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Characterization of ITO films prepared by electron shower method using ESCA

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The electrical resistivity of ITO films prepared by electron shower was $2x10^{-4}$ Ωcm at $2x10^{-4}$ Torr, but became $3x10^{-3}$ Ωcm after two months. It was due to decreasing oxygen deficiency. It was found that the amount of Sn donor was proportional to that of SnO, and that the ratio of the oxygen deficiency for donor to Sn donor was decided by using ESCA.

1. INTRODUCTION

Indium tin oxide (ITO), Sn-doped In_2O_3, films are transparent conducting films and are of use for transparent electrodes and solar cells. Most ITO films have been prepared by EB (electron beam) or by a sputtering method. The substrates are not only glass but also plastic for decreasing weight, for which the substrate temperature must be below 200 °C. In general, the conductivity and the adhesion of the films, however, decrease with decreasing substrate temperature.

Electron shower method is a new PVD method, and we have succeeded in fabricating a Cu film with high adhesion on a plastic film at about 200 °C, using this method [1]. When Cu thin films were coated on stainless steel by this method, the films did not delaminate before failure of the epoxy resin bond with a jig [2]. We estimated that the adhesion of the films was at least 400 times higher than that of films fabricated with conventional thermal vapor deposition. This was due to a change in the adhesion mechanism from physical adsorption to chemical adsorption; the Cu atoms formed oxides such as CuO and Cu_2O at the interface with oxygen on the surface of the stainless steel substrate.

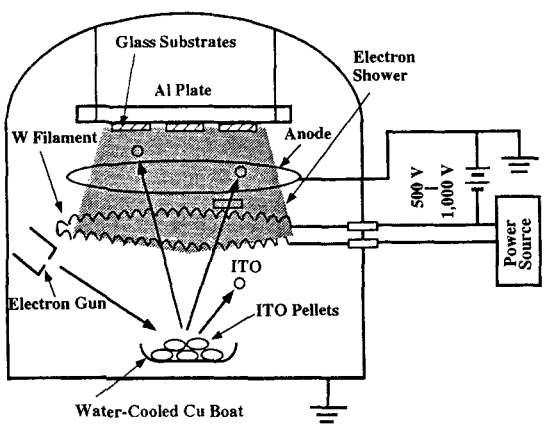

Figure 1. Schematic drawing of the electron shower apparatus.

When we fabricated ITO films using the electron shower without oxygen gas in a vacuum chamber, the resistivity of the film was $4x10^{-4}$ Ωcm, which was one order of magnitude smaller than that fabricated only with EB (electron beam). The cause of the decreasing resistivity was the increasing crystallization of the oxygen deficient ITO film. We use oxygen gas in this study and one of purposes of this study is to investigate the effect of oxygen gas on the ITO films fabricated with the electron shower.

In general, the resistivity of ITO is determined by the mobility of electrons and the carrier density which is decided by the amount of oxygen deficiency for donor and that of Sn for donor. Since these energy

levels of the donors are almost the same, it is difficult to decide the amounts of them. The other purpose of this study is to separate the amount of the oxygen deficiency from that of Sn donor by using ESCA.

2. EXPERIMENTAL

Fig. 1 shows a schematic drawing of the electron shower apparatus. The thermal electrons are emitted from a heated tungsten filament, and a potential of 500-1000 V is applied between the filament and a ring-shaped anode, so that the thermal electrons are accelerated toward the substrates and constitute an electron shower. The total current of the electron shower is 0.2 A. The substrates are white slide glass (soda glass) plates of 5x10x1 mm, of which temperature is 200 ^{o}C. After this bombardment of electron shower for 60 s to activate the substrates, ITO pellets, consisted of sintered In_2O_3 with 5 wt% SnO_2 are heated to evaporate ITO molecules by EB. The voltage and the current of EB are 5 kV and 0.1 A, respectively. The base pressure in the chamber is below $6x10^{-6}$ Torr and the pressure of oxygen is changed between 0 and $3x10^{-4}$ Torr. The film thickness is 0.15 μm and the growth rate of the film is 0.015 μm/min.

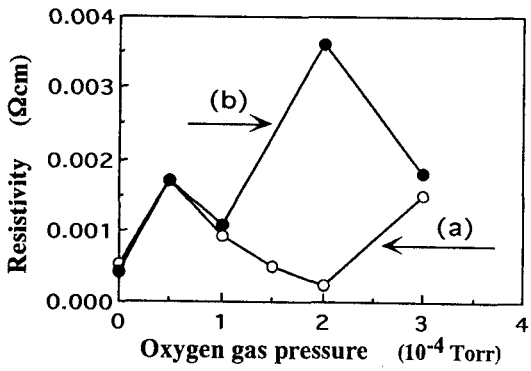

Figure 2. Relationship between oxygen gas pressure and the resistivity of the ITO films: (a) measured after a few days and (b) after 2 months.

3. RESULTS AND DISCUSSION

3.1. Resistivity

Fig. 2 shows the relationships between the resistivity of the ITO films and the oxygen gas pressure; the resistivities of (a) and (b) were measured after a few days and after two months, respectively. The graph (a) shows that the resistivity increased once and decreased with increasing oxygen gas pressure. It had a minimum ($2x10^{-4}$ Ωcm) at $2x10^{-4}$ Torr. The lowest value was $1x10^{-5}$ Ωcm at $2x10^{-4}$ Torr, but it was not reproducible. The graph (b) shows that the resistivity of the films fabricated at $2x10^{-4}$ Torr was changed from $1x10^{-5}$- $2x10^{-4}$ Ωcm to 10^{-3} Ωcm by leaving the films in air for two months. Therefore, these samples cannot be treated with the other samples.

The transmission of the films prepared without oxygen gas was 60-80 %, but was increased to above 90 % by using oxygen gas (above $1x10^{-4}$ Torr).

3.2. ESCA

Fig. 3 shows the spectra of oxygen (O 1^{S}) of the ITO films prepared by changing oxygen gas pressure, which were measured by ESCA. Fan and Goodenough [4] reported that there were two oxygen peaks: 530.0 and 531.6 eV. The first peak corresponded to O^{2-} ions whose neighboring In atoms had a full complement of six nearest neighbor O^{2-} ions, which was denoted by $O_{no\text{-}def}$ in fig.3. The second peak corresponded to O^{2-} ions in oxygen deficient regions, which was denoted by O_{def}. We can see that the peak height of $O_{no\text{-}def}$ increased with increasing oxygen gas pressure, but the amount of O_{def} for donor was decreased with it. The O_{def} peak was extremely high at $2x10^{-4}$ Torr, but became low with leaving it in air. Therefore,

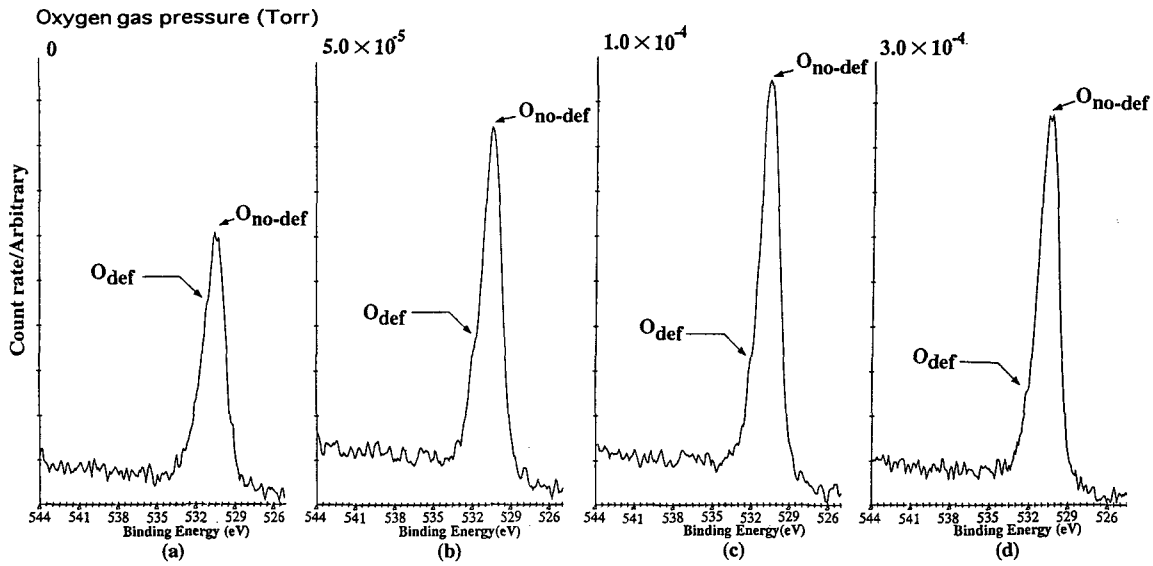

Figure 3. The effect of oxygen gas pressure on O 1^s ESCA spectrum of ITO films: (a) 0, (b) $5x10^{-5}$ (c)$1.0x10^{-4}$ and (d)$3.0x10^{-4}$ Torr.

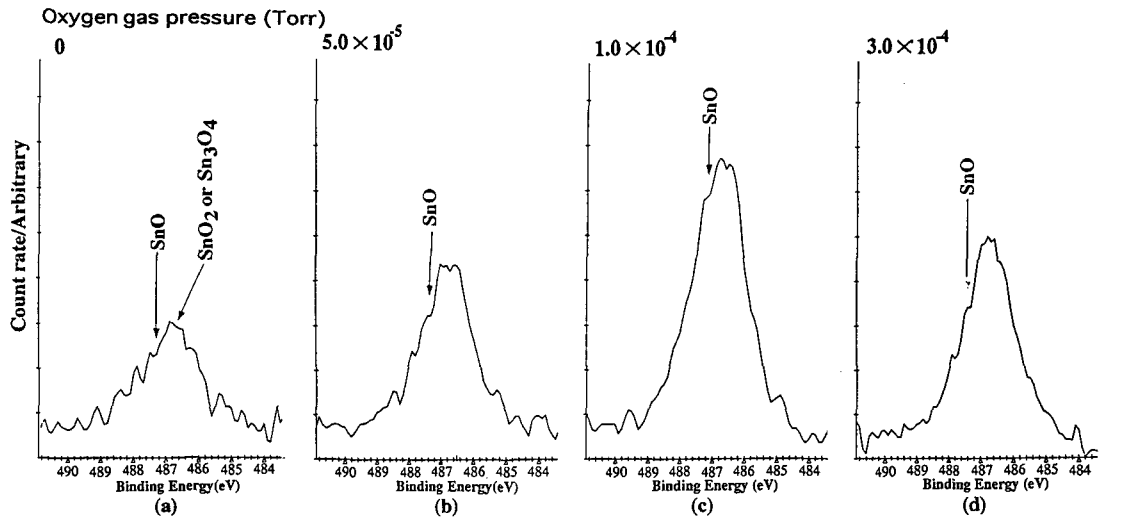

Figure. 4. The effect of oxygen gas pressure on Sn $3d^{3/2}$ ESCA spectrum of ITO films: (a) 0, (b) $5x10^{-5}$ (c)$1.0x10^{-4}$ and (d)$3.0x10^{-4}$ Torr.

the changing in resistivity to 10^{-3} Ωcm with time is due to the decreasing oxygen deficiency.

Fig. 4 shows the spectra of Sn $3d^{3/2}$ of the ITO films of fig. 3. The binding energies of metallic Sn, Sn_3O_4, SnO_2, and SnO were 484.9, 486.6, 486.7 and 487.2 eV, respectively [4]. Therefore, the peak of the spectra corresponded to Sn_3O_4 or SnO_2. Since the oxidation was enhanced in oxygen atmosphere, Sn changed from metallic Sn

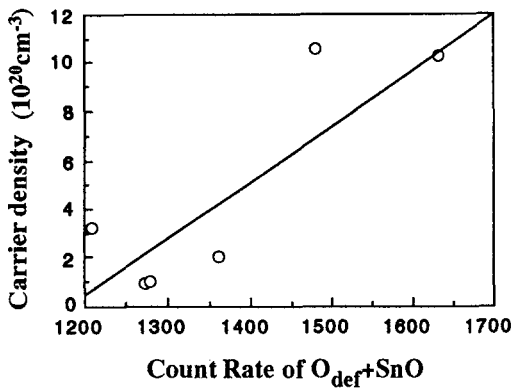

Figure. 5. Relationship between the resistivity and the sum of the count rates of O_{def} and SnO.

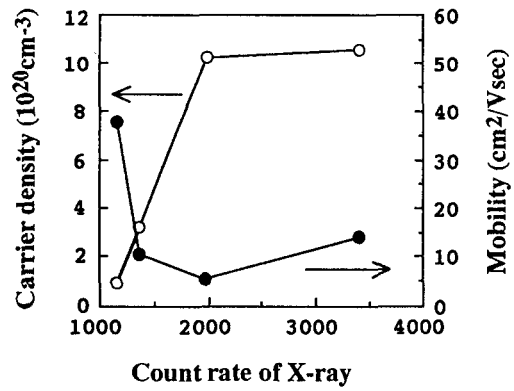

Figure. 6. The effects of (222) X-ray peak height on the carrier density and the mobility.

through SnO to SnO_2 with increasing oxygen gas pressure [5] Hence, it seemed the film contained a lot of Sn_3O_4 at no oxygen gas pressure, but a large amount of SnO_2 was contained at $3x10^{-4}$ Torr. The amount of SnO had a maximum at $1x10^{-4}$ Torr.

Fig. 5 shows the relationship between the count rate and carrier density; the horizontal axis is the sum of the count rates of O_{def} and SnO. All experimental data points obtained are approximately on a straight line. Since O_{def} is in proportion to the carrier density due to the oxygen deficiency, the carrier density due to Sn donor must be also proportional to the amount of SnO. It is found that we are able to obtain the ratio of oxygen deficiency to that of Sn donor. Mainly the amount of O_{def} decided the carrier density at no oxygen gas, and the amount of Sn donor (or SnO) decided it at $1x10^{-4}$ Torr.

Fig. 6 shows the effects of (222) X-ray peak height on the mobility and carrier density. In the case of the electron shower, the main peak was (222). The mobility decreased with increasing peak height, but the carrier density increased with it. In general, electron mobility of the ITO films prepared by a sputtering method increases with increasing crystallization, but the carrier density decreases with it. The behaviors of the carrier density and the mobility were reversed between the electron shower and the sputtering method. Since the X-ray peak height increases with increasing grain size, it is speculated that the ITO films prepared by the electron shower included more defects such as oxygen deficiency in a grain than that prepared by the sputtering method.

ACKNOWLEDGEMENT

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