Front. Optoelectron. China 2008, 1(3–4): 309–312
DOI 10.1007/s12200-008-0048-7

RESEARCH ARTICLE

Photoresponse of ZnO single crystal films

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Abstract The ohmic contact and photoresponse of a ZnO single crystal film by metalorganic chemical vapor deposition (MOCVD) were investigated. The electrical and photoresponsive changes in the ZnO film due to RF sputter deposition of SiO_2 (antireflection coating) were also discussed. The experimental results show that the non-alloyed Al/Au metallization scheme forms good ohmic contact on n-type ZnO, RF sputter deposition of SiO_2 induces defects which behave as carrier traps and prolong response time, and the photoresponse of ZnO epitaxial film deteriorates with time.

Keywords ZnO single crystal film, metalorganic chemical vapor deposition (MOCVD), photoresponse, antireflection coating (AR coating), RF sputter damage

1 Introduction

Besides infrared detection and laser detection, ultraviolet (UV) detection is another important technique that has become a new and absorbing photoelectric detecting technology used in both military and civilian industry products. UV radiation can be used in dosimetry, early missile threat warning, space-to-space communications, UV astronomy, water purification, flame detection, pollution monitoring, chemical/biological battlefield reagent detectors, and other applications [1]. Semiconductor UV detectors have the advantages of small size, wide spectral response range, high quantum efficiency, high dynamic range of operation, and low background noise [2], and are gaining more market share [3]. ZnO is a wide and direct bandgap semiconductor (bandgap: 3.4 V, responding to the cutoff wavelength of 365 nm) [4], so it is blind to infrared and visual light. Besides its larger photoresponse [5], ZnO is one of several good materials to manufacture solar-blind UV detectors. As a new semiconductor material, the investigation on ZnO is mainly focused on film growth [6–8] and p-type doping [9]. Many studies on the photoresponse of ZnO are limited to polycrystalline material [10–12]. The fabrication of ZnO detectors is also less compared to other types. To get a ZnO UV detector with good characteristics, single film growth, metal-semiconductor contact, and p-type doping should be further improved. The study on the polycrystalline ZnO deposited by RF sputtering shows that the photoresponse of ZnO contains two parts: a rapid and reproducible solid-state process [$h\nu \rightarrow h^+ + e^-$], where e and h represent electron and hole respectively, and a slow process with a large response. The latter is the photoresponse due mainly to the chemisorption and photodesorption of oxygen on the surface of ZnO film. The rising and falling time of the solid-state process cover several microseconds [5], the response of chemisorption-photodesorption is slow (a couple of seconds to minutes). The recovery time is long (several seconds to hours), and the response degenerates as time increases [10–12]. The ohmic contact and photoresponse of a ZnO single film grown by metalorganic chemical vapor deposition (MOCVD) were studied.

Translated from *Chinese Journal of Semiconductors*, 2006, 27(1): 96–99 [译自: 半导体学报]

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2 Experiments

The ZnO film was deposited on a R-plane $(01\bar{1}2)$ sapphire substrate by MOCVD. The X-ray diffraction (XRD) θ–2θ scan pattern of ZnO film is shown in Fig. 1. Diffraction peaks at $2\theta = 25.36^\circ$ and 52.28° corresponding to the $(01\bar{1}2)$ and $(02\bar{2}4)$ planes of sapphire substrate respectively. The strong diffraction peak at $2\theta = 56.68^\circ$ corresponding to the $(11\bar{2}0)$ ZnO is only 0.202°, indicating the high quality of ZnO film. The thickness of the film is 500 nm and its resistivity is about 200 Ω·cm after annealing in oxgen. To study the photoresponse of the ZnO film, Al/Au (100 nm/500 nm) were deposited by RF sputter deposition as the contact metal. Diffusion fields of interdigital (IDT) pattern was adopted and its figure length is 500 μm, width 10 μm, and spacing 10 μm. Then 60 nm SiO_2 was deposited on the detectors as antireflection (AR) coating, enhancing the UV transitivity and protecting the device from oxygen absorption. The measurement

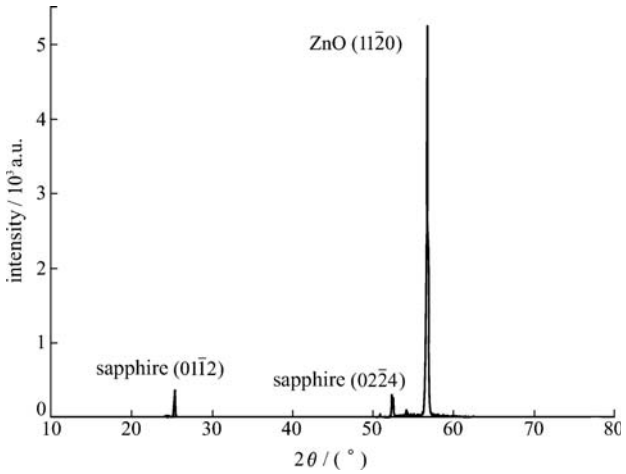

Fig. 1 XRD pattern of ZnO film

UV light source was a 150 W Xe lamp whose light power was calibrated by an optical power meter. The *I–V* characteristics were measured by an Agilent 4155C analyzer.

3 Results and discussion

3.1 ZnO ohmic contact

The *I–V* characteristics of ZnO single film under three different conditions are compared in Fig. 2. Figure 2(a) shows the *I–V* characteristics before and after AR coating without UV light illumination. Figure 2(b) shows the *I–V* characteristics of a newly deposited film and the one exposed to air for 5 months. The non-alloyed Al/Au was used as the contact metal. Figure 2(b) shows that dark current increases linearly when the bias voltage is −5–5 V, indicating that the non-alloyed Al/Au could form good ohmic contact on n-type ZnO, which is consistent with the result of Kim [13]. The result is also consistent with the fact that the enthalpy of formation for Al_2O_3 ($\Delta G^\circ_{298} = -1492$ kJ/mol) is much smaller than that for ZnO ($\Delta G^\circ_{298} = -324$ kJ/mol) [14]. During deposition, interdiffusion happened at the interface: some oxygen atoms outdiffused to the Al metal layer and Al atoms indiffused to ZnO layer [13]. It is noteworthy that the dissociation of the ZnO at the surface region is possible without an annealing process due to the strong reaction between Al and O in ZnO layer, which causes oxygen vacancy accumulation at the interface. Oxygen vacancies, acting as donors on ZnO film, increase the carrier concentrations to enable good ohmic contact by non-alloyed Al/Au on ZnO film. Low resistivity (200 Ω·cm) encourages the formation of ohmic contact. To avoid oxidation of the Al surface, more than 50 nm Au were deposited to further improve the ohmic contact. After AR deposition, ohmic contact becomes inferior as shown in Fig. 2(a).

3.2 *I–V* characteristics of ZnO film

The dark current is 3.5 mA under the bias voltage 5 V before AR coating, as shown in Fig. 2(b). But after AR

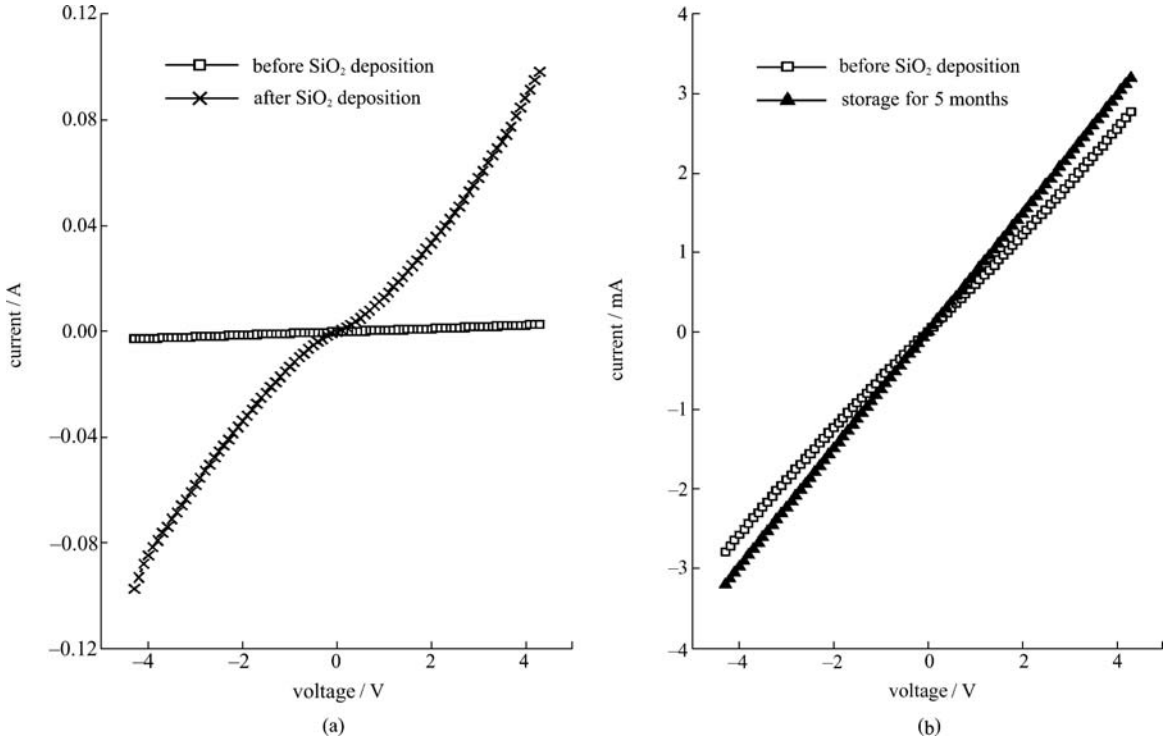

Fig. 2 (a) *I–V* characteristics comparison of ZnO film before and after AR coating deposition; (b) *I–V* characteristics comparison of ZnO film before AR coating deposition and stored in air for 5 months without AR coating

coating sputtered, the current increases 30 times to about 100 mA, as shown in Fig. 2(a). AR coating was deposited by RF sputtering and the SiO_2 is amorphous. The sputter deposition technique can damage the surface of semiconductor materials by the energetic species incident on the surface. The damage involves electrical, optical, structural, and stoichiometric modifications [15]. The electrode structure of the ZnO detector follows an IDT pattern. The simulation of the spatial electric field distribution on this structure shows that the electric field concentrates on the surface and has a low effective penetration depth [16]. As the electrode structure adopted and both electrodes are on the same side, damage produced by sputter deposition is easy to observe via the *I–V* characteristics of the detector. The *I–V* measurement result reveals that the sputter deposition of AR coating had produced damage on the surface of ZnO film and changed the electrical property remarkably. The bombardment of the energetic particle and high temperature due to the sputtering may fracture the Zn–O bond, thus increasing the oxygen vacancies and zinc Zn interstitials and decreasing the interface resistivity [17]. Because of the preferential sputtering of SiO_2, the deposited AR film cannot reach perfect stoichiometry and will also affect the *I–V* curve of ZnO.

3.3 Photoresponse

The measured dark and photoilluminated *I–V* characteristics are shown in Fig. 3. The current under UV light illumination is 10 times larger than dark current at 5 V bias, indicating that the ZnO film has a large UV photoresponse; it is a promising material for UV detector fabrication. Under constant UV radiant exposure, the photoilluminated currents increase linearly as bias voltage increases, indicating that the photoresponse has a linear relation with bias voltage and is consistent with the theory of semiconductor photoconductive detector [18].

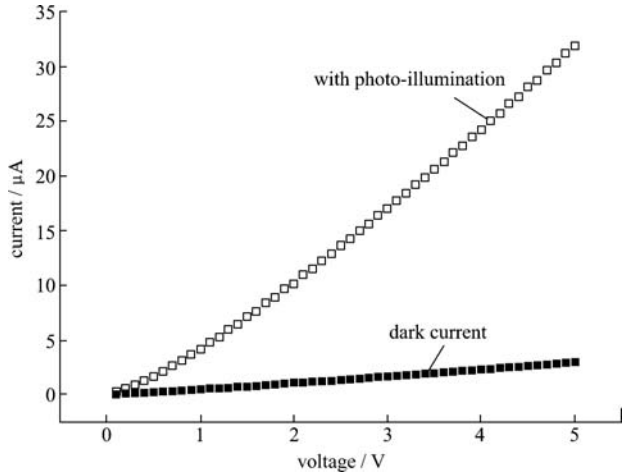

Fig. 3 Dark and photoilluminated *I–V* characteristics (before AR coating deposition)

Figure 4 shows the fall time of ZnO film under three different conditions. The fall time of the film exposed to air for 5 months is apparently longer than the newly deposited one, and its photoresponse is much bigger, consistent with the result of Zhang et al. [10]. It is concluded that not only the photoresponse of polycrystal ZnO, but also that of ZnO single film is affected by chemisorption-photodesorption of oxygen, and has the effect of aging. The recovery time of ZnO film before SiO_2 deposit is about several minutes; this time is significantly prolonged after SiO_2 deposit to about half an hour. This phenomenon indicates that the surface damage caused by sputtering introduces carrier defects into the ZnO bandgap, which acts as a trap center and decreases the recombination probability, i.e., increases the carrier lifetime τ. The light current caused by UV irradiation after AR coating deposit is bigger than before, as shown in Fig. 5. The light current caused by light irradiation can be expressed as [18]

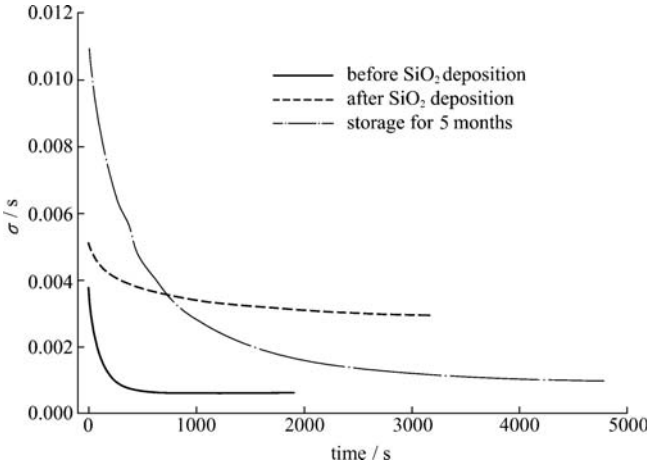

Fig. 4 Photoresponse comparison of ZnO film stored in air for 5 months, before and after AR coating deposition

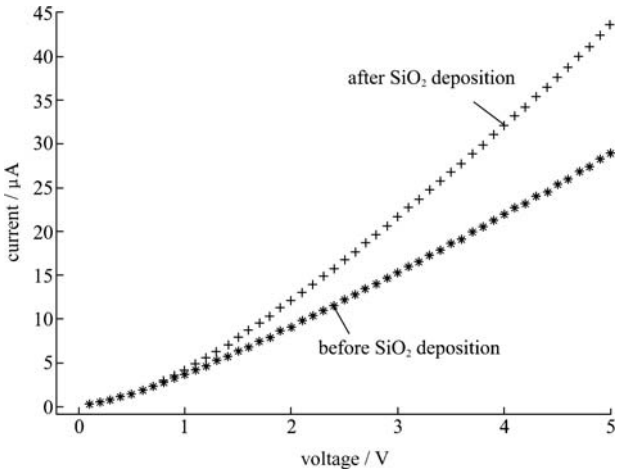

Fig. 5 Light current caused by UV light comparison before and after SiO_2 deposition

$$I_{\mathrm{ph}} = q\eta A_0 \Phi_{\mathrm{s}} g, \tag{1}$$

where I_{ph} is the light current caused by light irradiation, q is the electronic charge, η is the internal quantum efficiency, A_0 is the light sensitive area , Φ_{s} is the radiant flux and g is the photoconductive gain, which can be expressed as

$$g = \frac{\tau}{t_{\mathrm{tr}}} = \frac{\tau \mu_{\mathrm{e}} V_{\mathrm{b}}}{l^2}, \tag{2}$$

where τ is the carrier life time and t_{tr} is the transit time of carrier between the electrodes. Considering carrier mobility as a constant value, g can be expressed as a function of bias voltage V_{b}, and l is the electrode spacing. Figure 4 shows that the life time of ZnO film after AR coating deposited (τ_{aftr}) is longer than before (τ_{befr}). According to Eq. (2), the photoconductive gain after deposition (g_{aftr}) is bigger than before (g_{befr}). According to Eq. (1), it can be concluded that the light current after SiO_2 deposit is bigger than before. The results are consistent with the experimental data, which indicates that the RF sputter deposition of SiO_2 definitely introduces trap centers carrier into the ZnO bandgap.

4 Conclusion

The ohmic contact, I–V characteristics and photoresponse of ZnO single film deposited by MOCVD were investigated. The influence of SiO_2 AR coating deposition on ZnO film was discussed. Electrical and photoresponsive changes in the ZnO film due to RF sputter deposition of SiO_2 (antireflection coating) were also discussed. The results show that the non-alloyed Al/Au metallization scheme can form good ohmic contact on a ZnO single film. RF sputter deposition of SiO_2 introduces deep level defects to the surface of the ZnO film, which behaves as carrier traps and prolongs photoresponse time. The photoresponse of ZnO degenerates as time increases because of surface chemisorption-photodesorption. After exposure to the air for a period, the fall time of ZnO is prolonged.

Acknowledgements The work was supported by the special fund of elitist cultivation of Beijing (67002013200302).

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