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Study on the Influence Factors of Antimony Doped Tin Oxide Thin Films With High Conductivity Deposited *via* Mist CVD

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Abstract

High conductive (9.7×10^{-4} Ω cm) antimony doped tin oxide (ATO) thin films were successfully grown by mist CVD. In order to further improve the conductivity, we prepared SnO_x thin films using various solutions with different additive components; followed by identification of components contributing to high conductivity of the thin films. Experimentally, it was found that conductive tin oxide thin films could not be obtained by using only $SbCl_3$ solution, while high conductivity thin films were obtained by using both $SbCl_3$ and HNO_3 solutions. Higher conductive SnO_x thin films have been fabricated based on these results.

1. Introduction

Transparent conducting oxide (TCO) films are widely used in a variety of optoelectronic devices because of their low electrical resistivity and high optical transmittance. Among the various TCO thin films, one of most appropriate and popular material is tin oxide due to the high chemical stability, mechanical hardness, and heat resistant properties [1]. Previously, it was reported that the conductivity of tin oxide was improved by common dopants such as fluorine (F), indium (In), and antimony (Sb). As a doping material, anitmony has the characteristics of stable chemical nature, extensive origin and non-toxicity, these characteristics indicate that Sb is more suitable to prepare TCOs in comparison to F or In. Sb-Doped SnOx (ATO) thin films have been prepared by several methods, such as RF sputtering, chemical vapor deposition, dip coating, sol-gel coating, and spray pyrolysis [1-5].

In this research, ATO thin films were fabricated by mist chemical vapor deposition (CVD), which is one of the functional thin film fabrication techniques using precursor solutions under open-air atmospheric-pressure. Mist CVD is designed to achieve uniform flow and homogenous temperature in the fine channel reactor, which was previously reported in the literature [6].

2. Experimental

ATO thin films were deposited on quartz substrates under atmospheric pressure at 400°C. Tin(II) chloride dihydrate ($SnCl_2\cdot 2H_2O$) and antimony (III) chloride ($SbCl_3$) were used as the host precursor and the dopant, respectively. These materials dissolved in H_2O with a few mL of HCl (aq) and HNO_3 (aq). Especially, the tin precursor solution and antimony doping solution were added to different solution chambers in Mist CVD system. Quartz substrates were cleaned by acetone, isopropanol, and deionized water each for 2 min prior to the thin film fabrication. The detail condition of precursor solution preparation and film deposition are given in Table I.

Table I Experimental conditions

Solute A, concentration	$SnCl_2\cdot 2H_2O$, 0.02mol/L
Solute B, concentration	$SbCl_3$, 0.002mol/L
Solvent A	3% HCl (aq) + 1% HNO_3 (aq) + H_2O
Solvent B	HCl (aq) + HNO_3 (aq) + H_2O
Growth time	10min
Substrate	Quartz
Substrate temperature	400 °C
Growth system	Fine-channel type mist CVD system
Carrier gas	N_2
Dilution gas	N_2
Ultrasonic transducer	2.4MHz, 24V· 0.625A, 3

The thickness of sample (t) was measured by spectroscopic ellipsometer (J.A. Woollam Japan, WVASE). The sheet resistance (R_S) of thin films was studied by the Hall effect setup in the Van der Pauw configuration. The electrical resistivity (R) and conductivity (σ) of the thin films were determined by the relation $R = R_S \cdot t$ and $\sigma = 1/R$, respectively.

3. Results and discussions

Figure 1 shows the electrical properties and thickness of ATO thin films with different $SbCl_3$ ratios. Sb-Doped SnO_x (ATO) thin films were fabricated using 0%, 2%, 6%, 8%, 10% and 18% of $SbCl_3$ in doping solution. The thicknesses of ATO thin films were in the range from 200 nm to 300 nm. The resistivity of the thin films initially decreased with the ratio of $SbCl_3$ until 6%, then increased slightly again, the minimum value of resistivity (9.72×10^{-4} Ω cm) was obtain with the 6% $SbCl_3$. In comparison to non-doped SnO_x, Sb doping led to the increase in carrier density and Hall mobility. However, the carrier density increased and the Hall mobility decreased with the increase in Sb ratio.

In general, the substitution of Sn^{4+} by Sb^{5+} is the major possible reason for the decrease in resistivity, as previously reported in the literature [1]. Thus, it should be identified which component in solution contributes to the high conductivity of SnO_x in order to further improve the conductivity.

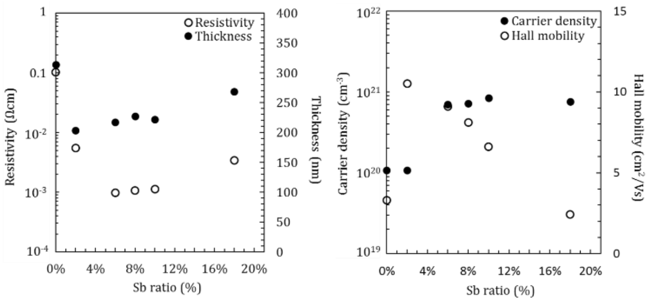

Fig. 1 Electrical properties and thickness of ATO thin films with different Sb ratios

In the preparation of the $SbCl_3$ solution, HCl (aq) was used to dissolve the $SbCl_3$. High concentration HCl (aq) of around 3.5% (*v*/*v*) was required for dissolving $SbCl_3$ to achieve 2 mmol/L in H_2O, although ATO thin films could not be fabricated by mist CVD. It is suspected that SnOx thin film was etched with high concentration HCl (aq) at the operating temperature around 300°C. However, only low concentration HCl (aq) around 0.84% (*v*/*v*) was needed for dissolving $SbCl_3$ to achieve 0.5 mmol/L in H_2O, which enabled the fabrication ATO thin films by mist CVD, while those ATO thin films showed a high resistance (>10^8 Ω cm).

The resistivity of thin films fabricated by different solutions are shown in Table II. It is obvious that, the resistivity of ATO thin films fabricated using $SbCl_3$ and HNO_3 solutions simultaneously, was much lower than the resistivity of films fabricated using either $SbCl_3$ or HNO_3 solution.

Table II Resistivity of films fabricating using different solutions

		$SbCl_3$	
		×	○
HNO_3	×	>10^8 Ω cm	>10^8 Ω cm
	○	7.62×10^{-3}Ω cm	9.72×10^{-4} Ω cm

Then conductive tin oxide thin films had been prepared with HNO_3 solution excluding $SbCl_3$. Figure 2 shows the relation between electrical properties and thickness of thin films and the HNO_3 concentration. The resistivity increased gradually with the increase of HNO_3 concentration, and lowest resistivity (7.62×10^{-3} Ω cm) was obtained when the concentration was 1%. Nitrogen (N) is multi valence nonmetallic element, so it is deduced that the substitution of Sn^{4+} and O^{2-} by N^{5+} and N^{3-} derived from HNO_3, may be one reason for obtaining the conductive thin films. In previous studies of fabricating ATO thin films, antimony doping ratio is regarded as the major factor of increasing conductivity. However, there were a few studies reported on nitrogen doping tin oxide [7, 8]. In these research, N_2 was used as the regular source of nitrogen, and they focused on the effect of nitrogen on the structural, electronic, optical and magnetic properties of tin oxides. In our research, it was found that the intrisic N existed in tin oxide thin films from XPS measurement (the images were not showed in paper). So the nitrogen originated from HNO_3 (aq) was considered as an important factor in fabrication of conductive thin films, and the concentration of HNO_3 affected the resistivity of the thin films. However, the resistivity of the tin oxide thin films fabricated using HNO_3 is larger than that of the ATO thin film (1.29×10^{-3} Ω cm), as reported in [9]. From the figure of carrier density and Hall mobility, it can be seen that carrier density initially increased with the increasing HNO_3 concentration, but decreased again for the further increase. Different from the changing tendency of carrier density, the figure did not indicate a clear relationship between Hall mobility and the HNO_3 concentration.

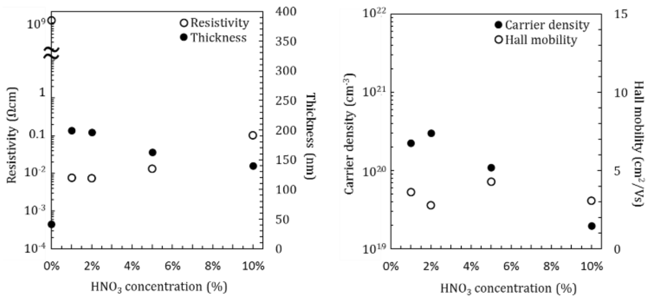

Fig. 2 Electrical properties and thickness of ATO thin films with different HNO_3 concentration

4. Conclusions

In this research, ATO thin films with high conductivity were successfully fabricated by mist CVD. To improve the conductivity of ATO thin films, the effect of each component in solution on the conductivity of ATO thin films was investigated. When 2% HNO_3 (aq) and 6% $SbCl_3$ in doping solution were used, the ATO thin films with low resistivity (9.72×10^{-4} Ω cm) was obtained. HCl (aq) is important for dissolving $SbCl_3$ in H_2O, however the excess HCl (aq) may etch the ATO thin films. Nitrogen originated from HNO_3 (aq) in the solution was obviously having a positive effect on obtaining ATO thin films with high conductivity. Study on the effects of $SbCl_3$ ratio and HNO_3 concentration on fabrication of ATO thin films by mist CVD is promising to improve the electrical properties of the ATO thin films.

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