Low-Resistivity Indium-Tin-Oxide Transparent Conducting Films: Dependence of Carrier Electron Concentration on Tin Concentration

Yutaka SAWADA[1,a,*], Shigeyuki SEKI[2,b], Takayuki UCHIDA[1,c], Yoichi HOSHI[1,d], Mei-Han WANG[3,e], Hao LEI[4,f], Li-Xian SUN[5,g]

[1]Center for Hyper Media Research, Tokyo Polytechnic University, Atsugi, Kanagawa, Japan

[2]Department of Electronic Engineering, Sendai National College of Technology, Sendai, Japan

[3]Scool of Mechanical Engineering, Shenyang University, Shenyang, China

[4]Suraface Engineering of Materials Division, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China

[5]School of Material Science and Engineering and Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin, China

[a]sawada@chem.t-kougei.ac.jp, [b]nariyuki@sendai-nct.ac.jp, [c]uchida@mega.t-kougei.ac.jp, [d]hoshi@em.t-kougei.ac.jp, [e]wangmhdicp@aliyun.com, [f]haolei@imr.ac.cn, [g]sunlx@guet.edu.cn

*Corresponding author

Keywords: ITO, Tin-doped In_2O_3, Spray chemical vapor deposition.

Abstract. Indium-Tin-Oxide (ITO, tin-doped In_2O_3) films with low resistivity (7.7×10^{-5} ohm cm) and high carrier electron concentration (1.8×10^{21} cm^{-3}) was successfully prepared by spray chemical vapor deposision in air and post-deposition annealing in reducing atmosphere in our previous papers; Y. Sawada et al., Thin Solid Films, 409 (2002) 46-50 and Y. Sawada, Materials Sci. Forum, 437-438 (2003) 23-26. Doping one tin ion generated two carrier electrons at low concentration of tin. The relation between carrier electron concentration and tin concentration are discussed in the present paper to propose a nobel defect model.

Introduction

Transparent conducting films of tin-doped In_2O_3 (Indium-Tin-Oxide, ITO) are used for solar cells, flat panel displays including touch panels etc. and usually deposited by magnetron sputtering. The authors reported elsewhere [1, 2] low-resistivity ITO films fabricated by spray chemical vapor deposition very cheaply. The lowest resistivity of the as-deposited in air was 1.8×10^{-4} Ω cm. This value was compatible with those deposited by magnetron sputtering. The post-deposition annealing in reducing atmosphere lowered the resistivity. The lowest resistivity was 7.7×10^{-5} Ω cm. In the present paper the carrier electron concentration of ITO films after the post-deposition annealing will be discussed as a function of tin concentration.

Experimental

The preparation and evaluation of the films were reported elsewhere [1, 2] in detail. Ethanol solution of $InCl_3.2.7H_2O$ and $SnCl_2.0.86H_2O$ was sprayed onto a glass substrate (Corning 7059) heated at 300-350^oC on a hotplate to deposit ITO films (approx. 200 nm). The films were annealed at 600^oC for 2 h in N_2-0.2%H_2 gas flow (300 mL/min) to lower the resistivity.

Results and Discussion

Figure 1 shows carrier electron concentration (n) of indium oxide films as a function of tin concentration (C_{Sn}) after annealing in reducing atmosphere. The C_{Sn} is tin concentration of

100×[Sn]/([Sn]+[In]), where [Sn] and [In] are the concentration (cm^{-3}) of tin and indium atoms, respectively, in indium oxide crystal.

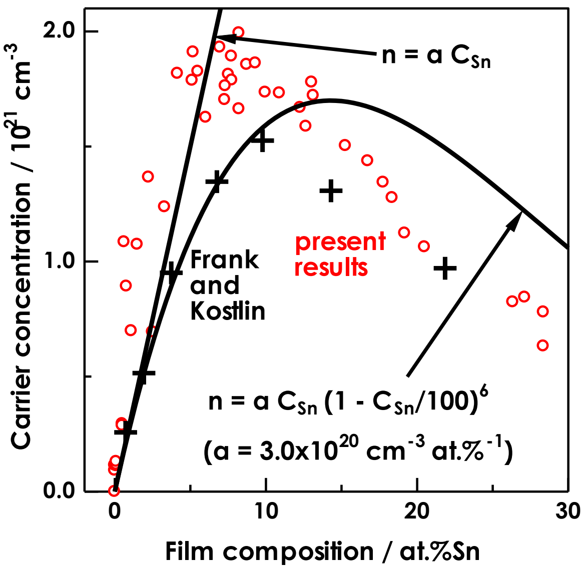

Fig. 1. Carrier electron concentration of indium oxide films as a function of tin concentration after annealing in reducing atmosphere: comparison with the results by Frank and Köstlin

This figure also shows the results by Frank and Köstlin [3] who deposited by spray CVD and annealed in reducing atmosphere. They interpreted that a Sn^{4+} ion at a In^{3+} site genaerates one carrier electron when interaction is negligible between the two neighbouring Sn^{4+} ions at low concentration of tin. This is expressed as Eq. 1 by Kröger-Vink notation [4] at low tin concentration.

$$SnO_2 \rightarrow Sn^{\bullet}_{In} + (3/2)O^{\times}_{O} + e' + (1/4)O_2 \qquad (1)$$

Carrier electron concentration (n) is expressed as

$$n = [Sn] = a\,CSn \qquad (2)$$

The constant $a = 3.0\times10^{20}$ cm^{-3} at.%$^{-1}$ is determined from the lattice constant (1.0118×10^{-7} cm) of In_2O_3 and number of metal ions (32) in a unit cell. At higher concentration of tin, carrier electron concentration is deviates from Eq. 2. They attributed to a formation of neutral defect complex $Sn^{\bullet}_{In\,2}\,O^{\times}_{i}$". They assumed two nearest-neighbor Sn^{4+} ions at In^{3+} site coupled with one interstitial O^{2-} ions to eliminate carrier electrons as Eq. 3.

$$2Sn{\bullet}In + 2e' + (1/2)O2 \rightarrow Sn{\bullet}In\ 2\ O\times i" \qquad (3)$$

The $O^{\times}_{i}$" is an interstitial oxygen ion (O^{2-}) located at a space called quasi-anion site of In_2O_3 lattice (C-rare earth oxide structure). They assumed that tin ions occupy only at "b-site" of In_2O_3 lattice and proposed Eq. 4 with 6 nearest-neighbor tin ions.

$$n = a\,CSn\,(1 - CSn/100)6 \qquad (4)$$

This equation satisfies their results at ≤ approx. 10 at.%Sn but fails to explain higher carrier electron concentrations of the present results.

The present results are shown in Figure 2 in order to compare with the results by Ohta et al. who deposited ITO film on a single crystal of zirconia by expensive pulsed laser deposition [5]. The present highest value (1.8×10^{21} cm^{-3}) agreed with their ones and our previous result [1, 2] at C_{Sn}, 5-7 at.%. The results fit with Eq. 5 at low concentration of tin (< approx. 3 at.%).

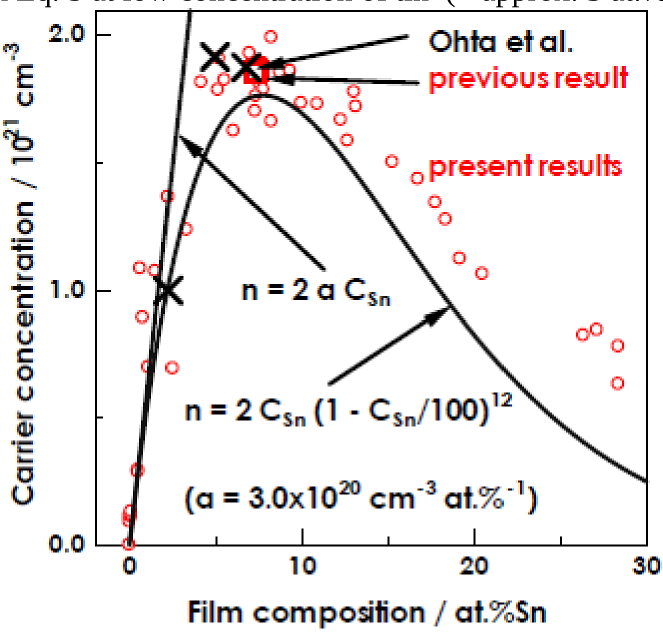

Fig. 2. Carrier electron concentration of indium oxide films as a function of tin concentration after annearing in reducing atmosphere: comparison with the results by Ohta et al. and our previous result.

$$n = 2\,[Sn] = 2\,a\,C_{Sn} \qquad (5)$$

This assumes that doping one tetravalent tin ion (Sn^{4+}) generates two carrier electrons (e^-) although it seems rather strange. In order to explain the present high carrier concentration, simulataneous formation of $Sn^{\bullet}_{In}$ and $V^{\bullet}_{O}$ was tentatively assumed to generate two carrier electrons as Eq. 6

$$SnO_2 \rightarrow Sn^{\bullet}_{In} + (1/2)O^{\times}_{O} + V^{\bullet}_{O} + 2e' + (3/4)O_2 \qquad (6)$$

$V^{\bullet}_{O}$ is an oxygen ion vacancy coupled with an electron. A novel model with 12 nearest-neighbor tin ions (both b- and d-site) is proposed.

$$n = 2\,a\,C_{Sn}\,(1 - C_{Sn}/100)^{12} \qquad (7)$$

This is a better fit with the present results although the defect mechanism explaining the phenomenon is not clear at present.

Structure and other properties of the present films will be demonstrated: the resistivity, carrier electron mobility, transmittance and reflectance, X-ray diffraction, FE-SEM photos etc.

Acknowledgements

The authors thank Mr. Takeshi AOYAMA for film preparation and Mr. Yoshiyuki SEKI for technical advice.

References

[1] Y. Sawada, C. Kobayashi, S. Seki and H. Funakubo, Thin Solid Films, 409 (2002) 46-50.

[2] Y. Sawada, Materials Sci. Forum, 437-438 (2003) 23-26.

[3] G. Frank and H. Köstlin, Appl. Phys., A27 (1982) 69-75.

[4] F. A. Kröger, “Chemistry of Imperfect Crystals, Vol. 2” (North-Holland, Amsterdam 1974) pp. 690-694.

[5] H. Ohta, M. Orita, M. Hirano, H. Tanji, H. Kawazoe and H. Hosono, Appl. Phys. Lett., 76 (2000) 2740-2742.