equation (1),

$$J \sim A_{\rm n}^* T^2 \exp\left(\frac{-q\left(\phi_{\rm bn} - \Delta\phi_{\rm n}\right)}{kT}\right) + A_{\rm p}^* T^2 \exp\left(\frac{-q\left(\phi_{\rm bp} - \Delta\phi_{\rm p}\right)}{kT}\right) \quad (1)$$

where $\phi_{\rm bn}$ and $\phi_{\rm bp}$ are the barrier heights at cathode and anode, respectively, $A_{\rm n}^*\ (=4\pi q m_{\rm n}^* k^2/h^3)$ and $A_{\rm p}^*\ (=4\pi q m_{\rm p}^* k^2/h^3)$ are the effective Richardson constants for electron and hole, respectively, while $\Delta\phi_{\rm n}$ and $\Delta\phi_{\rm p}$ are the image force lowering terms at cathode and anode, respectively. Knowing that the effective masses of electrons and holes in ZnO were $0.27m_0$ and $0.59m_0$ [19], respectively, we found that the Richardson constants for electrons and holes were 32 and 70 A cm^{-2} T^{-2}, respectively. Furthermore, it was found that the Schottky barrier height at the Pd/ZnO interface was 0.701 eV. It was also found that the dark current and photocurrent of the fabricated photodiode biased at 1 V were 1.19×10^{-8} and 3.83×10^{-6} A, respectively. In other words, we achieved a photocurrent-to-dark current contrast ratio of only 322. We should be able to improve the photocurrent-to-dark current contrast ratio by annealing the Pd electrodes. Previously, it has been shown that one can achieve a higher barrier height by annealing the Pd contacts on GaN [12–14]. We believe post-deposition thermal annealing could also enhance Schottky barrier height for Pd contacts on our n-ZnO epitaxial layers and reduce dark currents of our photodiodes. Such an experiment is underway and the results will be reported separately. Figure 3 shows measured spectral responsivities of the

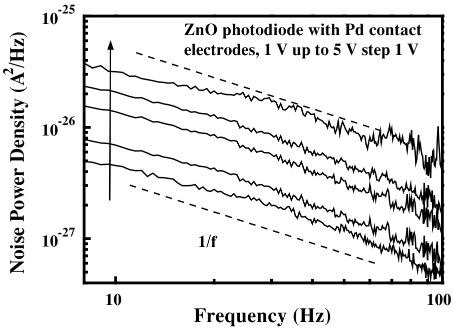

Figure 4. Low frequency noise spectra of the Pd/ZnO/Pd MSM photodiodes.

fabricated Pd/ZnO/Pd MSM photodiodes. As shown in figure 3, it was found that the photodiode responsivities were nearly constants in the below bandgap UV region (300–370 nm) while sharp cutoffs with a drop of two orders of magnitude occurred at approximately 370 nm. With an incident wavelength of 370 nm and 1 V applied bias, it was found that the maximum responsivity for the fabricated Pd/ZnO/Pd MSM photodiodes was 0.051 A/W. We can also calculate the quantum efficiency of our photodiodes from the measured spectra response by:

$$R = \eta \times \frac{q\lambda}{hc} \quad (2)$$

where η is the quantum efficiency, R is the measured responsivity, q is the electron charge, λ is the incident light wavelength, h is the Planck constant and c is the speed of light. Using this equation, we found that the quantum efficiency of our ZnO photodiodes was around 11.4%. Previously, Liang *et al* reported the fabrication of Ag/ZnO Schottky UV photodetectors on R-plane sapphire substrates [4]. They found that responsivity of their MSM photodiode could reach 1.5 A/W. The extremely large responsivity with quantum efficiency larger than 100% indicates that internal gain exists in their photodiode. Very recently, Lee *et al* have reported the optical properties of ZnO films grown on C-plane, A-plane and R-plane sapphire substrates [20]. They found that the ZnO film grown on the C-plane sapphire substrate has the smallest full-width at half-maximum (FWHM) values for both the x-ray diffraction peak and the photoluminescence peak for near-band-edge emission whereas that grown on the R-plane sapphire substrate has the largest FWHM values. Such a result suggests crystal quality of ZnO films prepared on R-plane sapphire substrates is poorer than those prepared on C-plane sapphire substrates. Thus, it is possible that the extremely large responsivity and the internal gain observed by Liang *et al* are originated from the defects in their ZnO film or from their metal/semiconductor interfaces [4].

Figure 4 shows low frequency noise spectra of the ZnO MSM photodiodes with Pd electrodes. From these curves, it was found that measured noise power densities, $S_{\rm n}(f)$, could be fitted well by $1/f^{\gamma}$ with $\gamma = 1$. The observed pure $1/f$ noise indicates that trapping states are distributed uniformly in energy for the device. For a given bandwidth of B, we could estimate the total square noise current by integrating $S_{\rm n}(f)$

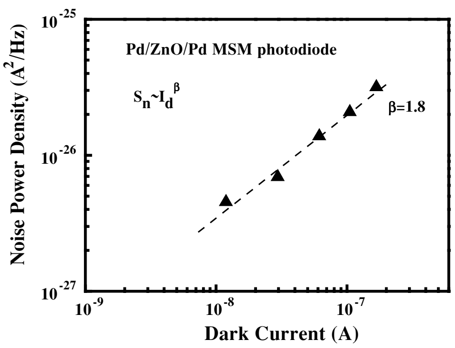

Figure 5. Noise power densities measured at 10 Hz as a function of current for the Pd/ZnO/Pd MSM photodiodes.

over the frequency range:

$$\langle i_n \rangle^2 = \int_0^B S_n(f)\,df = \int_0^1 S_n(1)\,df + \int_1^B S_n(f)\,df = S_0[\ln(B)+1]. \tag{3}$$

Here, we assumed $S_n(f) = S_n$ (1 Hz) for $f < 1$ Hz. Thus, the noise equivalent power (NEP) can be given by:

$$\mathrm{NEP} = \frac{\sqrt{\langle i_n \rangle^2}}{R} \tag{4}$$

where R is the responsivity of the photodiodes. The normalized detectivity, D^*, could then be determined by:

$$D^* = \frac{\sqrt{A}\sqrt{B}}{\mathrm{NEP}} \tag{5}$$

where A and B are the areas of the photodiode and the bandwidth, respectively. For a given bandwidth of 100 Hz and a 1 V applied bias, we found that NEP and corresponding detectivity $D^*$of our Pd/ZnO/Pd MSM photodiodes were 1.13×10^{-12} W and 6.25×10^{11} cm $Hz^{0.5}$ W^{-1} respectively. It should be noted that the D^* measured from our ZnO-based photodiodes was higher than those observed from GaN-based and ZnSe MSM photodiodes with a similar structure [21, 22]. Figure 5 shows the noise power density as a function of current for the Pd/ZnO/Pd MSM photodiodes measured at 10 Hz. It was found that measured noise power densities could be fitted well by the following equation:

$$S_n(f) = K\left(\frac{I_d^{\beta}}{f^{\gamma}}\right) \tag{6}$$

where $S_n(f)$ is the spectral density of the noise power, K is a constant, I_d is the dark current, β and γ are two fitting parameters. From figure 5, it was found that β and γ were 1.8 and 1, respectively. Such a result agrees well with Kleinpenning's model that spectral density of $1/f$ noise should be proportional to I_d^2 [23]. In other words, $1/f$ noise induced increase in current is related to the modulation of Schottky barrier height by uniformly distributed trapping states in our photodetectors.

4. Summary

In summary, ZnO epitaxial films were grown on sapphire substrates by MBE. Pd/ZnO/Pd MSM UV photodiodes were also fabricated. With an incident wavelength of 370 nm and 1 V applied bias, it was found that the responsivity for the photodiodes was 0.051 A/W, which corresponds to a quantum efficiency of 11.4%. Furthermore, it was found that NEP and the corresponding detectivity D^* of the Pd/ZnO/Pd MSM photodiodes were 1.13×10^{-12} W and 6.25×10^{11} cm $Hz^{0.5}$ W^{-1} respectively.

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