Extended Abstracts of the 2018 International Conference on Solid State Devices and Materials, Tokyo, 2018, pp785-786

Study on the Behaviors of HNO_3 in Highly Conductive Antimony Doped Tin Oxide Thin Films Deposited by Novel Mist CVD System

Li Liu[1], T. Kawaharamura[1, 2, 3], M. Ueda[2], G. T. Dang[3], S. Sato[1], S. Fujita[4], T. Hiramatsu[5], H. Orita[5]

[1] School of Systems Engineering, [2] Intelligent Mechanical System Engineering Course, [3] Research Institute,
Kochi University of Technology
185 Miyanokuchi, Tosayamada, Kami, Kochi, 782-8502, Japan
Phone: +81-887-57-2703 E-mail: kawaharamura.toshiyuki@kochi-tech.ac.jp, 198006k@gs.kochi-tech.ac.jp,
[4] Photonics and Electronics Science and Engineering Center, Kyoto University,
2 Katsura, Nishikyo-ku, Kyoto 615-8520, Japan
[5] Renewable Energy & New Technology Division, Toshiba Mitsubishi-Electric Industrial Systems Corporation (TMEIC)
Kobe International Business Center (KIBC) 509, 5-5-2 Minatojima-Minami, Chuo-Ku, Kobe 650-0047, Japan

Abstract

Antimony doped tin oxide (SnO_x:Sb) thin films with low resistivity (9.0×10^{-4} Ω cm) and excellent optical transmittance were successfully grown by novel mist CVD system in this work. Besides the effect of Sb doping ratio on the conductivity, it was found the HNO_3 in doping solution also has a positive effect on the conductivity of SnO_x films. In order to identify the contribution of HNO_3 to the conductivity, the behaviors of HNO_3 were studied by analyzing the optical, electrical, and chemical properties of high conductivity SnO_x thin films. The experimental results show that the moderate amount of HNO_3 in doping solution improved the conductivity. Compared to the SnO_x films fabricated using only $SbCl_3$ or HNO_3, the sample shown lower resistivity when both $SbCl_3$ and HNO_3 were used. Most likely, the change in valence state of N (V) and/or the substitution of N (V) for Sn (IV) increased the conductivity of SnO_x films.

1. Introduction

Transparent conducting oxide films (TCOs) are widely used in the fabrication of optoelectronic devices because of the high electrical conductivity and excellent optical properties [1-4]. The tin oxide (SnO_2), which is generally an n-type semiconductor with large band gap of 3.6 ~ 3.85 eV, high chemical stability, mechanical hardness, and heat resistance, is one of most promising TCOs [5-8]. Previous researches have verified that the metal oxides with dopants always exhibited higher electrical conductivity than non-doped ones. The common dopants for preparing highly conductive SnO_2 films are fluorine (F), indium (In), and antimony (Sb). As a doping material, Sb has the characteristics of stable chemical nature and extensive origin, illustrating it is more suitable to prepare high conductivity SnO_2 films than F and In [9]. $SbCl_3$ are the most common and frequently used dopant precursor when antimony doped tin oxide (SnO_2:Sb) films are fabricated, and the substitution of Sb (V) for Sn (IV) is thought to be the main reason for obtaining the high conductivity films.

In this work, the high conductivity SnO_x:Sb films were fabricated by novel mist CVD system with a special supply unit, which is composed of two solution chambers and one mixing chamber, this system has been reported in [10-12]. Based on the effects of Sb and HCl in dopant solution on the highly conductive SnO_x:Sb films have been studied in our previous researches, in order to further determine the factors of obtaining high conductivity, the behaviors of HNO_3 in dopant solution were studied by analyzing the optical, electrical, and chemical properties of thin films.

2. Experimental

SnO_x:Sb thin films were deposited on quartz substrates under atmospheric pressure at 400°C. Tin(II) chloride dihydrate ($SnCl_2\cdot2H_2O$) was selected as host precursor, and dissolved in a mixture solute of H_2O, HCl (aq), and HNO_3 (aq). The doping solution is composed of H_2O, HCl (aq), $SbCl_3$ and HNO_3 with different combinations. In order to avoid the complex reaction, the host precursor solution and doping solution were added to different solution chambers of novel mist CVD system and misted separately.

Sheet resistance (R_S) of sample was studied by the Hall effect setup in the Van der Pauw configuration. The electrical resistivity (R) and conductivity (σ) were determined by the relation $R = R_S \cdot t$ and $\sigma = 1/R$. X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical states of N, O, Sb and Sn. The chemical bond of film was determined in long-wavelength range from 1.7 to 30 μm by IR-VASE Mark II Ellipsometer (J.A. Woollam) under different measurement angles (55º, 65º and 75º)

3. Results and discussions

The resistivity of SnO_x:Sb films fabricated using different doping solutions are summed up in Table I. It is obvious that, the resistivity of films fabricated using both $SbCl_3$ and HNO_3 in doping solution, was much lower than that of films fabricated using either $SbCl_3$ or HNO_3 in doping solution. According to previous studies, the Sb doping was considered as the major factor for obtaining the conductivity thin films, there was few studies focus on the effect of other components. In our work, it was found that the HNO_3 was beneficial for increasing the conductivity of SnO_x:Sb films. Two possible reasons were given to explain the HNO_3 behaviors in the high conductivity film fabrication process. One reason is that the HNO_3 played a role of an oxidizing agent in the fabrication process, the reduction reaction of HNO_3 promoted generation of Sn (IV), and the substitution of Sb (V) for Sn (IV) resulted in the generation of conduction electrons when the SnO_x:Sb

films were fabricated. This idea can be confirmed by the following reaction:

$$6SnO_2 + 4H_3O^+ + 4NO_3^- \rightarrow 3SnCl_4 + 3SnO_2 + 4NO + 6H_2O$$

In addition to the HNO_3 acts as an oxidizing agent, another reason for the HNO_3 affects the conductivity of SnO_x:Sb films is considered that the N (V) derived from HNO_3 acts a dopant due to the N (V) has same valence state with Sb (V). This hypothesis will be verified later.

Table I Resistivity of films fabricated by different doping solutions

		$SbCl_3$	
		without	with
HNO_3	Without	$>10^8$ Ω cm	$>10^8$ Ω cm
	with	7.62×10^{-3}Ω cm	9.72×10^{-4} Ω cm

The XPS measurement was performed to determine the composition and chemical states of the SnO_x:Sb films fabricated by different doping solutions. Fig. 1 (a)-(d) show the N 1s, Sn 3d, O 1s core level, and valence band XPS spectra of SnO_x:Sb thin films. Because of the Sb signal was too weak to be observed, the XPS result of Sb was not included here. In Fig. 4(a), the N 1s XPS spectrum possessed a peak at ~ 400.3 eV, which is assigned to nitrogen located in NO_2- related groups. However, it is possible that the incorporation of N into SnO_x thin films was not surely verified due to the weak XPS N 1s intensity. In Fig. 4(b), the peaks at 486.8 eV and 495.2 eV correspond to the binding energy (BE) of Sn $3d_{5/2}$ and $3d_{3/2}$ levels in SnO_2, while in Fig. 4(c) the peak at 530.8 eV corresponds to the O 1s level in metal oxides. However, the BEs of Sn $3d_{5/2}$ in SnO_2 and SnO (486.5±0.5) are very close, causing difficulty in determination of the x value in the formula SnO_x. Based on intensities of Sn 3d and O 1s levels, the composition ratio [O]/[Sn] was calculated. For the SnO_x film fabricated using both $SbCl_3$ and HNO_3 in doping solution, the value of [O]/[Sn] was 1.34, and that ratio was 1.38 for the film fabricated using only HNO_3 in doping solution.

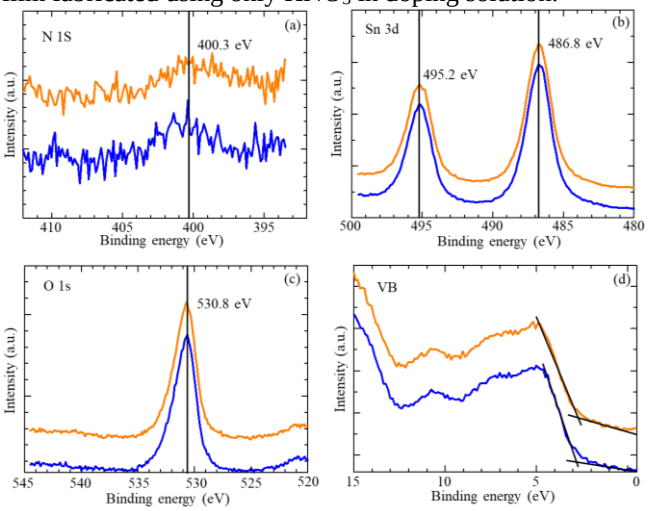

Fig. 1 XPS pattern of (a) the N 1s peak, (b) the Sn 3d peak, (c) the O 1s peak, and (d) VB (orange curve is the films fabricated using $SbCl_3$ and HNO_3; blue curve is the films fabricated using HNO_3)

Infrared spectroscopic ellipsometry was performed on the SnO_x films using IR-VASE in a wide spectral range from 250 to 8000 cm^{-1}. Fig. 2 (a) and (b) show the long-wavelength optical constants of SnO_x:Sb films fabricated using different dopant solutions. It can be seen that both samples had the similar band near 610 cm^{-1}, bands #1-2 (609 cm^{-1}) and #2-2 (610 cm^{-1}), which were attributed to the Sn-O vibration. For the film fabricated using both $SbCl_3$ and HNO_3 in doping solution, the band #2-1 (462 cm^{-1}) were assigned to the O-Sn-O stretching vibration. However, in the case of films fabricated using only HNO_3 in doping solution, the band #1-1 (489 cm^{-1}) corresponds to the O-Sn-O group, which showed a large shift compared to the band #2-1.

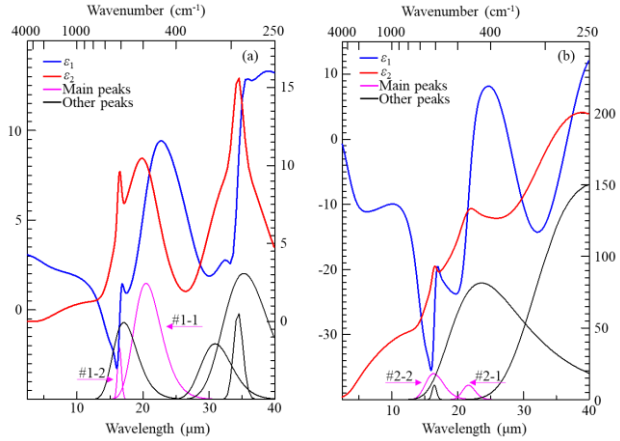

Fig. 2 Long-wavelength optical constants of (a) the film fabricated using HNO_3; (b) the film fabricated using both $SbCl_3$ and HNO_3

4. Conclusions

The SnO_x:Sb thin films with low resistivity (9.0×10^{-4} Ω cm) were successfully fabricated using novel mist CVD system. In this work, it was found that the HNO_3 in doping solution has a positive effect on the conductivity of SnO_x films. The experimental results show that moderate amount of HNO_3 in doping solution improved the conductivity, and the resistivity of the films fabricated using $SbCl_3$ and HNO_3 in doping solution was much lower than that using either $SbCl_3$ or HNO_3. The N (V) originated from HNO_3 acted as dopant and/or oxidizing agent were put forward to explain the behaviors of HNO_3 in the film fabrication process. Moreover, the XPS and IR-VASE results confirmed the tin oxide thin films fabricated using $SbCl_3$ and/or HNO_3 in doping solution were a mixture of SnO and SnO_2.

References

[1] J. Müller et al, Int. Solar Energy 77 (2004) 917.
[2] T. Minami, Thin Solid Films 516 (2008) 1314.
[3] D. S. Ginley and C. Bright, MRS Bull. 25 (2000) 15.
[4] E. Fortunato et al, MRS Bull. 32 (2007) 242.
[5] S. S. Lin et al, Appl. Surf. Sci. 380 (2016) 203.
[6] J. S. Jeng, Appl. Surf. Sci. 258 (2012) 5981.
[7] S. Dalui et al, Appl. Surf. Sci. 278 (2013) 127.
[8] T. M. Hammad and N. K. Hejazy, Int. Nano Lett. 2 (2012) 7.
[9] J. Montero et al, Sol Cells 94 (2010) 612.
[10] T. Hiramatsu et al, Japan, WO2016203595 A1, 2016-12-22
[11] T. Kawaharamura et al, The 64th JSAP Spring Meeting, Japan, 2017, p. 17a-502-10
[12] T. Kawaharamura et al, The 78th JSAP Autumn Meeting, Japan, 2017, p. 7a-C17-2.