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X-ray photoelectron spectroscopy study of highly-doped ZnO:Al,N films grown at O-rich conditions

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ABSTRACT

Highly-doped ZnO:Al,N films were grown under oxygen-rich conditions on Si substrates by magnetron sputtering using a layer-by-layer growth technique. An investigation of the highly-doped ZnO:Al,N films is attractive for obtaining *p*-type conductivity in ZnO films as well as for an improvement of performance of ZnO-based ultraviolet (UV) detectors. X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), X-ray emission spectroscopy (XES) and Secondary ion mass spectrometry (SIMS) were used for the samples characterization. An effect of high Al and N doping on structure and electronic properties of ZnO films was studied and discussed.

1. Introduction

Being a wide direct band gap material zinc oxide, ZnO (E_g ~3.3 eV at room temperature) has ecological and economic benefits over commercialized GaN, which is commonly used in the semiconductor industry [1]. At present, ZnO films still have been extensively investigated due to their promising applications in solar cells, gas- and bio-sensors, field emitters, transparent conductive electrodes, UV photodetectors and light emitting diodes, etc [2–9]. Extrinsic doping of ZnO is useful tool to tune its structure, optical and electronic properties. Therefore, clear understanding the doping effect on the ZnO films is an imperative for successful realization of high-performance devices. Naturally, ZnO has *n*-type conductivity. Nevertheless, there is still strong impetus towards achievement of stable *p*-type conductivity in ZnO, which is required for fabrication of different kinds of semiconductor devices. However, the latter is a great challenge due to a self-compensation effect caused by intrinsic *n*-type defects (oxygen vacancies (V_O), zinc interstitials (Zn_i) and zinc antisites (O_{Zn}) [10]) and by the incorporation of hydrogen as an unintentional donor as well as due to low solubility of doping elements in ZnO lattice [11]. The simultaneous doping (co-doping) of ZnO by acceptor (N, P or As) and donor (Al, Ga or In) impurities allows to increase the solubility of acceptor impurities and to reduce their ionization energy [12]. Therefore, the co-doping is promising for the realization of stable *p*-type conductivity in ZnO.

On one hand, the achievement of p-type conductivity in ZnO is important for designing of ZnO UV detectors based on p-n-junction. It is believed that p-type conductivity in ZnO could be achieved by the nitrogen impurity doping. But this matter is still controversial and has been debated up to now [13–15]. In particular, as was shown in our previous works [16,17] acceptor nitrogen doping of ZnO thin films did not lead to p-type conductivity. Nevertheless, even without being electroactive dopants, the nitrogen species can be very useful for improvement of the photovoltaic properties (the photoconductivity and the photoresponse rate) for different types of ZnO-based UV photodetectors. Recently, we proposed the mechanism underlying giant enhancement of the photoresponse rate of ZnO-based UV photodetectors [18]. This enhancement is triggered by reducing the density of hole-trapping centers. Another way of the improvement of the photoresponse speed of photodetectors is enhancement of the carrier concentration in ZnO films by

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donor doping [19]. Therefore, the nitrogen and aluminum co-doping of ZnO also is promising for development of highly efficient photodetectors based on ZnO films due to the increased solubility of nitrogen in the oxide lattice and the enhancement of the carrier concentration in ZnO films by Al donor doping. Moreover, such co-doping also may lead to improvement of the ZnO films structure [20]. Earlier, we reported the effect of the incorporation of small amount of nitrogen and aluminium species into ZnO films on the energy distribution of the electronic states within the valence-band region as well as on altering values of binding energies of the XPS core-levels associated with zinc and oxygen atoms [21]. To our best knowledge, the influence of high concentrations of nitrogen and aluminium on the electronic structure of ZnO films grown under O-rich conditions has not been studied yet in details. Although, synthesis of the ZnO films in oxygen rich mode is perspective for improvement the performance of ZnO-based devices [22,23]. Thus, it is very important to clarify the electroactive behaviour of the Al an N dopants. Here, we gain deep insight into the physical nature of the effect of high Al-N doping on the electronic structure of ZnO:N, Al films deposited under O-rich conditions.

2. Experimental

2.1. Sample preparation

ZnO films co-doped by nitrogen and aluminum were deposited on p-Si (ρ_s = 9 Ohm □) substrates by radio-frequency (rf) magnetron sputtering using the layer-by-layer growth method [24]. Before loading substrates into deposition chamber the last ones were cleaned in acetone, ethanol and deionised water during 10 min for each stages. Immediately after, the substrates were dried in nitrogen flow. Using start-stop technique (i.e. introducing interruptions at film growth) the films were grown by three stages. The total time of deposition was 18 min. Zinc disk (99.99% purity) with Al (99.99% purity) inserts was used as a target. The area of Al inserts was 1.4% of the Zn target area. Nitrogen-aluminum doping was performed during ZnO films growth by adding the nitrogen (N_2) to oxygen-argon working gas mixture in the deposition chamber. The nitrogen pressure was changed from 0.4 to 0.8 Pa by step 0.2 Pa. The rf discharge power was maintained at 200 W. The pressure of oxygen and argon were about 0.9 and 1 Pa, respectively. The substrate temperature was fixed at 270 °C. The target-substrate distance was approximately 7 cm.

2.2. Characterization

The crystal structure was investigated by X-ray diffraction (XRD) using DRON-4 diffractometer, utilizing Cu-Kα radiation (λ = 0.1542 nm). The elemental analysis of ZnO:N films was done by ZEISS EVO 50 XVP SEM using energy dispersive X-ray spectroscopy (EDX) furnished INCA 450 (OXFORD Instruments).

Measurements of XPS valence-band and core-level spectra were carried out in a sublimation ion-pumped chamber having a base pressure less than 5×10^{-10} mbar of the UHV-Analysis-System (SPECS, Germany) equipped with a PHOIBOS 150 hemispherical energy analyzer. The energy scale of the XPS spectrometer was calibrated by setting the measured Au $4f_{7/2}$ and Cu $2p_{3/2}$ binding energies (BEs) of pure reference metallic samples to 84.00 ± 0.05 eV and 932.66 ± 0.05 eV, respectively, with regard to the Fermi energy, E_F. The XPS spectra were excited by Mg Kα source of X-ray radiation (E = 1253.6 eV) and were recorded at a constant pass energy of 25 eV. The charging effects were taken into account in reference to the C 1s line (284.6 eV) of adventitious carbon as it is recommended for such kind of materials [25,26]. Furthermore, for the ZnO:N, Al film with the highest nitrogen concentration we have measured the XES Zn Lα (transition $L_{III} \rightarrow M_{IV,V}$) and O(N) Kα (transition $K \rightarrow L_{II,III}$) bands representing the energy distribution of the Zn 3d, 4s and O(N) 2p states, respectively. The technique of measurements of the above XES bands is the same as described in detail in Refs. [27,28]. Briefly, an RSM-500 spectrometer equipped with a diffraction grating (600 groves/mm, radius of curvature of R = 6026 mm) and a secondary electron multiplier VEU-6 (CsI photocathode) was used. Spectrometer electron gun operated at U_a = 5.2 kV and I_a = 1.5 mA was used for excitation of the XES Zn Lα and O Kα bands. The energy resolution, ΔE_{min}, of the RSM-500 spectrometer within the energy regions corresponding to positions of the measuring XES bands was estimated to be less than 0.3 eV. The concentration profiles of elements for ZnO:N, Al films were studied by secondary ion mass spectrometry (SIMS) technique using a CAMECA IMS6F micro-analyser. SIMS measurement was performed with cesium (Cs+) primary beam, with the beam current kept at 200 nA. The size of the eroded crater was about 200 μm × 200 μm and the secondary ions were collected from a central region of 40 microns in diameter. Defect distributions were characterized by the RBS (Rutherford Backscattering) method in channeling mode [29].

3. Results and discussion

The concentrations of nitrogen and aluminium as well as O/Zn stoichiometric ratio were defined by using the EDX spectroscopy. The concentration of aluminium in ZnO:Al,N films was found to be approximately 2.4 at. %. When nitrogen pressure in deposition chamber was changed from 0.4 to 0.8 Pa with step 0.2 Pa the nitrogen incorporates in ZnO:Al,N films with concentrations 2.3, 3.6 and 4.3 atomic %, respectively. With increasing of nitrogen concentration the O/Zn stoichiometric ratio in films decreases as 1.48, 1.41 and 1.25, respectively. Therefore, the oxygen pressure in deposition chamber of 0.9 Pa leads to O-rich conditions in all deposited films and the enhancing of nitrogen concentration results in decreasing of oxygen concentration in ZnO:Al,N films. So, we have an interesting case for analyzing of the films structure as well as electronic properties of O-rich high-doped ZnO:Al,N films.

The influence of high concentration of nitrogen on structure of ZnO:Al,N films was analyzed by XRD measurements (Fig. 1). All ZnO:Al,N films have (002) and (004) diffraction peaks of hexagonal wurtzite ZnO (accordingly with JCPDS card number 36-1451) that correspond to *c*-axis orientation of crystallites in the film plane. With increasing nitrogen concentration from 2.3 to 4.3 at.% the structure of ZnO:Al,N films gradually changes: the full width at half maximum (FWHM) of diffraction peak ZnO (002) increases from 0.69 to 1.12° as well as the position of (002) peak shifts to smaller angle side from 34.41 to 34.07°, respectively. Such increasing of FWHM of (002) peak for co-doped ZnO films testifies decreasing grain size in films as estimated by Scherrer's formula [30]. The deterioration of structure for ZnO:Al,N films is caused by increasing nitrogen incorporation into ZnO lattice. The shift of (002) peak position of ZnO in small angle side is related to expansion of ZnO lattice (*d*-spacing value) caused by substitution of oxygen on nitrogen ions or nitrogen molecules which have bigger ion radius then oxygen one [31]. When nitrogen concentration in ZnO lattice rises to 4.3 at.%, the peak (321) of cubic Zn_3N_2 (corresponding to the JCPDS card number 35-0762) appeared (Fig. 1, XRD pattern 3). No other phases corresponding to AlN, or Al_2O_3 were detected. The increase in nitrogen concentration in ZnO:Al,N films leads to (i) gradual increasing of FWHM of XRD (002) peak and (ii) shift of the main peak towards smaller angle side. This is due to the deterioration of ZnO crystal structure, which is caused by nitrogen incorporation into ZnO lattice (Zn-N bond formation). High nitrogen partial pressure in reactive chamber leads to the formation of Zn_3N_2