Journal of Korean Institute of surface Engineering
Vol. 29, No. 6, Dec., 1996

OPTICAL PROPERTIES OF INDIUM OXIDE AND INDIUM TIN OXIDE FILMS PREPARED BY SPUTTERING

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ABSTRACT

Thin films of indium oxide and indium tin oxide have been prepared by d.c. magnetron sputtering onto the fused silica substrates kept at 90, 200 and 300℃. In order to elucidate the optical absorption process in low energy region below 3 eV, we have analyzed the absorption coefficients obtained from reflectance and transmittance measurements for these films based on the Lucovsky model. It has been found for the first time that a defect center in the band gap is located at 0.8~1.4 eV below the Fermi level in all films and arises from oxygen vacancies in their films. The optical absorption in low energy region is explained to be dominated by the transition of electrons trapped at the positively charged (+2e) oxygen vacancies with s-like nature to the conduction band formed from the 5s-orbit in indium atoms.

INTRODUCTION

Optical properties on thin films of indium oxide (IO) and indium tin oxide (ITO) have been studied for optoelectronic applications such as transparent electrodes for solar cell and flat panel displays[1]. In this connection, the development of ITO with high transmissivity and low resistivity is recently needed in order to satisfy commercial demands for large area flat panel diplays in full color with higher switching speeds[2].

However, it is unsatisfied for this purpose, because the general understanding is not yet established for optical and electrical properties of ITO[2]. In particular, the optical absorption in low energy region below about 3 eV, which plays an important role for the optical properties at a long wavelength, has not been studied for the ITO films.

The purpose of the present study is to elucidated the optical absorption in low energy region below 3 eV for these films by an analysis of optical absorption coefficients obtained from reflectance and transmittance measurements based on the Lucovsky model[3]. All the films have been deposited by d.c. magnetron sputtering under the well controlled conditions, e.g., an oxygen partial pressure, substrate temperatures and tin contents in the target.

Experimental method

Thin films of IO and ITO have been prepared by d.c. magnetron sputtering onto the fused silica substrates kept at 90, 200 and 300℃. The sputtering target, 12.7㎝ in diameter, was a hot-pressed target of pure In_2O_3 and SnO_2 (5 and 10wt.%) doped In_2O_3, respectively. The sputtering gas was the mixture of Ar (60 sccm) and O_2 (0~2 sccm) at 0.8 Pa. The deposition rate of these films was about 10Å/s at d.c. power of 1 W㎠ and then the thickness of deposited films was 100~400 nm. All the films were confirmed to have the ordinary polycrystalline structure compared with a standard cubic In_2O_3 (ASTM Card 6-0416) from X-ray diffraction measurements[1].

The reflectance and transmittance of the IO and ITO films have been measured at 300 K in the wavelength range 200~800 nm using a spectrometer (Hitachi Co. U3400). From these measurements, the optical absorption coefficient α as a function of photon energy $h\nu$ has been determined in order to investigate the optical absorption process in low energy region below 3 eV for IO and ITO specimens.

Data analysis on optical absorption coefficient

In order to elucidate the optical absorption process in low energy region below 3 eV for the IO and ITO films, we have analyzed the optical absorption coefficient α obtained from the reflectance and transmittance measurements on the basis of the Lucovsky model[3]. This model has been successfully used for the studies on the optical absorption in crystal silicon doped with indium acceptor and on a hole trapped level (A center) and dangling bond D^- states in hydrogenated amorphous silicon[3,4], and is presented by

$$\sigma OPT^{\infty} (hv-Et)^{3/2}/(hv)^3 \quad (1)$$

where OPT is an optical cross section, Et denotes the threshold energy related to the optical absorption process such as the transition of electrons trapped at a localized level to the conduction (or valence) band. In this model, the ion core potential is assumed to be a delta function, and two possible transitions are involved as follows[3-5]: (A) In the case where the density of states (DOS) are parabolic at the band edge, the optical transition is dominated by the forbidden transition of the electrons (or holes) trapped at the neutral center to the conduction band (or to the valence band), where both localized wave functions at initial and final states are in the same band. (B) In the case of the band edge with the linear DOS, it is dominated by the forbidden transition of electrons (or holes) trapped at the reversely charged center to the conduction band (or to the valence band) within the same band. Actually, when the Lucovsky model is applied to the study of localized levels in semiconductors, we notice the change in absorption coefficient, $\Delta\alpha \propto (\sigma_n - \sigma_p)\Delta n$, where σ_n/σ_p denotes the optical cross section for electronsholes and Δn is the steady state change in trapped electrons (or holes) caused by a prolong illumination on the specimen.

In the present study, the $\Delta\alpha$ corresponds to an incremental deviation from the straight line on α in semilog plots of α against hv in the intermediate energy region ($h\nu = 2.54$ eV), where the straight line denotes an exponential band tail. The $\Delta\alpha$ emerges clearly towards to the lower energy below 3 eV as will be shown in Fig. 1. In the present analysis,

we use the Lucovsky plots of $(\Delta\alpha)^{2/3}(h\nu)^2$ v.s. h and determine the threshold energy Et in Eq. (1), i.e., a localized level.

Results and discussion

Figure 1 shows experimental results of the optical absorption coefficient plotted as a function of $h\nu$ for four ITO specimens deposited at a substrate temperature Ts=200℃ from the target with 5 wt.% SnO_2 as an parameter of oxygen flow rates 0, 0.2, 0.5, and 2.0 sccm. It is seen from this figure that the values of α at $h\nu=3\sim4$ eV are well presented by the straight lines showing the exponential band tail. In contrast, in low energy region below 3 eV they increasingly deviate from the straight line and the linear portion of α lengthens as an oxygen flow rate increases from 0 to 2 sccm, which corresponds to oxygen partial pressure of about 2.8×10^2 Pa. These facts are related to the increase in the direct allowed transition energy Eg from a different part of k-space than the maxima of the valence band to the Fermi level, i.e., the highest energy level filled by electrons in the conduction band : The increase in Eg is originated from the increase in the number of electron created by oxygen deficits (i.e., oxygen vacancies) depending to the oxygen partial pressure PO_2. For instance, for the specimens shown in Fig. 1, Eg=3.8 eV for $n=8\times10^{20}cm^{-3}$ at $PO_2=2.8\times10^2$ Pa and Eg=3.5 eV for $n=5\times10^{19}cm^{-3}$ at $PO_2=1.0\times10^2$ Pa, where electron concentration n is determined from Hall coefficient measurements.

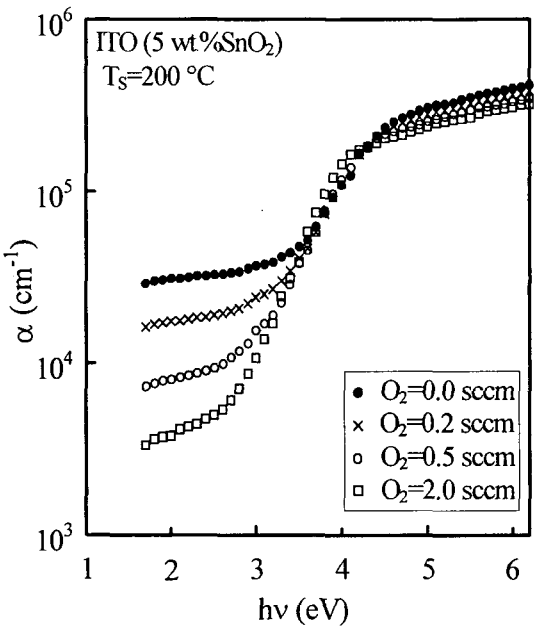

Fig 1. Absorption coeffient α plotted against photon energy hv for indium tin oxide films deposited from a target In_2O_3 with 5 wt. % SnO_2, ITO(5 wt.% SnO_2), at a substrate temperature T_s=200℃, as an parameter of oxygen flow rates(O_2=0, 0.2, 0.5 and 2.0 sccm) in the sputtering gas of mixture of Ar with 60 Sccm and O_2

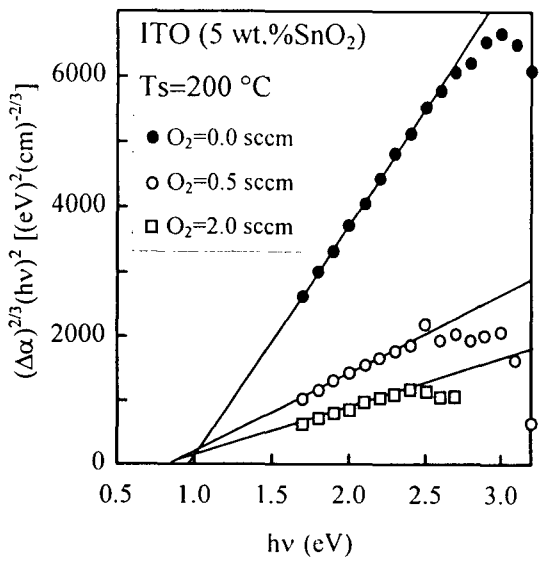

Fig 2. Lucovsky plots, $(\Delta\alpha)^{2/3}(hv)^2$ versus hv, for ITO (5 wt.% SnO_2) dilms deposited at Ts =200℃ using the sputtering gas of mixture of Ar with 60 Sccm and O_2 with 0, 0.5 and 2.0 sccm, respectively, shown in Fig. 1

Figure 2 shows the Lucovsky plots of $(\Delta\alpha)^{2/3}(h\nu)^2$0, $(\Delta\alpha)^{2/3}(h\nu)^2$ v.s. h for the specimen (5wt.%SnO_2) at Ts=200℃ obtained from the data shown in Fig. 1. It is seen from this figure that the calculated data points are well presented by the straight lines and from the extrapolation of its straight-line to $(\Delta\alpha)^{2/3}(h\nu)^2=0$, the threshold energy Et in Eq. (1) is given as 0.8~1.0 eV. This threshold energy is considered to show that a localized (defect) level exists in the ITO films, and its physical origin will be discussed later. For other specimens, we have also performed the Lucovsky plots and their results are shown in Fig. 3. In Fig. 3, the threshold energy Et is plotted against an atomic ratio O/In showing a stoichiometric deficiency of oxygen atoms, where the composition of the films is determined by the ESCA with the use of standard In_2O_3 specimen. It is seen from Fig. 3 that for the indium oxide the values of Et are larger than those of the ITO with 5 and 10 wt.% SnO_2 on the whole. This seems to be related to an evidence that the intrinsic band gap Egd for the direct allowed transition, indicating the transition from the valence band at k=0 to the conduction band bottom, is larger for the IO (Egd=3.4~3.5 eV) compared to those of all the ITO (Egd=2.8~3.1 eV), which were obtained from the plots of Eg v.s. $\eta^{2/3}$, where Eg was obtained from the α^2 v.s. $h\nu$ plots. However, as shown in Fig. 3, it is difficult to explain the change in Et for the IO at Ts=200 and 300℃ markedly depending on the O/In for the present. In contrast, the values of Et for the ITO with 5 and 10 wt.% SnO_2 lie around 1.0 eV with increasing O/In without having a strong dependence on O/In, except for that of the ITO(10 wt.% SnO_2) at Ts=300℃

In view of the fact that in Fig. 3 the content of oxygen in the IO and ITO films markedly deviates from the stoichiometric composition (O/In=1.5) of In_2O_3 and such oxygen deficits in the ITO play an important role in determining the electrical and optical properties[1], we propose an energy band model as shown in Fig. 4 : In this figure, the threshold energy Et obtained from the Lucovsky plots

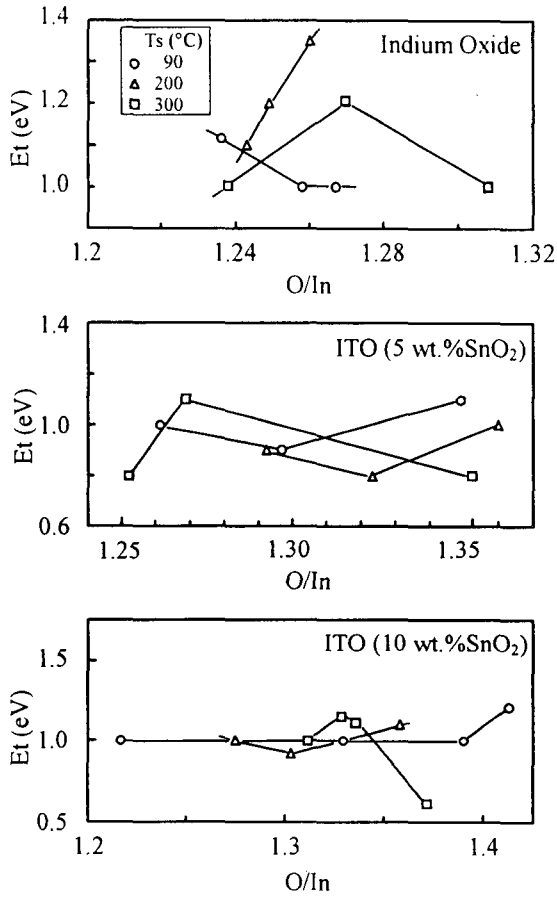

Fig 3. Threshold energy Et, obtained from Lucovsky plots as shown in Fig. 2, plotted against the atomic ratio O/In showing a stoichiometric deficiency of oxygen atoms for films of indium oxide, ITO(5 wt.% SnO_2) and ITO (10wt.% SnO_2) deposited at T_s=90, 200 and 300℃ The threshold energy Et denotes a localized energy in the hand gap locates Fermi level, vacancies (see text)

in Fig. 2 is considered to be coincident with a defect level located below the Fermi level EF. An origin of this defect level is discussed as follows.

According to the standard model[6] for the indium oxide materials, the conduction electrons ($>10^{19}cm^{-3}$) can result either from the oxygen vacancies acting as doubly charged donors, providing two electrons each, or from the tin acting as a singly charged donor on an indium atomic site. In this connection, it is well known that such the electron creation due to the oxygen vacancies predominates than that due to the tin even for the ITO films highly doped with tin[1]. This is also understood from the present ESCA results that the tin content in the ITO deposited by using the target with 20 wt.% SnO_2 is less than ~9 at.%. Furthermore, it is also known[7] that the direct band gap in the ITO is influenced by oxygen vacancies, which are changed by annealing.

Accordingly the origin of the present defect level should be associated with the oxygen vacancies : The oxygen vacancies are considered to behave as the positively charged (+2e) sites, and to be neutralized by trapping nearly free electrons in the specimen at thermal equilibrium and at dark state. Therefore, in this circumstance the defect level Et corresponds to a transition energy of electrons at the neutralized sites into the conduction band caused by a light illumination. Such the transition is consistent with the case (B) as described above, i.e., the forbidden transition of electrons trapped at the reversely (+2e) charged center to the conduction band within the same band where the band edge has the linear DOS. From a condition of the transition between the same bands, the defect level is a s-like band, because the conduction band in the In_2O_3 crystal is known to be the s-band originated from the 5s-orbit in indium atoms in this crystal with a bixbyite structure[8].

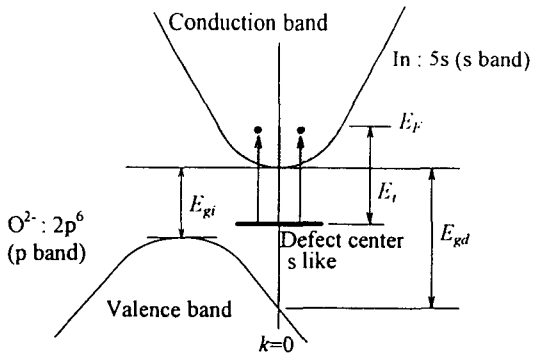

Fig 4. Diagram of proposed band model, which characterizes the defect center existing in indium oxide and ITO films.

CONCLUSION

Thin films of indium oxide and indium tin oxide have been prepared by d.c. magnetron sputtering onto the fused silica substrates kept at 90, 200 and 300℃ from the targets of In_2O_3 and SnO_2 (5 and 10 wt.%) doped In_2O_3, and at 0.8 Pa using the mixture of Ar (60 sccm) and O_2 (0~2 sccm). In order to elucidate the optical absorption in low energy region below 3 eV for these films, we have analyzed the absorption coefficient obtained from reflectance and transmittance measurements based on the Lucovsky model. It has been found for the first time that the defect center in the band gap is located at 0.8~1.4 eV below the Fermi level in all films and arises from oxygen vacancies in their films. The optical absorption in low energy region has

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