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SOME PHYSICAL PROPERTIES OF SPRAY DEPOSITED SnO_2 THIN FILMS

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Thin films of tin oxide (SnO_2) were deposited on various substrates by spray pyrolysis technique using $SnCl_2$ as precursor. The as-prepared films were characterized for their electrical, optical and structural properties. Films deposited on optical glass showed the better electrical properties as compared to those deposited on other substrates. Further, fluorine- and antimony- doped SnO_2 films were deposited on these substrates. The fluorine- doping resulted in enhancing both the electrical and optical properties of these films. On the other hand antimony- doping enhanced the electrical properties of the films but decreased the optical properties. The preferred orientation (211) of undoped films was found shifted to (200) for both the dopants. The change in orientation was reflected in SEM studies as they have different grain shapes. The minimum sheet resistance of 1.8 and 2.2 Ω/□ obtained for the films SnO_2:F and SnO_2:Sb deposited on glass are the lowest among the reported values for these materials prepared from $SnCl_2$ precursor. The 42 % transmittance of undoped films found increased to 85 % on fluorine- doping (15 wt. %) but decreased to 20 % on antimony-doping (2 wt. %).

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1. Introduction

Thin films of tin oxide (SnO_2) that are coming under the category of transparent and conducting oxides are useful as solar windows in photovoltaic devices. Although the investigation on tin oxide has commenced in 1930s [1], the increased performance and application of this material lead to work on it till date [2]. The sensitivity of this material to various gases is excellent and this has motivated the research on SnO_2 based sensors to a great extent [3-5]. The detailed literature survey suggested that the work on this material from $SnCl_2$ precursor is very scarce [6]. The advantage of $SnCl_2$ precursor is cost effective which suits the intention of the present work to prepare low-cost, high conducting SnO_2 films. The films in the present study are hence prepared with this cost effective precursor on various substrates. This study revealed that the films produced on optical glass have excellent electrical properties. Further, fluorine- and antimony- doped SnO_2 films were deposited on optical glass alone by retaining the same parameters.

2. Experimental details

Thin films of tin oxide were deposited on various substrates by employing the homemade spray pyrolysis experimental setup. The substrates used were the optical glass, corning 7059, pyrex and fused quartz. The schematic diagram of the experimental setup is given elsewhere [6]. The films were prepared with the optimized substrate temperature of 400 °C [7-8]. An 11 g of $SnCl_2{\cdot}2H_2O$

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dissolved in concentrated HCl by heating at 90 °C for 10 minutes and subsequently diluted with methanol formed the starting solution. For fluorine- doping ammonium fluoride (NH_4F) dissolved in doubly distilled water was added to the starting solution. Whereas for antimony- doping antimony-tri-chloride ($SbCl_3$) dissolved in isopropyl alcohol was added. The overall amount of solution in each case was prepared up to 50 ml and the same amount of solution was sprayed on pre-heated substrates. The repeated experiments of each deposition showed that the films could be reproduced easily. An extensive care was taken in giving sufficient spray interval between successive sprays for the substrates get back to deposition temperature after undergoing thermal decomposition. This has resulted in the proper decomposition of the films that in turn produced the lowest ever sheet resistance values reported for the doped SnO_2 films from $SnCl_2$ precursor. The electrical studies were carried out by Hall measurements in van der Pauw configuration. The surface morphology was studied using JSM 840 scanning electron microscopy. A Philips X' Pro X-ray diffractometer has been used for obtaining XRD patterns. The transmittance and reflectance spectra are obtained using Hitachi U-3400 double beam spectrophotometer.

3. Results and discussion

3.1. Undoped SnO_2 films deposited on various substrates

Electrical properties

The negative sign of Hall coefficient confirmed that the films are n-type. The variation of resistivity as a function of temperature showed that the films are degenerate in nature. The sheet resistance (R_{sh}) and resistivity (ρ) obtained for various substrates are shown in Fig. 1. It is perceptible from the figure that the lowest R_{sh} and ρ values are obtained for the films those deposited on optical glass (OG). The lowest R_{sh} value of 38.2 Ω/□ obtained for the films deposited on OG was found increased to 72.1 Ω/□ for those deposited on pyrex glass (PG). The Hall mobility and carrier concentration obtained for the films deposited on various substrates are shown in Fig. 2. The Hall mobility of 109.6 $cm^2\ V^{-1}\ S^{-1}$ obtained for the films deposited on OG found to increase to a maximum of 132.5 $cm^2\ V^{-1}\ S^{-1}$ for those deposited on PG. On the other hand the highest carrier concentration value of 1.2×10^{19} obtained for the films deposited on OG was found decreased for the films deposited on other substrates.

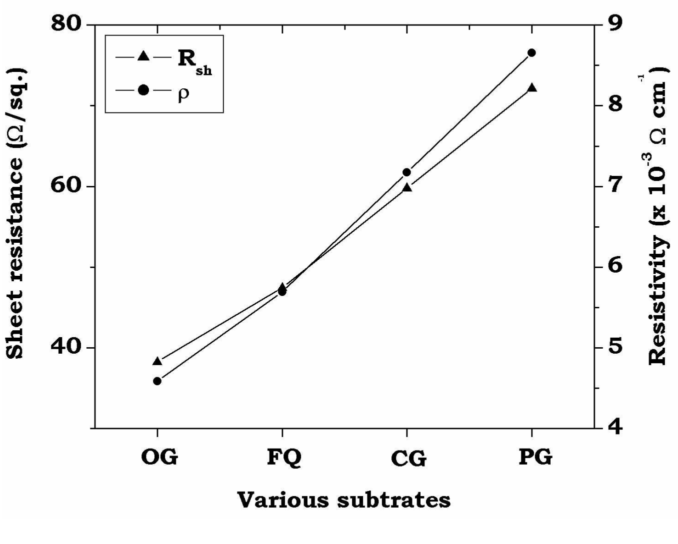

Fig. 1. Sheet resistance (R_{sh}) and resistivity (ρ) obtained for undoped SnO_2 films on various substrates: OG-Optical glass; FQ-Fused quartz; CG-Corning 7059 and PG-Pyrex.

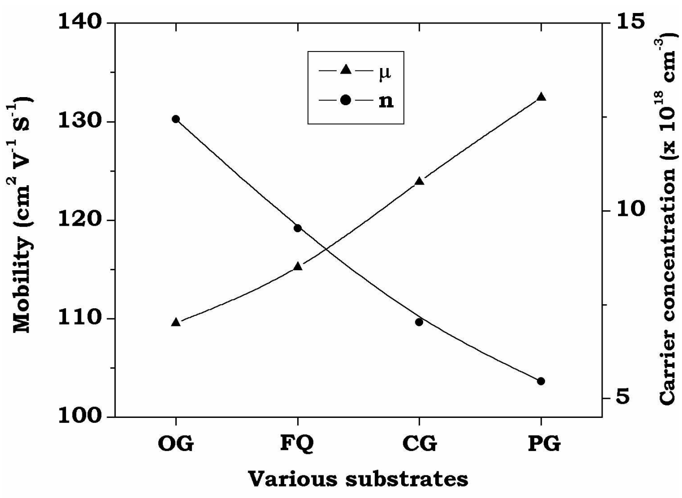

Fig. 2. Hall mobility (μ) and carrier concentration (n) obtained for undoped SnO_2 films deposited on various substrates.

Optical properties

The transmittance spectra recorded for the films deposited on various substrates in the wavelength range of 300-1300 nm is shown in Fig. 3. The transmittance spectrum of film quoted on OG is shown comparatively with doped films in Figs. 6 & 7. An uncoated (blank) substrate of each type has been used as the reference for obtaining the transmittance spectra. The figure shows that the film deposited on FQ has the maximum transmittance than those deposited on other substrates. The difference in transmittance between the films deposited on FQ and CG is feeble. Whereas the film deposited on PG show a comparable decrease in transmittance in the visible and near NIR region. Although the transmittance of films deposited on OG showed slightly lesser value, conductivity was considerably better than other substrates. Further, the figure of merit calculated from Haacke's formula [9] showed higher values for the films deposited on OG than other substrates. The figure of merit is a parameter that gives a better measure for the suitability of materials for window materials. Hence, the films deposited on OG are suitable for to be used as solar window provided both the conductivity and transmittance have been increased further. Hence the further work has been carried out with the same deposition parameters and keeping OG as substrate for fluorine- and antimony-doping.

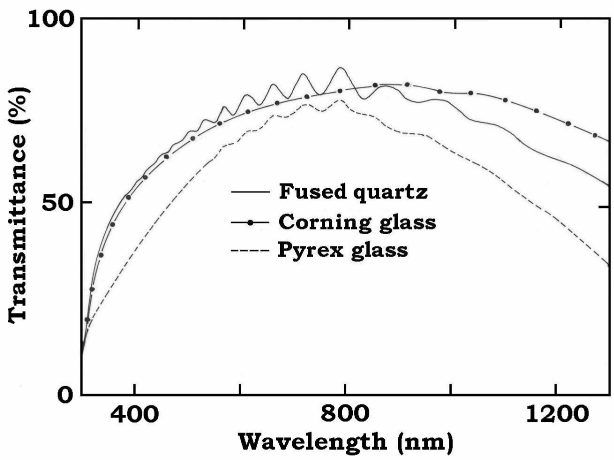

Fig. 3. Transmittance spectra of undoped SnO_2 films deposited on various substrates.

3.2. Doped SnO_2 films deposited on glass

3.2.1. Structural properties

With the parameters reported in section 3.1, the films of fluorine- and antimony- doped SnO_2 were deposited on optical glass substrates for different doping concentrations. It is found that the 15 wt. % of fluorine- doping and 2 wt. % of antimony- doping produced the best electrical properties. Hence in the foregoing discussion undoped films on optical glass are compared with the films doped with these two doping levels. The X-ray diffraction studies showed that the films are polycrystalline in nature with tetragonal rutile structure (JCPS card no. 41-1445). The XRD patterns obtained for undoped, 15 wt. % fluorine- and 2 wt. % antimony- doped SnO_2 films are shown in Fig. 4. It is perceptible from the figure that the undoped films grow along the preferred orientation of (211) whereas all the doped films grow along (200). Presence of other orientations such as (110), (101), (310), (301) and (321) have also been detected with considerable intensities for the undoped films. Whereas the secondary peaks are negligibly small for the doped films as compared to undoped films.

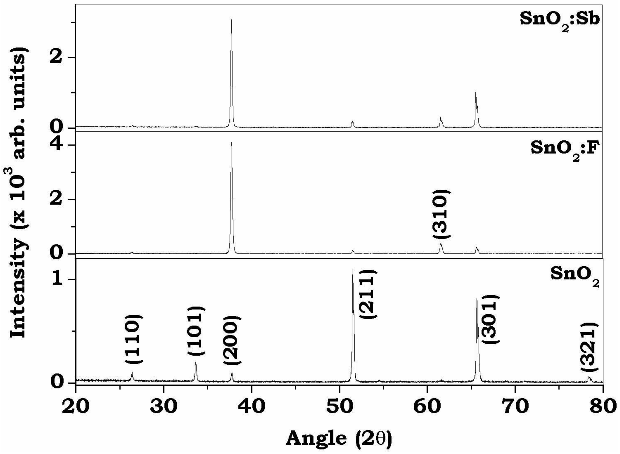

Fig. 4. XRD patterns of undoped and fluorine- and antimony doped SnO_2 thin films deposited on optical glass substrates.

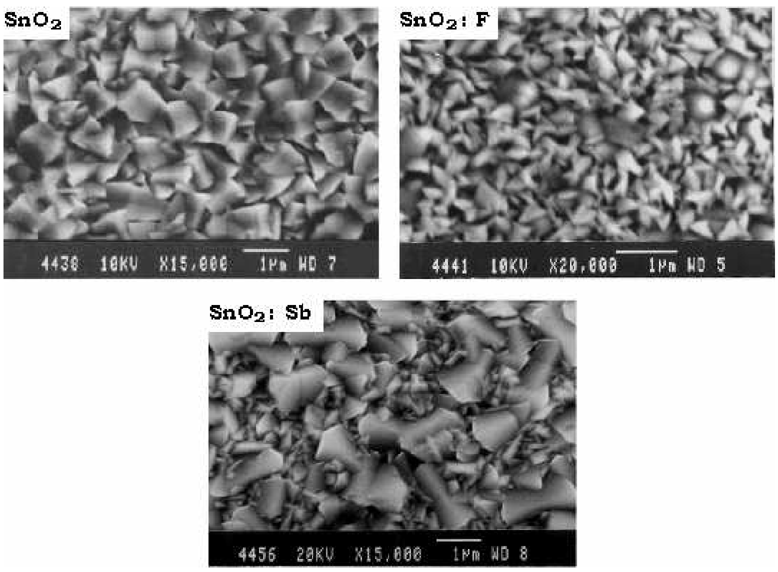

Fig. 5. SEM micrographs of undoped and fluorine- and antimony- doped SnO_2 thin films deposited on optical glass substrates.

The SEM micrographs obtained for undoped, 15 wt. % fluorine- and 2 wt. % antimony-doped SnO_2 films are shown in Fig. 5. As seen in the XRD patterns the difference in the preferred orientation of pure and doped films, the grain size of these films have different shapes as examined by SEM. The undoped films have the grains of regular rectangular shaped grains whereas the fluorine- and antimony- doped films have the characteristic needle shaped grains reported for doped SnO_2 films [10]. The morphology shown for antimony- doped films is look like cauliflower.

3.2.2. Electrical properties

The films prepared with 15 wt. % of NH_4F showed a tremendous increment in both conductivity and transmittance. The sheet resistance (38.2 Ω/□) of undoped films found decreased to a minimum of 1.8 Ω/□ for the films prepared with 15 wt. % of NH_4F. This minimum sheet resistance is found to be the lowest among the reported values for SnO_2:F thin films prepared from $SnCl_2$ precursor [6]. The films prepared with 2 wt. % of $SbCl_3$ as well showed a tremendous increment in conductivity but the transmittance has been reduced much. The sheet resistance of undoped films found decreased to a minimum of 2.2 Ω/□ for the films prepared with 2 wt. % of $SbCl_3$. This minimum sheet resistance is found to be the lowest among the reported values for SnO_2:Sb thin films prepared from $SnCl_2$ precursor [7]. The electrical data obtained from Hall measurements for undoped, fluorine- and antimony- doped SnO_2 films are given in Table 1.

Table 1. Electrical data of SnO_2 films deposited on optical glass.

Material	Sheet resistance (Ω/□)	Resistivity ($\times 10^{-4}$ Ω-cm)	Hall mobility ($cm^2 V^{-1} S^{-1}$)	Carrier concentration ($\times 10^{20} cm^{-3}$)
SnO_2	38.2	46.3	109.5	0.12
SnO_2:F (15 wt. %)	1.8	2.1	22.1	13.3
SnO_2:Sb (2 wt. %)	2.2	2.9	12.0	16.8

3.2.3. Optical properties

The transmittance and reflectance spectra of both pure and 15 wt. % NH_4F doped SnO_2 films are shown comparatively in Fig. 6. The transmittance was found increased from 42 % to 85 % (800 nm) for this doping level. The figure clearly shows the increase in transmittance due to doping at visible range of wavelength. The plasma edge occurs at wavelength of ~1700 nm for the fluorine-doped films. The reflectance of pure SnO_2 shows the maximum of ~10 % at wavelength above 1500 nm whereas it shows negligible reflectance at the wavelength below ~1000 nm. On the other hand SnO_2:F show a reflectance value of ~10 % in the lower wavelength and show the maximum of ~ 50 % at 2500 nm.

The transmittance and reflectance spectra of pure and 2 wt. % $SbCl_3$ doped SnO_2 films are shown comparatively in Fig. 7. The transmittance of pure SnO_2 was found decreased drastically to a value of 20 % from 42 % (800 nm). The figure clearly shows the decrease in transmittance due to doping at visible range of wavelength. The plasma edge occurs at wavelength of ~1300 nm for the antimony- doped films. Antimony- doped SnO_2 show an increase in reflectance above 1500 nm and show the maximum of ~ 25 % at 2500 nm.

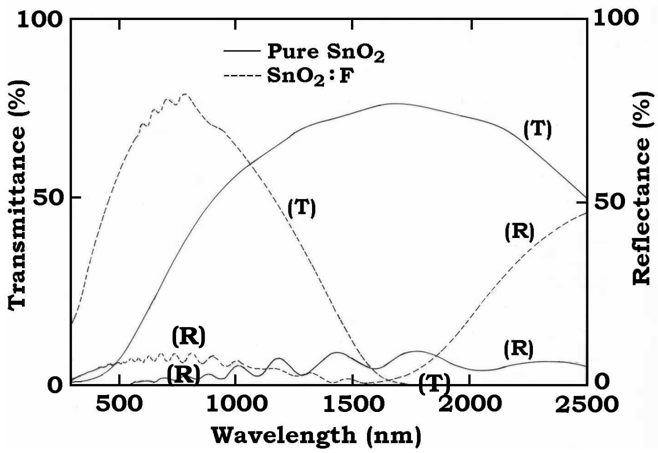

Fig. 6. Comparison of transmittance and reflectance spectra of undoped and 15 wt. % fluorine-doped SnO_2 films deposited on optical glass substrates.

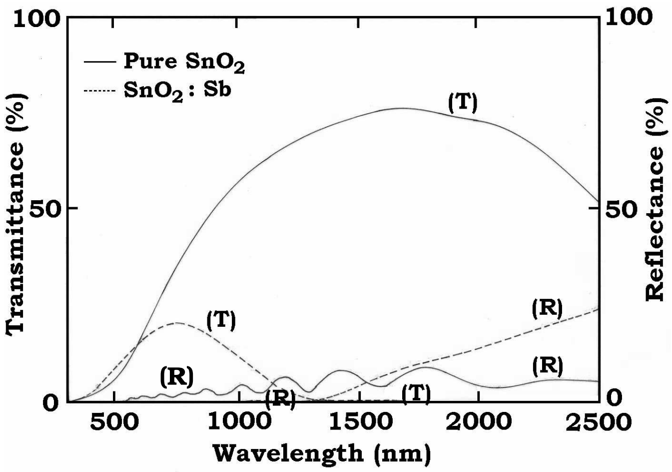

Fig. 7. Comparison of transmittance and reflectance spectra of undoped and 2 wt. % antimony- doped SnO_2 films deposited on optical glass substrates.

The effect of antimony- doping on decreasing the transmittance by a striking difference in the present study can be explained as follows. The film colour turns from milky white to blackish blue on 2 wt. % of antimony- doping. This blackening of film colouration must result from light absorption [11]. It is known fact that a material containing an element in two different oxidation states or in a mixed oxidation state (like SnO_2:Sb) manifests abnormally deep and intense colouration. Electron transfer between the different oxidation states of the element causes intense light absorption, which is termed as the interaction colour. There are evidences for this colouration [12,13]. Further, the heavy doping of antimony- may lead to increase in the degenerate (metallic) nature of the films, which results in light absorption. The reason for arriving to this conclusion is that these films are showing poor transparency even though they are transparent to naked eye. Hence the decrease in transmittance due to antimony- doping is attributed to light absorption.

The high Infrared (IR) reflectivity is one of the main requirements in solar energy conversion process. In flat plate collectors, the escape of thermal energy in the form of IR radiation reduces the conversion efficiency considerably [14]. Thus, it is desirable to have high IR reflectivity for a material that is to be useful in solar energy conversion. The IR reflectivity (R) of the films reported in the present study were calculated using the relation $R = 1/(1 + 2\,\varepsilon_0\, c_0\, R_{sh})^2$, found in Frank et al. [15] that is valid over a wide range in the IR region ($\varepsilon_0\ c_0 = 1/376\ \Omega^{-1}$). As this relation is indirectly proportional to sheet resistance (R_{sh}) and a material should have minimum R_{sh} to have high R-values. The R-value of 69 % obtained for pure SnO_2 films was found increased to a maximum of 98 % for the films doped with both 15 wt. % of NH_4F and 2 wt. % of $SbCl_3$. It is found from these results that SnO_2:F films have both high transmittance and reflectance. The combination of high R and T values make the SnO_2:F films suitable for the photo-thermal conversion of solar energy. Whereas, SnO_2:Sb films have considerable low transmittance but high IR reflectance of SnO_2:Sb, which suggests that these films are useful in flat plate collectors and in different electrode processes [9,15,16].

4. Conclusions

Thin films of tin oxide were deposited on different substrates and found that the optical grade glass substrates showed better electrical and optical properties. Further the films were doped with fluorine- and antimony- with the same parameters. The minimum sheet resistance obtained for the doped films (both F and Sb) was found to be the lowest among the reported values for these materials prepared from $SnCl_2$ precursor. The transmittance of the undoped films found increased on fluorine-doping whereas decreased on antimony- doping. The preferred orientation of the undoped films found shifted on doping and was reflected in SEM studies as they have different grain shapes.

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