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Advanced ion beam technology for versatile oxide thin film formation

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Abstract

Various oxide films, such as SnO_2, In_2O_3, Al_2O_3, SiO_2, ZnO, and Sn-doped In_2O_3 (ITO) have been deposited on glass and polymer substrates by 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, crystallinity, and microstructure of the films were controlled by changing assisted oxygen ion energy and arrival ratio of assisted oxygen ion to evaporated atoms. IBSD method has been carried out for understanding the growth mode of the films on glass and polymer substrate. Relationships between microstructure and electrical properties in ITO films on polymer and glass substrates were intensively investigated by changing ion energy, reactive gas environment, substrate temperature, etc. Smooth-surface ITO films ($R_{rms} \leqslant 1$ nm and $R_{p-v} \leqslant 10$ 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. In the case of Al_2O_3 and SiO_2 films, the oxygen and moisture barrier properties were also improved by IAR surface treatment. The experimental results of the oxide films prepared by the ion beam technologies and its applications will be represented in detail.

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Keywords: Oxide films; Ion-assisted deposition; Ion beam sputter deposition; Ion-assisted reaction

1. Introduction

Various oxide films are used in industrial fields such as transparent electrodes for flat panel displays and solar cells, barrier coatings, gas sensors, anti-reflection and anti-static coatings, IR reflecting coatings. In our groups, the growth and modification of various oxide films such as SnO_2, In_2O_3, Sn-doped In_2O_3, ZnO, Al_2O_3, SiO_2, and TiO_2 by using ion beam technology have been intensively studied since 1992. During last decades, new and/or modified methods of thin film preparation have been introduced in literature [1] aimed on precise control of the film properties, improvement of the functionalities providing new applications. These methods are physical and chemical vapor deposition (PVD and CVD), dc or rf magnetron sputtering, pulsed laser deposition (PLD), spray pyrolysis, sol–gel synthesis, etc. The advantage of the utilized ion beam technologies is the possibility to control precisely the technological process and finally material properties such as microstructure, non-stoichiometry, morphology, crystallinity, etc. [2].

In this paper, we review the experimental results and discuss our research activities for improving material properties of oxide film and interfacial properties with polymer substrates by advanced ion beam technologies. Low energy

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ion irradiation under reactive gas environments, called ion-assisted reaction (IAR), has been used for surface modification of polymer substrates. Ion-assisted deposition (IAD) and ion beam sputter deposition (IBSD) have been used for thin film growth on glass and polymer substrates. 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 [1].

2. Details of research activities

2.1. Control of material properties of SnO_{2-x} and In_2O_3 films by IAD

The first research of our group was started from SnO_2 film growth using ion-assisted deposition [3–6]. The SnO_2 films have been widely used in various industrial fields such as opto-electronic devices, solar cells, anti-reflection coatings and gas sensors [7–9]. Among various deposition methods for SnO_2 film fabrication, the ion-assisted deposition is very effective because it can control non-stoichiometry and structural properties of the film precisely by changing of the average arrival ratio of oxygen gas ions to Sn metal particles and assisted ion energy [10]. Besides, ion-assisted deposition (IAD) enables to get high quality thin films by controlling nuclei at an initial stage of thin film growth [2].

The SnO_{2-x} films were deposited on SiO_2/Si or glass substrates at 300–500 °C by oxygen ion-assisted deposition. Sn metal was evaporated by using thermal evaporator and oxygen ions were generated by using a cold hollow cathode-type 5-cm-gridded ion gun. The oxygen ions were accelerated to the ion energy of 500 eV and the current density of the beam was changed from 3.5 to 17.5 μA/cm^2 by changing the discharge current. The arrival ratio of oxygen to tin was converted into an average impinging energy (E_a) which was changed from 25 to 100 eV/Sn atom.

The oxidation state and chemical shift between tin and its oxides were investigated by quantitative Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). The effect of average impinging energy on the microstructure of SnO_{2-x} films was observed by SEM. The details of experimental conditions were explained elsewhere [3–6].

We briefly summarize the results of AES and XPS analysis for tin oxide films deposited at various average impinging energies. As shown in Fig. 1a, the transition peak observed at 415.6 eV due to the bulk plasmon loss provides a useful indicator of pure tin metal [11]. The characteristic AES transition line of Sn $M_4N_{4,5}N_{4,5}$ for pure Sn was observed at 436 eV. The line shifted to lower kinetic energy by as much as 4 ± 1.0 eV for the film deposited at $E_a = 25$ eV/atom as shown in Fig. 1b. The AES line shifted further to lower kinetic energy by as much as 6 ± 1.0 eV from the films deposited at $E_a = 50$ eV/atom (Fig. 1c) to stoichiometric tin oxide powder (Fig. 1f). The atomic ratio

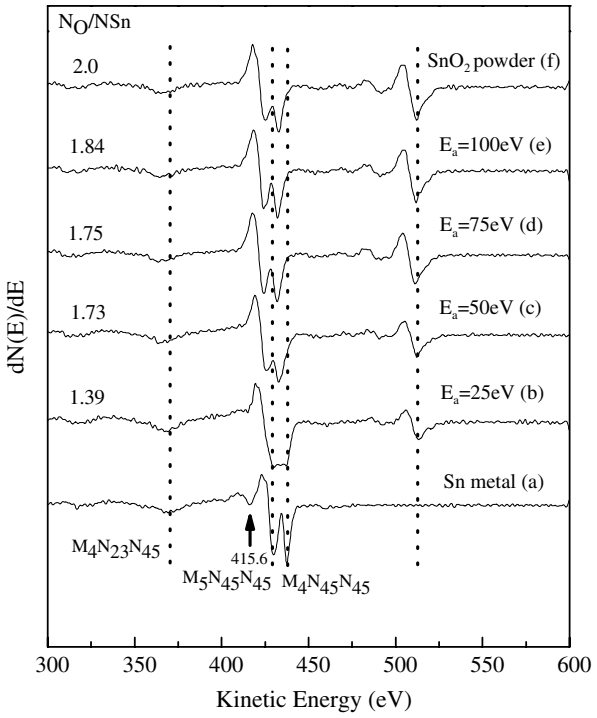

Fig. 1. Derivative Auger electron spectra for (a) pure tin metal, (b)–(e) as-deposited tin oxide films by IAD at various average energies, and (f) pure SnO_2 powder.

(N_O/N_{Sn}) of SnO_{2-x} films were determined from the ratio of peak-to-peak heights of Sn $M_4N_{4,5}N_{4,5}$ and O $KL_{2,3}L_{2,3}$ in AES spectra. The N_O/N_{Sn} increased from 1.39 to 1.84 as E_a increased from 25 to 100 eV/atom.

Fig. 2 shows the Sn 3d core-level XPS spectra of SnO_{2-x} thin films and stoichiometric tin oxide powder. The spectrum represents the Sn 3d spectrum corresponding to a tin oxide film that contains both Sn metal and SnO phase. The binding energy of Sn $3d_{5/2}$ increases by 1.74 ± 0.02 eV and 2.23 ± 0.02 eV in the films deposited at $E_a = 25$ eV/atom and 100 eV/atom, respectively. The shift of 2.29 ± 0.02 eV occurred in tin dioxide powder. The chemical shift of the tin $M_4N_{4,5}N_{4,5}$ in AES and Sn $3d_{5/2}$ peak in XPS for the tin oxide films and the standard tin dioxide powder are observed apparently in Figs. 1 and 2. From AES and XPS analysis, the chemical state and stoichiometry of SnO_{2-x} films approach those of the standard tin dioxide powder with increasing of the average impinging energy, i.e., the relative arrival ratio of oxygen to tin.

The changes in microstructure of the SnO_{2-x} films with the E_a values correspond to those in chemical state and composition of the films. Fig. 3 shows the SEM micrograph of tin oxide films deposited at various E_a values. It is seen that the film deposited at $E_a = 25$ eV shows oxygen deficient Sn-metallic phase but the films at $E_a = 100$ eV have the typical grain shapes of SnO_2 phase.

In summary, the non-stoichiometry and microstructure of SnO_{2-x} films were effectively controlled by changing the average impinging energy of assisted oxygen ion to Sn atom.