Physica B 404 (2009) 1550–1552

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Ultraviolet photovoltaic characteristics of silver nanocluster doped ZnO thin films

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ARTICLE INFO

Article history:
Received 1 December 2008
Received in revised form
11 January 2009
Accepted 14 January 2009

PACS:
73.50.pz
78.20.-e
78.40.fy

Keywords:
Nanocluster
Zno thin films
Laser-induced voltage

ABSTRACT

We reported on the ultraviolet laser-induced photovoltaic effect of a silver nanocluster doped ZnO thin film on fused quartz substrate. An open-circuit photovoltage of about 1 ns full width at half-maximum was observed under the illumination of a 266 nm pulsed laser in duration of 25 ps. When the film was irradiated by a 308 nm laser pulse for 20 ns, a transient photovoltaic signal of ~29 mV occurred with a full width at half-maximum of about 20 ns. A possible mechanism of the observed phenomena is discussed based on the microstructure characteristics.

1. Introduction

ZnO is a promising short-wavelength optoelectronic material because of its direct wide band gap (3.37 eV at 27 K), large exciton binding energy (60 meV) and high transparency (>80%) in the visible wavelength region [1–4]. Significant efforts have been directed toward the fabrication of ZnO thin film and nanowire devices [5–8]. Over the past years a great deal of physical properties has been investigated in doping ZnO thin films. Lim et al. reported the fabrication of ZnO based LEDs using sputter deposited P-doped ZnO as the p-type layer [9]. Ye et al. used N–Al codoping for p-type doping and fabricated ZnO LEDs on Si with sputter deposition [10]. Myong et al. obtained highly conductive Al-doped ZnO thin films [11]. Ataev et al. reported a resistivity of $1.2\times10^{-4}\,\Omega$cm for Ga-doped ZnO thin films grown by chemical-vapor deposition [12].

In this paper, we report the ultraviolet (UV) photovoltaic response of Ag-doped ZnO thin films deposited at different temperature. The transient voltage signals with a full width at half-maximum (FWHM) of ~1 ns have been observed at room temperature when the films are irradiated by a 266 nm laser for a duration of 25 ps. When the film was irradiated by a 308 nm laser pulse for 20 ns, a transient photovoltaic signal of ~29 mV occurred with a FWHM of ~20 ns.

2. Experimental

The films were prepared on fused quartz substrates by pulsed laser deposition (PLD). A KrF excimer laser (wavelength: 248 nm, pulse width: 30 ns, energy density: 1 J/cm^2) was used for ablation of a ZnO mosaic target (1/4 area of the target was uniformly covered with high-purity silver slices in the shape of a sector). In our experiment, the repetitive frequency of the laser was 4 Hz, the O_2 pressure was 5×10^{-4} Pa, and the temperature of the substrates varied from 350 to 550 °C. All the samples were cooled to room temperature under an O_2 pressure of 5×10^{-4} Pa in the chamber.

The microstructure of the films was analyzed by scanning electron microscopy (SEM). For the photovoltaic measurements a quadruple Nd:YAG laser (wavelength 266 nm) was used as the light source at room temperature in air with a pulse energy of 1 mJ and a light spot of 6 mm in diameter. The photovoltaic signals

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doi:10.1016/j.physb.2009.01.017

were monitored with a 500 MHz oscilloscope terminated into 50 Ω. Under the same condition, the 308 nm excimer laser was used as the light source to irradiate the samples. The UV-visible absorption spectrum was also measured as a function of wavelength.

3. Results and discussion

Fig. 1 presents typical open-circuit photovoltages transient of Ag-doped ZnO films deposited at different temperature (350 °C, 450 °C and 550 °C). Under pulsed 266 nm laser irradiation of 25 ps duration, the photovoltaic signals had FWHMs of 0.9, 0.8 and 1.0 ns and peak photovoltages of 29, 72 and 28 mV for 350, 450 and 550 °C, respectively. Furthermore, Fig. 1(d) shows the temporal response of the Ag-doped ZnO film to a 20 ns 308 nm laser pulse. The peak photovoltage reaches ~29 mV. The FWHM and 10–90% rise times are ~20 and ~10 ns, respectively, which are limited by the excitation laser.

To characterize the photogenerated carriers of the samples used in present study, we determined the optical absorption spectrum from the optical transmission measurement using a SpectraPro500i spectrophometer. Fig. 2 shows the UV-visible absorption spectrum of Ag-doped ZnO films as a function of the wavelength. The sharp absorption edge is at ~370 nm, which is agreement with the optical band-gap of ZnO and the experimental results. This property demonstrates that the production of the photongenerated carries plays a crucial role in the process of laser induced voltage in this system.

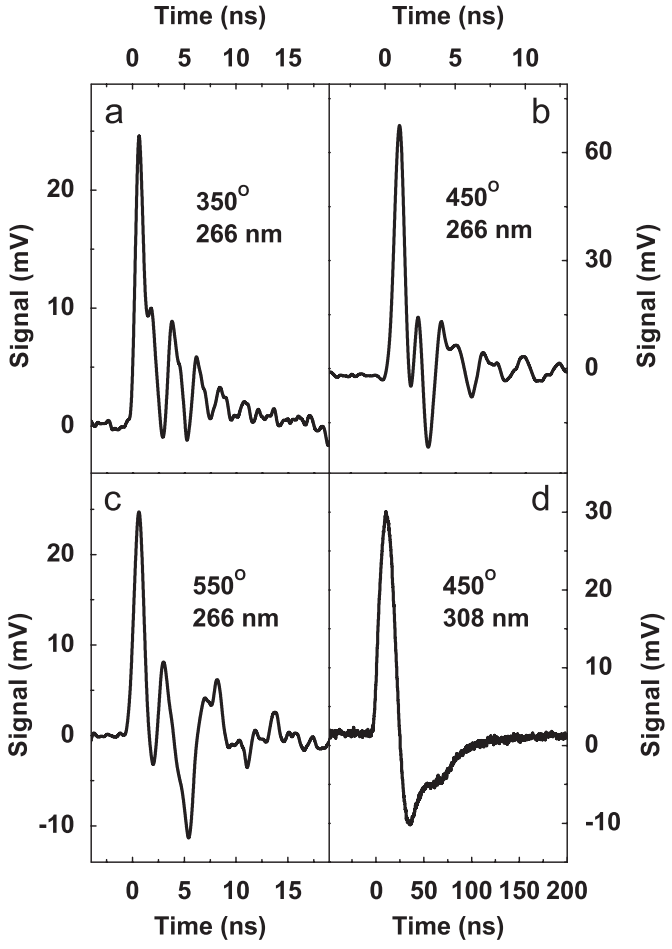

Fig. 1. Open-circuit photovoltages of Ag-doped ZnO films deposited at (a) 350 °C, (b) 450 °C and (c) 550 °C under the excitation of 266 nm laser. (d) Shows the photovoltage of the sample deposited at 450 °C under the excitation of 308 nm laser.

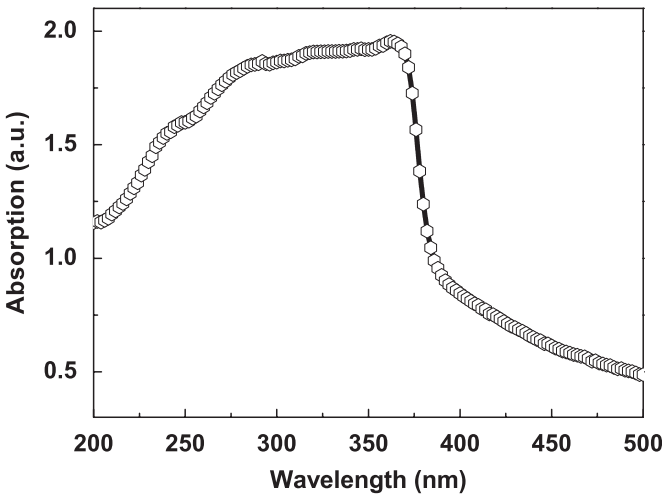

Fig. 2. UV-visible absorption of Ag-doped ZnO film.

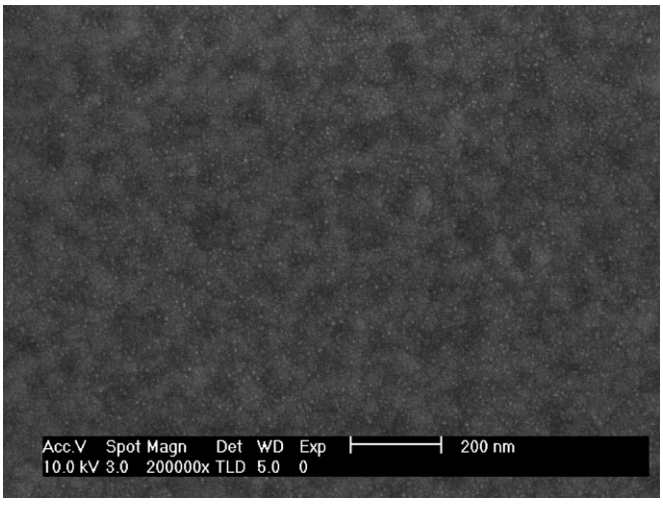

Fig. 3. SEM morphologies of Ag-doped ZnO films deposited at 350 °C.

Figs. 3 and 4 show the SEM morphologies of Ag-doped ZnO films deposited at 350 and 550 °C, which is different from that at 450 °C reported in Ref. [13] where the silver nanocluster uniformly distribute in the films and three largest size of clusters are denoted by 18.2, 16.2 and 14.2 nm [13]. From the SEM image the Ag-doped ZnO films consist of grains separated by grain boundary (GB), and Ag would preferentially choose to sit in vicinity of grain boundaries due to its large ionic radius.

We also studied the photovoltaic effect of ZnO films without Ag under the same condition and no voltaic signal appeared in our oscilloscope, indicating that Ag clusters in vicinity of grain boundaries play an important role in the present photovoltaic characteristics. Thus, a simplified model can be given on the origin of the photovoltaic signal. There is a chemical potential shift $\Delta\mu$ between the GB region and the grain, which might induce a depletion layer in the GB region and the build-in voltage V_b is given by $\Delta\mu$, $V_b = \Delta\mu$. Shu-Ting Kuo et al. calculated the electrostatic barrier of one-grain boundary of Ag-doped ZnO was approximately 2 V [14]. When the laser irridiates the sample, electron-hole pairs can be excited in the grains and GB regions

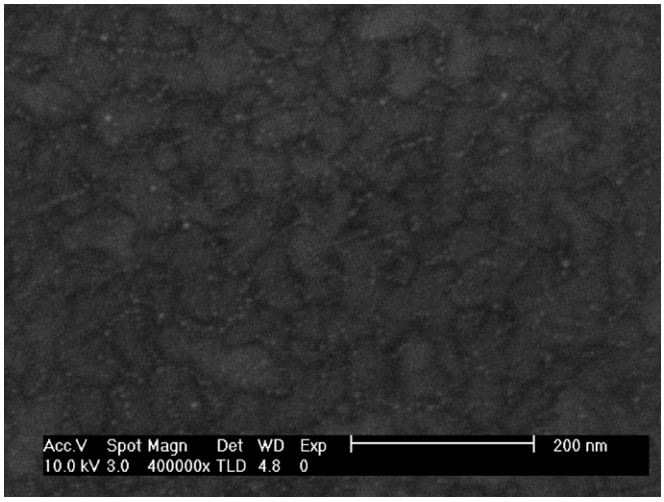

Fig. 4. SEM morphologies of Ag-doped ZnO films deposited at 550 °C.

since an energy gap of ZnO between occupied and empty electronic states is smaller than UV photon energies (4.0 eV for 308 nm and 4.7 eV for 266 nm). And then the nonequilibrium carriers are separated by the built-in electric field near the GB, eventually, leading to the appearance of an instant photovoltage.

Since the sample is polycrystalline, there should be an equal number of grains with photogenerated carriers shifting in one direction as in the opposite direction, hence there should be not net current flow and no photovoltage signal. This is not the case. In fact, it is uncertain why there is an overall preferred direction for the flow of the photogenerated current. This behavior may be due to the asymmetry of the lattice which induces an asymmetric moving of the excited carriers in a preferred direction. Further study on the nature of the photovoltaic properties of such a system is under way.

4. Conclusions

In summary, the Ag nanocluster doped ZnO thin films have been prepared on fused quartz substrates by PLD. Under the irradiation of UV pulsed laser of 266 nm and 308 nm, the films showed transient photovoltaic signals with the response times of ~1 and ~20 ns. Since UV photon energy is higher than the energy gap of ZnO, the electron-hole pairs are excited in the film under UV laser, and separated by the built-in electric field near the GBs, leading to the photovoltaic effect.

Acknowledgements

This work has been supported by NCET, NSFC, RFDP, Key Project of Chinese Ministry of Education (No. 107020), and Beijng Natural Science Foundation (No. 4082026).

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