Electrical properties of silver Schottky contacts to ZnO thin films

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ZnO thin films are deposited on Al/Si substrates by the pulsed laser deposition (PLD) method. The XRD and SEM images of films are examined. Highly c-axis oriented ZnO thin films which have uniform compact surface morphology are fabricated. The size of surface grains is about 30 nm. The Schottky barrier ultraviolet detectors with silver Schottky contacts are made on ZnO thin films. The current-voltage characteristics are measured. The ideality contact factor between Ag and ZnO film is 1.22, while the barrier height is 0.908 e V. After annealing at 600 °C for 2h, the ideality factor is 1.18 and the barrier height is 0.988 eV. With the illumination of 325 nm wavelength UV-light, the photocurrent-to-dark current ratios before and after annealing are 140.4 and 138.4 biased at 5 V, respectively. The photocurrents increase more than two orders of magnitude over the dark currents.

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Zinc oxide (ZnO) is a wide direct bandgap semiconductor of II-VI group materials. The wide bandgap energy of 3.37 eV at room temperature and large exciton-binding energy of 60 meV make ZnO the good physical and chemical properties. In the applications of ZnO[1,2], it is a key point that high-quality metal-ZnO contact could be successfully fabricated on ZnO thin films. Using the Schottky contacts we can fabricate ZnO-based Schottky detectors with metal-semiconductor-metal (MSM) structure[3-5]. At present, the growth of p-ZnO through doping is still so difficult that we cannot fabricate good quality p-n junction. So MSM structure is appropriate for ZnO-based UV detectors. Thus the study of ZnO-based Schottky contacts has practical significance.

In this paper, the mainly experiment equipment is pulse laser deposition (PLD) system (as shown in Fig.1). In experiment, four targets are metal Al, ZnO doping Al (AZO, the mount of Al is 3% in mass), ZnO, and metal Ag. The purities of all the targets are better than 99.99%. The substrates are *n*-Si (111) with 450 μm thickness. Before substrates are put into vacuum chamber, the pretreatment program is as follows: (1) silicon chips are rinsed using deionized water; (2) they are utrasonic cleaned for 10 minutes using acetone and ethanol respectively; (3) substrates are rinsed using deionized water repeatedly; (4) silicon chips are etched in 5% HF for 5 minutes to remove surface oxidation layer; (5) substrates are soaked for 10 minutes in deionized water; then high-purity N_2 is used to blow drying chips and the substrates are put into vacuum chamber for 5 minutes. During experiments, the background vacuum keeps better than 2×10^{-5} Pa. 500 nm thickness Al thin films are deposited on silicon substrates at 200°C as ohmic electrodes. At the same time, the aluminum films are also buffer layer of ZnO growth[6]. As the difference of thermal expansion coefficient between ZnO and silicon is very large, which are $4.75\times10^{-6}K^{-1}$ and $2.6\times10^{-6}K^{-1}$ respectively, ZnO thin film will shrink more than silicon substrates when the temperature declines from growth temperature to room temperature. Large numbers of cracks probably appear on ZnO thin films because of big tensile stress. Deposition of Al layer before the growth of ZnO film is helpful to grow high-quality ZnO thin film on silicon substrate. Then, 250 nm AZO layer and 450 nm ZnO layer are deposited on the Al/Si substrates successfully at 400°C. The ZnO epitaxial layer is deposited at 2.6 Pa in pure O_2. At last, 200 nm thickness Ag layer is deposited on the ZnO films as Schottky electrode. In experiments, KrF excimer laser runs at 248 nm laser wavelength, 20 ns pulse width and 2 J/cm^2 energy density.

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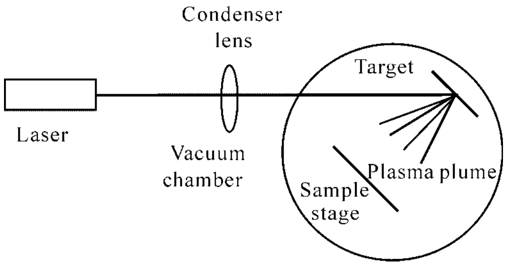


Fig.1 Structural diagram of PLD

Fig.2 is the structural diagram of samples, which shows the MSM structure model of Schottky UV-detector. Samples are tested by step profiler, scanning electron microscopy (JSF6100) and X-ray diffraction (BD2000). The current-voltage (I-V) characteristics of samples are also measured and analyzed.

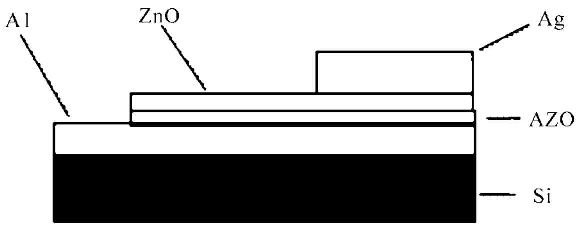


Fig.2 Structural diagram of the samples

Fig.3 (a) is the SEM image of ZnO layer. We can find that compact ZnO grains are well-distributed on the film surface. This result is caused by the growth polarity of ZnO surface grains. Sakurai et al reported that ZnO thin film had smooth surface on bulk ZnO substrate (-c axis) while on bulk ZnO substrate (+c axis) ZnO epilayer consisted of hillocks and columns[7]. Such phenomenon also appears in our samples. The hillocks are well-distributed on the ZnO surface, which have smooth surface and size of 30 nm. These hillocks consist of ZnO grains on +c facet. ZnO epilayer has high crystal quality that shows uniform and compact surface grains. Fig.3 (b) is the SEM image of Ag/ZnO/AZO/Al/Si cross-section. Every part of the multilayer structure is clearly distinguished without serious diffusion. From up to down, they are metal Ag, ZnO, AZO, metal Al, and Si substrate respectively. Without question, the high-quality samples have been fabricated. The thicknesses of Ag, ZnO/AZO and Al layer are about 200 nm, 700 nm and 500 nm estimated by Fig.3(b) respectively, which are consistent with the result by step profiler, Ag 211.4 nm, ZnO/AZO 709.8 nm, Al 498.3 nm.

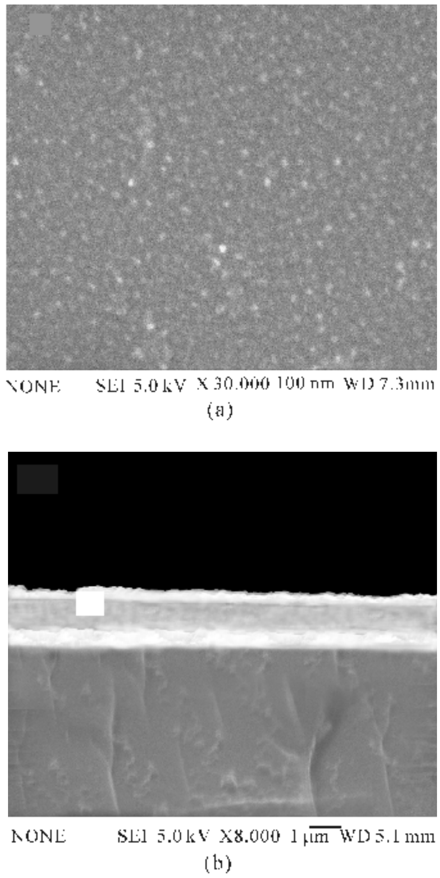


Fig.3 SEM images of samples. (a) ZnO/AZO/Al/Si; (b) Ag/ZnO/AZO/Al/Si.

Fig.4 (a) is the XRD image of ZnO epilayer. It is clearly to find that a peak of ZnO (002) is at $2\theta = 34.22^{\circ}$ with a FWHM of 0.32°. Such a result indicates that the ZnO film has good crystal quality and is preferentially grown in c-axis direction. The size of ZnO grains can be calculated by the strength, position, FWHM of ZnO (002) peak. According to Scherrer equation $D = 0.9\,\lambda/(\Delta\theta\, cos\ \theta)$, D is the size of ZnO grains, λ is the wavelength of X-ray, θ is the diffraction angle of ZnO (002) peak. The size of ZnO grains calculated by the equation is 30.02 nm, which is consistent with the value estimated by SEM image. Fig.4 (b) is the XRD image of Ag/ZnO/AZO/Al/Si multilayer structure. The peaks occurred at $2\theta = 34.22°$ and $2\theta = 37.88°$ are ZnO (002) peak and Ag (111) peak respectively. It indicates that high-quality Ag single thin films are deposited on the ZnO epilayer successfully.

I-V characteristics of MSM structure are measured at room temperature. Then the sample is dealt with vacuum annealing at 600 °C for 2 h. And its *I-V* characteristics are shown in Fig.5. For comparison, the vertical axis of Fig.5 (a) is transformed to logarithmic form shown in Fig.5(b).

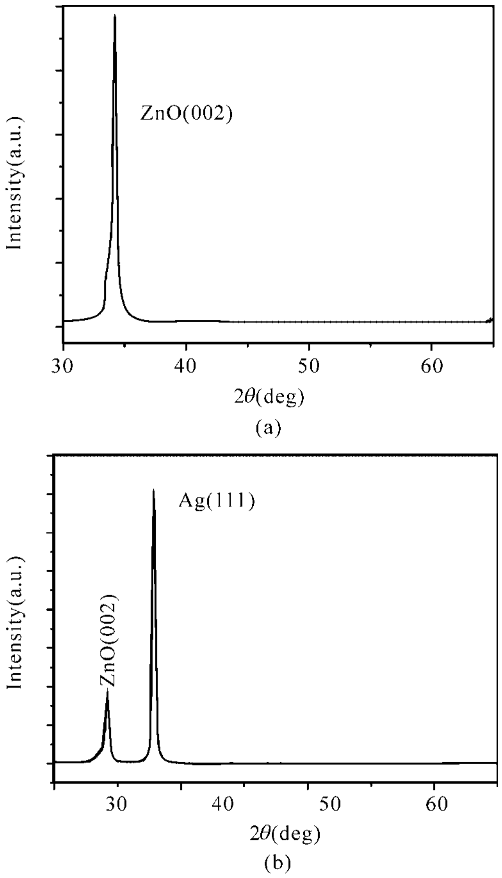


Fig.4 X-ray diffraction patterns. (a) ZnO/AZO/Al/Si; (b) Ag/ZnO/AZO/Al/Si.

It is clear from Fig.5 that annealing can improve the characteristics of metal-ZnO contacts and the quality of MSM devices[8,9].

According to the semiconductor theory, the femi energy levels of metal and ZnO are equal in the case of Schottky contacts. The current-voltage (I-V) curve shows rectifying characteristics. By thermionic emission theory, the current is given by $I=I_s$ [exp (qV/nkT)-1], where n is the ideality factor, k is Boltzmann's constant, T is the absolute temperature. The saturation current I_s is given by $I_s=AA^*T^2$ exp [-$q\Phi_B/kT$], where A is the Schottky contact area, A^* is the effective Richardson constant (theoretically A^*=32 Acm^{-2} K^{-2} for ZnO using m^*=0.27 m_0), and Φ_B is the barrier height. At room temperature. T=300 K, qV>>3 kT, so $I=I_s$ [exp (qV/nkT)], making a transform by nature logarithm, ln I=ln I_s+ (qV/nkT). The barrier height and ideality factor can be obtained by the ln I-V curves.

Fig.6 is the ln I-V characteristics of detectors. Fitting the ln I-V curves over the range 0.1 V < V < 0.5 V, we get the ideality factors 1.22 and 1.18 before and after annealing, respectively. The barrier heights of Ag-ZnO Schottky junctions are about 0.908 eV and 0.988 eV, respectively. At present, the excellent ideality factor of Schottky contacts on

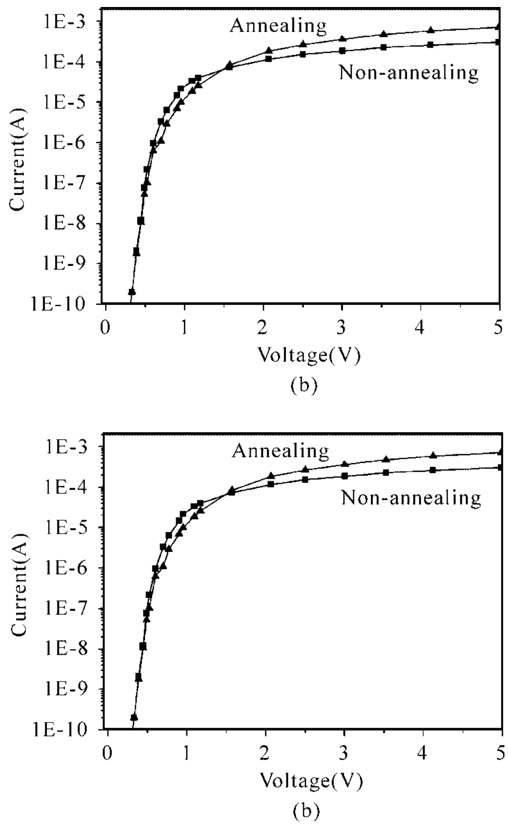


Fig.5 *I-V* characteristics of the detectors

n-ZnO materials is about 1.3, and the barrier heights are ranged from 0.56 eV to 0.92 eV[10-12] . In this paper, annealing causes changes of barrier height in certain extent. New interface phases appear in the contact interface layer by interactions between metal and ZnO at high temperature. The different phases have different work function, which leads to different changes of contact barrier. Moreover, diffusion from metal to ZnO layer increases the electron density of ZnO layer. And the fimi energy level moves towards to the bottom of conduction band. From Fig.6, as forward voltage increases, contact barrier heights increase both before and after annealing. When Ag and ZnO layers are not ideal contacts, there is a complex interface layer between the metal and ZnO layer. The potential on interface layer changes along with the electrical field in ZnO layer. And it leads to the change of contact barrier at last. In other word, the barrier height increases along with the forward voltage.

When the detectors are exposited to the light, high energy photons are captured by ZnO layers and a larger number of photo-generator carriers are produced. If a proper bias voltage is added on the detector, the photo-generator carriers will directionally flow to produce photo current. Fig.7(a) and (b) are the I-V characteristics of detectors under dark and 325 nm UV-light, respectively. From Fig.7(a), before annealing the dark current is 303.2 μA and the photo current is

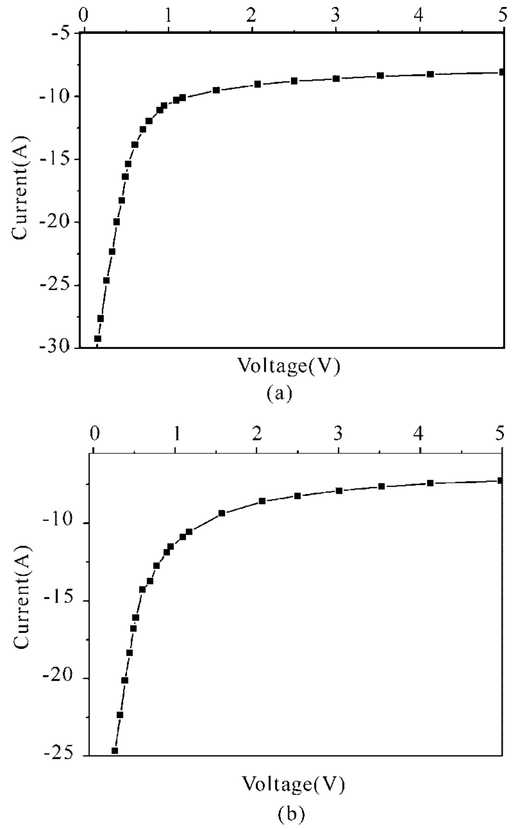
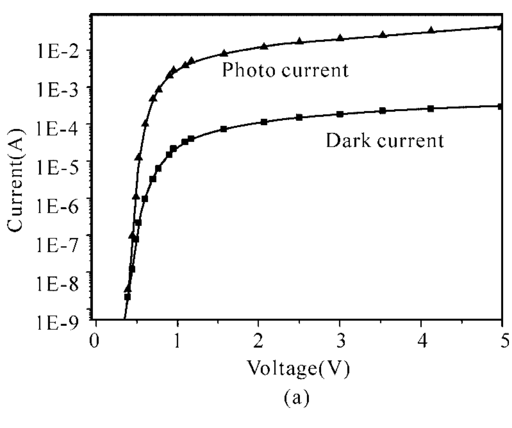


Fig.6 In *I-V* characteristics of detectors

42.58 mA under 5 V bias voltage. The photocurrent-to-dark current ratio is 140.4. After annealing, the dark current is 709.8 μA under 5 V that is also very low. The photo current is 98.23 mA under 5 V bias voltage.

The photocurrent-to-dark current ratio is 138.4. Under 325 nm UV-light, the photocurrent increases more than two orders of magnitude over the dark current. Such samples are proper for Schottky UV detectors.

In summary, the contacts between silver and ZnO thin films are studied in this paper. High-quality ZnO thin films are successfully prepared on Si (111) substrates by PLD. The Schottky barrier ultraviolet detectors with silver Schottky con-



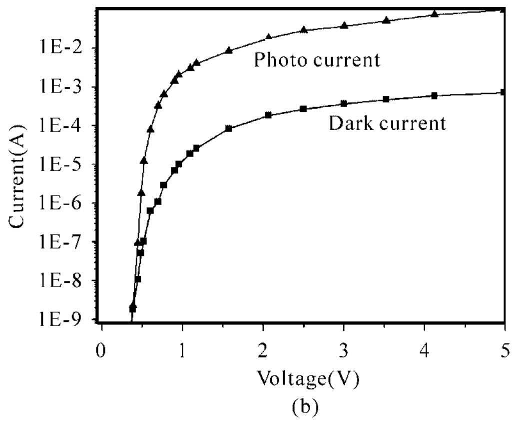


Fig.7 *I-V* characteristics of the detectors at dark (a) and 325 nm illumination(b)

tacts are made on ZnO thin films. The ideality factors are 1. 22 and 1.18 before and after annealing at 600 °C while the contacts barriers are 0.908 eV and 0.988 eV, respectively. Under the illumination of 325 nm wavelength UV-light, the photocurrent-to-dark current ratios before and after annealing are 140.4 and 138.4 biased at 5 V bias, respectively. The photo currents increase more than two orders of magnitude over the dark currents. Such results indicate that using the samples good Schottky barrier UV-detectors can be prepared successfully.

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