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Band gap engineering of indium zinc oxide by nitrogen incorporation

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ABSTRACT

The effects of nitrogen incorporation in indium zinc oxide films, as grown by RF reactive magnetron sputtering, on the structural, electrical and optical properties were studied. It was determined that the variation of the N_2/Ar ratio, in the reactive gas flux, was directly proportional to the nitrogen percentage measured in the sample, and the incorporated nitrogen, which substituted oxygen in the films induces changes in the band gap of the films. This phenomenon was observed by measurement of absorption and transmission spectroscopy in conjunction with spectral ellipsometry. To fit the ellipsometry spectra, the classical and Adachi dispersion models were used. The obtained optical parameters presented notable changes related to the increment of the nitrogen in the film. The band gap narrowed from 3.5 to 2.5 eV as the N_2/Ar ratio was increased. The lowest resistivity obtained for these films was $3.8 \times 10^{-4}\ \Omega\,\mathrm{cm}$ with a carrier concentration of $5.1 \times 10^{20}\ \mathrm{cm}^{-3}$.

1. Introduction

The In_2O_3-ZnO (IZO) system has demonstrated excellent optical and electrical properties, such as high optical quality, high mobility, surface uniformity and chemical and thermal stability in various environments. For these reasons, IZO has been widely used in applications, such as transparent contacts for solar cells, light emitting diodes and several other optoelectronic devices [1–6]. For the application of IZO in optoelectronic devices, one of the relevant properties is the optical band gap, which closely depends on the change of the growth conditions, the doping impurities and, consequently, the carrier concentration. In recent years, the best control in the thin film deposition techniques allows for the design of band structures with nearly arbitrary and continuous band-gap variations showing that band-gap engineering is a powerful technique for the design of new semiconductor materials and devices. In this way, there are many reports related to the production of shifts in the band gap of IZO [6–9]. Several of these works modified the band gap by changing the ratio between indium and zinc metal or including new metallic species within of the IZO matrix, which often results in a more complicated, costly and less reproducible process, and the shifts of the band gap are relatively small. However, before this work, nobody has studied or reported the band gap engineering of the IZO system by substituting oxygen with nitrogen.

In the present work, a method to change the optical band gap of IZO films grown by RF reactive magnetron sputtering is reported. The synthesis and the optical, structural and electrical characterization of the IZON thin films obtained by RF reactive magnetron sputtering are presented. The nitrogen incorporation in the films is also studied as a function of the nitrogen concentration in the sputtering atmosphere. The refractive index and extinction coefficient were determined as a function of the photon energy using spectroscopic ellipsometry (SE). The optical constants derived from the experimental techniques are presented, and a significant study of the optical band gap was realized from the dependence of the absorption coefficient on the photon energy. Optical band gap shifts as large as 1 eV are observed for the IZON films.

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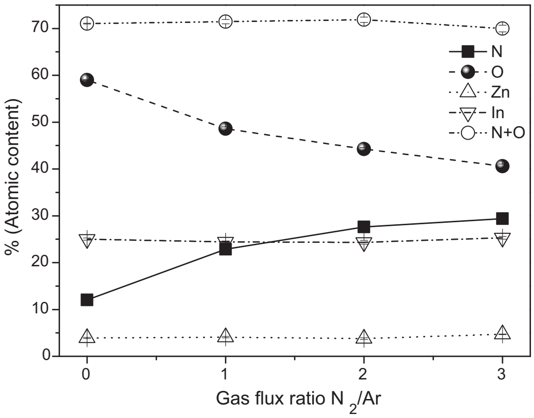

Fig. 1. Atomic percentages for the different species present in the IZON films as a function of the gas flux ratio N_2/Ar in the reactive atmosphere.

2. Experimental details

Indium zinc oxynitride thin films were deposited on Si(1 0 0) substrates and corning glass substrates by RF reactive magnetron sputtering under different nitrogen concentrations in the reactive atmosphere. IZO (In_2O_3/ZnO, 90/10 wt.%, with a purity of 99.99%) was used as the sputtering target. For this purpose, the deposition chamber was evacuated to a base pressure lower than 1.5×10^{-6} Torr. Room temperature sputtering depositions were performed with Ar (99.995%) and N_2 (99.99%) as the reactive sputtering gases at a total pressure of 6×10^{-3} Torr. The gas flux ratio N_2 (sccm)/Ar (sccm) was set at: 0/5, 5/5, 10/5 and 15/5. The deposited films were characterized in a Jeol Scanning Electron Microscope, model JSM-6390LV. An X-ray energy dispersive spectrometer (INCA X-sight Oxford Inst. Model 7558) was attached to the microscope. The crystalline structure of the IZON thin films was studied in a Siemens D-5000 diffractometer using the Cu Kα line (λ = 0.1541 nm). The X-ray diffraction patterns were obtained in a grazing angle mode at 1.5°. The electrical resistivity, mobility, and carrier concentration were measured in an Ecopia HMS-3000 Hall Effect Measurement System, using the Van der Pauw configuration. The optical transmittance was measured in a Perkin Elmer Lambda 35 UV–vis spectrophotometer in the wavelength range from 300 to 1000 nm. Finally, spectroscopic ellipsometry (SE) measurements were acquired in a Yobin Ivon Ellipsometer, model UVISEL, in an energy range from 1.5 to 4.5 eV. The latter measurements were employed to find the refractive index and extinction coefficient of the films by comparison with the theoretical computer-calculated spectra of the films using the software provided with the ellipsometer (Psi-Delta 2.0).

3. Results and discussion

3.1. Thin film composition

X-ray energy dispersive spectroscopy (EDX) analysis confirmed the presence of In, Zn, O and N in all the deposited films. The atomic concentrations are shown in Fig. 1. As the ratio of nitrogen increased in the reactive gas flux, the amount of nitrogen in the films increased. At the same time, the percentage of oxygen in the film decreased, inversely proportional to the amount of nitrogen incorporated. In addition, the atomic percentages of indium and zinc in the films did not change with the N_2/Ar gas flux ratio. In Fig. 1, the sum N + O is also plotted, and its behavior with the varying N_2/Ar gas flux ratio is nearly constant. These results directly suggest that oxygen ions are partially substituted by nitrogen ions in the structure of the film. Even when no nitrogen flux was supplied to the sputtering chamber (0 N_2/5 Ar), the background nitrogen inside was enough to be introduced in the films. This finding is most likely observed due to the large affinity of nitrogen for indium [10]. In fact, this feature has led to improvement of the incorporation of nitrogen in the films. However, the increment of nitrogen in the films could lead to the appearance of new phases besides the original phases that were present in the sputtering target used for depositing these films.

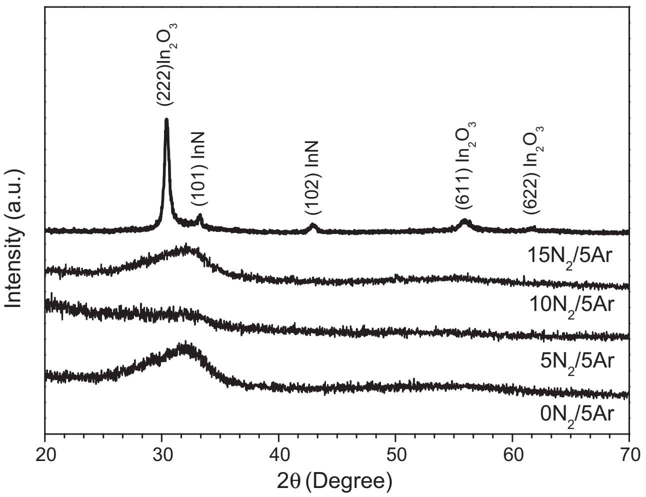

Fig. 2. XRD spectra of the IZON thin films as a function of the growth parameters.

Fig. 2 shows the XRD pattern obtained for the different films. For the first three conditions of deposition, amorphous films were generated, and the related spectra showed a broad band in the diffracted intensity associated with the amorphous phase in the range of 20–40° with the maximum approximately 32.4°. This band is related to the IZO matrix, so it is not possible to observe any effect of nitrogen for these cases. However, the films deposited with a gas flux ratio of 15 N_2/5Ar showed a sharp peak at $2\theta = 30.5°$ associated with the (2 2 2) plane of the In_2O_3 bixbyite structure. This peak has been previously reported for the In_2O_3-ZnO system [11–15]. In addition, four peaks located at 33.2°, 43.5°, 56.1° and 61.7° corresponded to the (1 0 1) and (1 0 2) planes of the hexagonal structure of pure InN and the (6 1 1) and (6 2 2) planes of In_2O_3 bixbyite structure. The XRD results showed that for the largest N_2 flux in the chamber, the active N species formed by the RF readily competed for sites and substituted oxygen in the films, as confirmed by EDX, leading to the formation of additional crystalline phases of InN in the films.

3.2. Electrical properties

The carrier concentration (n), the mobility (μ) and the resistivity (ρ) of the IZON thin films were analyzed as a function of the N_2/Ar gas flux ratio. Fig. 3 shows the evolution of the electrical properties. All of the films presented n-type conductivity, which is the typical conductivity reported for IZO films [14–17]. The carrier concentration was related to the nitrogen in the films, i.e., the carrier concentration decrease was inversely proportional to the amount of nitrogen incorporated in the films. The electrical conduction in intrinsic indium oxide (In_2O_3) is due to free electrons originating from two mechanisms. The related mechanisms are oxygen vacancies and the excess of indium atoms in the films [18]. Nevertheless, a complementary scenario for n-type electrical conductivity is expected for intrinsic zinc oxide (ZnO). In addition to interstitial zinc in the films, oxygen vacancies are historically attributed as free charge carriers via the formation of shallow donor levels [19]. However, first-principles calculations