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# Doping efficiency of oxygen vacancy for ITO and InO thin films

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The effect of oxygen vacancy on carrier density for indium tin oxide (ITO) and Indium oxide (InO) films has been investigated. Hot-cathode Penning discharge sputtering (HC-PDS) in the mixed gasses of argon and oxygen was applied to fabricate the ITO and InO films. Density of oxygen vacancy was estimated using a high-energy ion beam technique. The electrical properties of the films such as resistivity, carrier density and mobility were estimated by Van der Pauw method. Doping efficiency of oxygen vacancy could be obtained from the relationship between oxygen vacancy and carrier density. The doping efficiency of ITO films resulted in a quite small value. Comparing the doping efficiencies of ITO and InO films, effect of tin donor on carrier density was also discussed.

## 1 Introduction

Indium tin oxide (ITO) films exhibit high transmittance in the visible region and high electrical conductivity [1]. Due to these properties, ITO films have been widely used in optoelectronic applications, e.g. transparent electrodes of flat panel displays. With the recent considerable increase in technological demands for flat panel displays, ITO films with excellent quality have become necessary to accommodate these demands.

ITO films have been fabricated by various methods, for example, spray pyrolysis (SP), electron beam evaporation (EB), chemical vapor deposition (CVD) and magnetron sputtering (MS). We have used hot-cathode Penning-discharge sputtering (HC-PDS), to fabricate ITO films [2]. This method has several independent parameters for production of films. So we can easily change the oxygen concentration in the film. Using this method, we are investigating the effect of oxygen or other metallic compositions on film quality.

There are two kinds of source of carrier production for ITO film. One is Sn donor, the other is oxygen vacancy donor. To fabricate excellent films, control of carrier production is a key technique. Therefore the estimation and consideration of doping efficiency are important. There have been few studies on doping efficiency of Sn or oxygen vacancy, except some earlier reports [3,4]. We have already indicated that the resonant RBS was useful technique to estimate oxygen content in ITO films [5,6]. Using the resonant RBS, density of oxygen vacancy was estimated nondestructively. As a result, the doping efficiency of oxygen vacancy was estimated.

In this paper, we estimate doping efficiency of oxygen vacancy of ITO films and InO films, firstly. Comparing the carrier density of ITO films with that of InO films on the same condition of oxygen concentration, the doping efficiency of Sn donor were also estimated.

## 2 Experimental

Hot-cathode Penning-discharge sputtering (HC-PDS) was applied to fabricate ITO and InO films. The sputtering conditions during HC-PDS deposition is shown in Table 1. As seen in Table 1, a $In_2O_3$ target which contain $5wt\%$ $SnO_2$ was used to fabricate ITO films and a pure $In_2O_3$

Table 1. Sputtering conditions of HC-PDS method.

| | |
|---|---|
| Target | $In_2O_3$–$SnO_2$ ($SnO_2$: 5wt%)<br>$In_2O_3$ |
| Substrate | Corning7059 |
| Base Pressure | $5\times10^{-6}$ Torr |
| Ar+$O_2$ Pressure | $5\times10^{-4}$ Torr |
| $O_2$ Pressure | $5\times10^{-6}$~1, $0\times10^{-4}$ Torr |
| Target Voltage (Vt) | −100V |
| Target Current (It) | 30mA |
| Anode Voltage (Va) | 50V |
| Anode Current (Ia) | 0. 6A |
| Substrate Temperature (Ts) | 300℃ |
| Thickness | 1000Å |

target was used to fabricate InO films. Only the oxygen partial pressure of the sputtering parameters was varied in order to obtain the films with different oxygen contents.

The oxygen content of as-deposited ITO and InO films was investigated by means of $^{16}O(\alpha,\alpha)^{16}O$ resonant backscattering of a 3.045 $MeV$ $^4He^{2+}$ ion beam [7]. Resonant RBS is a rapid, quantitative and depth-sensitive technique which has been applied for compositional analysis of oxide films [8-10].

The electrical properties of resistivity, carrier density, and Hall mobility were measured by the van der Pauw method [11].

# 3 Results and Discussion

Comparing XRD patterns of ITO with InO films, Sn atoms cause no effect on crystallinity, suggesting that most of Sn atoms occupy In atom sites for $In_2O_3$ bixbyite structure substitutionally. Then when Sn atoms are electrically active, it is expected that one Sn atom produces one free electron. From this point of view, we estimate the doping efficiency of Sn. From the comparison of electrical properties, both films had nearly equal electron mobilities for different oxygen concentrations.

Figure 1 shows the relationship between carrier density and oxygen concentration for ITO films. The doping efficiency of the oxygen vacancy was estimated from the slope of the least squares fit to the experiment. The obtained doping efficiency was 0.089. It was found that doping efficiency of the oxygen vacancy for ITO film was quite low.

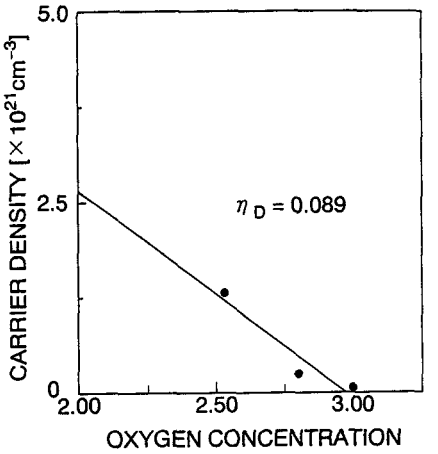


Figure 1. Carrier density of ITO films as a function of oxygen concentration estimated when In concentration is defined as 2.0. The solid line is a least-squares fit to the experiment.

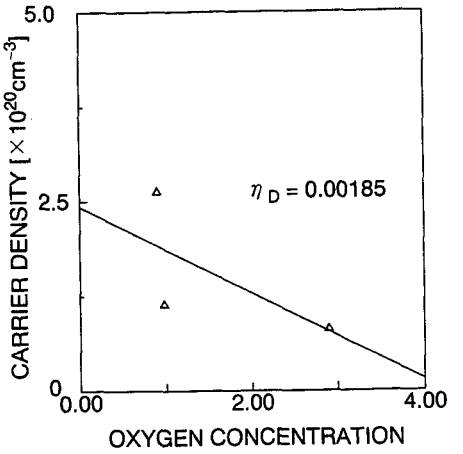


Figure 2. Carrier density of InO films as a function of oxygen concentration.

Figure 2 shows the relationship between carrier density and oxygen concentration for InO films. The doping efficiency of the oxygen vacancy was estimated in the same way as ITO films. The obtained doping efficiency was 0.00185. It was found that doping efficiency of the oxygen vacancy for InO film was extremely lower than that for ITO. This might be due to low carrier density, resulting in the small change of carrier density against the oxygen content. Bellingham et al. reported the doping efficiency of oxygen vacancy for InO films was quite low, about 0.1 [12]. Also in our previous report the doping efficiency of oxygen vacancy for post-annealed ITO films indicated quite low [13]. From these results, mechanism of doping of oxygen vacancy was not so simple. And also it is not yet clear the reason of extremely lower efficiency of InO compared with ITO.

Next, the doping efficiency of Sn was estimated. From a result of electron probe micro analysis (EPMA), tin content in the films are the same as that in the target. Then it is possible to estimate the number of Sn atoms in the film. On the assumption that all Sn atoms in the films were electrically active, the carrier density from Sn donor was obtained as a difference in carrier density between ITO and InO films of same oxygen content which were estimated by resonant RBS. Table 2 shows the doping efficiencies of Sn for the films with different oxygen contents. As the oxygen content in the films decreased, the doping efficiency of Sn increased. According to Köstlin et al. and Manifacier et al., each Sn atom donates one electron for ITO films with doping concentration of 0 to 4 at% tin for indium. However this model is not recognized for ITO films with more tin concentration [3,4]. Our result suggests that the Sn doping efficiency is subject to change for oxygen content in the film, and every Sn atom which occupies In site does not always produce one electron.

# 4 Conclusions

We have investigated the relationship between the oxygen content and electrical properties of ITO and InO films. Doping efficiencies of oxygen vacancies of ITO and InO film were estimated. It was found that both doping efficiencies were quite low and there was large difference between ITO and InO films. The reason of difference is not yet clear. From the results of XRD pattern and electrical properties of ITO and InO films, Sn atoms in the InO film caused no effect on crystallinity and mobility, suggesting that most of Sn atoms occupy In atom sites for $In_2O_3$ bixbyite structure. Also doping efficiency of Sn donor of ITO film was estimated. From the result, it was found that the model that each Sn atom donate one electron is not complete. And the doping efficiency of Sn donor depended on oxygen content in ITO film.

Table 2. Estimation of doping efficiency of Tin.

| oygen content x* | 2.5 | 2.75 | 3.00 |
|---|---|---|---|
| carrier density of ITO n(ITO) [/cm3] | $1.29\times10^{21}$ | $6.13\times10^{20}$ | $7.00\times10^{19}$ |
| carrier density of InO n(InO) [/cm3] | $1.00\times10^{20}$ | $8.64\times10^{19}$ | $7.00\times10^{19}$ |
| $\Delta n$ = n(ITO)-n(InO) [/cm3] | $1.19\times10^{21}$ | $5.27\times10^{20}$ | 0 |
| doping efficiency of Sn $\eta$ (Sn) | 0.839 | 0.371 | 0 |

* In composition is defined as 2.0.


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