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Study on chemical state of Sn in ITO by Mössbauer spectrometry

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ABSTRACT

^{119}Sn Mössbauer studies on Sn-doped In_2O_3 (ITO for Indium Tin Oxide) powders with different Sn doping concentrations were carried out. Transmission Mössbauer spectra exhibited that all Sn atoms in ITO were in 4+ state. Deconvolution analysis of the spectra made it possible to distinguish between electrically active Sn and inactive dopants, and hence to estimate the amounts of them in the material. Steady increase in the ellectrically inactive Sn, such as $Sn^{\cdot}{}_2O_i''$ and $(Sn_2O_4)^x$, was clearly observed with increasing Sn doping concentration in the powders. Carrier densities were estimated for the each sample, taking account of the concentration of the active Sn dopants, which was in good agreement with the measured values for splayed ITO films.

1. INTRODUCTION

Tin-doped In_2O_3 (ITO) is an n-type, highly degenerated, wide-gap semiconductor, which shows low resistivity ($\sim 10^{-4}\Omega$cm) and high transmittance (above 80%) in visible region. ITO thin films have been applied to optelectronic devices, such as transparent electrodes of flat panel displays and solar cells. With recent demands for large size and high quality flat panel displays, ITO films are required to have extremely low resistivity less than 10^{-4} Ωcm. The electrical and optical properties of the ITO thin films had been extensively investigated[1,2]. Both of these properties are intimately associated with microstructure[3-7] and lattice defects[8, 9] of the films.

Chemical state of Sn in this material is one of the most important key factors to achieve the lower resistivity, since substitutional four-valent Sn on In^{3+} site ($Sn_{In}^{\cdot}$) is one of the dominant donor sites. A phenomenon that doping efficiency decreases with increasing Sn doping concentration at about 5-10 atomic% has been reported[1], which was considered to originate in the presence of electrically neutralized dopants at higher doping concentrations. There were a few reports on the chemical states of Sn in ITO[10-15], however, the mechanism of donor compensation effect has been cleared. Frank et. al. proposed[8] two models of neutralized Sn dopants, such as $Sn^{\cdot}{}_2O_i$ and $(Sn_2O_4)^x$, which were comprised of interstitial oxygen anion (O_i'') and substitutional tin ($Sn_{In}^{\cdot}$) on indium site. Their models could explain the dependence of the carrier density on the Sn doping concentration, however no evidence for existence of such defects has been reported.

Mössbauer spectroscopy is one of the powerful technique for investigations on lattice defects, since the spectra are sensitive to symmetry of coordination around the Mössbauer atoms. In order to clarify the presence of the neutralized Sn and doping mechanism, ^{119}Sn Mössbauer studies on Sn in ITO powders with different Sn doping concentrations were performed in view of crystal structure.

2. EXPERIMENTALS

ITO Powders were prepared by sintering the mixtures of In_2O_3 and SnO_2 powders with Sn concentrations of 0.5, 2.5, 5.0, 7.0, and 10at% at

1500 ℃ for several hours under atmospheric condition.

Transmission Mössbauer spectra of the ITO powders were obtained using a NaI(Tl) scintilation counter. 1mCi $Ba^{119m}SnO_3$ was used as γ-ray source. The isomer shifts were referred to SnO_2 at room temperature. The velocity was calibrated using a 10mCi $^{57}Co(Rh)$ source and enriched ^{57}Fe foil as an absorber. The spectra were fitted as a sum of three doublets (sub-spectrea) composed of Lorentzian curves by the non-liner least-squares program. In order to assign the sub-spectrum to Sn in the different chemical state, electric field gradient and asymmetric parameter at each Sn site was calculated with point charge approximation.

3. EXPERIMENTAL RESULTS

The obtained spectra were fitted with the three doublets, assuming that each sub-spectrum was Lorentzian. The goodness of the fitting (χ^2) was about 1.0, which was considered to be very satisfactory. The sub-spectra were named COMP.1, COMP.2, and COMP.3, respectively, in order of magnitude of quadrupole splitting. Different quadrupole splitting values imply that Sn is located at the different sites. The isomer shift (IS) relative to SnO_2, quadrupole splitting (QS), and relative area of each spectrum are listed in Table 1. At lower Sn concentration (<5.0at%), each fitting spectrum consists of two sub-spectra. On the other hand, the fitting spectra consist of three sub-spectra at higher Sn concentration (≧ 5.0at%). The IS values of all components indicated that all Sn atoms in the ITO powders were in 4+ states. Neither Sn^{2+} nor metallic Sn were detected in the samples. The QS values of all components became larger with increasing doping concentrations, which should be the results of increasing local disorder around the dopant Sn. The relative areas of COMP.2, and COMP.3 showed steady increase with increasing Sn concentration.

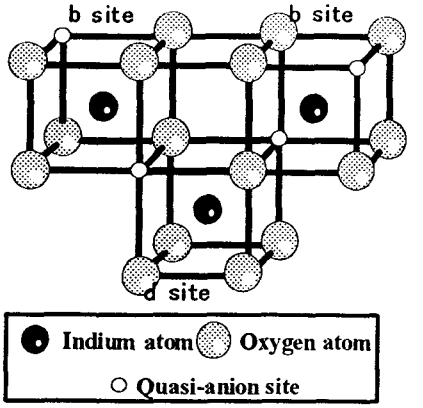


Fig. 1 The crystal structure of In_2O_3 host lattice

4 DISCUSSIONS

4.1 Crystal Structure of ITO distorted

Before discussing the relationship between defect models and Mössbauer results, a short descrepion of crystal structure of the ITO is required. X-ray diffraction patterns of the all ITO powders showed clear In_2O_3 cubic bixbyite structure without any SnO_2 peaks. There are two non-equivalent In atom sites in In_2O_3 crystal. In the unit cell, 8/32 of indium atoms occupy the center of trigonally distorted oxygen octahedron (b site) and the remaining 24/32 located at the center of more distorted octahedra (d site)[16]. Both of the Indium sites are surrounded by six oxygen atoms and adjacent to quasi-anion sites. A part of In_2O_3 lattice is shown in Fig. 1.

4.2 Defect Models in ITO

The doping mechanism had been investigated by several author in terms of interstitial Sn atoms[17] or Sn_3O_4-like phase[10].

Parent et. al.[11,12], by means of EXAFS, reported that interstitial Sn atoms did not exist in view of radial structure functions. And a detail XPS

Table1. Obtained Mossbauer parameters and relative areas

Sn conc. (at%)	COMP.1 IS (mm/sec)	COMP.1 QS (mm/sec)	COMP.1 area (%)	COMP.2 IS (mm/sec)	COMP.2 QS (mm/sec)	COMP.2 area (%)	COMP.3 IS (mm/sec)	COMP.3 QS (mm/sec)	COMP.3 area (%)	χ spur
0.5	0.17	0.5	80	0.23	0.47	20	-	-	0	1.038
2.5	0.17	0.65	68	0.22	0.61	32	-	-	0	1.003
5.0	0.15	0.7	62	0.16	0.68	36	0.16	0.21	2	1.004
7.0	0.12	0.75	36	0.15	0.67	61	0.13	0.21	3	1.118
10	0.11	0.84	26	0.15	0.78	69	0.12	0.21	5	1.004

analysis of Sn 3*d* spectra[13] suggested no evidence for existence of Sn_3O_4-like phase.

The most reliable defect models were proposed by Frank et. al.[8], which were summarized as follows.

$Sn_b^{\cdot}$, $Sn_d^{\cdot}$:

Sn^{4+} on In^{3+} (b or d) site ; effective dopant

$Sn^{\cdot}{}_2O''_2$:

O^{2-} on interstitial quasi-anion site, loosely bound to two Sn^{4+} which don't occupy nearest neighbor In^{3+} positions ; neutralized dopant.

$(Sn_2O_4)^x$:

Strongly bound complex, similar to Ca_2F_4, composed of two nearest neighbor Sn^{4+} ,surrounded by three nearest neighbor O^{2-} on regular anion sites, and one interstitial O^{2-} on quasi-anion site in the In_2O_3 lattice. ; neutralized dopant.

According to these defect models, there are four kinds of Sn atoms in the ITO.

Each Sn species should be under different electric field gradient resulting in different QS in the Mössbauer spectrum. Point charge calculations of electric field gradients and asymmetric parameters were performed in order for the assignment of individual sub-spectrum to Sn atoms on the different site, since magnitude of the QS is nearly proportioned to the electric field gradient The calculated electric field gradients (**EFG**) and asymmetric parameters (η) are listed in Table 2. Based on the results in Table1 and Table2, it is considered that COMP.1 could be assigned to $Sn_b^{\cdot}$, COMP.2 could be assigned to $Sn_d^{\cdot}$ or $Sn^{\cdot}{}_2O''_2$, and COMP.3 could be assigned to $(Sn_2O_4)^x$. The relative area of COMP.2 increased abruptly at higher (>5at%) Sn doping concentration, where doping efficiency started to decrease[1] with increasing Sn concentration. This suggest that the amount of $Sn^{\cdot}{}_2O''_2$ (neutralized Sn) is considered to have increased at higher Sn doping concentration around 5at%.

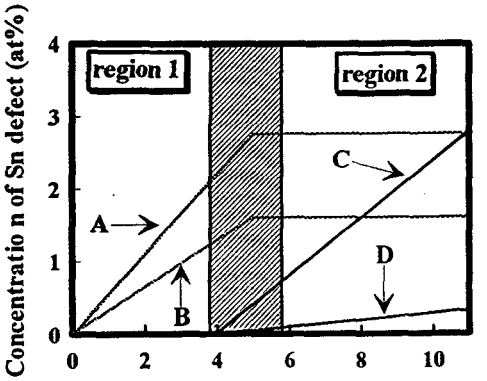
Table 2
The calculated values of EFG and asymmetric parameter (η)at different locations of Sn atoms

	EFG ($\times 10^{17}$V/cm^2)	η
$Sn_b^{\cdot}$	12.1	0.0
$Sn_d^{\cdot}$	6.1	1.0
$Sn^{\cdot}{}_2O''_2$	6.1	0.0
$(Sn_2O_4)^x$	0.0	-

Since the relative area of each component sub-spectrum implies amount of Sn species located at the corresponding chemical state, the concentrations of each Sn defect could be estimated using the relative areas of sub-spectra.

The dependence of the each defect concentration in the powder ITO on the Sn doping concentration is given in Fig.2. The concentrations of electrically active dopants, such as $Sn_b^{\cdot}$, and $Sn_d^{\cdot}$, linearly increased with increasing Sn concentration at lower doping concentration (region 1 in the Fig.2) and saturated at higher doping concentration around 5at% (region 2 in the Fig.2). The concentration of $Sn_b^{\cdot}$ was higher than that of $Sn_d^{\cdot}$, which should be caused by the more similar configuration of oxygen atoms around the b sites to the one around Sn atom in the SnO_2 rutil crystal structure. The amounts of neutralized dopants, such as interstitial defect [$Sn^{\cdot}{}_2O''_2$] and neutral complex [$(Sn_2O_4)^x$] appeared and linearly increased with increasing Sn concentration at the higher Sn concentration. These neutral defects cannot donate the free electron and exist as the neutral impurity scattering centers in the ITO, which cause the decreasing in the doping efficiency and hence the mobility of free carriers.

It was reported that the host network was distorted with Sn doping , which was consistent with steady increase in QS values with increasing Sn concentration because the distortion of the host



Doping concentration (Sn at%)
A : $Sn^{\cdot}_b$, effective dopant
B : $Sn^{\cdot}_d$, effective dopant
C : [$Sn^{\cdot}{}_2O_i''$], neutral defect
D : [Sn_2O_4], neutral complex

Fig. 2
Dependance of defect ccopncentration on doping concentration

network should induce the increase in of host network induce the increase of the electric field gradient and the asymmetric parameter around the dopant Sn atoms.

4.3 Estimation of Carrier Density

Carrier densities of the samples were estimated on the basis of Fig.2, assuming that the only $Sn_b^{\cdot}$ or $Sn_d^{\cdot}$ donate one electron. Comparison was made between the estimated carrier densities for powder samples from the Mössbauer analysis and the measured values for films deposited using spray pyrolysis technique, because the spray pyrolysis was not so non-equilibrium technique compared with sputtering or another PVD technique. In Fig.3, both of the values were plotted as a function of the doping concentrations. In this figure, the estimated values were in good agreement with the measured values for the films, indicating that the analysis and the assignments should be reasonable.

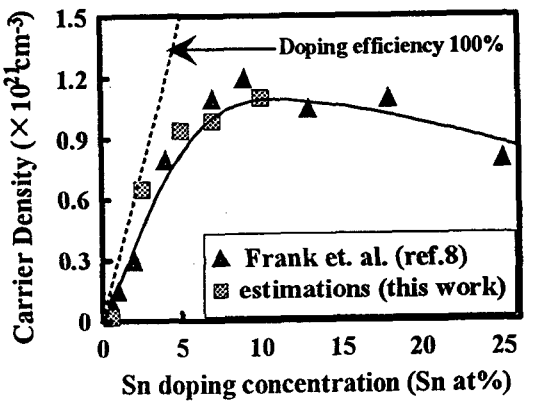


Fig. 3
Comparison between the estimated and measured carrier dinsity

5. CONCLUSIONS

In this study, the Mössbauer results could be successfully related to the electrical properties of ITO films.

The deconvolution analysis of ^{119}Sn Mössbauer spectra of the powder ITO made it possible to distinguish the electrically active and inactive Sn dopants. The steady increase in neutralized Sn dopants, such as $Sn^{\cdot}{}_2O_i^{''}$ and $(Sn_2O_4)^x$, were clearly observed with increasing Sn doping concentration in the powders, which demonstrated the low doping efficiency with highly doped ITO.

The estimated carrier densities of the powders from the Mössbauer results were in good agreement with that of ITO film deposited by spray pyrolysis.

These two results suggested that both (i) increasing the electrically active Sn substituted to In atoms ($Sn_b^{\cdot}$ or $Sn_d^{\cdot}$) and (ii) decreasing the electrically neutralized Sn which are exist only as neutral scattering centers ($Sn^{\cdot}{}_2O''_2$ or $(Sn_2O_4)^x$) should be important to obtain ITO films with the extremely low resistivity.

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