Preparation and Characterization of Tin Oxide based Transparent Conducting Coating for Solar Cell Application

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Abstract: Transparent conducting coatings for solar cell application have been the subject of research over a number of years. The transparent conducting coatings were prepared by oven drying process on glass plates at various temperatures and various concentrations of the starting material stannous chloride ($SnCl_2.2H_2O$). Structural, morphological, optical, and electrical properties of the resulting plates were studied by XRD, Inverted Microscope, UV Visible and Hall Effect Measurement method. XRD showed a homogenous morphology of the coating. The minimum grain size of SnO_2 was found to be 22 nm as calculated by XRD using Debye Scherrer Formula. The change in electrical conductivity and optical transmittance were found to be a function of the change in heating temperature, heating time and molar concentration of the starting materials. The coating prepared at 350°C for about 300 seconds with molar concentration 0.1M of the starting material showed low level of electrical resistivity (3.81E-02 Ω-cm) and high level of transmittance (transmittance maximum 79.2% at 600 nm). The use of this transparent conducting electrode in a Dye Sensitized Solar Cell depicted the voltage of 315 mV and the resistance of 300 KΩ. All of the results indicate that the developed coating could be used in solar cell application.

Keywords: Tin Oxide, Transparent conducting coating, Surface morphology, Electrical property, Optical property.

1 Introduction

Solar energy conversion has the potential to satisfy the electricity and even the total energy consumption of the world. Indeed, one hour of solar irradiation on earth is equivalent to the total world energy consumption in one year (about 130 PWh). Photovoltaic (PV) or the direct conversion of sunlight into electricity is a promising technology which can be easily installed without affecting neither the landscape nor the natural environment if directly integrated into building. One of the technological key points is the transparent conductive films (TCFs) used for front contact, barrier layer or intermediate reflector [1].

Transparent conducting films (TCFs) are optically transparent and electrically conductive in thin layers. TCFs can be fabricated from both inorganic and organic materials. Inorganic films typically are made up of a layer of TCO (transparent conducting oxide), generally in the form of indium tin oxide (ITO), fluorine doped tin oxide (FTO) and doped zinc oxide usually aluminum doped zinc oxide ZnO:Al (AZO). Organic films are being developed using carbon nanotube networks and graphene [2,3].

High optical transparency and high electrical conductivity are two critical parameters in the choice of electrodes for many optoelectronic devices, such as liquid crystal displays, light emitting diodes, solar cells and touch panels [4]. Currently, tin-doped indium oxide (ITO) and fluorine-doped tin oxide (FTO) are used as the primary choice for transparent conductive electrodes (TCE) for such applications due to their high electrical conductivity and optical transparency [5,6].

However, the high cost of the indium source and the high processing temperature for its production has resulted in the quest for new electrode materials for optoelectronic device applications. Various alternatives have been pursued by different groups towards this objective, among which thin metal films [7,8] and metal grids [9,10] have shown a performance comparable to ITO. However, these approaches suffer from the requirement for high vacuum equipment for processing and fabrication. Carbon nanotube (CNT) films [11,12] and more recently, graphene films [13,14] have been successfully used as TCE in organic light emitting diodes [15,16] and solar cells,[17,18] and have attracted significant interest.

However, their performance in terms of sheet resistance and transparency are still inferior to ITO. Thus there is a need to continue the quest for new cheap and reliable materials that can be used in a highly scalable method for a TCE material

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with comparable performance in terms of sheet resistance and transparency to that of ITO.

In the last decade, among the known oxide, tin oxide (SnO_2) semiconducting film has been intensively used in the field of microelectronics and stable gas sensors, specifically in recognition of volatile organic compound (VOC). Application of SnO_2 films are not limited to the research laboratory but are used commercially in environmental monitoring, industrial electronic sensor, and liquid crystal displays etc. [19].

Undoped SnO_2 is an n-type semiconductor material with a direct bandgap of about 4 eV and indirect bandgap of about 2.6 eV, refractive index of about 1.9 and a tetragonal rutile structure. The film is highly transparent, chemically inert, and mechanically hard. Owing to its low resistivity and high transmittance, SnO_2 thin films are used as a window layer in solar cells [20]. This films act as a window for light to pass through to the active material beneath (where carrier generation occurs), as an ohmic contact for carrier transport out of the photovoltaic. This type of thin film of metal oxides of binary compound without any intentional impurity doping has been developed. The optical and electrical properties of tin oxide thin films have been performed for a dye sensitized solar cell.

Doped or undoped tin oxide films can be deposited by several methods such as Thermal Evaporation, [21,22] Chemical Vapor Deposition, [23,24] R.F. Magnetron Co-sputtering, [25,26] Laser Pulse Evaporation [27] and Spray Pyrolysis [28]. A simple oven drying technique has been used here being less expensive.

The present analysis is focused on optimization, for depositing good tin oxide thin film by oven drying and to investigate structural, optical and electrical properties of SnO_2 thin film at molar concentration 0.1M.

2 Experimental Sections

2.1 Materials

The starting material stannous chloride, $SnCl_2.2H_2O$ was obtained from MERCK with a purity >98% and was used without further purification. The acid, HCl and alcohol, Methanol were obtained from BDH with a purity >99% and were used as received. The solutions were prepared in doubly distilled water for the present study.

2.2 Deposition method of SnO_2 thin film

To prepare thin film, 0.1 M solution of the stannous chloride was prepared at first. Then coating solution of varying percentages of stannous chloride, hydrochloric acid and methanol (**table 1**) was prepared. The solution was then stored for a while. In the meantime one clean glass slide was taken and washed by distilled water and then dried in a woven. Then four pieces of scotch adhesive tape (5-6 cm long) was applied on any face of glass slide to make a rectangular shape of desired size. The glass substrate was then carefully cleaned with dilute HCl and finally cleaned with acetone. The stored solution was then applied in the rectangular shape on the glass slide by using glass rod. The glass slide with solution on one of its faces was annealed and sintered in a furnace (Muffle Furnace). After that the furnace was turned off and the slide was allowed to cool slowly to room temperature.

Table 1. Percentages of solutions for sample preparation

	$SnCl_2$ Solution (%)	Methanol (%)	HCl (%)
Sample 1	83.33	8.33	8.33
Sample 2	76.92	7.69	15.38
Sample 3	71.43	7.14	21.42
Sample 4	66.67	6.67	26.67

2.3 Characterization of SnO_2 thin film

The structural properties and particle size of the deposited SnO_2 film was characterized by XRD using X'PertPRO XRD model number-PW 3040.The optical transmittance spectra of the deposited films were recorded in the wavelength range of 400 nm to 900 nm using UV-Visible spectrophotometer model T-60A (PG electronics U.K.). Finally, the electrical resistivity of samples was examined by Hall Effect Measurement System Model No: HMS5000/AMP55T (Hi-TECH Scientific Equipments, Kolkata).The contacts of the four probes were made by silver paste. The Microscopic analysis was performed by inverted microscope Serial No-21107 (Gippon INC Limited, Japan.).

3 Results and Discussion

3.1 Structural and micro-structural analysis of SnO_2 film

Structural analysis of the deposited SnO_2 film was carried out by using CuKα radiation, source having wavelength1.5406 Å. The X-ray diffraction patterns of the samples of four different formulations deposited by oven drying technique at 350°C temperature for 300 seconds are shown in **figure 1**.

The XRD patterns of the undoped tin oxide thin films of four different formulations reveal that these films are polycrystalline in nature. The grain size of SnO_2 thin film D, is estimated by the Debye-Scherrer formula [29].

$$D = \frac{0.9\,\lambda}{\beta\,cos\,\theta} \tag{1}$$

Where, D = Crystalline grain size.
β = FWHM (full width and half maxima) of the observed peak.
λ= wave length of the X-ray diffraction
θ = Angle of diffraction
Sample containing 8.33, 15.38, 21.42 and 26.67% HCl has

an average particle size of 52, 25, 22 and 36 nm respectively. Tin oxide crystal nucleation occurred at 350ºC as can be seen from the X-ray diffraction pattern. A small change in HCl percentage has a strong effect on crystalline size as well as grain size. The diffraction pattern of the sample has no peaks indicates the amorphous nature of the film. The presence of sharp and well defined XRD patterns and strong peaks (**figure 1**) indicate that SnO$_2$ has large crystalline size or that SnO$_2$ particles are crystalline in nature [29]. The peak intensity decreases when the HCl percentage is raised to15.38% and 21.42%. It is because of the breakdown of bond of intermediate polymer molecules [30]. Heating temperature also has an effect on crystal formation or nucleation. So a variation in the crystal size as well as particle size of 26.67% HCl content can occur due to
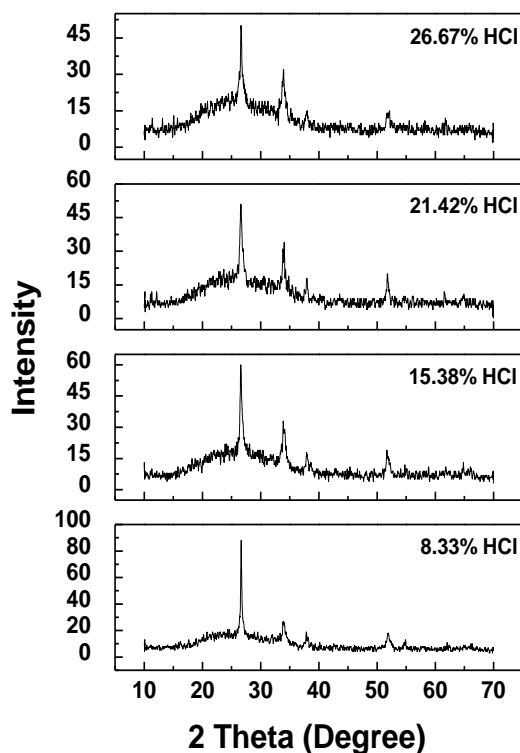

Figure 1. XRD of SnO$_2$ thin film annealed at temperature 350°C for 300 seconds.

temperature variation. It is found that the XRD peaks become gradually broader with increase in HCl content, indicating smaller particle size.

3.2 Optical property of SnO$_2$ thin film

Concentration of the starting material (solution) highly affects the nature of the film mainly its grain size, growth of the film and optical characteristics [31,22].
Higher concentration has the problem of rendering opacity to the film. On the other hand very lower concentration disturbs the growth of SnO$_2$ film. In this case concentration optimization is very important. Annealing temperature plays an important role in the film formation. When temperature is below 300°C, solution will undergo incomplete thermal

decomposition giving foggy film whose transparency as well as electrical conductivity will be very poor. Where the optimum temperature is in the range of 300-400°C complete oxidation of solution takes place. Duration of heating also has an effect on film transparency. The transmittance spectra as a function of wavelength in the range 400-900 nm for four samples are shown in **figure 2.**
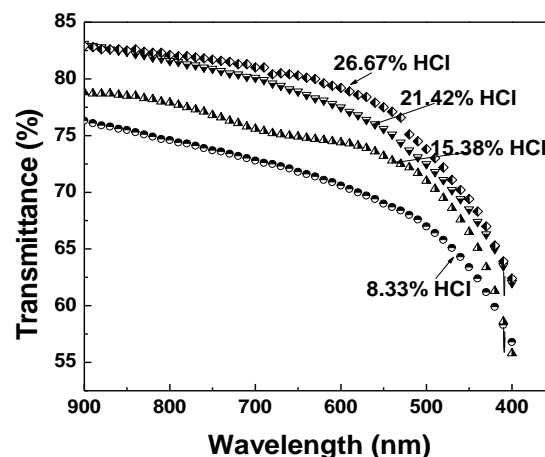

Figure 2. The transmittance spectra as a function of wavelength.
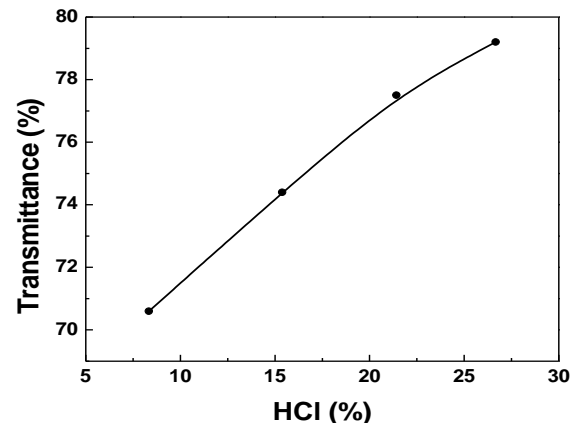

Figure 3. Transmission spectrum of SnO$_2$ thin film against percentage HCl.

HCl content in the solution affect the optical property of the film. The HCl render the solution transparency mostly, due to the breakdown of the intermediate polymer molecules [30].
The percentage transmittance of thin film increases with the percentage of HCl content. (**figure 3**).

3.3 Electrical property of SnO$_2$ thin film

Hall Effect measurements were done using the Vander Pauw technique in order to determine the dominant charge carrier type, charge carrier mobility and charge carrier concentration. Oxygen vacancies and interstitials Sn ions play an important role as charge carriers. Oxygen vacancies can be created by controlling the substrate temperature or ambient oxygen pressure. At high annealing temperature

number of Sn interstitials can be decreased due to evaporation. So a controlled annealing temperature can inhibit this problem. The electrical resistivity of four different samples against temperature is shown in **figure 4.**

The effect of temperature on the annealed SnO_2 film is limited (**figure 4**). But the effect of HCl on the film formation is clear from **figure 5**. Methanol in the solution helps in the decomposition of stannous chloride solution and forms a SnO_2 film on a heated substrate in air [32].
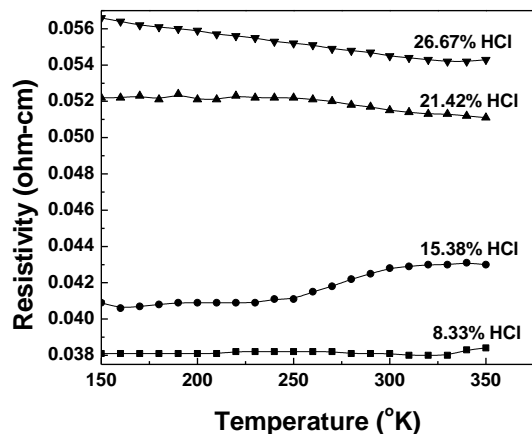

Figure 4. The electrical resistivity of four different samples as a function of temperature.
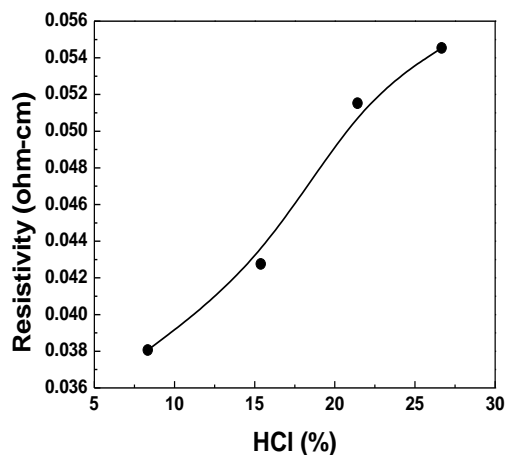

Figure 5. Resistivity of thin film against percentage HCl

HCl content in the solution break the intermediate polymer molecules and create porosity. Due to the high porosity electrons are scattered at the grain boundaries of the particles. Grain boundaries act to limit the mobility of the electrons by charge trapping at lattice defect sites; leading to a high resistivity [33]. Structures with large and closely packed crystallites exhibit higher electron mobility and carrier density and consequently lower electrical resistivity [34].

3.4 Microscopic analysis

Microscopic analysis gives brilliant image of the particle of

material. The microscopic image of four different samples is given in **figure 6**.

From inverted optical micrograph of 8.33% HCl containing film, it is obvious that the surface is smooth and less porous. Structures with large and closely packed crystallites exhibit higher electron mobility and carrier density and consequently higher electrical conductivity. On the other hand less porosity or closely packed crystallites leads the film low transparent. When the percentage of HCl content increases then the porosity is also increases due to the breakdown of intermediate polymer molecules. This makes the film high resistive and high transparent. And this is obviously true for the percentage of 15.38, 21.42 and 26.67 HCl. This is why 26.67% HCl containing sample has higher resistivity and higher transmission of visible light.
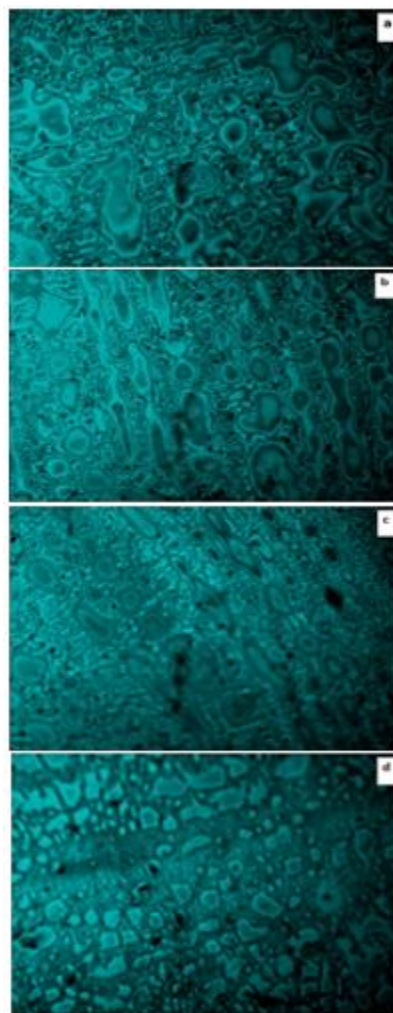

Figure 6. a, b, c and d represents the optical micrograph of 8.33, 15.38, 21.42 and 26.67% HCl containing thin film respectively.

4 Conclusions

In summary, we demonstrated the application of oven drying technique to obtain high quality stannous oxide films on

glass substrates. The electrical resistivity of the film was characterized by Hall Effect measurement system and found to be 3.81E-02 Ω-cm as good one. The UV-Visible spectrometer analysis showed transmission of visible light maximum 79.2% at 600 nm wavelength. The XRD result showed a regular, smooth morphology. The deposited film was found to be polycrystalline. The Microscopic analysis showed large and closely packed crystallites which exhibited higher electron mobility and carrier density and thus lower electrical resistivity.

Acknowledgement

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