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Study of the Improved conductivity of Indium-tin Oxide Films Cosputtered with Zinc Oxide at Room Temperature from Thermal Degradations

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Abstract-- In this paper, the thermal stability of indium-tin oxide (ITO) and cosputtered indium-zinc oxide (IZO) films annealed under reducing gas, oxygen, and atmosphere ambient were investigated. The associated carrier concentration and crystalline structure evolutions were responsible for the thermal degradation mechanisms. By introducing the evidence investigated from the thermal degradations, an IZO film prepared at room temperature possessed low film resistivity was further concluded to be the oxygen atoms being captured by zinc atoms and resulted in a high carrier concentration originated from the formation of the oxygen vacancies in ITO domains.

1. Introduction

IZO films at atomic ratios [Zn / (Zn + In) at.%] raged from 20 to 50% has attracted considerable attention for its superior conductivity and surface uniformity to ITO films prepared at room temperature [1-2]. In our previous work, we had successfully prepared an IZO film with lowest film resistivity at an atomic ratio around 30% at room temperature using a novel rf magnetron cosputtering system with ITO and zinc oxide (ZnO) targets [3]. Although the lower resistivity of IZO films was attributed to the appearance of an amorphous-like $Zn_kIn_2O_{3+k}$ structure [4], the improved mechanism on the film resistivity was still demanded to further control the application reliability. Moreover, the investigation of the thermal stability was also a key issue for employing in the associated optoelectronic devices operated at elevated temperatures.

In this paper, ITO films and cosputtered IZO films at an atomic ratio of 32% were thermally annealed at various temperatures under reducing gas (95% Ar + 5% H_2), oxygen, and atmosphere ambient. The associated thermal degradations were determined by the evolutions of the electrical properties. In addition, the crystalline structure evolutions annealed under reducing ambient were also observed from X-ray diffraction (XRD) measurements. By means of the thermal stability investigations, the physical mechanism of an IZO film prepared at room temperature possessed superior film resistivity was thus comprehended.

2. Experimental procedure

Figure 1 shows the rf magnetron cosputtering system to deposit pure ITO films and IZO cosputtered films at an atomic ratio of 32% on sapphire substrates at room temperature. Detailed descriptions for this cosputtering technology were reported elsewhere [4]. Sequentially, these as-deposited samples were thermally annealed under reducing gas, oxygen, and atmosphere ambient at various temperatures for 30 min. The related electrical properties were measured by a Hall-effect system (HMS-3000). Crystalline structures were examined by a Siemens X-ray diffractometer (D-500).

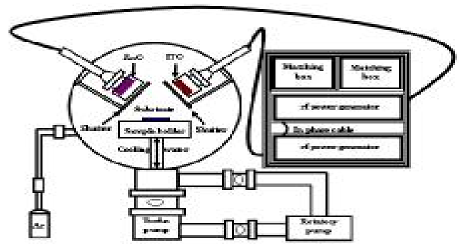

Fig. 1 Schematic of rf magnetron cosputtering system

3. Experimental results

The electrical characteristic of ITO and IZO films depend on the annealing temperatures under reducing gas is shown in Fig. 2. The low resistivity of the as-deposited IZO film was mainly due to the apparent increase in carrier concentration. At an annealing temperature of 300°C, an obvious decrease in film resistivity of ITO films originated from the higher carrier concentration was detected while that of IZO films only showed limited improvement. At an annealing temperature reaching 500°C, the film resistivity of ITO and IZO films was increased. The increased resistivity for an ITO film was originated from the marked decrease in Hall mobility while that of an IZO film was attributed to the loss of carrier concentration. The crystalline structure evolutions of ITO and IZO films annealed at various temperatures under reducing gas ambient are shown in Figs. 3(a) and 3(b). The as-deposited ITO film was poly-crystalline structure while that of IZO film was an amorphous one. XRD diffraction patterns of annealed ITO films were dominated by the poly-crystalline structure expect for the sample annealing at 700°C. Concerning about IZO films annealed at various temperatures, XRD diffraction patterns evolved from amorphous structures to poly-crystalline ones at an annealed temperature of 500°C. The poly-crystalline structures were identified as mixture of

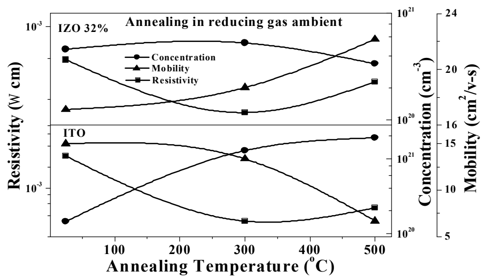

Fig. 2 Electrical properties as functions of annealing temperatures under reducing gas ambient.

ITO and $Zn_2In_2O_5$ structures. The metal-like In phase was predominated over XRD diffraction pattern of ITO and IZO films at an annealing temperature of 700°C and exhibited the insulating properties corresponded to the resistivity of 10^5 Ω cm. Since hydrogen atoms introduced from the annealing

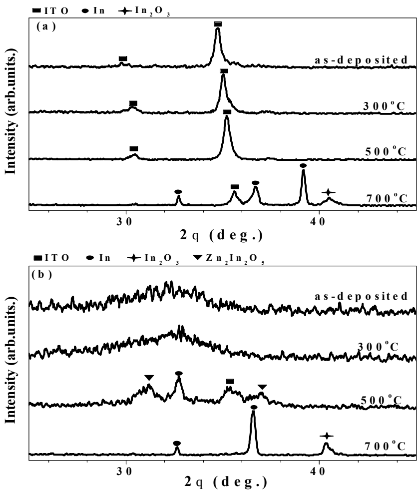

Fig. 3 Crystalline structure evolutions of (a) ITO and (b) IZO films annealed under reducing gas ambient.

gas were prone to react with oxygen atoms and sequentially formed the oxygen vacancies, the related carrier concentration was suggested to be markedly improved. However, the increase in carrier concentration of an IZO film annealed at 300°C was unapparent. This revealed that the chemical bond of Zn-O was more stable than that of In-O originated from the nature of its lower oxidation potential [5]. Moreover, in spite of a higher Hall mobility of an IZO film annealed at 500°C was measured due to the improvement of crystalline structure, the carrier concentration was decreased due to the substitution of In^{3+} sites by Zn^{2+} ions resulted from the appearance of $Zn_2In_2O_5$ structure. In addition, the appearance of the metal-like In phase at an annealing temperature of 700°C was attributed to the depletion of oxygen atoms in these films.

ITO and IZO films annealed at temperatures of 500 and 700°C under oxygen and atmosphere ambient were processed to provide an evidence of zinc atoms being prone to react with oxygen atoms. The electrical properties as functions of annealing temperatures under oxygen and atmosphere ambient are shown in Figs. (4) and (5). The carrier concentration evolutions of IZO films were markedly reduced while those of ITO films were nearly unchanged after annealing. This indicated that more oxygen atoms were

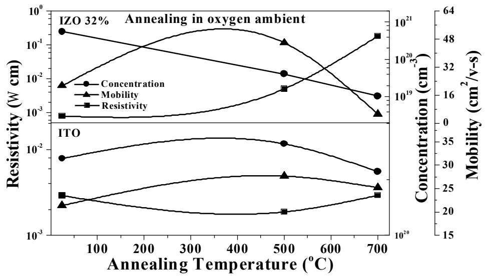

Fig. 4 Electrical properties as functions of annealing temperatures under oxygen ambient.

introduced in IZO films. As a result, the resistivity of IZO films was increased with annealing temperatures. Considering about IZO films thermally annealed under atmosphere ambient, the carrier concentration evolutions were more alleviative due to the less oxygen atoms than annealed under oxygen ambient. Incorporated with the thermal stability investigations, the oxidation of zinc atoms in IZO films annealed under oxygen and atmosphere ambient was responsible for the apparent reduction on the carrier concentration. In addition, since the formation of oxygen vacancy was a consequence of the increase in carrier concentration, the physical mechanism for the superior resistivity of an IZO film prepared at room temperature was attributed to the formation of oxygen vacancies in ITO domains resulted from the introduction of zinc atoms while cosputtered with a ZnO target.

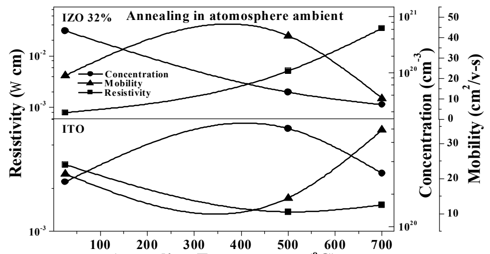

Fig. 5 Electrical properties as functions of annealing temperatures under oxygen ambient.

4. Conclusions

In this paper, the thermal degradation of indium-tin oxide (ITO) and cosputtered indium-zinc oxide (IZO) films annealed under reducing gas, oxygen, and atmosphere ambient were investigated. The thermal degradation mechanism for films annealed under reducing gas ambient was attributed to the exceeding formation of oxygen vacancies and resulted in the appearance of the metal-like In phase. The thermal degradation mechanism of IZO films annealed under oxygen and atmosphere ambient was concluded to be the oxygen atoms attracted by zinc atoms due to their low oxidation potential. As a result, the achievement of a lower resistivity from the amorphous IZO film prepared at room temperature was further clarified to be originated from the elimination of oxygen atoms in ITO domains by zinc atoms introduced from cosputtered ZnO target and resulted in the abundant oxygen vacancies.

Acknowledgments

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