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Annealing behaviour of electron-beam deposited tin dioxide films

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Abstract. The sheet resistivity of tin dioxide films deposited by electron-beam evaporation has been studied during annealing, both as a function of time and temperature. The annealing behaviour of SnO_2 films under the above two different conditions is consistent. A qualitative interpretation has been given for the decrease and the minimum observed in the resistivity. The increase in resistivity has been confirmed by scanning-electron micrographs. The films were also characterized by x-ray diffractometry.

Keywords. Tin dioxide films; electron beam evaporation; annealing behaviour; sheet resistivity.

1. Introduction

Thin transparent conducting films of SnO_2, because of their wide application in solar cells, have currently become a subject of intense investigation. The SnO_2 film is a transparent conductor which is sometimes known as Nesa glass (Ishiguro *et al* 1958). The optical and electrical properties of SnO_2 films were studied by Arai (1960) who found them to be polycrystalline *n*-type degenerate semiconductor with a free carrier density of 7×10^{18}–$1{\cdot}7 \times 10^{19}$ cm^{-3} and an energy band gap of about 3·5 eV. The change in the conductivity of the material (SnO_2) in thin films as compared to that in bulk arises due to anion oxygen defects.

It is known (Raccanelli and Madalena 1976; Viscrian and Georgescu 1969; Shanthi *et al* 1980) that post-annealing treatment of SnO_2 films can result in change of electrical properties. It has recently been reported (Ghosh *et al* 1978; Nagatoma *et al* 1979) that the annealing of SnO_2 films plays an important role in the improvement of the performance characteristics of SnO_2/Si solar cells. It has been found that on annealing the resistivity of pure SnO_2 single crystals reduces and that of the SnO_2 films deposited by hydrolysis of an ether-alcohol solution of Sn $(OC_2H_5)_4$ first decreases and then increases drastically on annealing at temperatures higher than 500°K (Jarzebeski 1976). But no satisfactory explanation is available for the phenomenon.

As far as the authors are aware, investigations on the annealing behaviour of electron beam deposited SnO_2 film, which are important in solar cells, have not been reported. The present work was therefore undertaken.

2. Experimental

2.1 *Sample preparation*

SnO_2 films were prepared by electron-beam evaporation at a pressure $\sim 10^{-6}$ torr. Undoped SnO_2 (99·90%) was evaporated by an electron-beam gun onto chemically

cleaned glass substrates at room temperature (300°K). An evaporation rate of 4 Å sec^{-1} was maintained to produce films of SnO_2 with approximately uniform thickness of about 1300 Å. The thickness of the films was measured during evaporation by a quartz crystal thickness monitor and also by the interferometry method.

2.2 *Resistivity measurement*

The resistivity of the films was measured in a furnace during annealing as a function of time. The temperature of the furnace was maintained constant (± 5°C). The sheet resistivity of SnO_2 films was also measured during annealing as a function of temperature in the range (623–808 K). The temperature of the furnace was regulated at approximately 3°C/min. The temperature was measured with a chromel-alumel thermocouple. X-ray diffraction measurements of the films were made (Philips x-ray diffractometer, model No. PW-1140/90) and scanning electron micrographs taken (SEM-501, Philips make).

3. Results and discussion

The sheet resistivity of the as-deposited SnO_2 films was very high (> 20 MΩ) and decreased with annealing in air. The variation of sheet resistivity as a function of time during isothermal annealing at different temperatures is shown in figure 1. The as-deposited or unannealed SnO_2 films (evaporation temperature above 1800°C) are expected to be amorphous in character as shown by its high resistivity. This amorphous character is confirmed by x-ray diffractometric characterisation (figure 2a). The peaks of the x-ray diffraction pattern show crystallization with time during annealing at 717, 701 and 688 K respectively (figure 2) as also indicated by decrease in resistivity. As expected, the general shape of the isothermal annealing curves (figure 1), at different temperatures is very similar.

It was observed that the time at which the films became conducting increases as the annealing temperature decreases. This is expected because the thermally activated process of transformation from the amorphous to the polycrystalline phase will slow down with decrease of annealing temperature. This also explains the broadening of the minima with decreasing annealing temperature. The decrease in sheet resistivity with time (figure 1) may be attributed to the reduction in defect density as shown by the x-ray diffraction results, and in addition chemisorption of oxygen also takes place which further reduces the resistivity of the films (Shanthi *et al* 1980). The sheet resistivity attains a minimum when the defect distribution may be assumed to be in equilibrium (Chopra 1969). The increase in the observed resistivity after the minimum is dominated by the formation of pores and further increase in size of the pores. The SEM photographs (figures 3a, b) corresponding to 37 and 60 min annealing give only pores with their size increasing.

The variation in sheet resistivity with temperature on annealing the SnO_2 film in air is plotted in figure 4. The film showed irreversible decrease in sheet resistivity, perhaps due to the reduction of defect density with increasing temperature. This mechanism governing the resistivity of films is well known (Maissel and Glang 1970). The minimum nearly corresponds to the Debye temperature of SnO_2 [$\sim 500°$ K], so that the largest

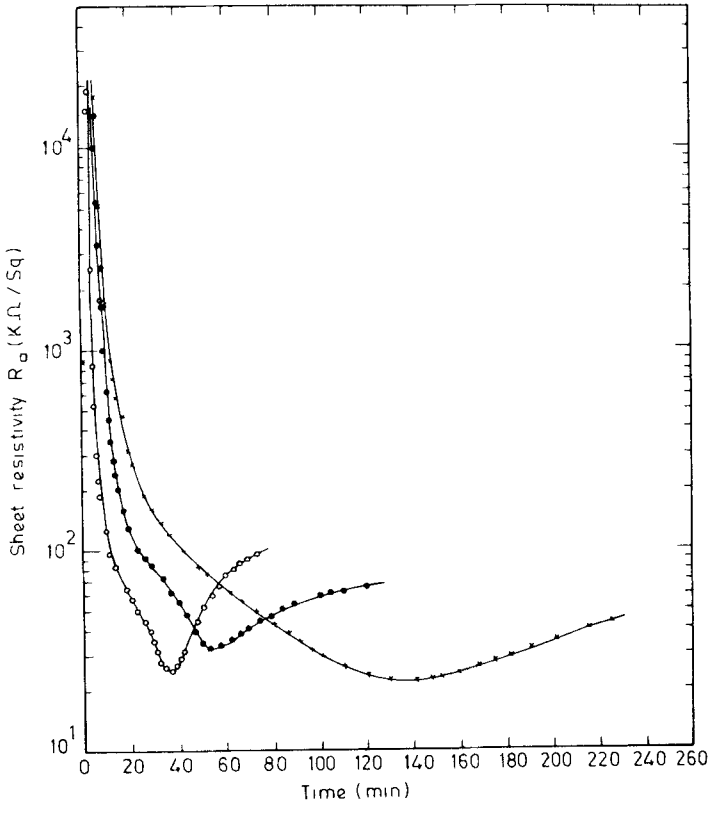

Figure 1. Sheet resistivity *vs* time for SnO_2 films deposited on glass substrate during isothermal annealing (o)-701 K; (•)-688 K; (×)-660 K.

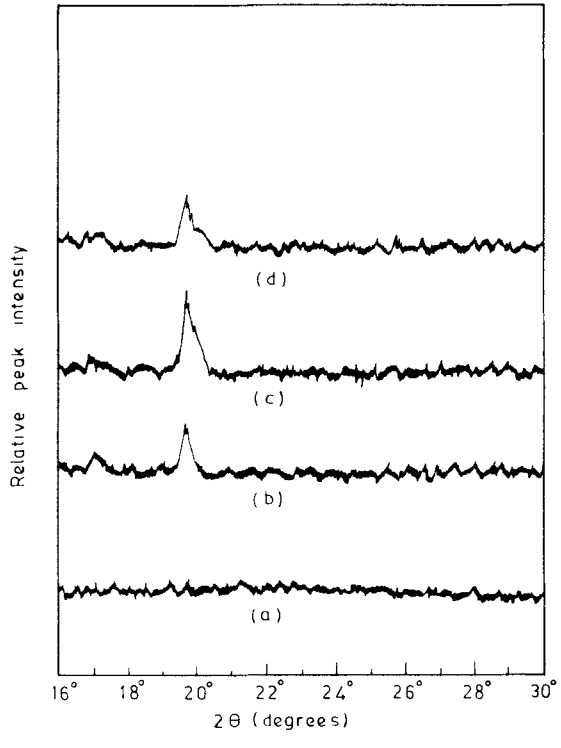

Figure 2. X-ray diffraction pattern for SnO_2 films deposited on glass substrate. **a**. Unannealed films, **b**. $t = 4$ min annealed at 717 K, **c**. $t = 37$ min annealed at 701 K, **d**. $t = 1$ hr annealed at 688 K.

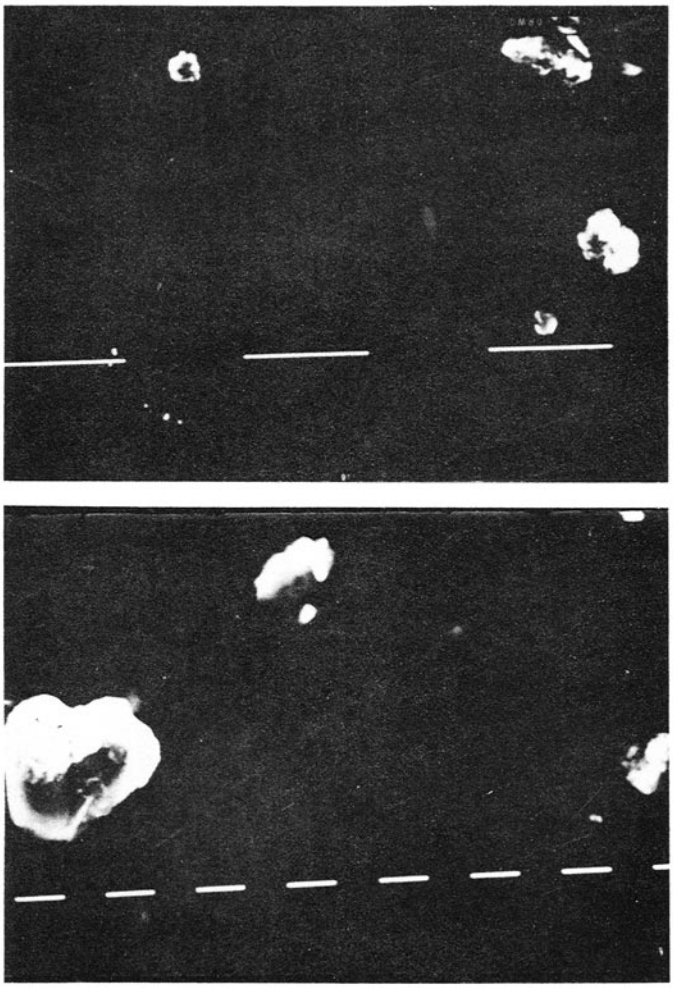

Figure 3. Scanning electron micrograph of SnO_2 films deposited on a glass substrate annealed at 701 K, **a.** annealed for 37 min (magnification: 160 × 1·1). **b.** annealed for 1 hr (magnification 640 × 1).

part of the lattice defects is removed because of the maximum frequency of the lattice vibrations (Chopra 1969). Therefore, beyond this point the resistivity increases.

We have attempted here to give a qualitative interpretation of the results obtained on the annealing behaviour of tin dioxide films. A quantitative study is in progress.

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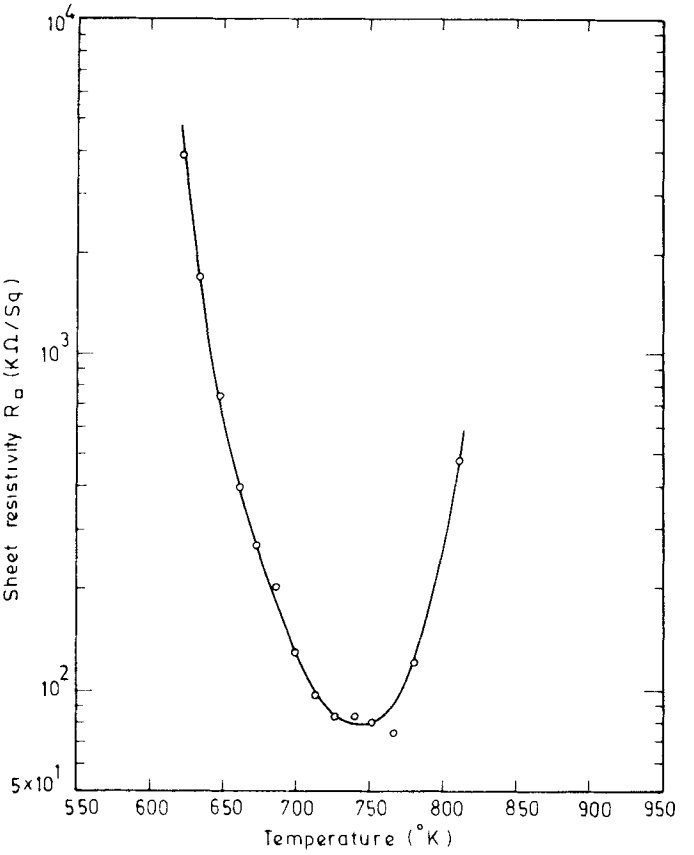

Figure 4. Sheet resistivity *vs* temperature for SnO_2 film deposited on a glass substrate.

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