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Crystallization and Electrical Properties of Doped and Undoped Indium Oxide Films

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The crystallization process and the electrical properties of amorphous tin-doped indium oxide (ITO) films have been studied in contrast with those of undoped indium oxide (IO) films. Amorphous ITO and IO films were prepared by magnetron sputtering succeeded by annealing in the air at various temperatures. ITO films showed higher crystallization temperature compared with that of IO films, suggesting an excess free energy caused by the repulsion between the active donors (Sn^{4+}). The analysis of the electrical properties alternated with the phased annealing of films provided essential information for understanding the conduction mechanisms of ITO. It was also revealed that the amorphous IO/ITO films showed oxidation around 100°C in contrast with crystalline IO/ITO films with the oxidation temperature above 200°C.

Key words: Indium oxide films, Doping of tin, Electrical properties

I. Introduction

Tin doped indium oxide (ITO) is a highly degenerate wide-gap semiconductor that is extensively used in flat panel displays as transparent electrodes in thin film form. Recent high-quality low energy-consumptive flat panel displays require ITO films to be as conductive as possible and a lot of efforts for growing ITO films with even lower resistivity have been done.[1-4)] It is also required that the substrate temperature during deposition of ITO should be lower than 200°C in order to prevent the degradation of color-filters of flat panel displays. However, it is hard to cope with both low temperature deposition and low resisitivity of ITO films since the crystallization temperature of ITO is around 180°C. Shigesato et al.[5,6)] revealed that tin (Sn) was no longer an active dopant in amorphous ITO films deposited by ion-plating and the free electrons were liberated from oxygen vacancies. However, the systematic study of room temperature deposited ITO films and the optimum annealing conditions below 200°C for lower resistivity have not yet been elucidated. In this study, therefore, detailed examination of annealing temperature dependence of structural and electrical properties of both indium oxide (IO) and ITO films were performed. The aim of this study is to understand the mechanisms of crystal growth and electrical conduction of low temperature deposited IO/ITO films and to establish crystal growth process for low resistivity films.

II. Experimental

IO and ITO films were deposited by DC and RF magnetron sputtering system. The starting material for IO and ITO films were sintered oxide pellets of In_2O_3 and In_2O_3 (10 wt%SnO_2), respectively. Soda-lime glass was used as a substrate and the substrate was not initially heated. Argon gas was used as a sputtering gas and the crystal structure of as-deposited IO/ITO films were controlled by changing target-substrate distance (T-S) and the total pressure during growth (Ptot). As deposited IO/ITO films showed amorphous structure (asdep-a) when T-S distance and Ptot during growth were kept at relatively large value, while lower T-S and Ptot led to crystalline structure of IO/ITO films (asdep-c).[7)] Further ex-situ annealing of IO/ITO films was performed in the air by an electric furnace. The crystal structure of IO/ITO films were investigated by x-ray diffraction (XRD) and the electrical properties of IO/ITO films were investigated by Fan-der-Pauw method combined with Hall effect measurements at room temperature.

III. Results and Discussion

Fig. 1 shows the transition of the XRD patterns of an asdep-a IO film with increasing annealing temperature. A clear (222) diffraction peak of In_2O_3 was observed above the annealing temperature of 160°C, and the crystallization temperature of the asdep-a IO film was determined to be between 150 and 160°C. However, asdep-a ITO films showed crystallization temperature between 180 and 190°C, which is higher than that of IO films by 30°C (Fig. 1(b)). The substitutional Sn for In, which is an active donor in ITO, is positively charged in In_2O_3 host material.[8)] As a result, the active donors (substitutional Sn) were repulsive each other

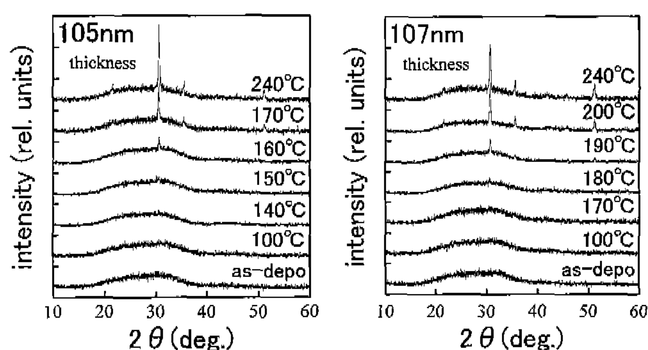

Fig. 1. XRD patterns of asdep-a IO (a) ITO and (b) films annealed at various temperatures.

and the lattice constant increases with increasing Sn content.[9] This means that the doping of Sn need excess energy against this repulsion between the active donors. This is why ITO films showed crystallization temperature higher than that of IO films.

The annealing temperature dependence of resistivity, carrier density and carrier mobility of IO and ITO films are shown in Fig. 2 and 3, respectively. Asdep-a IO/ITO films are shown by the solid markers and the asdep-c IO/ITO films are shown by the open markers, respectively in Figs. 2 and 3. As-deposited IO and ITO films showed no remarkable difference in carrier density, suggesting that the carrier generation in amorphous IO/ITO films were dominated by the oxygen vacancies instead of substitutional Sn atoms in the case of crystalline ITO films.[5] It is worth noticing that the asdep-a IO films and asdep-c IO films showed different behavior, which is conspicuous in the annealing temperature dependence of carrier density (Fig. 2(b)). The asdep-a IO films showed clear drop in carrier density above the annealing temperarure of 100°C. However, the asdep-c IO films showed a clear drop in carrier density above 200°C. According to the above discussion on active donors, these data suggest that the oxygen vacancies are extinguished by

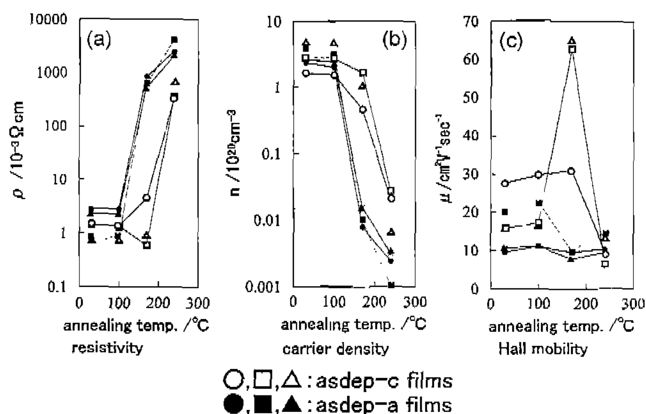

Fig. 2. The annealing temperature dependence of resistivity, carrier density and carrier mobility of IO. Asdep-a IO films are shown by the solid markers and the asdep-c IO films are shown by the open markers, respectively.

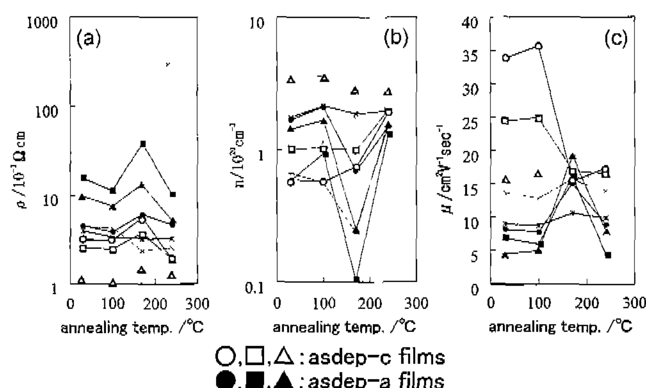

Fig. 3. The annealing temperature dependence of resistivity, carrier density and carrier mobility of ITO. Asdep-a ITO films are shown by the solid markers and the asdep-c ITO films are shown by the open markers, respectively.

the oxidation of films during annealing in air. One important result here is that the asdep-a IO films are easy to be oxidized at lower annealing temperature compared with asdep-c IO films. The electrical properties of asdep-a IO films are more sensitive to annealing conditions compared with that of asdep-c IO films.

In the case of ITO films, asdep-a ITO films showed a clear decrease in carrier density at 180°C and it increased again above 200°C. This drop of carrier density also attributed to the oxidation of asdep-a IO/ITO films above 100°C. The increase of carrier density above 200°C reflect the increase of substitutional Sn, which act as active donor for free electron. However, the asdep-c ITO films showed no clear drop in carrier density. The carrier mobility of asdep-a ITO films showed clear peaks at 180°C(Fig. 3(c)). The increase of carrier mobility from 100°C to 180°C is attributed to the decrease in the ionized impurity scattering center based on oxygen vacancies. The drop of carrier mobility above 180°C is due to the increase in the neutral impurity scattering centers consisted of substitutional Sn combined with interstitial oxygen.[8] The asdep-c ITO films showed monotonous decrease in carrier mobility, which is also attributed to the neutral scattering centers discussed above.

IV. Conclusion

Asdep-a ITO films showed crystallization temperature higher than that of IO films by 30°C. This is due to the substitutional Sn atoms, which are positively charged active donors in In_2O_3 host material, were repulsive each other and the doping of Sn need excess energy against this repulsion between the active donors. It was also revealed that the asdep-a IO/ITO films showed oxidation around 100°C in contrast with asdep-c IO/ITO films with the oxidation temperature above 200°C. The behavior of the electrical properties of asdep-a/-c IO/ITO films were elucidated on the basis of ionized impurity scattering caused by the oxygen vacancies and the neutral impurity scattering caused by the sub-

stitutional Sn combined with interstitial oxygen.

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