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Microstructure of vacuum-deposited tin thin films

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Tin thin films of equal thickness were vacuum deposited on NaCl substrates at different deposition rates both in high vacuum (2×10^{-5} Torr) and poor vacuum (1×10^{-3} Torr). These films were examined by electron microscopy and the grain size and density in the films were determined. It was found that both in poor and high vacuum, as the deposition rate was increased the grain size decreased and grain density increased. However, the deposition rate must be increased by an order of magnitude in order to observe large changes in the grain size and density. It was also observed that the films prepared in poor vacuum, especially at low deposition rates, consist of islands with jagged edges. These observations have been interpreted on the basis of nucleation theory and the effect of adsorbed/chemisorbed gases on island growth in these films.

1. Introduction

Epitaxial growth and the microstructure of vacuum-deposited tin thin films prepared under different growth conditions have attracted the attention of several workers. This is because the microstructure influences the properties of these films, especially the superconducting properties, which find application in cryogenic computing devices [1–3]. Osaka *et al.* [4] studied the epitaxial growth of tin films and found that the film islands are composed of faceted particles when grown at lower substrate temperatures, while they consist of spherical particles at high substrate temperatures. Shimaoka [5] found that if a lateral electric field is applied or an electron bombardment is carried out during the evaporation there is a preferential epitaxy of Sn films, while Patel and Damodara Das [6] found that initially polycrystalline films, when bombarded with electrons, agglomerate into single crystalline islands. Damodara Das and Gopalakrishnan [7] found that an applied electric field during growth decreases the resistivity of Sn films at low strengths and increases it at high strengths, thus indicating the influence of the field on the microstructure. On the other hand, Murr *et al.* [8, 9] found no effect on the microstructure of tin films due to an applied electric field during growth. Malhotra *et al.* [10] studied the effect of substrate temperature and deposition rate on the microstructure and found that tin films grown at a temperature of about two-third the melting point at a rate of 0.6 nm sec^{-1} are single crystalline. Singh *et al.* [11, 12] studied the effect of substrate temperature and thickness on island density and island size of Sn thin films and evaluated the saturation density and the activation energy for diffusion. Hill *et al.* [13] studied the effect of oxygen and structure on the superconducting properties of Sn films, while Watton [14] finds that the superconducting transition temperature is altered by the grain size of the films.

In the above studies, the effect of various growth parameters such as electric fields, substrate temperature and electron bombardment on the structure of the films has been studied, but the vacuum during deposition has been good, either 10^{-8} to 10^{-9} Torr or 10^{-5} to 10^{-6} Torr. The present paper aims at the study of the extent of the influence of ambient gases in poor vacuum conditions (10^{-3} Torr) on the morphology and microstructure of vacuum-deposited tin thin films and the effect of deposition rate. It is expected that considerable changes occur in the microstructure of the films deposited in poor vacuum due to

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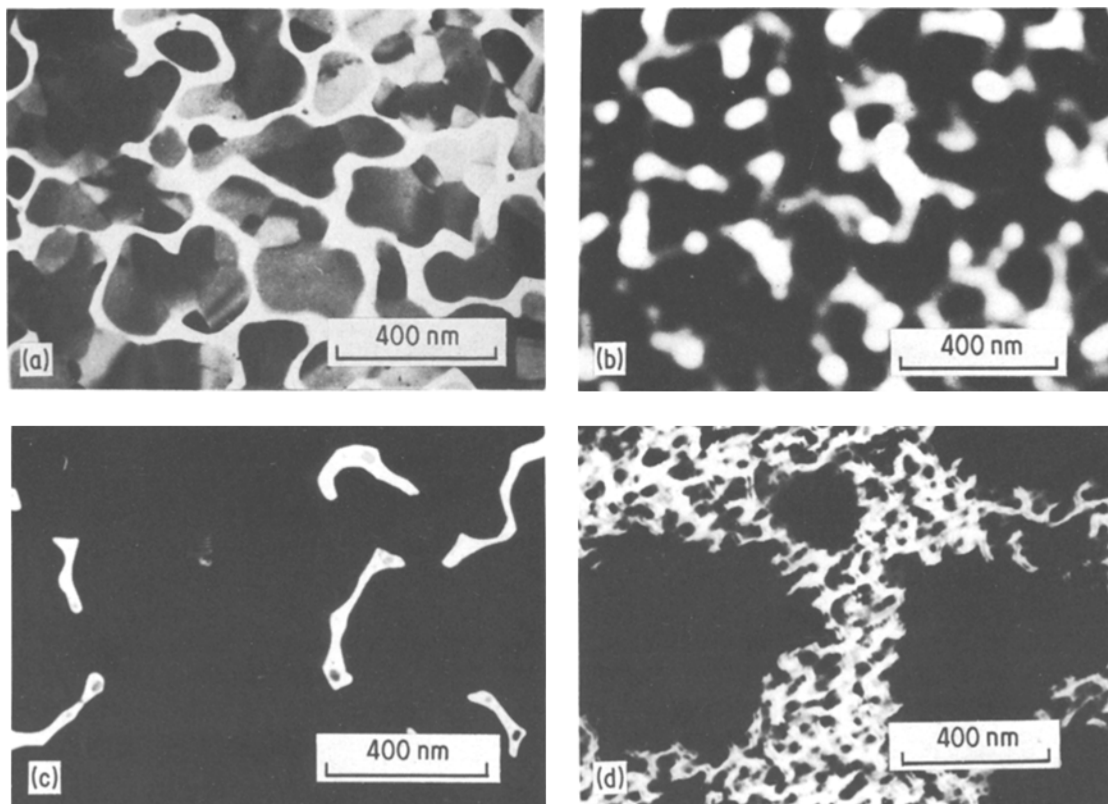

Figure 1 Electron micrographs of tin thin films of 50 nm thickness deposited at (a) 2, (b) 1, (c) 0.3 and (d) 0.014 nm sec^{-1} in a vacuum of 2×10^{-5} Torr.

gas-vapour atom interactions which have a direct bearing on the properties of the films.

2. Experimental procedure

Thin films of β-Sn of equal thickness (50 ± 3 nm) were prepared by vacuum deposition from a flat molybdenum boat at different deposition rates onto freshly cleaved NaCl surfaces, in both high vacuum (2×10^{-5} Torr) and poor vacuum (1×10^{-3} Torr). After removal from the NaCl surfaces, the films were examined in transmission and by a selected area diffraction technique in an electron microscope. The film thicknesses were measured by multiple beam interferometry and the deposition rates were deduced.

3. Results

Figs 1a to d show the electron micrographs of the films of almost the same thickness (50 ± 3 nm) grown in a vacuum of 2×10^{-5} Torr at deposition rates of 2, 1, 0.3 and 0.014 nm sec^{-1}, respectively. It is seen from the figures that as the deposition rate decreases there is an increase in the size of the grains. However, it is evident that for the first three deposition rates (which are of the same order of magnitude) there is only a small change in the grain size of the films, while for the last deposition rate (where the order of magnitude is changed) a marked change is observed. It is also evident from the figures that the density of grains decreases with a decrease in the deposition rate. It is interesting to note that the film formed at the rate of 0.014 nm sec^{-1} has grains with jagged edges. Figs 2a and b show the plots of grain size and grain density of the films of Fig. 1 against deposition rate, n, and log of deposition rate, respectively. Fig. 2b shows that the change in grain size is linear with respect to log of deposition rate. Even though Fig. 2a indicates a near linear dependence of grain density on deposition rate, Fig. 2b shows that the dependence is not simply linear but is more complex.

Figs 3a to d are the electron micrographs of the films of almost the same thickness (50 ± 3 nm) grown in a vacuum of 1×10^{-3} Torr at deposition rates of 2.5, 1.7, 0.25 and 0.11 nm sec^{-1}, respec-

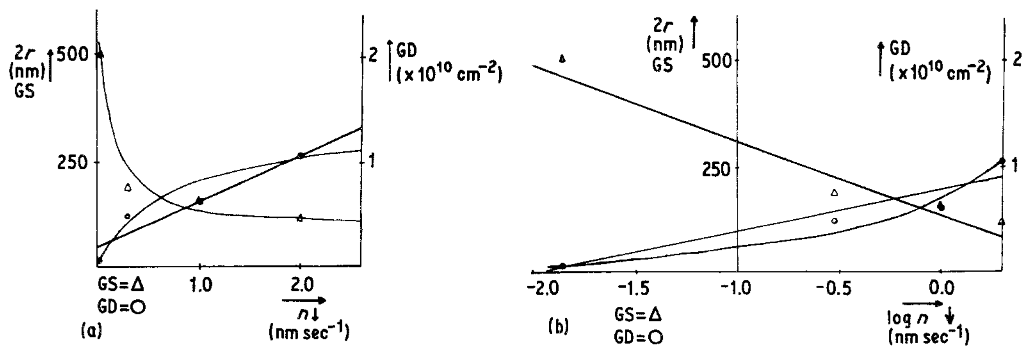

Figure 2 Plots of grain size ($2r$) and grain density against (a) deposition rate, n and (b) $\log n$ for the films of Fig. 1.

tively. Figs. 4a and b show the plots of grain size and grain density of films of Fig. 3 against deposition rate and log of deposition rate, respectively. It can be seen from the micrographs and plots of Figs 3 and 4 that similar dependences of grain size and grain density on deposition rate occur in the case of films prepared in poor vacuum. However, it should be noted that the increase in grain size and grain density with a decrease and an increase respectively in the deposition rate is larger in the case of poor vacuum films. Furthermore, here films grown at low deposition rates of 0.25 and 0.11 nm sec^{-1} also have jagged grains. However, it should be noted that the above deposition rates are 20 and 10 times larger than 0.014 nm sec^{-1}, the rate for which jagged grains were observed at 2×10^{-5} Torr vacuum.

4. Discussion

The final island size and island density in a thin film will be determined by the size of the critical nuclei and saturation nucleation density [15, 16],

Figure 3 Electron micrographs of tin thin films of 50 nm thickness deposited at (a) 2.5, (b) 1.7, (c) 0.25 and (d) 0.11 nm sec^{-1} in a vacuum of 1×10^{-3} Torr.

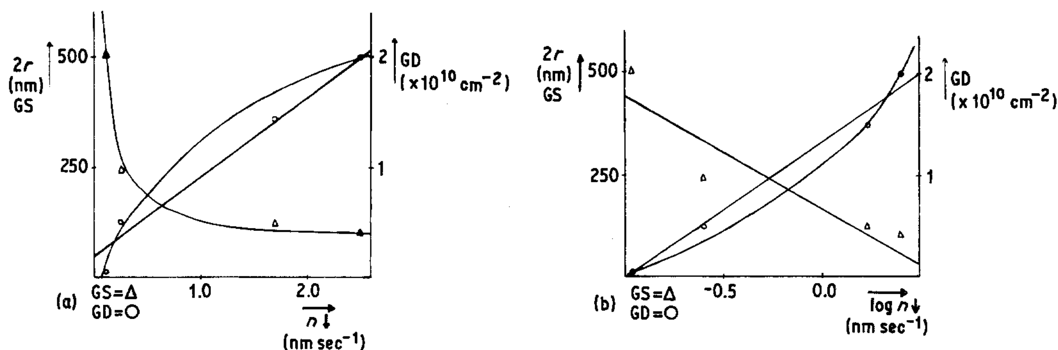

Figure 4 Plots of grain size ($2r$) and grain density against (a) deposition rate, n and (b) log n for the films of Fig. 3.

growth and coalescence of islands [16] and island–gas interactions [16]. The nucleation theory predicts [15, 16] that a decrease in the deposition rate (a) increases the size of the critical nucleus, and hence, the size of the nuclei, and (b) increases the nucleation frequency, and hence, the number of nuclei by decreasing the critical free energy of condensation. However, because of the logarithmic dependence of the "free energy in the bulk" on the deposition rate, a large change (in the order of magnitude) in the deposition rate is essential for any observable changes in the size of the critical nuclei and the nucleation frequency, and hence, in grain size and grain density of the final films. Thus the observation that island size and density of the films are found to alter to a significant extent only when there is a change in the deposition rate by an order of magnitude, and the observed nature of the changes in both high and poor vacuum films, can be explained on the basis of the nucleation theory. It can also be concluded that despite other phenomena like grain growth, coalescence and adsorbed and chemisorbed gases influencing the final island structure of the films, the latter is significantly controlled by the critical nuclear size and the nuclear density.

The observations that the films formed in poor vacuum show larger changes in grain size and grain density with changes in deposition rate, have a different microstructure, and have grains with jagged edges at comparatively higher deposition rates, indicate that the ambient gases, especially oxygen and water vapour, have a strong influence on the microstructures of these films. As is known, during the deposition process, gas molecules (water vapour and oxygen) will be constantly striking the substrate surface, and the number of these striking per second (per unit area) in poor vacuum will be larger. At very low deposition rates the ratio of the number of gas molecules to the number of metal atoms striking the substrate surface per second will be very large, so that at any given instant of time a large number of gas molecules will be present on the substrate surface. It is understandable that these gas molecules, because of their chemical and physical affinity to the metal atoms, obstruct the migration of metal atoms and metal atom clusters from one site to another, and hence necessitate the growth of only the isolated large nuclei already formed. The observation of very irregular shapes of grains which give them a jagged appearance at low deposition rates (compare with Figs 1d, 3c and 3d) supports the above statement about the influence of impinging gas molecules on the film structure.

Earlier workers such as Powell *et al.* [18, 19], Casewell [20] and Preece *et al.* [21–23] have studied the chemisorption and the influence of residual gases like oxygen, nitrogen and others on the microstructure and properties, and they also find a significant influence of residual gases, especially oxygen, on tin film microstructure, epitaxy and properties. Powell *et al.* [18, 19] find that tin exposed to oxygen at a pressure as low as 5×10^{-6} Torr at room temperature contains both the tin oxides. Hence, adsorption and chemisorption of oxygen at higher pressures of 1×10^{-3} Torr in the present case is naturally expected. Casewell [20] finds that specific residual gases like O_2, H_2, CO_2, etc., reduce the surface mobility of adsorbed Sn atoms, while Preece *et al.* [21, 22] find that the presence of oxygen changes the orientation of Sn films formed, and they attribute this to reduced surface mobility of adsorbed tin atoms during the growth of the film. Preece *et al.* also find different orientations of tin films when formed in 10^{-8} Torr and 10^{-5} Torr vacua. Thus their observations too support our attribution of changes in micro-

structure of tin films to interactions between gas and metal atoms.

It is possible that some of the Sn atoms interact with oxygen and other gases during transit to the substrate and condense as oxide molecules. However, selected area diffraction patterns of the films did not reveal any presence of oxides in the film. Preece *et al.* [23] were also not able to locate crystalline SnO in the films deposited at 10^{-5} Torr but found abnormal reflections in electron diffraction patterns which could be attributed to the presence of oxygen. This is possibly because the oxides are present in small traces only on the surfaces of islands as has been observed by Auger and EEL spectroscopy by Powell *et al.* [18, 19].

5. Conclusions

It can be concluded from the present study that variation of island density and island size of films vacuum-deposited at both high and poor vacua is significantly controlled by the critical nuclear size and saturation nucleation density even though other processes such as grain growth, coalescence of grains and adsorption/chemisorption of gases influence the final island structure. The jagged edges of the islands observed in films formed at low deposition rates and in poor vacuum are attributed to the chemisorption of oxygen on the growing islands and gas–metal atom interactions during transit.

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