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XPS study of nitrogen-implanted ZnO thin films obtained by DC-Magnetron reactive plasma

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Abstract

We have synthesized pure and N-doped ZnO films by reactive plasma in a DC-Magnetron sputtering system. Nitrogen was implanted by using an ion gun attached to an electron spectrometer. The films were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and scanning electron microscopy (SEM) to investigate their composition and microstructure. XPS revealed the presence of two well-resolved peaks in N 1s spectra at about 396.2 and 404.3 eV. The peak at 404.3 eV has been assigned to zinc nitrite while the peak at 396.2 eV to zinc nitride. After annealing the sample at 250 °C in air for 1 h, one single peak, located at 399.1 eV, was observed. We suggest that this is due to the decomposition of nitrite and the formation of oxynitride.
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Keywords: ZnO thin films; XPS; DC sputtering; Nitrogen doping

1. Introduction

Zinc oxide is a wide gap semiconductor ($E_g = 3.37$ eV) that has been extensively studied in the past because of its electrical and optical properties used in a wide variety of technological applications such as gas sensor devices [1], transparent electrodes [2–4], piezoelectric devices [5] and varistors [6]. It has recently gained a tremendous interest because of its potential use for the fabrication of blue light emitting diodes (LED) and laser diodes (LD) [7]. Indeed, ZnO is currently considered as the main competitor of another direct gap II–VI compound GaN ($E_g = 3.5$ eV). However, the free exciton energy in ZnO (60 meV) is about three times larger than that in GaN (21–25 meV). In addition, ZnO has the advantage to be more resistant to radiation damage [8]. One of the major obstacles hindering the use of ZnO in optoelectronics is the difficulty to obtain p-type samples. Nitrogen is a good acceptor candidate for ZnO [9]. It was successfully used to dope another II–VI compound ZnSe [10–11]. Many authors tried to obtain p-type conductivity by doping ZnO with N [12–27], As [28–30], P [31], and by co-doping samples with (N, Ga) [32–33] and (N, Al) [34]. In reference [13], it was shown that ion implantation of high-energy nitrogen ions (50–380 keV) in ZnO single crystals induced a high concentration of defects without changing the type of conductivity. In this work, we have used an ion gun attached to the electron spectrometer to introduce low-energy nitrogen ions (2 keV) in ZnO thin films that were prepared by DC-Magnetron reactive plasma. Such low energy is expected to minimize the concentration of defects induced in the thin film samples. X-ray photoelectron spectroscopy (XPS) technique was used to monitor the behavior of nitrogen in the implanted films before and after annealing. Hall measurements were also performed using van der Pauw method in order to check the evolution of the electrical properties of the films.

2. Experimental

The ZnO films of less than 1-μm thickness were deposited on glass substrates by reactive plasma in a home-made DC-Magnetron sputtering system. The experimental conditions were as follows: diameter of the Zn target 5 cm, distance between the target and substrates 3 cm, initial pressure in the vacuum

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chamber 5×10^{-7} mbar, oxygen pressure 10^{-4}–10^{-3} mbar, total (Ar + O_2) pressure during sputtering 60–90 mbar, high voltage 850 V, and current 40–60 mA.

Nitrogen was implanted by bombarding the films with N^+ ions of energy 2 keV for 15 min. The target current was about 1.5 μA and the nitrogen pressure in the chamber was 2×10^{-7} mbar. Subsequently, the film was annealed ex situ under air at 250 °C for 60 min.

XPS spectra were recorded by using an electron spectrometer of the type VG-ESCALAB MKII equipped with a dual X-ray source (Mg/Al) and an ion gun (Type EXO5). We have used the aluminum anode (Kα, 1486.6 eV). The energy resolution of the spectrometer was about 1 eV at pass energy 20 eV. Zn 2p, C 1s, O 1s and N 1s lines were systematically recorded. Since different surfaces (as grown, sputtered, and annealed) of the sample were compared in the study, it was realized that the adventitious C 1s line, which is traditionally used as a reference for correcting charge shift, was not appropriate. Furthermore, we have verified that the chemical shift in Zn $2p_{3/2}$ between metallic and oxidized Zn is very small (0.2 eV) [35]. Therefore, the charge shift correction of the binding energies was done by using the Zn $2p_{3/2}$ line (E_b = 1021.8 eV) as a reference.

The microstructure of the films was observed by scanning electron microscopy (SEM) (JEOL-JSM6460). The microscope was equipped with a liquid-nitrogen cooled silicon detector to perform energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) experiments were carried out using a fully automated X-ray diffractometer (Bruker XRD-D8). The incident photons were produced from a Cu anode (Kα, λ = 1.5418 Å).

3. Results and discussion

The microstructure and composition of the films were characterized by SEM, XRD, and XPS. Fig. 1 shows an SEM image of the cross section of such a film. It shows that the thickness of the film is 0.75 μm. The image also reveals the polycrystalline structure of the film and some surface roughness. Fig. 2 shows the XRD pattern of two films labeled Film 1 and Film 2. Film 1 corresponds to the film displayed in Fig. 1. It was prepared under 80 mbar total (Ar + O_2) pressure and a partial oxygen pressure $P_{O_2} = 4.7 \times 10^{-6}$ mbar (P_{O_2} = oxygen pressure/total pressure). Film 2 was prepared at higher partial oxygen pressure (2×10^{-5} mbar), the other parameter being similar to those of Film 1. We have also reported on the same figure the XRD patterns that we have obtained from a pure zinc foil and ZnO powder for comparison. The XRD diagrams show a very strong (0 0 2) diffraction peak indicating a strong texture of the films with a preferential orientation parallel to this direction. In addition, the width of the (0 0 2) peak of Film 2 (FHWM = 0.2790°) is much broader than that observed in Film 1 (FHWM = 0.2199°). This result is probably related to a smaller size of the grains in Film 2. By using Sherrer's relation between the grain diameter *D* and the FHWM, that is $D = \lambda/(\mathrm{FWHM} \times \cos\theta)$, we obtain about 40 nm grain size for Film 1 and 30 nm for Film 2. The difference in the grain size of the two films could be related to the difference in the partial pressure of oxygen during growth. However, more systematic study is needed to confirm this assumption.

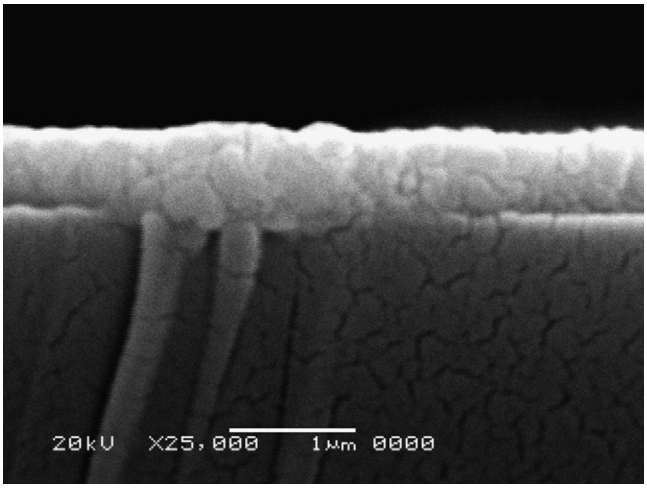

Fig. 1. SEM image of ZnO thin film deposited on glass substrate. Notice the polycrystalline structure of the film.

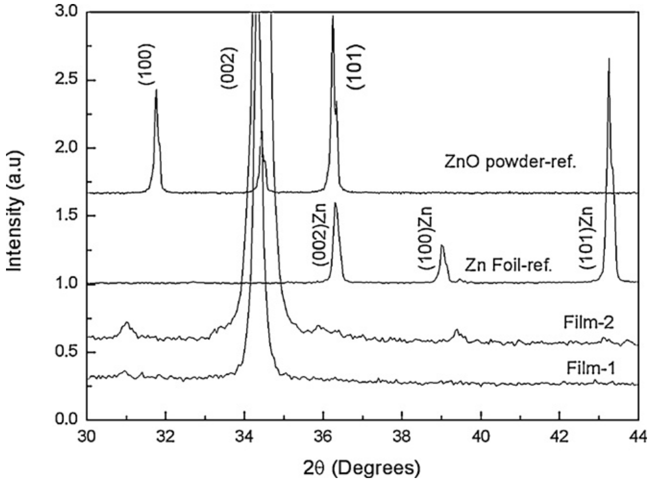

Fig. 2. XRD patterns of two ZnO films labeled Film 1 and Film 2. The XRD patterns of ZnO powder and metallic Zn foil are also shown as references.

Fig. 3 shows the N 1s region of the N-implanted ZnO thin film (labeled Film 2) before and after annealing. Before annealing, the N 1s spectrum reveals two distinct peaks at about 396.2 and 404.3 eV. After annealing the sample at 250 °C in air for 1 h, the two peaks merged into a single one located at about 399.1 eV. The literature shows that the binding energy of the N 1s line is very sensitive to the chemical environment of the nitrogen atom. It varies from 396 to 408 eV [35]. Shinn and Tsang [36] discussed the 1s binding energy of chemisorbed nitrogen on Cr/W(1 1 0) film. They detected four different peaks at 396, 397.5, 400, and 405 eV in the N 1s XPS spectra, and identified them with four different types of bonding configuration for chemisorbed nitrogen. The peak at 396 eV was assigned to atomic nitrogen (β-N), the 397.5 eV peak to well screened molecular nitrogen (α-N_2), the 400 eV peak to terminally bonded well screened molecular nitrogen (γ-N_2), and the 405 eV peak to terminally bonded poorly screened molecular nitrogen (γ-N_2). Their annealing study also showed that

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