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On the growth of transparent conductive oxide ternary alloys Zn–Ir–O (ZIRO) by the means of rf magnetron co-sputtering

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ABSTRACT

We report here on an alternative approach for forming p-type transparent conductive oxide ternary alloys Zn–Ir–O (ZIRO) by the means of rf magnetron co-sputtering of Ir and zinc nitride targets in a mixed argon and oxygen plasma. The structural and optical properties of ZIRO thin films formed on both glass and Si (100) substrates have been studied by Energy Dispersive X-ray spectrometry (EDX), X-Ray Diffraction (XRD), Raman and optical spectrophotometry. The EDX results outlined that the Ir incorporation in ZIRO alloys saturates at 3.3% when the rf co-sputtering is done in a plasma containing above 2% O_2. XRD and Raman spectroscopy analysis revealed that all films were polycrystalline containing only the ZnO and IrO_2 phases. The presence of Ir in ZIRO thin films does affect their optical transparency below 500 nm while it remains comparable to that of ZnO above 500 nm down to the infrared spectral range. Moreover the physical properties of the ZIRO films have been studied after sequentially annealing in air or forming gas (95% N_2–5% H_2) at elevated temperatures up to 700 °C. All ZIRO films were found to remain highly resistive (MΩ range) regardless of annealing treatment conditions. The optical transparency of these films was found to be further reduced upon annealing at temperatures above 500 °C.

1. Introduction

ZnO is a wide band gap semiconductor (Eg ~3.3 eV) with high exciton binding energy (~60 meV), has good transparency and its conductivity (when doped with Al) approaches that of the widely used n-type indium–tin–oxide (ITO). As a result, ZnO is the ideal material to replace ITO on many applications in the emerging field of transparent electronics and optoelectronics. ZnO exhibits intrinsic n-type conductivity due to native defects such as oxygen vacancies, zinc interstitials, and antisite zinc, which act as donors. It can also be easily doped by group III elements (Al, Ga, In) to give high quality n-type ZnO [1]. However, achieving p-type ZnO in a controllable, reproducible and reliable manner remains a technological challenge [2]. Many attempts have been made to introduce acceptors in an effort to obtain p-type doping however with limited success due to either low solubility of acceptors in ZnO or self-compensation effects caused by the native defects which act as donors compensating the deliberately introduced acceptors [3]. These attempts have concentrated on single doping by group V elements (N, As, Sb), acceptor-donor co-doping such as N–Al, P–In, N–Zr, N–B, and N–Mg, or even by dual-acceptor doping like N–As and N–P ([3] and references therein). Nevertheless none of these attempts have managed to solve the serious reproducibility and stability issue of p-type ZnO.

A different class of p-type zinc oxide with iridium has attracted attention recently [4,5], due to some remarkable features on their electronic structure. Despite the very limited available data on the Zn–O–Ir system, theoretical calculations have shown [4] that while low Ir doping can lead to hole trapping processes inhibiting p-type conduction and transparency, high Ir concentrations reduce diffusion barriers for hole hopping through the lattice and thus hole trapping cannot play an important role in p-type conductivity in materials such as Ir-doped ZnO (ZnO:Ir) or the spinel $ZnIr_2O_4$. Similar findings concerning p-type conduction have been reported for spinel structures containing zinc such as, ZnM_2O_4, M = Co, Rh [5]. Recently, sputtered ZnO–IrO_2 films, containing more than 35 at.% Ir, exhibited resistivity of around 10^{-3} Ωcm and transmittance at 550 nm around 33%, but only after annealing in air at 500 °C for 20 h the transmittance was increased to 60% with no appreciable change in resistivity [6].

In a previous investigation we had shown [7] that by employing zinc nitride target it was possible to fabricate n-type or p-type N-containing ZnO depending on the amount of oxygen in the Ar plasma. In the present work we are exploring an alternative approach on the formation of p-type transparent conductive oxide ternary alloys Zn–Ir–O

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(ZIRO) by means of rf magnetron co-sputtering of Ir and zinc nitride targets in a mixed argon and oxygen plasma. We report here on the morphological, structural and optical properties of the Ir containing ZnO films and on the impact of the post deposition annealing (up to 700 °C) on the physical properties of these films.

2. Experimental details

A reference sample of ZnO film was fabricated by rf sputtering, using a commercially available 6 in. in diameter zinc nitride target (Zn:N = 1:1, purity 99.95%) in plasma containing Ar and O_2 gasses (purities 99.999% and 99.95 N, respectively). The ZIRO films were grown by rf co-sputtering of metallic Ir and ZnN targets in plasma containing Ar and O_2 gasses. The rf sputtering target for ZIRO film growth was realized by placing metallic Ir pellets (diameter 10 mm and thickness 2 mm, purity 99.95%) on the surface of zinc nitride target. The rf sputtering growth experiments were performed at 100 W rf power (power density 19.7 W/cm^2), total pressure of 0.67 Pa (5 mTorr) consisting of 0–10% O_2 in Ar gas and the distance between the target and the substrates was kept constant at 11 cm. The sputtering target conditioning was achieved by sputtering cleaning step before and after each deposition run for 30 min at 100 W rf power and 0.67 Pa Ar plasma. The films with nominal thickness around 170 nm were deposited on unintentionally heated substrates: Si (100) substrates, from which the native oxide had been removed by immersing them in 10% HF solution, as well as on fused silica (dimensions: 1 in. × 1 in. × 1 mm), which were cleaned in organic solvents and dried in N_2 gas before placing them in the sputtering system. The ZnO and ZIRO films thickness was determined by using a profilometer (Veeco Dektak 150). The post deposition annealing treatments of the films were performed successively at 300 °C, 500 °C and 700 °C in a Rapid Thermal Annealing (RTA) system in flowing forming gas for 1 min or heated in air in a furnace for 10 min (step 15 °C/min). The forming gas was 95% N_2-5% H_2 and the flow rate was 450 sccm (standard cubic centimeter per minute).

The structural, optical and electrical measurements could be performed on films deposited on a single glass substrate with the appropriate patterns for the characterization methods employed. The patterns were formed by means of a photoresist, employing standard photolithographic technique, followed by thin film deposition and lift-off.The XRD technique was employed to examine the structure of the films by using the Cu K_α X-rays of a Rigaku RINT-2000 system. Both θ/2θ and Grazing Incidence XRD (GIXRD, θ = 1°, 2θ = 20–90°) configurations were utilized to extract the crystallographic properties of the films. For a selected number of films overnight scans were performed in order to get more accurate information of the films' grains orientation. Information about preferred orientations was taken by comparing experimental data with those of the Joint Committee on Powder Diffraction Standards (JCPDS) database. The surface morphology was investigated by a Field Emission Scanning Electron Microscope (SEM, JEOL 7000) operating at 15 kV, equipped with an Energy Dispersive X-ray (EDX) spectrometry system. The latter was used, at the working distance of 10 mm, for evaluating the atomic percentage of Ir in films deposited on Si substrates following the expression at.% Ir = Ir/(Zn + Ir + O).

Raman scattering measurements were utilized to investigate the existence of iridium related bonds. The system employed was a NICOLET Almega operating in the conformal mode. The laser beam of 473 nm excitation line with power of 10 mW was focused on a spot size of 2 μm in diameter. The scattered light was detected by a charge coupled device (CCD) detection system. The electrical properties of the films were determined by Hall-effect measurements using the four-probe Van der Pauw technique. The transmittance of the films was measured using a Perkin Elmer Lambda 950 UV/VIS/NIR spectrophotometer at λ = 250–2500 nm. From the transmittance spectrum and by employing the standard Tauc plot procedure [8], an estimation of the direct optical energy gap (E_{gap}) was made using the equation $(\alpha h\nu)^2 = A(h\nu\text{-}E_{gap})$, where α is the absorption coefficient, hv is the photon energy, h is the Planck's constant and A is a constant. By plotting $(ahv)^2$-vs-hv and extrapolating the linear region of the resulting curve, the E_{gap} could be extracted at the interception with the energy axis.

3. Results and discussion

3.1. Properties of as-prepared ZIRO films

Before investigating the properties of Ir-containing ZnO, zinc oxide films (used as a reference in this study) were grown from the zinc nitride target in plasma containing up to 10% of O_2 in Ar. By increasing the amount of O_2 in plasma from 0% to 10%, the deposition rate decreased by one order of magnitude, from 7.1 nm/min to 0.7 nm/min due to the atom of oxygen being lighter than that of argon. Even though the nitrogen sputtered from the zinc nitride target could be detected in the plasma during deposition [9], the existence of nitrogen in the structure of the grown ZnO films could not unambiguously be detected by the EDX technique since its signal was almost at the detection limit of the system as well as overlapping with the oxygen peak thus we are concluding that any nitrogen content in the structure of the ZnO films should be less than 1%.

For achieving the incorporation of Ir into n-type ZnO films, Ir pellets were placed onto the zinc nitride target in the sputtering chamber. In a preliminary rf sputtering growth experiment we investigated the Raman features of films depositing using an increasing number of Ir pellets (up to 2 pellets) on the target in order to get information on the presence of possible Ir-related compounds. The results are depicted in Fig. 1 along with the signal from the Si substrate for comparison. It was found that the Raman peak seen at around 725 cm^{-1}, demonstrated an intensity increase as a function of the number of Ir pellets on the target surface. This peak is the characteristic Raman active mode B_{2g} of IrO_2 [10]. The A_{tg} Raman mode, which is generally appearing very close to the B_{2g} mode, at around 752 cm^{-1} [10] could not be distinguished due to the broadening of the B_{2g} mode. The other characteristic phonon mode of IrO_2, E_g, at around 550 cm^{-1} arising from the stretching mode of Ir–O_2 bonds [6,10–12] could not be seen due to the strong phonon mode of Si substrate (520 cm^{-1}). In Fig. 1 we cannot clearly discern any Raman modes for ZnO due to the fact that polycrystalline ZnO thin films have a low Raman scattering efficiency when they assume a decreased crystalline order due to the presence of the IrO_2 phase.

Since the concentration of Ir in ZnO has been reported to affect drastically the electrical and optical properties of Zn–O–Ir films [4,6,12], in this work we focus on the properties of zinc oxide films fabricated

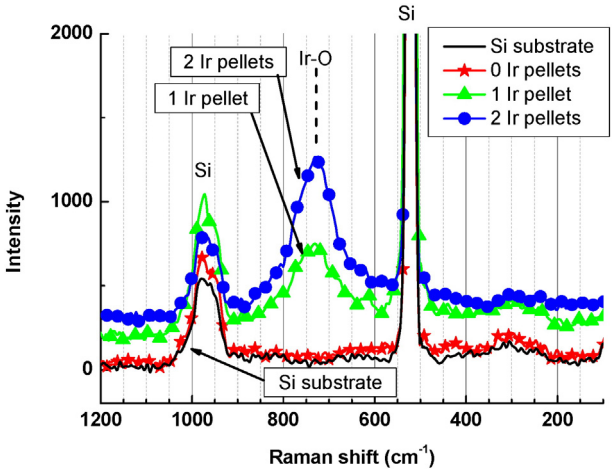

Fig. 1. Raman spectra of films containing increasing number of Ir pellets. The Si substrate spectrum is also shown.

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