A study on nucleation, growth and grain boundary reflection in thin tin nanofilms

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Abstract. The present work incorporates a study on nucleation, and growth due to the changes in the nano-structural properties as a function of thickness and grain boundary reflection in tin thin nanofilms. Thickness happens to be one of the important and crucial nanofilm preparative parameters which dictates majority of properties like, nano-structure, electrical, optical and morphological texture of evaporated tin nanofilms. Hence, we have selected tin nanofilms in the thickness range 20-160 nm, in order to study the thickness dependence of their nano structural and electrical properties, in the temperature range 77-450 K, in detail. All the films were grown in a conventional vacuum coating unit under a pressure of \(\sim 10^{-6}\) Torr at room temperature of 22 °C, onto cleaned glass substrates. The tin film nano-structure was analyzed by Transmission Electron Microscope (TEM). The nano structural properties can be tuned to the desired level and application by the proper choice or proper combination of deposition parameters. And it is found to depend upon the nature of the substrate material, environment and the binding force between the substrate material and evaporated tin atoms.

1. Introduction

The present work is the extension of the earlier work reported on thin tin films\([1,2]\). Thin film science has received tremendous attention in the recent years for their applications in diverse fields such as, microelectronic industries, military weapons systems, space science, solar energy utilization, cell phones, smart devices, computer note books and gas sensors etc.\([3-8]\). Thickness plays an important role in thin films as it is a significant parameter, which affects the optical, electrical, nano-structural properties considerably. Thin film properties mainly depend on the preparative conditions, film nano-structures, presence of defects and impurities.

Tin has low resistivity, low melting point, high temperature coefficient of resistance and negative thermo-electric power in the bulk form. Tin develops a milky white surface because of its un-specular reflection. Therefore tin is rendered unsuitable for mirror coatings. However, it is used as one of the components in solder material and its oxides and compounds are widely used in the
fabrication of solar cells and liquid crystal displays[9,10] and other semiconductor devices. In view of the above mentioned interesting properties of tin metal in the bulk form, a study on nucleation, growth and electrical properties in thin tin nanofilm form has been undertaken herewith. There are several steps involved in the growth process from nucleation to final film formation stage. By the knowledge of the nanostructure, it is possible to select a material of specific thickness for specific application in order to suit it for conduction or insulation mechanisms. By varying the deposition parameters the electrical, optical and nano-structural properties of films can be regulated.

2. Theoretical section

The electrical resistivity of thin films, based on the Fuchs-Sondheimer(FS) theory [11,12] is given by

$$\rho = \rho_0 / \left( 1 + \frac{3}{8} \frac{(1-p)}{\lambda} \right), \quad \lambda > 0.1$$  \hspace{1cm} (1)

where $\rho$ = resistivity of thin film,
$\rho_0$ = the resistivity of the infinitely thick film,
$\lambda$ = the ratio of the film thickness($t$), to the conduction electron mean free path($l$),
$p$ = the specularity parameter.

The second term on the Right Hand Side(RHS) of Eq.(1) is contribution to the electrical resistivity from size effect. Taking into account of the grain boundary scattering, which is predominant in very thin films, Mayadas - Shatzkes (1970) modified the above equation as [13]

$$\rho = \rho_0 / \left( 1 + \frac{3}{8} \frac{(1-p)}{\lambda} + \frac{3}{2} \alpha' + \ldots \right)$$  \hspace{1cm} (2)

where $\alpha' = l(R)/d(1-R)$ = the scattering power of grain boundaries which depends upon the electron mean free path($l$) and average grain size($d$) and $R$ being the grain boundary reflection coefficient. The third term on the RHS of Eqn. (2) is contribution to the electrical resistivity from grain boundary scattering.

3. Experimental Section

The vacuum coating unit used in the present investigation is the ‘Hind High Vacuum Coating Unit, Model 12A4D’, to grow thin films of tin in this work. The film thickness was controlled by means of an in-built Quartz Crystal Digital Thickness Monitor (Model DTM-101). Tin was evaporated from a molybdenum boat, and the distance between the boat and the glass substrate was around ~22 cm. Tin of purity 99.99% was thermally evaporated by resistive heating technique on to cleaned glass slides. The glass slides were cleaned initially in chromic acid, ultrasonically and at last by the ionic bombardment method. Thin tin films in the thickness range 20-160 nm have been grown on to thus cleaned glass substrates at the rate of 0.5 nm/s under a pressure of ~10^{-6} Torr at room temperature of 22°C. After growing the films, they were taken out of the vacuum chamber for nano-structural analysis and temperature dependent resistivity measurements in the range 77-450 K. The sample preparation technique in order to view image for TEM analysis is given below:

3.1 For TEM
Nano-films were grown in the conventional vacuum chamber on freshly cleaned glass substrates for their structural studies. The films were removed from the glass substrates by immersing them in distilled water. Afterwards, these films were mounted on carbon coated copper grids (having 200 meshes/cm²). All the films were examined with Hitachi Transmission Electron Microscope for bright field image.

3.2 For grain boundary reflection measurement

We have initially measured the resistance of tin nanofilms by four probe technique [12], at temperatures 77, 300 & 450 K as a function of thickness. For observing the effect of temperature on \( \rho_0 \), \( l \) and \( \rho \); the plots \( \rho \) vs \( t \) have been drawn at temperature 77, 300 and 450 K, in the thickness range 40-160 nm for tin nanofilms, which is shown in Fig. 1, since tin exhibits a positive TCR, Fig. 2 shows the plot of \( (\rho \times t) \) vs \( t \) at 77, 300 and 450 K for tin nano films. These are found to be straight lines yielding values for slopes as \( \rho_0 \), and intercepts give values for \( \frac{1}{\rho_0} \), which are given in Table I. The grain boundary reflection coefficient (R) was determined from the resistivity data and its average values at temperatures 77, 300 & 450 K are listed in the same table I.

![Figure 1](image.png)

**Figure 1.** Resistivity, \( \rho \times 10^8 \Omega \text{ m} \) Versus Thickness \( t \) for tin nano films based upon Fuchs – Sondeimer theory (lower curve) and Experimental (upper) curve based on Mayadas - Shatzkes theory.
Figure 2. $\rho t \times 10^{17} \Omega \text{m}^2$ versus Thickness ($t$) for tin nano films ($t > 80$ nm).

The symbols used in the graph are the actual measured data points.

Figure 3. Grain Boundary Reflection coefficient average ($R_{av}$) Versus thickness ($t$) for tin nano films with linear fit.
### Table 1. (For tin nanofilms)

| Temperature, K | Infinitely thick tin film resistivity $\rho_0 \times 10^5$ $\Omega$ m | Conduction Electron mean free path $l$ (nm) | Specularity Parameter $\rho$ | Average grain boundary reflection coefficient $R_{av}$ |
|---------------|-------------------------------------------------|------------------------------------------|-----------------------------|----------------------------------|
| 77            | 5.01                                            | 196                                     | 0                           | 0.53                             |
| 300           | 11                                              | 143.4                                   | 0                           | 0.74                             |
| 450           | 15                                              | 111                                     | 0                           | 0.92                             |

4. Results and Discussion

4.1 The morphology and nanostructure were analyzed using TEM. The TEM images of Sn films reveal that the observed morphological and nano-structural modification induce changes in electrical properties. It is found that there was no electrical continuity of the tin films below the 40 nm thickness. The initial stages of the growth of the film is formation of nucleation centres/islands structures as shown in Fig. 4 (a). No physical connections between the nuclei/islands exist and hence no electrical continuity is achieved. The small islands are dense populated. As the thickness increases, the smaller islands merge with bigger islands and well crystallized with various nano crystalline morphology as depicted in Fig. 4 (b) [15]. Both grains and sub-grains are clearly visible in the TEM nanographs. Similar type of results were obtained by T. M. Rajkumar et.al. for Cd chalcogenide films [14]. As the thickness increases the island structures merge with forming a semi continuous or quazi-continuous structure, with bigger voids, which has been shown in the Fig. 4 (c). Further if we increase the thickness, again the quazi-continuous structures merge with neighboring ones and the voids between the structures will be reduced as shown in the Fig. 4 (d). With the further increase in the thickness almost the entire structure becomes continuous and the film became opaque, to the incident electron beam in the TEM and thus film helps in the conduction of current.
Figure 4. TEM images of thin tin nanofilms for different thicknesses and magnifications.

4.2 Grain Boundary Reflection Coefficient Analysis

In case of tin films, the thickness dependence of electrical resistivity graph approaches the saturation value of $15 \times 10^8 \, \Omega \, m$ after about a thickness of 100 nm, for the resistivity measurement.
done at 300 K, 8 & 19 $10^8$Ω m respectively, for the measurements taken 77 & 450 K, as shown in the Fig. 1. However, we obtained the infinitely thick film resistivity ($\rho_\infty = 11 \times 10^8$ Ω m) which is same as that of the bulk tin value ($\rho_B = 11 \times 10^8$ Ω m) [15] from the plot of ($\rho x t$) vs t (Fig. 2). Tin being a metal of low melting point in the bulk form, has a low resistivity even in the thin film form. Because, low melting point metals produce large crystal, preferentially oriented to the substrate[18]. This has been confirmed by the TEM study on tin films. We have estimated the average island (crystal ) size as 31.1 nm for 30.0 nm thickness tin nanofilm from Fig. 1(b).

We did not see the electrical continuity of tin films below 30 nm thickness which has also been reported by Pal and Sen (1977) [19], Kong et al. (1977) [20] and Stolecki et al. (1979) [21]. Although there is a fairly good agreement between the Fuchs theory and our experimental points of resistivity data, for higher film thicknesses, there is a wide difference between the Fuchs theoretical curve and our experimental data for lower thickness films (< 80 nm). This is mainly due to the grain boundary scattering and is predominant in lower thickness films. The Fuchs theory considers only size effect but disregards the scattering of electrons from grain boundaries.

So, Mayadas-Shatzkes (M-S) theory [13] takes into account the grain boundary scattering in addition to the Fuchs size effect. The M-S theory is in good agreement with our experimental $\rho$ data throughout the thickness range. Similar type of deviation between the Fuchs and experimental curves for the resistivity data has been reported for other substances like Yb [22], Ni[23], Pd [24], and Sm [25] films. By knowing the difference between the Fuchs and M-S theoretical $\rho$ curves, we have estimated the value of $R$, the grain boundary reflection coefficients, for the $\rho$-$t$ data, measurements done at temperatures 77, 300 and 450 K. The values of $R$ calculated closely agrees with that reported by Pal and Sen (1977) [21].

For the tin films. M – S theory holds good to our experimental data for $p = 0$, for all the $p$ versus $t$ data at temperature 22, 300 and 450 K, indicating total diffuse scattering of conduction electrons. From this value of $p$, we have calculated the electron mean free paths ($\lambda$) which have been given in Table I. It is clear from the table I that as the temperature of Sn nano film is decreased, the value of conduction electron mean free path increases due to decrease in the amplitude of thermal vibrations of the Sn-lattice. The average grain boundary reflection coefficient decreases with the decrease in temperature, again due to decrease in the amplitude of lattice vibrations, as shown in Fig. 3.

5. Conclusion

We have depicted the thickness dependence of nano-structural properties of thin tin films starting from nucleation, growth and final film formation mechanisms. The structure of the nanostructure is found to depend upon the thickness and preparative conditions. The observed morphological and nano-structural modifications induce changes in the electrical properties of tin films. By judicial adjustments of deposition parameters, one can grow films of specific nanostructure/thickness for specific applications as required for optical and electrical devices. The F-S theory considers only size effect and neglects grain boundary scattering. The M-S theory considers the grain boundary scattering also. Our experimental results
for tin nano films closely fits with M-S theory for the entire range of film thickness and temperature. The electron mean free path and grain boundary reflection coefficient are found to be temperature dependent in tin nano films.

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Supplementary data for Tin

Fig. 1 Resistivity, $\rho \times 10^8 \, \Omega \cdot m$ Versus Thickness (t) for tin nano films based upon Fuchs–Sondeimer and Mayadas–Shatzkes theories.

| Thickness (t) in nm | Resistivity due to Fuchs $\rho_f \times 10^8 \, \Omega \cdot m$ | Experimental resistivity value at 77 K $\rho_e \times 10^8 \, \Omega \cdot m$ | Resistivity due to Fuchs $\rho_f \times 10^8 \, \Omega \cdot m$ | Experimental resistivity value at 300 K $\rho_e \times 10^8 \, \Omega \cdot m$ | Resistivity due to Fuchs $\rho_f \times 10^8 \, \Omega \cdot m$ | Experimental resistivity value at 450 K $\rho_e \times 10^8 \, \Omega \cdot m$ |
|---------------------|-------------------------------------------------|---------------------------------|-------------------------------------------------|---------------------------------|-------------------------------------------------|---------------------------------|
| 40                  | 14.5                                           | 21.5                            | 25.8                                            | 30                              | 30.6                                            | 39.5                            |
| 50                  | 12.6                                           | 17                              | 22.8                                            | 26.5                            | 27.5                                            | 34                              |
| 60                  | 11.4                                           | 14                              | 20.8                                            | 22.5                            | 25.4                                            | 30                              |
| 70                  | 10.5                                           | 12                              | 19.5                                            | 20.5                            | 23.9                                            | 26                              |
| 80                  | 9.8                                            | 9.8                             | 18.4                                            | 18.4                            | 22.8                                            | 22.8                            |
| 100                 | 8.9                                            | 8.9                             | 16.9                                            | 16.9                            | 21.2                                            | 21.2                            |
| 120                 | 8.2                                            | 8.2                             | 15.9                                            | 15.9                            | 20.2                                            | 20.2                            |
| 140                 | 7.8                                            | 7.8                             | 15.2                                            | 15.2                            | 19.5                                            | 19.5                            |
| 160                 | 7.4                                            | 7.4                             | 14.7                                            | 14.7                            | 18.9                                            | 18.9                            |
Fig. 2 $\rho \times t, (\times 10^{17} \ \Omega \ m^2)$ versus Thickness (t) for tin nano films (t > 80 nm).

| Thickness(t) in nm | $\rho \times t, (\times 10^{17} \ \Omega \ m^2)$ at 77 K | $\rho \times t, (\times 10^{17} \ \Omega \ m^2)$ at 300 K | $\rho \times t, (\times 10^{17} \ \Omega \ m^2)$ at 450 K |
|-------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|
| 80                | 784                                                | 1472                                               | 1824                                               |
| 100               | 890                                                | 1690                                               | 2120                                               |
| 120               | 984                                                | 1908                                               | 2424                                               |
| 140               | 1092                                               | 2128                                               | 2730                                               |
| 160               | 1184                                               | 2352                                               | 3024                                               |
Fig. 3 Grain Boundary Reflection Coefficient average ($R_{av}$) Versus thickness ($t$) for tin nano films with linear fit.

| Temperature in K | $R_{av}$ |
|------------------|----------|
| 77               | 0.53     |
| 300              | 0.74     |
| 450              | 0.92     |