Optical and electrical properties of SnO₂ films prepared by chemical vapour deposition

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Abstract. Transparent and conducting SnO₂ films are prepared at 500°C on quartz substrates by chemical vapour deposition technique, involving oxidation of SnCl₂. The effect of oxygen gas flow rate on the properties of SnO₂ films is reported. Oxygen with a flow rate from 0.8–1.35 lmin⁻¹ was used as both carrier and oxidizing gas. Electrical and optical properties are studied for 150 nm thick films. The films obtained have a resistivity between 1.72×10^{-3} and 4.95×10^{-3} ohm cm and the average transmission in the visible region ranges 86–90%. The performance of these films was checked and the maximum figure of merit value of 2.03×10^{-3} ohm⁻¹ was obtained with the films deposited at the flow rate of 1.16 lmin⁻¹.

Keywords. Chemical vapour deposition; figure of merit; SnO₂ film; transparent conducting film.

1. Introduction

Tin oxide films are being used in a variety of applications, such as transparent heating elements, transparent electrodes and antistatic coatings (Manifacier and Fillard 1981). In the last few years interest in tin oxide films has further increased because of their potential application in semiconductor-insulator-semiconductor (sis) solar cells (Nagatomo *et al* 1979; Ghosh *et al* 1980). In the present study a simple and inexpensive chemical vapour deposition (cvd) method involving oxidation of SnCl₂ has been selected for the deposition of SnO₂ films for solar cell application. Murthy and coworkers (Murthy *et al* 1983; Murthy and Jawalekar 1983) deposited SnO₂ films using a similar method and studied the effect of deposition temperature (range: 300–500°C) on their properties. It was reported that the films deposited at 500°C have low resistivity with uniform and large grain size (0.303 μm). Thus, 500°C was considered as the optimum deposition temperature for deposition of SnO₂ films. The aim of the present work is to study the effect of oxygen flow rate on the electrical and optical properties, and to find out the optimum oxygen flow rate for the deposition of SnO₂ films. In the present study, the depositions are carried out at 500°C with an oxygen flow rate between 0.8 and 1.35 lmin⁻¹. The dependence of electrical and optical properties on the oxygen flow rate is also reported.

2. Experimental details

An open tube cvd system has been used to deposit SnO₂ films. The schematic experimental set-up is shown in figure 1. Chemically and ultrasonically cleaned Pyrex or quartz substrates (about 4 cm² in area) were loaded into quartz reactor tube and

Figure 1. Schematic of the CVD experimental set-up for the deposition of SnO_2 films.

placed inside the constant temperature zone. The deposition temperature was maintained at the required value within $\pm 2^\circ\text{C}$ by using a temperature controller. Anhydrous stannous chloride produced by heating $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (purity 99.9%) was used as a source material. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was heated to its melting point (248°C) and oxygen (purity 99.9%) gas was bubbled through it, which acts as a carrier and oxidizing gas. While heating to this temperature, the stopcock S_1 was adjusted to position L_1 so that water vapour could be vented out. After adjusting the required oxygen flow rate the vapours are allowed to pass through the gas mixing bulb to the heated substrates by turning S_1 to position L_2 . The bulb was continuously heated to avoid any condensation of vapours inside the bulb. Any required dopant vapours can also be introduced through the stopcocks S_3 and S_5 . However no doping was carried out in this study and therefore S_3 and S_5 are kept closed.

The thickness of the film was measured by an optical interference method. The sheet resistance was measured by the conventional four-probe technique. For this measurement direct current through the films was maintained low (1 mA) and was passed for less than 30 sec to avoid heating of the films. The optical transmission in the visible region was measured using a spectrophotometer (Aminco DW2A).

3. Results and discussion

The properties of SnO_2 films are strongly dependent on deposition parameters, such as deposition temperature (T), deposition time (t) and oxygen flow rate (F). All the depositions were carried out in the flow range $0.8\text{--}1.35\text{ lmin}^{-1}$ at 500°C and the effect of oxygen flow rate on electrical and optical properties is discussed in detail. Films deposited on quartz substrates were used for electrical and optical measurements.

3.1 Electrical properties

The variation of film thickness (d), deposited in the flow range $0.8\text{--}1.35\text{ lmin}^{-1}$ with deposition time (t) is shown in figure 2. It can be seen that d also increases with F . This is because at higher flow rates more SnCl_2 vapours will be carried out from the source flask by oxygen and thereby the rate of deposition will be greater, hence the thickness. The dependence of sheet resistivity (R_{sh}) on the film thickness, deposited in the flow range $0.8\text{--}1.35\text{ lmin}^{-1}$ is shown in figure 3. It can be observed that R_{sh} decreases with d and the variation of R_{sh} is less beyond 150 nm. To study the effect of oxygen flow rate on R_{sh} and resistivity ρ , a fixed thickness film should be deposited under different flow conditions. In this case 150 nm film thickness has been chosen to study the effect of oxygen flow rate. To deposit 150 nm thick film, in the flow range $0.8\text{--}1.35\text{ lmin}^{-1}$, the corresponding deposition times are found out from figure 1 and the films are deposited accordingly. The variation of R_{sh} and ρ with F for these films are shown in figure 4. It can be seen from these curves, that initially when F is increased, R_{sh} and ρ decrease and passes through a minimum value at 1.16 lmin^{-1} and a further increase in F results in increase in R_{sh} and ρ .

The above results can be explained in the following way. It is well known that the SnO_2 is an oxygen-deficient semiconductor and SnO is an insulator. At low flow rates all the tin atoms may not be oxidized to the SnO_2 state. A few molecules in the SnO phase may also be present, resulting in relatively high resistivity. As the flow rate is

Figure 2. Variation of SnO_2 film thickness on deposition time at various oxygen flow rates.

increased, the concentration of SnO may decrease, thereby decreasing ρ . Thus ρ reaches a minimum and SnO_2 obtained in this region will have the optimum concentration of oxygen vacancies to give rise to the lowest ρ . As the flow rate is increased further, the oxygen content in the reaction tube increases. This may result in infilling of the oxygen vacancies in the SnO_2 , and hence the oxygen-deficient SnO_2 becomes nearly stoichiometric SnO_2 . Thus ρ again increases as F increases.

3.2 Optical properties

The transmission spectra in the visible region 400–800 nm was recorded for 150 nm thick SnO_2 films, deposited in the flow range of 0.8–1.35 l min⁻¹. From these spectra the

Figure 3. Dependence of SnO_2 film sheet resistivity on film thickness at various oxygen flow rates.

average transmission ($T_{r(av)}$) is calculated and is plotted as a function of F (figure 4). It can be seen from this curve that the transmission initially decreases as F increases, and is minimum for films deposited at 1.16 lmin^{-1} . The reason for this is an increased absorption by free carriers with an increase in F . It is also evident from resistivity curve, that ρ decrease as F increases. As ρ decreases the carrier concentration increases and hence the absorption by the free carriers also increases. A further increase in F results in increase in transmission. This is again because ρ increases and hence the absorption by free carriers decreases. This explains the variations of transmission with F .

Figure 4. Variation of sheet resistivity (R_{sh}), resistivity (ρ), average transition ($T_{r(av)}$) and figure of merit (ϕ_{TC}) with oxygen flow rate (F).

3.3 Figure of merit

In order to compare the performance of the films deposited at various flow rates, the most commonly used definition of figure of merit ϕ_{TC} as proposed by Haacke (1976) has been used. It is defined as

$$\phi_{TC} = T_r^{10}/R_{sh},$$

where T_r is the transmission and R_{sh} is the sheet resistivity. The variation of ϕ_{TC} as a function of oxygen flow rate is shown in figure 4. It can be seen that the films deposited at a flow rate 1.16 lmin^{-1} exhibit the maximum ϕ_{TC} . The highest figure of merit $2.03 \times 10^{-3} \text{ ohm}^{-1}$ obtained in this study is of the same order of magnitude as reported by Kane *et al* (1975) and Shanthi *et al* (1982).

The above results show that the optimum oxygen flow rate for the deposition of SnO₂ films is 1.16 lmin^{-1} . The corresponding film properties are $R_{sh} = 115 \text{ ohm. square}^{-1}$, $T_{r(av)} = 86.5\%$ and $\phi_{TC} = 2.03 \times 10^{-3} \text{ ohm}^{-1}$.

4. Conclusions

In this study tin oxide films deposited by cvd technique involving oxidation of SnCl₂ at 500°C with an oxygen flow rate between 0.8 and 1.35 lmin^{-1} . Electrical and optical properties are studied as a function of oxygen flow rate. On the basis of figure of merit values it is concluded that 1.16 lmin^{-1} is the optimum flow rate for the deposition of SnO₂ films.

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