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Material properties and growth control of undoped and Sn-doped In_2O_3 thin films prepared by using ion beam technologies

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Abstract

Undoped (IO) and Sn-doped In_2O_3 (ITO) films have been deposited on glass and polymer substrates by an advanced ion beam technologies including ion-assisted deposition (IAD), hybrid ion beam, ion beam sputter deposition (IBSD), and ion-assisted reaction (IAR). Physical and chemical properties of the oxide films and adhesion between films and substrates were improved significantly by these technologies. By using the IAD method, non-stoichiometry and microstructure of the films were controlled by changing assisted oxygen ion energy and arrival ratio of assisted oxygen ion to evaporated atoms. Relationships between structural and electrical properties in ITO films on glass substrates were intensively investigated by using the IBSD method with changing ion energy, reactive gas environment, and substrate temperature. Smooth-surface ITO films ($R_{rms} \leq 1$ nm and $R_{p-v} \leq 10$ nm) for organic light-emitting diodes were developed with a combination of deposition conditions with controlling microstructure of a seed layer on glass. IAR surface treatment enormously enhanced the adhesion of oxide films to polymer substrate. The different dependence of IO and ITO films' properties on the experimental parameters, such as ion energy and oxygen gas environment, will be intensively discussed.
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Keywords: Undoped In_2O_3; Sn-doped In_2O_3; Ion-assisted deposition; Ion beam sputter deposition; Ion-assisted reaction

1. Introduction

For at least a few decades, new and/or modified methods of thin film preparation have been introduced to control the properties of a film more precisely for improving the functionalities and making new applications. There are various methods, such as evaporation, chemical vapor deposition (CVD), dc or rf magnetron sputtering, pulsed laser deposition (PLD), spray pyrolysis, sol-gel synthesis, etc., for material preparations including film deposition and surface modification [1]. Of those techniques, ion beam technologies are highly advantageous and advanced due to their controllability. The ion beam techniques enable the precise control of material properties such as microstructure, non-stoichiometry, morphology, crystallinity, etc. [2].

The ion beam technologies are undergoing industrialization process with the development of new ion sources and vacuum technologies. The application of ion beam technologies for the preparation of oxide materials is highly attractive because during this process the activation energy for forming the film can be supplied to the growing film in a defined manner [3]. Various oxide films are used in industrial fields such as transparent electrodes for flat panel displays and solar cells, gas sensors, anti-reflection and anti-static coatings, IR reflecting coatings. In our groups, the growth and modification of In_2O_3 and Sn-doped In_2O_3 by using ion beam technology have been intensively studied since 1995. Ion-assisted deposition (IAD) and ion beam sputter deposition (IBSD) have been used for thin film growth on glass and polymer substrates. Low energy ion irradiation under reactive gas environments, called ion-assisted reaction (IAR), has been used for surface modification of polymer substrates. In this paper, we review the experimental results and discuss the relationship between microstructure and electrical properties of both IO and ITO films and interfacial properties with polymer substrates.

2. Details of experimental conditions and results

2.1. Control of material properties of undoped In2O3 films by IAD

In_2O_3 and ITO are well known as n-type degenerate semiconductors that exhibit the high electrical conductivity and high transmittance in the visible range simultaneously and

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thus are widely used as transparent electrode for flat panel displays [4]. Various fabrication methods have been reported for getting the high quality indium oxide films. Among them, the ion-assisted deposition (IAD) method is very advantageous because microstructure, crystallinity and chemical composition of determining the ultimate electrical and optical properties are easily controlled by the assisted ion energy and the arrival ratio of oxygen ion to metal atom [5].

We deposited the undoped In_2O_3 films by ion-assisted deposition using a cold hollow cathode-type ion source [6–8]. Pure O_2 gas (2 ml/min) was introduced into the ion source for producing oxygen ions and indium vapor was provided by thermal evaporation. The deposition rate of In vapor was fixed at 0.1 nm/s and the final film thickness was 200–300 nm. The current density and energy of the oxygen ions was varied from 7.8 to 19.1 μA/cm^2 and from 60 to 500 eV, respectively. The glass substrate was in situ heated at 200 °C by a halogen heater. Chemical composition of indium oxides was investigated by quantitative Auger electron spectroscopy (AES). The other details of the experimental conditions are given in previous reports [6,7]. The parameters related to the assisted ion beam for preparation of In_2O_3 films are listed in Table 1.

Fig. 1 shows the AES derivative spectra of the indium oxide films prepared at different assist ion energies. As shown in Fig. 1, The N_O/N_{In} ratio for all deposited films was lower than that of standard In_2O_3 powder, which meant that the films were non-stoichiometric. The N_O/N_{In} ratio of the conventionally evaporated In_2O_3 film was 1.30, whereas that of the films deposited by oxygen ion assist was changed between 1.37 and 1.45 with the ion energy. The ionized oxygen was more reactive to metal than non-ionized oxygen and then the larger N_O/N_{In} ratio of the films deposited by oxygen ion assist was caused by the enhanced reactivity of ionized oxygen to indium atoms. From the AES results, it seemed that the chemical composition did not depend on the assist ion energy.

Fig. 2 shows the SEM photographs of the evaporated In_2O_3 film and ion-assisted In_2O_3 films deposited at 60 and 500 eV as a function of the arrival ratio (γ). As shown in Fig. 2(a), the evaporated film ($\gamma=0$) has a grain structure which consists of granular and equi-axed crystallites. When the films were prepared with ion assist and a different structure between 60 eV and 500 eV is observed. In the case of 60 eV, the film show the change from grain to domain structure as the γ value is increased; however, the films formed with 500 eV assist ions still show the grain structure irrespective of the values. One

Table 1
Parameters of In_2O_3 films preparation by IAD

Sample label	Oxygen ion energy (eV)	Arrival ratio (γ)	Current density (μA/cm^2)	Average energy (eV/In atom)	N_O/N_{In} ratio
Evaporated film				<1.0	1.32
Ion-assisted films	60	0.13	7.8	4.0	1.43
		0.22	13.4	6.5	1.43
		0.31	19.1	9.0	1.45
	500	0.13	7.8	32.0	1.42
		0.22	13.4	55.0	1.42
		0.31	19.1	75.0	1.45

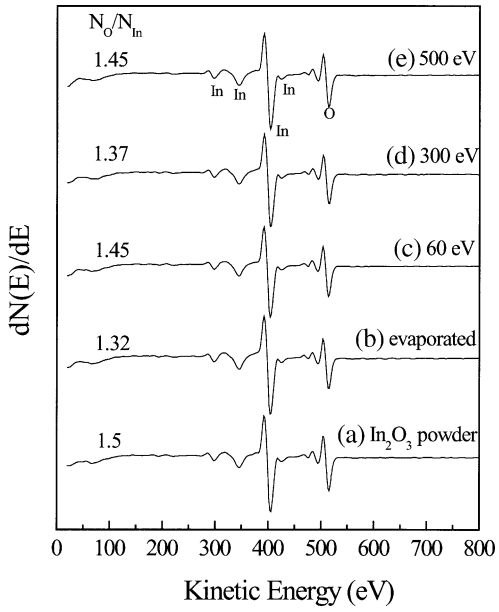

Fig. 1. Derivative Auger electron spectra for (a) pure In_2O_3 powder, (b) evaporated In_2O_3, and (c)–(e) as-deposited indium oxide films by using IAD at various average energies (arrival ratio $\gamma=0.31$).

domain consists of many sub-grains oriented into the same direction and the domain boundaries separate the sub-grains gathered in one direction [9]. The difference of microstructures in the In_2O_3 films fabricated at each ion energy is induced due to the energetic ion bombardment effect on the thin film formation. Under a low energy ion (<300 eV), the primary effect of the ion bombardment is to enhance ad-atom mobility, whereas the radiation damage to the growing film is a dominant effect at higher ion energies [6,7]. Kamei et al. [10] showed that the domain structure resulted from the anisotropic resputtering of the grains having the different crystalline orientations by the ion bombardment at 20–30 eV. Therefore, it can be said that the domain structure of the films deposited at 60 eV resulted from the enhanced ad-atom migration on the surface and the re-sputtering of grains at near surface by the low energy bombardment. However, in the case of 500 eV oxygen ion bombardment, the radiation damage is more effective than the enhancement of ad-atom mobility, and the defect sites act as nucleation sites to form the fine grain structure.

Fig. 3 shows the electrical properties of In_2O_3 measured by four point probe and Hall effect measurement. The electrical resistivity of the evaporated film is 8.9×10^{-4} Ω cm and with increasing γ, the electrical resistivity of the films deposited at 60 eV increases slightly from 5.1×10^{-4} to 8.8×10^{-4} Ω cm, whereas that of the films deposited at 500 eV increases abruptly from 2.6×10^{-3} to 7.3×10^{-2} Ω cm. Although the evaporated film has low resistivity, the film is not suitable as a transparent conductor because the film does not show the high transmittance in the visible range.

In undoped In_2O_3 films, because the free carriers are supplied by the oxygen vacancies [11], the carrier concentration is dependent on the non-stoichiometry of the films. However, as shown in Fig. 3(a), in spite of the same N_O/N_{In}

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