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Electrical and optical properties of Zn–In–Sn–O transparent conducting thin films

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ABSTRACT

Indium tin oxide (ITO) is one of the widely used transparent conductive oxides (TCO) for application as transparent electrode in thin film silicon solar cells or thin film transistors owing to its low resistivity and high transparency. Nevertheless, indium is a scarce and expensive element and ITO films require high deposition temperature to achieve good electrical and optical properties. On the other hand, although not competing as ITO, doped Zinc Oxide (ZnO) is a promising and cheaper alternative. Therefore, our strategy has been to deposit ITO and ZnO multicomponent thin films at room temperature by radiofrequency (RF) magnetron co-sputtering in order to achieve TCOs with reduced indium content. Thin films of the quaternary system Zn–In–Sn–O (ZITO) with improved electrical and optical properties have been achieved.

The samples were deposited by applying different RF powers to ZnO target while keeping a constant RF power to ITO target. This led to ZITO films with zinc content ratio varying between 0 and 67%. The optical, electrical and morphological properties have been thoroughly studied. The film composition was analysed by X-ray Photoelectron Spectroscopy. The films with 17% zinc content ratio showed the lowest resistivity ($6.6\times10^{-4}\,\Omega\,cm$) and the highest transmittance (above 80% in the visible range). Though X-ray Diffraction studies showed amorphous nature for the films, using High Resolution Transmission Electron Microscopy we found that the microstructure of the films consisted of nanometric crystals embedded in a compact amorphous matrix. The effect of post deposition annealing on the films in both reducing and oxidizing atmospheres were studied. The changes were found to strongly depend on the zinc content ratio in the films.

1. Introduction

Transparent conductive oxides (TCOs) are optoelectronic materials gaining importance in the technology and research field thanks to their conductivity, high transparency and industrial process compatibility [1]. They have a wide range of passive and active applications in solar cells [2,3], flat panel displays [4], electrochromic windows [5] or gas sensors [6]. Films can be deposited by a wide variety of techniques such as sputtering [7], sol–gel [8], spray pyrolysis [9], thermal evaporation [10], pulsed laser deposition [11], low pressure chemical vapour deposition [12], etc. The three primary polycrystalline inorganic materials for transparent conducting thin films are In_2O_3, SnO_2 and ZnO [13]. These materials are strongly degenerated n-type semiconductors with a band gap over 3.1 eV and, therefore, transparent in the visible wavelength range. Among the TCO thin films, indium oxide doped with tin oxide (ITO) is widely used due to its unique electrical (~$1\times10^{-4}\,\Omega\,cm$) and optical (~85% in visible region) properties. Nevertheless, indium is a rare material [14] and therefore it is expensive. Moreover, the high deposition temperature needed to obtain good electrical and optical properties [15] is another disadvantage to fabricate devices on plastic substrates. Besides, doped ZnO seems to be a promising material to substitute indium tin oxide because of its comparable electrical and optical properties [16], and zinc is an abundant material on the Earth's crust [17]. Amorphous semiconductors are preferred over polycrystalline ones when they are to be deposited over active layers as it happens in thin film transistors [1] or solar cells [18], because of their low processing temperature. Amorphous oxide semiconductors formed by Zn, Sn or In have relatively high mobilities because the bottom of the conduction band is formed by spherically symmetric 4 s or 5 s orbitals with isotropic shapes and, therefore direct overlap with next 4 s or 5 s orbital is possible [19]. This property allows them to behave similar to their polycrystalline phase [20].In order to reduce the use of In and enhance the use of Zn, we have deposited a multicomponent material formed by In–Sn–Zn–O (ZITO) varying the Zn content ratio from 0 to 67%. We present the structural, electrical and optical properties as well as the electrical properties after annealing in oxygen and hydrogen atmospheres.

2. Experimental details

ZITO layers were deposited by radiofrequency (RF) magnetron co-sputtering of ZnO and ITO at room temperature. Both materials were sputtered simultaneously in a pure argon atmosphere onto a rotating substrate. The targets were of 3 inch in diameter and had a purity of 99.995% in the case of ZnO and 99.99% for ITO (In_2O_3 doped with

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10 wt,% SnO_2). A series of samples with varying Zn content ratio were achieved by keeping a constant rf power (50 W) to ITO and changing the power to ZnO from 0 to 150 W in steps of 25 W (see Table 1 for sample identification). The targets to substrate distance were fixed at 12 cm and a rotation speed of 10 rpm was given to the substrate to get a uniform film onto 5×5 cm^2. The substrate was Corning glass (1737 F) and the pressure was kept at 0.35 Pa. The deposition time was adjusted to get layers with the same thickness. (~215 nm).

The film thickness was measured using a Dektak 3030 profilometer. Thickness was measured on different parts of the sample and average value was taken with a tolerance of $\pm$20 nm. The structure of the films was analysed by X-ray diffraction (XRD) using a PANalytical X'Pert PRO MPD Alpha1 powder system using copper K_α radiation ($\lambda = 1.5406$ Å) as the source. Moreover, samples were studied by High Resolution Transmission Electron Microscopy (HRTEM) using a JEM JEOL 2100 system. The film composition was analysed by X-ray Photoelectron Spectroscopy (XPS) with a PHI 5500 Multitechnique System from Physical Electronics. The optical transmission and reflectance spectra were recorded by using a spectrophotometer (Perkin Elmer Lambda 950). The sheet resistance was measured by using a four point probe system (Jandel RM3). Mobility and carrier concentration were determined from the Hall effect measurements by using standard Van der Pauw method in a magnetic field of 0.3 T.

Two kinds of thermal annealing treatments were performed to the samples at 300 °C. A set of samples was annealed at atmospheric pressure with an oxygen flow of 4 sccm for one hour. Another set of samples was annealed in hydrogen for 1 h at a pressure of 1 Pa.

3. Results and discussion

The atomic content ratio of Zn, Sn and In in the co-sputtered films was analysed by XPS and the Zn content ratio in the films was estimated as [Zn]/([Zn] + [In] + [Sn]). The Zn content ratio in the films varied from 0 for ITO to 67% for ZITO150 (Table 1). It increased almost linearly with the power given to the ZnO target as can be seen in Fig. 1. The Zn, In and Sn concentration ratio is presented in Table 1.

The initial analysis of the films with XRD showed the films were amorphous with a wide peak as shown in Fig. 2. Similar XRD spectra has been reported earlier for ZITO samples deposited by co-sputtering [21,22]. This could be easily understood on the fact that, during the low temperature sputter deposition (in this case no intentional heating was applied); species reached the unheated substrate and did not receive extra energy to enhance the formation of polycrystalline layers. Nevertheless, it can be seen a smooth peak corresponding to the substrate at 24.7° as well as another broad peak moving to higher angles as the Zn content ratio increased. In the case of ITO, the broad peak corresponds to 31.1° and shifts to 34.4° in case of ZITO150. These peaks can be interpreted as the (111) peak of In_2O_3 byxbyite structure referenced at 30.6° [23] changing gradually to ZnO (001) wurtzite peak referenced at 34.4° [24]. It suggested that some short range order could be present in the film structure. Due to the forehead mentioned reasons we cannot conclude that ZITO structure was purely amorphous, and hence we performed HRTEM on two samples.

Table 1
Sample identification with the rf power delivered to the targets and cation content in the films measured by XPS.

Sample	PITO (W)	PZnO (W)	In (%)	Zn(%)	Sn(%)
ITO	50	0	89.3	0	10.7
ZITO25	50	25	75.5	17.1	7.5
ZITO50	50	50	57.6	36.6	5.8
ZITO75	50	75	46.7	48.5	4.8
ZITO100	50	100	41.8	53.8	4.4
ZITO125	50	125	34.5	62.8	2.7
ZITO150	50	150	30.2	67.3	2.6

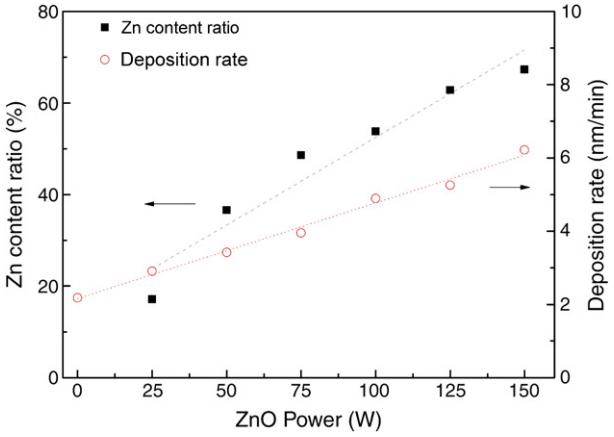

Fig. 1. Zn content ratio estimated from the XPS and the deposition rate for the ZITO samples deposited with different ZnO power. Lines are just a guide for eyes.

ZITO25 and ZITO100 which were deposited on the insulating Corning glass substrates were carefully analysed using HRTEM and the images obtained can be seen in Fig. 3. Column A shows the images corresponding to ZITO25 whereas column B shows the images corresponding to ZITO100. Three images for each sample are shown, the first one corresponds to the selected-area electron diffraction pattern, the second a cross-section view of the samples, and the last one is a HRTEM image taken at a magnification of 800,000, where crystallographic planes can be observed. In case of ZITO25, which corresponds to a zinc content ratio of 17%, diffraction pattern (Fig. 3.A1) shows identifiable peaks proving the polycrystalline nature of the sample. The brighter peaks correspond to In_2O_3 (211), ZnO (002), In_2O_3 (440) and In_2O_3 (622). Every peak can be associated to either In_2O_3 or ZnO, suggesting that no other ternary species are formed at room temperature. The fuzzy ring containing each peak, gives evidence of an amorphous matrix [25] within which the nanocrystals are embedded. In Fig. 3.A2, an amorphous initial growth layer of about 10 nm was observed followed by a 200 nm film. The thickness is in agreement with that measured using the profilometer. In the high resolution image (Fig. 3.A3) the atomic planes can be observed. We identified the inter atomic planar distance, $d_{(002)}$ of ZnO as 0.264 nm. However, ZITO100 shows a completely different selected-area electron diffraction pattern (Fig. 3.B1). In this case few faint peaks corresponding to In_2O_3 (440) can be seen, but the fuzzy rings show

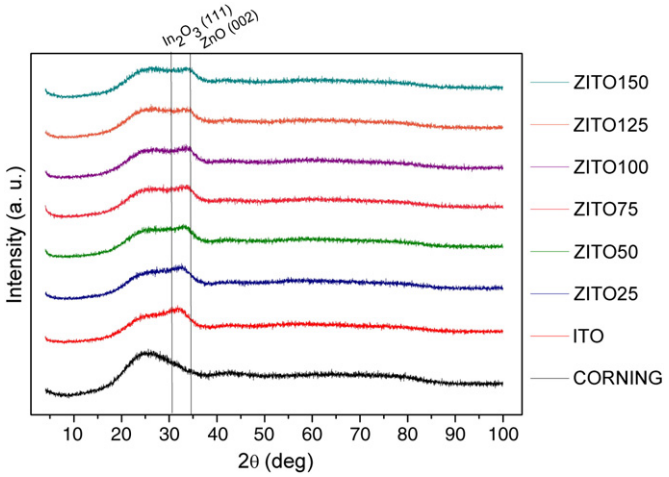

Fig. 2. The XRD spectra of the ZITO films deposited with different ZnO powers. Lines indicate In_2O_3 byxbyite (111) peak at 30.6° [23] and ZnO wurtzite (001) peak at 34.4° [24].