Growth and Characterization of Co-Doped Fluorine and Antimony in Tin Oxide Thin Films Obtained by Ultrasonic Spray Pyrolysis*

Thitinai GAEWDANG** and Ngamnit WONGCHAROEN**

** Department of Applied Physics, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang

3 Moo 2, Chalongkrung Rd., Ladkrabang District, Bangkok, 10520, Thailand.

E-mail: kgthitin@kmitl.ac.th

Abstract

Fluorine (F)-doped, antimony (Sb)-doped, fluorine and antimony co-doped tin oxide (SnO_2) thin films were prepared by ultrasonic spray pyrolysis technique using SnCl_2 , NH_4F and SbCl_3 as precursors of Sn, F and Sb elements respectively. F and Sb doping concentrations carried out from 1 to 20 wt% and 1 to 4 wt% in F-doped and Sb-doped SnO_2 films respectively. In F and Sb co-doped SnO_2 films, the proportions of F and Sb to Sn in starting solution were 15 and 2 wt% respectively. XRD patterns showed that the preferred orientation of $\text{SnO}_2\text{:F}$, $\text{SnO}_2\text{:Sb}$ and $\text{SnO}_2\text{:F,Sb}$ is dependent on the doping concentration. The variation of doping concentration and preferred orientation of the films was reflected in their morphology as investigated by SEM. The electrical properties of the films were performed by Hall effect measurements in van der Pauw configuration. The minimum resistivity values of $\text{SnO}_2\text{:F}$ and $\text{SnO}_2\text{:Sb}$ were found in the films doped with 15 wt% of F and 2 wt% of Sb. However, The minimum of resistivity value of F and Sb co-doped SnO_2 films is not better than neither the one of F-doped nor the one of Sb-doped SnO_2 films. The optical transmission of $\text{SnO}_2\text{:F}$ films was found to increase with increasing in F doping concentration. Whereas the optical transmission of $\text{SnO}_2\text{:Sb}$ was found to decrease with increasing in Sb concentration. The F and Sb co-doped SnO_2 films annealed in three different conditions at 500 °C show the lower transmission values than the value obtained in the as-prepared $\text{SnO}_2\text{:F,Sb}$ films.

Key words: SnO_2 Thin Films, F and Sb Doping, Electrical Properties, Optical Properties

1. Introduction

Tin oxide films have a wide range of applications due to its high electrical conductivity and high transparency in visible and near infrared region of solar radiation. These films are used as transparent electrodes in gas sensors (1), solar cells (2) and in photovoltaic devices (3). It is demonstrated that appropriate doping can enhance the conductivity of these films. The reason for the enhancement in conductivity is that the suitable dopant atoms introduce more free carriers, normally electrons in the case of almost all transparent conducting oxides. In general, these materials are n-type conducting characteristics.

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Thin films of tin oxide can be prepared by various techniques such as chemical vapor deposition, r.f. sputtering, spray pyrolysis, etc. Among the various deposition techniques available, spray pyrolysis is the most convenient method because of its simple and inexpensive experimental setup, ease of adding doping materials, high growth rate and mass production capability for uniform large area coatings, which are desirable for industrial applications. SnO_2 :F films are very attractive because of their good adhesion to many polycrystalline and amorphous substrates such as glasses, metals and oxides. The reports on F and Sb co-doped SnO_2 thin films are very scarce. Hence, the main objective of the present work is to prepare transparent and high conductivity F and Sb co-doped SnO_2 from $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ precursor and to investigate its structural, electrical and optical properties.

2. Experimental Details

Thin films of undoped, F-doped, Sb-doped, F and Sb co-doped SnO_2 were prepared by a home-made ultrasonic spray pyrolysis experimental setup. Stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) of 0.2M was used as precursor of tin. The tin precursor dissolved in concentrated HCl and subsequently diluted with methanol served as starting solution. NH_4F and SbCl_3 dissolved in deionized water were added into the starting solution in order to dope the films; the variation of proportions of F and Sb to tin in starting solution were 5 to 20 and 1 to 4 wt % respectively. In the case of F and Sb co-doped SnO_2 films, the proportions of F and Sb to tin were 15 and 2 wt% respectively. The starting solutions were heated at 90°C for 15 min. The amount of spray solution prepared was 200 ml for all depositions. The well-cleaned slide glass was used as substrate. During deposition process, the substrate temperature was kept at 400°C . The carrier gas flow rate was maintained a pressure of 5 kPa and deposition time is 15 min using ultrasonic wave with frequency 17 MHz to generate mist of solution. The obtained films were annealed in air, vacuum and N_2 ambients for 30 min. X-ray diffraction (XRD) measurements using CuK_α radiation were performed to study the preferential orientation and crystallinity of the films. Grain size and surface morphology were revealed in accordance to SEM. The optical transmission spectra of films were measured in the wavelength ranging from 300 to 2,500 nm. The electrical properties studies were carried out by Hall effect measurements in van der Pauw configuration.

3. Results and Discussion

The formation of SnO_2 films from the SnCl_2 solution gives rise to a transitory formation of the compound SnO . The chemical reactions taking place are

Simultaneously, the decomposition of ammonium fluoride takes place according to the equation (4)

The decomposition temperature of ammonium fluoride is quite low. Therefore, it takes place almost instantaneously and forms a cloud of HF in the vicinity of the growing SnO_2 films. There is a possibility of chemical reaction between the growing SnO_2 films and the halo-acid. In this case, the following reaction would take place

and this would obviously result in retarding the formation of the layers. The law of mass action of these equations suggests that the externally added dopant increases the rate of backward reaction through the fourth power dependence of HF concentration. Hence, HF will determine the rate of deposition of the SnO_2 films by the competition between the rate of formation of SnO_2 and the rate of etching of SnO_2 (4). Since HF is a product from the doping NH_4F . Thus, the deposition rate can be correlation to the amount of dopant. The increase in deposition rate with the increase in the amount of NH_4F doping has already reported by Elangovan and Ramamurthi (5).

Fig.1 XRD patterns of $\text{SnO}_2\text{:F}$ films prepared with different F concentrations.

Fig.1 shows the XRD patterns of $\text{SnO}_2\text{:F}$ thin films prepared with different fluorine concentrations. The films were found to be of cassiterite type with a tetragonal rutile structure. The calculated values of lattice parameters “a” and “c” of undoped SnO_2 are 4.735 and 3.192 Å respectively, and found to be in good agreement with the standard data (6). The lattices parameters “a” and “c” simultaneously with increasing fluorine doping concentration. Undoped and F-doped SnO_2 films grow along the preferred orientation (200). The preferred growth of (200) plane increases with increasing fluorine doping concentration. Small difference in preferred growth of Sb-doped SnO_2 films are observed in Fig. 2. The Strongest intensity of the (200) plane is observed in SnO_2 films prepared with 2 wt % Sb doping. However, the preferred growth of (200) plane is disappeared in the SnO_2 films doped with F (15 wt %) and Sb (2 wt %) (as shown in Fig. 3).

XRD patterns of F and Sb-doped SnO_2 films annealed in air, vacuum and N_2 ambient at 500 °C are shown in Fig. 4. The absence of preferred growth of the co-doped SnO_2 films was observed in vacuum annealing condition. In contrast, the preferred orientation of (200) plane of co-doped SnO_2 films was displayed in air annealing condition. However, the (211) diffraction plane is predominant in the co-doped SnO_2 films annealed in N_2 ambient.

The films obtained by this method were smooth, uniform adherent and transparent in visible light region. The preliminary estimation of film thickness was obtained from the mass of the deposited materials using the gravimetric method. The standard density value of tin oxide (6.994 g/cm³) was used for the calculation (7). The film thickness was consequently verified with the cross-sectional SEM micrographs and found that the values are in agreement with our preliminary estimation.

Fig.2 XRD patterns of SnO_2 :Sb films prepared with different Sb concentrations.

Fig.3 XRD patterns of SnO_2 :F,Sb films prepared with 15wt% of F and 2 wt% of Sb.

The SEM micrographs of SnO_2 :F films prepared with different fluorine concentrations are shown in Fig. 5. The undoped SnO_2 films show large grains whereas all the doped films show the characteristic needle shaped grains. The undoped films have the grains of bigger in size and of almost uniform whereas all the F-doped films contain fine needle shaped grains. The morphology shown for 20wt.% F-doped films has very fine grains.

The SEM micrographs for SnO_2 :Sb films prepared with different antimony doping concentrations are shown in Fig. 6. The smaller grains started appearing on the surface, once the antimony doping has commenced. The number of smaller grains increased with increase in Sb doping. The needle shaped grains has appeared on the surface of Sb-doped films for those having preferred orientation along (200) plane. For the films doped with 2 wt% of Sb, the biggest needle shaped grains were observed. As seen from the XRD patterns, these films have the preferred orientation are along (200) plane. Thus, SEM micrographs is in good agreement with XRD patterns.

Fig.4 XRD patterns of $\text{SnO}_2\text{:F,Sb}$ films annealed at 500°C with different conditions.

Fig.5 SEM micrographs of $\text{SnO}_2\text{:F}$ films prepared with different concentrations.

The SEM micrographs of SnO_2 films doped with 15 wt% of F and 2 wt% of Sb are also shown in Fig. 7. Annealing conditions may lead to increase in grain size. However, two types of grain size, large and small size, are appeared in the F and Sb co-doped SnO_2 films annealed in vacuum. But grains of almost similar size observed in the films annealed in N_2 ambient. However, the films annealed in air show irregular shape with different sizes.

Fig.6 SEM micrographs of $\text{SnO}_2\text{:Sb}$ films preped with different concentrations.

Fig.7 SEM micrographs of $\text{SnO}_2\text{:F,Sb}$ films annealed at 500 °C with different conditions.

The electrical measurements were carried out using Hall measurements in van der Pauw configuration. The negative sign of Hall voltage confirmed that the films are n-type conducting. The variation of electrical resistivity, Hall mobility and carrier concentration of the $\text{SnO}_2\text{:F}$ films a function of film F doping concentration are plotted in Fig. 8. It is found that the electrical resistivity value decreases with increasing fluorine concentration initially to reach a minimum value ($1.43 \times 10^{-3} \Omega \text{ cm}$ at 15 wt% of F) that afterwards increases for further increase in doping. When F is incorporated in SnO_2 films, each F⁻ anion substitute an O^{2-} anion in the lattice and the substituted O^{2-} anion introduces more free electron (8). This results in an increase of free electrons and hence decreases the value of resistivity. The increase in the value of resistivity beyond a certain doping concentration of F probably represents a solubility limit of F in the SnO_2 lattices. The excess F atoms do not occupy the proper lattice positions to contribute to the free carrier concentration, while at the same time increase the disorder of the structure leading to an enhance in resistivity. This was observed in the films beyond 15 wt% of F doping.

Fig.8 Variation of resistivity, Hall mobility and carrier concentration of SnO₂:F films.

The Hall mobility of the films decreases with increasing F doping concentration in the whole doping range of this study. The Hall mobility of the undoped SnO₂ films was 46.3 cm²/Vs and found to decrease to a value of 11.9 cm²/Vs for 15 wt % of F. On contrary, the carrier concentration of the undoped films is found to increase from 1.6 × 10¹⁹ for the undoped films to 3.8 × 10²⁰ cm³ for 15 wt % of F. In the case of SnO₂:F films, F appears to be the most favored substituent because of the following reasons (5): (i) its ionic size (F⁻: 1.33 Å) very closely matches with that of oxygen (O²⁻: 1.32 Å), (ii) the energy of Sn-F bond (~26.75 D°/kJmol⁻¹) is comparable to that of the Sn-O bond (~31.05 D°/kJmol⁻¹) and (iii) since the charge on the F⁻ is only half of the charge of the O²⁻, Coulomb forces that bind the lattice together are reduced (5). Thus, geometrically the lattice is nearly unable to distinguish between F⁻ and O²⁻. But this increase does not precede much further. The reduction in carrier concentration for higher doping levels suggests a probable interstitial incorporation of the dopant, taking place in the SnO₂ lattice. The corresponding peak value of carrier concentration has been obtained for the films prepared with 15 wt % of NH₄F.

The variation of electrical resistivity, Hall mobility and carrier concentration of SnO₂:Sb films are plotted in Fig. 9 with Sb doping concentration. The resistivity decreases to minimum value being 1.6 × 10⁻³ Ω cm on 2 wt% of Sb but then increase for the doping of Sb above 2 wt %. the color of the films varied from milky white for undoped SnO₂ to light blue for low concentrations of Sb (1 wt %). The intensity of the blue color gradually increases with increase in doping concentration and became blackish-blue beyond 3 wt % of Sb. Hall mobility of the films decreases with increasing Sb doping concentration in the whole doping range of present study. On the other hand, the carrier concentration increases with increase in F doping initially but then decreases for the further increase in Sb doping. The electrical measurements of the present work suggest that the 2 wt % of Sb doping is the optimum doping level for achieving better electrical properties.

The variation in the electrical resistivity of SnO₂ thin films with Sb doping can be explained on the basis of the presense of Sb in two oxidation states namely Sb⁵⁺ and Sb³⁺. When SnO₂ is doped with Sb, a part of the lattice Sn⁴⁺ atoms are replaced by Sb⁵⁺ resulting in the generation of conduction electrons and thus reducing the resistivity (5). Hence continuous a of resistivity is observed until Sb concentration lower 2 wt %. Beyond 2 wt % of Sb doping, a part of the Sb⁵⁺ ions may probably reduces to the Sb³⁺ state resulting in the formation of acceptor sites and concurrent loss of carriers (5) and hence an increase in resistivity occurs. Kojima et al.(9) have verified the reduction of Sb⁵⁺ and Sb³⁺ by an estimation of the lattice parameter of the Sb-doped SnO₂ films. Since, the ionic radius of Sn⁴⁺ is less than Sb³⁺ but higher than that of Sb⁵⁺, an increase in the lattice parameter of SnO₂ phase is observed beyond 2 wt% of Sb doping. This reduction of Sb⁵⁺ to Sb³⁺ can be attributed as the reason for the increase in resistivity above an optimum level of Sb doping (2 wt%).

Fig.9 Variation of resistivity, Hall mobility and carrier concentration of SnO₂:Sb films.

In order to prepare F and Sb co-doped SnO₂ films, F and Sb concentrations as 15 and 2 wt % were used. The electrical resistivity, Hall mobility and carrier concentrations are shown in table 1. These values obtained in F and Sb co-doped SnO₂ films are not better than neither the ones of F-doped SnO₂ films nor the ones of Sb-doped SnO₂ films. It may imply that, in the case of coexistence of F and Sb dopant in SnO₂ films, first and foremost the suitable amounts of F and Sb doping concentration should be evaluated. Among different annealing conditions F and Sb co-doped SnO₂ films annealed in N₂ ambient show the best results (as shown in Table 2).

Table1 Important parameters of undoped and doped SnO₂ films.

Parameters	SnO ₂ (undoped)	SnO ₂ :F (15 wt%)	SnO ₂ :Sb (2 wt%)	SnO ₂ :F,Sb (15,2 wt%)
Resistivity (x10 ⁻³ Ω cm)	8.6	1.4	1.6	2.3
Hall Mobility (cm ² /V.s)	46.3	11.9	26.2	37.7
Carrier Concentration (x10 ¹⁹ cm ⁻³)	1.6	38.1	15.2	7.4

Table 2 Important parameters of F and Sb co-doped SnO₂ films annealed in different Ambients.

Parameters	Annealing Ambients			
	As-prepared	N ₂	Vacuum	Air
Resistivity (x10 ⁻³ Ω cm)	2.3	1.5	2.1	3.4
Hall Mobility (cm ² /V.s)	37.7	24.9	31.3	49.8
Carrier Concentration(x10 ¹⁹ cm ⁻³)	7.4	17.1	9.7	3.7

The optical transmission of SnO₂:F films with different F doping concentrations is shown in Fig.10. The transmittance of the F-doped SnO₂ films was found to increase with increasing in F doping concentration. The transmittance value of about 93 % for 15 wt % of F doping (at 600nm). The color of the undoped SnO₂ films is milky white and became colorless on 15 wt % of F doping. The lowest transmittance at wavelength above 1,500 nm is observed in the SnO₂ films doped with 15 wt % of F.

Fig.10 Transmittance spectra of $\text{SnO}_2\text{:F}$ films with different F concentrations.

The optical transmission of $\text{SnO}_2\text{:Sb}$ films for different Sb doping concentration is shown in Fig.11. The transmittance of the Sb-doped SnO_2 films, in contrast to the F-doped SnO_2 films, was found to decrease with increasing in Sb concentration. The lowest transmittance at wavelength above 1,500nm is observed in the SnO_2 films doped with 2 wt % of Sb. The decrease in transmittance with increase of Sb doping can be explained as follows. Kojima et al. have studied the blackening of oxide thin films, which were heavily doped with antimony. They reported that the blackening must result from light absorption in the films. It is a known fact that a material containing an element in two different oxidation states or in a mixed oxidation state (like $\text{SnO}_2\text{:Sb}$) reveals abnormally deep an intense coloration (9). The transmittance of $\text{SnO}_2\text{:Sb}$ films with increase in doping concentration may be due to the increasing absorption by free electrons. Heavy doping of Sb may lead to increase in the degenerate nature of the films, which results in light absorption. Hence, the transmission spectra recorded for different doping levels of Sb show a consistent decrease with increasing Sb doping concentration.

Fig.11 Transmittance spectra of $\text{SnO}_2\text{:Sb}$ films with different Sb concentrations.

Fig.12 shows the optical transmission of the F and Sb co-doped SnO_2 films annealed with different conditions. The F and Sb co-doped SnO_2 films without annealing show the highest transmittance of 78 % (at 1,000 nm). But the all annealed films at 500 °C show the lower transmission value than the value obtained in the as-prepared SnO_2 films. However, the similar optical transmission of $\text{SnO}_2\text{:F,Sb}$ films annealed in three different conditions are observed. It may suggest that annealing ambients probably are less influence on the F and Sb co-doped SnO_2 films than the annealing temperature. Further efforts are on to find out the optimum value of F and Sb amounts of co-doping in SnO_2 films achieving the best electrical resistivity and optical transmission values.

Fig.12 Transmittance spectra of $\text{SnO}_2\text{:F,Sb}$ films with different doping concentrations.

4. Conclusion

Thin films of F-doped, Sb-doped, F and Sb co-doped SnO_2 were successfully prepared by ultrasonic spray pyrolysis technique using SnCl_2 , NH_4F and SbCl_3 as the source of Sn, F and Sb respectively. XRD patterns show that undoped, F-doped and Sb-doped SnO_2 films grow along the preferred orientation (200) whereas the preferred growth of (200) plane is disappeared in the SnO_2 films doped with 15 wt % of F and 2 wt % of Sb doping concentration. The minimum values of resistivity of F-doped and Sb-doped SnO_2 films were found to the films corresponding to doping concentration 15 wt % of F and 2 wt % of Sb. However, the minimum value of resistivity of F and Sb co-doped SnO_2 films is not better than neither the one of F-doped nor the one of Sb-doped SnO_2 films. The optical transmission of $\text{SnO}_2\text{:F}$ films was found to increase with increasing in F doping concentration. Whereas the optical transmission of $\text{SnO}_2\text{:Sb}$ was found to decrease with increasing in Sb concentration. The F and Sb co-doped SnO_2 films annealed in three different conditions at 500°C show the lower transmission value than the value obtained in the as-prepared SnO_2 films. Further efforts are under progress to find out the optimum value of F and Sb co-doping contents which will give rise to the better resistivity and optical transmission values reported in this article.

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