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THE PREPARATION AND PROPERTIES OF PECVD-MADE SnO₂ THIN FILMS

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Abstract - High quality films of undoped SnO₂, which have potential applications for a-Si solar cells, were deposited on soda lime glass at the relatively low temperature of 200°C from the anhydrous Sn Cl₄-O₂ reaction system by plasma-enhanced chemical vapour deposition (PECVD). Typically, the films have a sheet resistance of 50 ohm per square with an average optical transparence of more than 90% in the 400-800nm wavelength range. The influences of the main control deposition parameters on electrical and optical properties of the resulting SnO₂ films were studied.

1. Introduction

SnO₂ thin films are currently actively investigated since their high transparency and electrical conductivity, and chemical stability would be of unique value in numerous optoelectronic applications. These properties are shared with only a few other materials, and many techniques for their depositions have therefore been developed. Deposition temperature usually ranging from 450 to 750°C are necessary in these processes. Sputtering is one of the most extensively used techniques for the deposition of transparent conducting oxide films. Although lower temperature are used in the rf sputtering, the properties of the resulting films are very difficult to control. Ghandi et al. (1) have reported
highly transparent films of SnO\textsubscript{2} deposited at room temperature and base on the reaction of rf plasma-activated oxygen with tetramethyltin. In this letter a new technique is presented for the deposition of SnO\textsubscript{2} films with both high transmission and conductivity, based upon the reaction of SnCl\textsubscript{4} with oxygen at lower temperature of 200\degree C by plasma-enhanced chemical vapour deposition (PECVD).

2. Experimental

The deposition of SnO\textsubscript{2} films was performed in a vertical reactor, 30 cm in diameter. rf excitation at 13.75 MHz was used to create the oxygen plasma in this system. A mechanical pump resulted in a pressure below 10\textsuperscript{-2} torr. A total system pressure of 1.5 torr was maintained for all deposition described in this work. To obtain uniform films, the grounded pedestal, on which the samples were located, rotated at the speed of 10 cycles per minute during growth. Nitrogen was bubbled through the saturator containing the anhydrous SnCl\textsubscript{4} source which was maintained at the temperature of 45\degree C. Each of the gases used in this work was fed to chamber through a needle valve, and monitored by means of a flow gauge. Chamber pressure was measured by a thermocouple gauge. A round polyflon plank, 45 mm in diameter, was placed between the two electrode plates. This served to effectively change the gas distribution within the reaction chamber, and greatly improve the uniformity of the deposited SnO\textsubscript{2} films.

In operation, the system was pumped down to a base pressure of below 10\textsuperscript{-2} torr. Nitrogen carrying SnCl\textsubscript{4}, oxygen and additional nitrogen were together introduced to the chamber until the total system pressure of 1.5 torr was achieved. Then, the rf power was applied. A plate voltage and current of 1200 V and 70 mA, respectively, were maintained during these experiments. This was followed by plasma excitation for the desired deposition time. 1.5 mm thick 4.0 x 5.0 cm soda lime glasses, on which SnO\textsubscript{2} films were deposited, were employed. The substrate temperature was monitored during the growth run for evidence of change. For our work, this temperature changed by less than 10\degree C over an entire run.

3. Results and Discussion

3.1 Films of undoped SnO\textsubscript{2} prepared by PECVD at optimum growth conditions are fairly uniform. Scanning electron micrographs at 10,000X magnification exhibit a very fine-grained size of about 0.2 \mu m. X-ray diffraction patterns reveal
that the films are polycrystalline, and do not show preferred orientation.

3.2 The effects of deposition variables on film properties were explored to find optimum process conditions. The variables include source and substrate temperatures, reactant and carrier gas flow rates, and growth rates of the films.

Fig. 1 shows the relation between film thickness and growth time for SnCl\textsubscript{4} and O\textsubscript{2} flow of 1.5 and 0.4 lmin\textsuperscript{-1}, respectively, and corresponds to a growth rate of 103 Åmin\textsuperscript{-1} for this set of experimental conditions. Film thickness was measured by means of a multiple-beam interferometer. In our system, the higher growth rate (about 100-130 Åmin\textsuperscript{-1}) at low pressure is primarily due to the high electron temperature achieved because of the rf excitation, but changing the substrate temperature was found to have a strong influence on the conductivity of the film. Films deposited at low substrate temperature showed high sheet resistance R\textsubscript{sh} and hence low figure of merit Q (equal to R\textsubscript{sh} L\textsubscript{n}T\textsuperscript{2}), T-average visible transmission in the 400-800 nm wavelength range). The low conductivity may be due to small film thickness caused by low deposition rate and presence of unreacted stannic chloride. Substrate temperatures in excess of 150°C in our system were found necessary to oxidize SnCl\textsubscript{4} vapour for forming tin oxide films. All works were conducted at a fixed temperature of 200°C, which was found to yield optimum deposition rates and excellent properties of the films.

Fig. 2 gives a plot of deposition rate versus nitrogen flow carrying SnCl\textsubscript{4} vapour. The growth rate initially increases sharply with increasing SnCl\textsubscript{4} flow from 0 to 0.4 lmin\textsuperscript{-1}. Later it saturates to a value of about 150 Åmin\textsuperscript{-1}. The
mechanism of SnO₂ film formation has been thoroughly examined by Ghoṣhtagore (3).

According to Rideal-Eley mechanism, the reaction of Sn Cl₄ has been found to take place at the surface of the substrate with an absorbed oxygen atom. Obviously, when the excitation power is given, increasing Sn Cl₄ vapour reacts to fixed atomic oxygen on the surface of the substrate, forming SnO₂ film with increasing thickness. However, reactor operation at Sn Cl₄ flow in excess of 2.5 lmin⁻¹ led to formation of large amounts of particulate matter in the system, resulting in hazy films. This appears to be the limiting factor for the increasing in N₂ flow carrying Sn Cl₄.

Fig. 3 offers the dependence of Rsh, T and Q on oxygen flow. As seen in Fig. 3, oxygen flow has the stronger influence on Rsh, and the weaker on T. To receive high figure of merit, it is concluded that the optimum oxygen flows range between 0.2-0.6 lmin⁻¹.
Fig. 4 describes the variation of $R_{sh}$, $T$, and $Q$ as a function of nitrogen flow through SnCl$_4$ source. Films deposited at the low nitrogen flow (i.e., low SnCl$_4$ concentration) show high $R_{sh}$ and hence low $Q$. The films made between 1.5-2.5 lmin$^{-1}$ are superior with high transmission, low sheet resistance and hence high figure of merit. Higher SnCl$_4$ flows led to the deterioration of the film characteristics as said above.

![Graph](image)

**FIG. 4.** $R_{sh}$ (△), $T$ (○) and $Q$ (•) versus $N_2$ flow carrying SnCl$_4$ vapour.

Fig. 5 depicts transmission spectra in the wavelength of 400-800 nm for three SnO$_2$ films fabricated at three different oxygen flow rates: 0.2, 0.4, 0.85 lmin$^{-1}$, and the same SnCl$_4$ flow of 1.5 lmin$^{-1}$. Films produced at the oxygen flow rates between 0.2-0.7 lmin$^{-1}$ always have high average light transmission of more than 90% and low sheet resistance/less than 60 ohm per square. At higher oxygen flow rates (more than 1.0 lmin$^{-1}$), the deposition rate was high and the films become foggy, resulting in an increase in resistance, a decrease in transmission and hence in figure of merit as shown in Fig. 3.
It is well-known that the only way to obtain good transparent conductors is to create electron degeneracy in a wide band gap (greater than 3eV) oxide by controllably introducing non-stoichiometry and/or appropriate dopants. The n-type conductivity of undoped SnO₂ is primarily due to its non-stoichiometry. But for our work, in the deposited films from chloride (Sn Cl₄) the corporation of chlorine ions into the lattice also contributes to the conductivity.

Finally, fast and low temperature (400°C) annealing with forming gas in an open quartz tube system was effectively employed to increase the conductivity of the film deposited not at the optimum conditions. It was also observed that annealing has a minor influences on the film of the optimum growth condition.

3.3 The surface compositions of SnO₂ films were observed with X-ray photoelectron spectroscopy (XPS). From XPS measurements, it is found that elements existing on the surface of SnO₂ films were Sn(IV), Sn(II), O, and C. Chlorines were not observed on the surface, which may be incorporated into SnO₂ lattice either interstitially or substitutionally (4). According to the transport property model(5), free carriers may be trapped on surface states. These surface states here were identified to be Sn(II).

3.4 F-doped SnO₂ films were also made and excellent results were obtained. Freon, as F dopant, was used to produce F-doped SnO₂, which greatly decrease the sheet resistance, and increase the optical transmission of the films. Typically, the F-doped SnO₂ films have a sheet resistance of 20 ohm per square and an
average optical transmission of more than 90% in the 400-800nm wavelength range. Further efforts are been done on the F-doped SnO₂ films.

4. Summary

This paper describes a new CVD process for the deposition of highly conductive SnO₂ films based on the oxidation of Sn Cl₄. Undoped films with Rsh of 50 ohm per square and average transmission of more than 90% were obtained at optimum conditions. The F-doped SnO₂ films exhibit excellent sheet resistance and optical transmission. This new technique has the advantages of simple apparatus, low deposition temperature, and good reproducibility. We can conclude that the SnO₂ films made by PECVD, which are used as transparent electrically conducting antireflection films of a-Si solar cells, are very promising materials.

REFERENCES

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