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# Size and temperature effects on thermoelectric power of $\beta$ -tin thin films

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Tin thin films of thicknesses in the range 500–7000 Å have been prepared by vacuum deposition at room temperature at a pressure of  $5 \times 10^{-5}$  Torr on glass substrates. Thermal electromotive forces (emfs) of these films have been measured after aging as a function of temperature difference. It is found that the thermoelectric power of the films is independent of temperature in the range studied (300–425 °K). It is also found that the thermoelectric power of the films obeys the inverse thickness dependence predicted by size effect theories. The electronic mean free path is evaluated to be 530 Å.

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## INTRODUCTION

The thermoelectric power is one of the most sensitive electronic properties of a material. The thermoelectric power of a material in the thin film state is a function of thickness as a consequence of scattering of electrons from the surfaces—both external and grain boundary—and the changing external surface to volume ratio with thickness. There have been several studies on transport properties of tin in the thin film state but only a few on the thermoelectric power. Fujita *et al.*<sup>1</sup> have studied the thermoelectric power of tin films at low temperatures (3.7–8 °K) and found that it varies as  $S = aT + bT^2$  in the above range of temperatures. They have explained the variation of “ $a$ ” (in the equation) with thickness on the basis of the mean free path theory of size effect. The values of “ $a$ ” and “ $b$ ” obtained by them were found to be in agreement with the values of Altukhov and Zavaritskii<sup>2,3</sup> who studied the thermoelectric power of tin in the bulk state at low temperatures and the effect of impurities on it. Zavaritskii and Altukhov<sup>2</sup> have found that both the phonon and the electronic components of thermoelectric power of tin at low temperatures increase several times with increasing impurity concentration. They used as impurities Cd, In, Sb, Te, and Pb up to 0.2%. Fryer *et al.*<sup>4</sup> studied the thermoelectric power of bulk polycrystalline tin between 4.2 and 280 °K and found that it varied from sample to sample. They ascribed this variation not to impurities but to anisotropy in the thermoelectric property of tin and to the fact that the different samples had different preferred orientations. They also found that at very low temperatures (below 12 °K) the thermoelectric power is negative, it becomes positive at 12 °K, increases up to 30 °K, then decreases and again becomes negative between 60 and 100 °K. It remains negative till 280 °K. They also found that the thermoelectric power did not vary linearly in any part of the region. Their results below 12 °K are in agreement with the results of earlier workers like De Vromen,<sup>5</sup> Puller,<sup>6</sup> and Van Baarle *et al.*<sup>7</sup> Van Baarle *et al.*<sup>7</sup> also found that the thermoelectric power of tin single crystals, especially the phonon drag component, showed anisotropy between 3.7 and 9 °K. Zhilik<sup>8</sup> measured the thermoelectric power and its temperature coefficient for tin films of different thicknesses in the temperature range 113–273 °K and found them to be functions of thickness. He only qualitatively attributed this variation to surface area

increase and crystal defects without recourse to any theoretical explanations. It is seen from the above that even though there has been some work on the thermoelectric properties of tin, it is only at very low temperatures, except for the work of Fryer *et al.*<sup>4</sup> Also, there is very little work on tin in the thin film state, except that of Zhilik<sup>8</sup> and the recent work of Fujita *et al.*<sup>1</sup> which is again at very low temperatures. Thus all the works pertain to  $\alpha$ -tin (cubic and semiconducting) which is the stable structure below 291 °K. The present paper describes the studies on the thermoelectric power of  $\beta$ -tin thin films i.e., above room temperature and up to about 425 °K and explains the results on the basis of the size effect theories of thermoelectric effect.

## EXPERIMENTAL

$\beta$ -tin thin films of thicknesses between 500 and 7000 Å were prepared by vacuum deposition onto clean glass substrates held at room temperature at a constant deposition rate in a vacuum of  $5 \times 10^{-5}$  Torr. A large quantity of the material was taken in the boat (about 1 g.) and the required, much smaller quantity of the material was evaporated to keep the current through the boat during an evaporation, constant. The films of different thicknesses were prepared in individual evaporations and the thickness were measured “*in situ*” using a quartz crystal thickness monitor. The lateral dimensions of the films were 2.5 and 7 cm and the source to substrate distance was 20 cm. The films were aged for more than 48 hours in a dessicator to anneal out residual defects, and were then mounted on the thermoelectric power measuring setup one at a time. The chamber enclosing the measurement setup was evacuated to a vacuum better than  $5 \times 10^{-5}$  Torr and the thermoelectric power measurement was carried out. The thermoelectric power measurement setup consisted of a massive copper heat sink, which was in good thermal contact with the base plate of the vacuum system. To this copper sink was clamped one end of the experimental film to maintain its temperature constant. This end was the cold end of the film. To the other end of the film was clamped a mini copper heater (60 W power) which could be heated resistively by means of a nichrome tape wound heater coil in it. This end of the film could be heated uniformly by controlling the power to the miniheater by a variable power supply. Thus, the thermoelectric power measurement on the

experimental films could be carried out by the integral method using the above setup. The temperatures of the hot and cold ends of the film were measured using copper-constantan thermocouples which were clamped right on to the experimental film mechanically. The thermal emf developed across the tin film was measured with respect to copper wires as a function of hot end temperature while the cold end temperature was constant at 300 °K within  $\pm 0.5$  °K. The emfs were measured with a high impedance (10 M $\Omega$ ) digital millivoltmeter. The maximum hot end temperature was about 425 °K. X-ray diffractograms and electron diffraction patterns of the films revealed that they were polycrystalline, but with a fibrous structure, (100) planes of the grains ( $\beta$ -Sn structure, tetragonal) being parallel to the substrate. These observations are also in accordance with those of Patel and Mysorewala.<sup>9</sup>

**RESULTS**

Figure 1 shows the plot of thermal emf against the temperature difference between hot and cold ends for a 1000-Å film of  $\beta$ -tin. The thermal emfs were recorded both during heating and cooling and it can be seen from the figure that the plots for heating and cooling agree within the experimental errors. This implies that during the heating process defects, if any, are not removed so that the defect concentra-

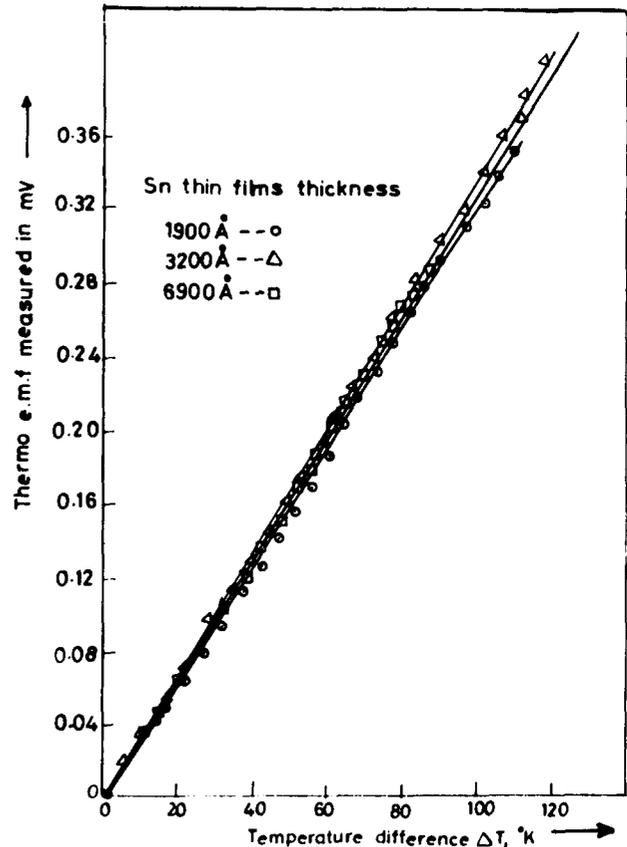
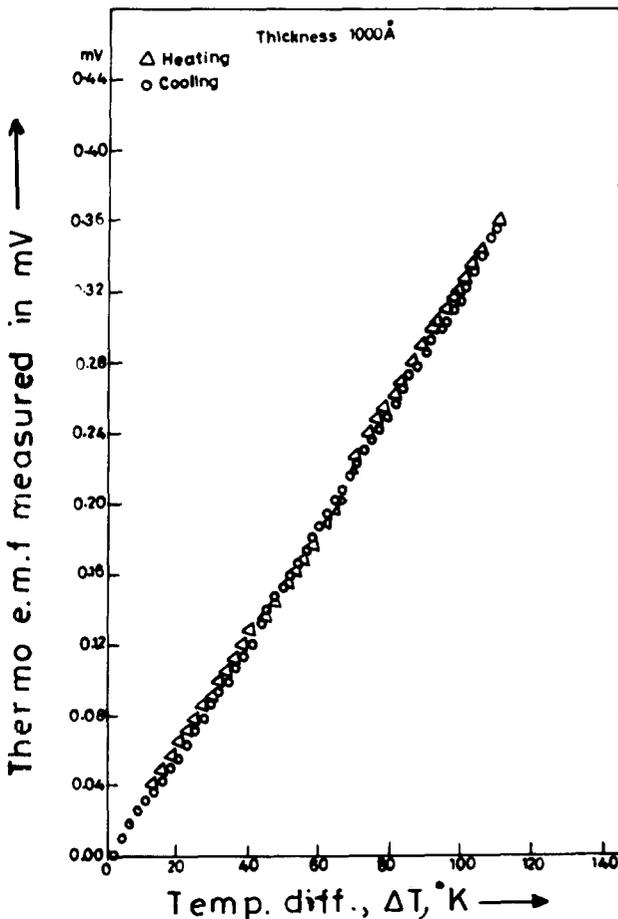
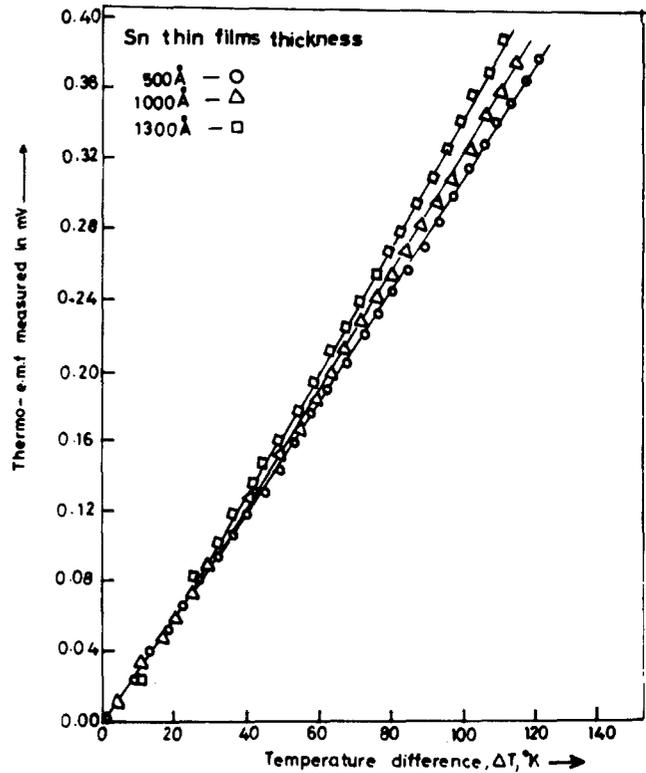


FIG. 1. Plot of thermal emf against temperature difference between hot and cold ends for a 1000 Å thick  $\beta$ -tin film during heating and cooling.

FIG. 2. Plots of thermal emf against temperature difference between hot and cold ends for  $\beta$ -tin films of thicknesses 500, 1000, 1300, 1900, 3200, and 6900 Å.

tion, if any, is unaltered by the heating process. Hence, it can be concluded that aging for 48 hours has removed any defects present in the film and hence during the heating, the defect concentration is unaltered or alternatively the heating process has not altered the initial defect concentration. Therefore, during measurements, the residual defects, if any, remain unaltered.

Figures 2(a) and (b) show the plots of thermal emf against temperature difference for  $\beta$ -tin films of thickness 500, 1000, 1300, 1900, 3200, and 6900 Å. It is seen that the thermal emf is nearly linear with respect to temperature difference within experimental errors, and that it increases as the film thickness increases for a given temperature difference.

From the plots of thermal emf against temperature difference, thermoelectric power of the films with respect to bulk copper was calculated at different temperatures. Figure 3 shows the plots of this thermoelectric power against temperature for the films of different thicknesses. It can be seen that thermoelectric power is independent of temperature for all the films in the temperature range 300 to 425 °K, within experimental errors. It is also seen that thermoelectric power increases (from about 3.21 to 3.46  $\mu\text{V}/^\circ\text{K}$ ) as the thickness increases.

Figure 4 shows the plot of average thermoelectric power of  $\beta$ -tin films with respect to copper in the range 300–425 °K as a function of thickness of the films. It is a typical plot depicting the size effect on thermoelectric power of thin films. It is seen that the thermoelectric power of the thinnest film is the lowest and it increases rapidly with increasing

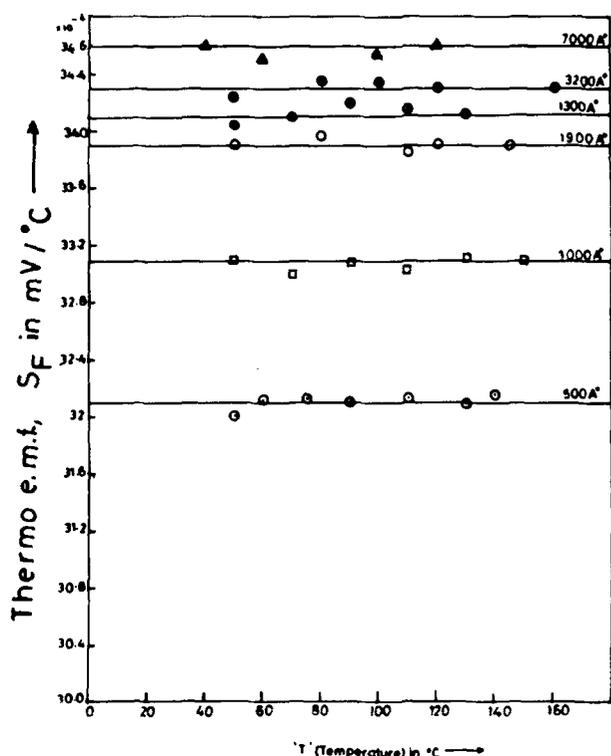


FIG. 3. Plot of thermoelectric power against temperature for  $\beta$ -tin films of different thicknesses.

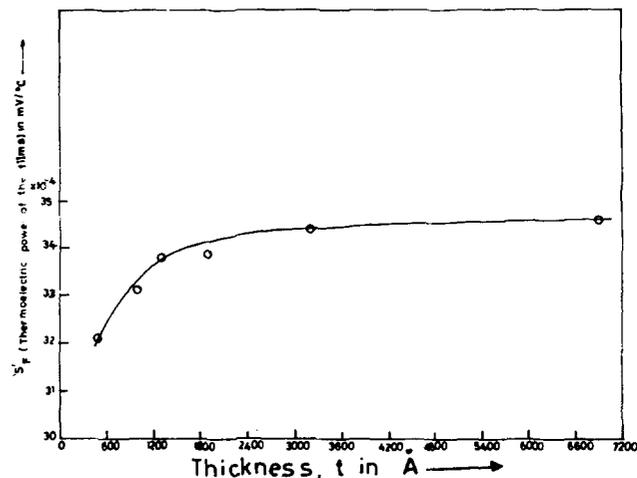


FIG. 4. Plot of thermoelectric power against film thickness for  $\beta$ -tin films.

thickness up to about 2000 Å and thereafter increases slowly with a further increase in thickness, attaining saturation. This is a typical behavior of thermoelectric power due to size effect. Figure 5 shows the plot of thermoelectric power against reciprocal thickness and it is seen that it is linear. The intercept on the y axis, as will be seen later gives the “grain boundary thermoelectric power”  $S_g$  of polycrystalline tin with respect to copper and is found to be 3.48  $\mu\text{V}/^\circ\text{K}$ . Taking the value of absolute thermoelectric power of bulk copper at 300 °K to be 1.83  $\mu\text{V}/^\circ\text{K}$  (Cusack and Kendall<sup>10</sup>) the absolute “grain boundary thermoelectric power” of polycrystalline tin can be evaluated as  $-1.65 \mu\text{V}/^\circ\text{K}$ . Earlier results on  $\beta$ -tin are not available for comparison.

## DISCUSSION

The transport properties—like electrical conductivity, thermoelectric power, magnetoresistance, Hall effect; and others—of a material in the thin film state are significantly different from the properties of the same material in the bulk state. This is because as the thickness of a metal/semicon-

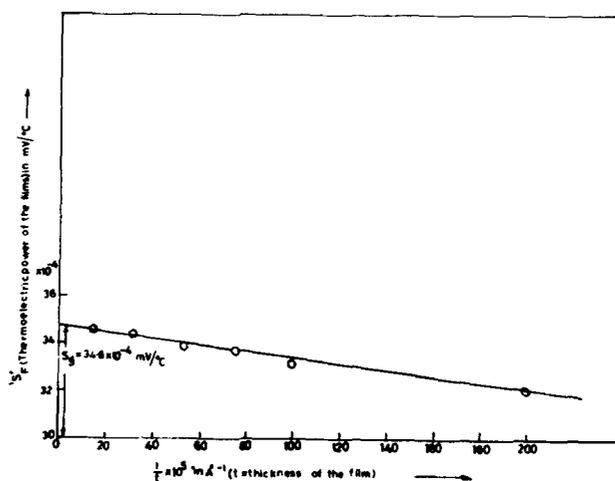


FIG. 5. Plot of thermoelectric power against reciprocal thickness for  $\beta$ -tin films.

ductor film becomes comparable in magnitude with the electronic mean free path of the material, the film surfaces impose a geometrical limitation on the motion of conduction electrons and hence on the effective value of the mean free path. Physical effects arising out of this geometrical limitation of the mean free path are termed classical size effects or mean free path effects.

The classical size effect theory for a free electron model was worked out by Fuchs<sup>11</sup> for a spherical Fermi surface and was later extended by Sondheimer<sup>12,13</sup> to include magnetic field effects. Fuchs-Sondheimer treatment is a statistical analysis based on the Boltzmann equation for the distribution of conduction electrons. One of the basic assumptions made in their theory is that the electrons are scattered from the film surfaces either diffusely or specularly. In the former case every free path of the electrons is terminated by collision at the surface so that the distribution function of the electrons leaving each surface is independent of direction. In the latter case the electrons are elastically scattered from both the surfaces of the film with a reversal of the velocity component normal to the film surface. It is further assumed that some constant fraction  $p$  of the free electrons is scattered specularly from both the surfaces while the rest are scattered diffusely. The fraction  $p$  is assumed to be independent of electron wavelength, the angle of incidence of the electron onto the surface and the thickness of the film. The relaxation process for surface scattering is taken to be essentially that for the bulk scattering. The assumption that the film is single crystalline is also inherent, as the theory does not take into account scattering by grain boundaries that would be present in a polycrystalline film.

According to this classical size effect theory, the thermoelectric power  $S_F$  of a thin film of thickness  $t$  is given by<sup>14</sup>

$$S_F = S_B \left[ 1 - \frac{3}{8}(1-p) \frac{U}{1+U} \frac{\lambda_B}{t} \right] \quad (1)$$

for thickness  $t > \lambda_B$ , the bulk electronic mean free path. Here  $S_B$  is the bulk thermoelectric power given by<sup>15</sup>

$$S_B = \frac{-\pi^2 k^2 T}{3 e E_F} (U + V).$$

$p$  is the specularly parameter giving the fraction of electrons specularly scattered (without change in the longitudinal velocity component) from the surfaces of the film and  $U$  is the rate of change of mean free path with energy evaluated at the Fermi energy,

$$\left( \frac{\delta \ln \lambda_B}{\delta \ln E} \right)_{E=E_F}$$

and is equal to 2 according to the Bloch quantum theory of metallic conduction and hence  $\lambda_B \propto E^2$ , and

$$V \left( \frac{\delta \ln A}{\delta \ln E} \right)_{E=E_F},$$

the rate of variation of Fermi surface area with energy, evaluated at the Fermi energy. Even though the above expression is an approximation valid for  $t > \lambda_B$ , it is found to be valid for  $t/\lambda_B$  up to 0.1 without much error. The above expression (Eq. 1) is strictly valid for monocrystalline films as it does not take into account the contribution to the ther-

moelectric power due to grain boundary scattering.

Recently, Pichard *et al.*<sup>16</sup> have obtained an expression for the thermoelectric power of a polycrystalline thin film using an effective mean free path model<sup>17</sup> taking into account the scattering by the grain boundaries (proposed by Mayadas and Shatzkes<sup>18</sup>). In this model it is shown that an effective relaxation time  $\tau_g$ , and hence an effective mean free path  $\lambda_g$  can be defined for describing the simultaneous background and grain boundary scattering of electrons. The relaxation time  $\tau_g$  can be approximately equated to the product of bulk relaxation time  $\tau_B$  (used in the Fuchs-Sondheimer theory) and a function  $F(\alpha)$ , of the parameter  $\alpha$  governing the grain boundary scattering ( $\alpha$  is given by  $\alpha = (\lambda_B/a_g)(r/1-r)$ , where  $\lambda_B$  is the bulk mean free path,  $a_g$  the grain size, and  $r$  the grain boundary reflection coefficient). Then it is shown that expressions similar to those of Fuchs-Sondheimer can be obtained to describe the transport parameters—like resistivity,  $\rho$ , temperature coefficient of resistance (TCR),  $\beta$ , thermoelectric power,  $S$ , and others—of polycrystalline films in which grain boundary scattering is significant, by replacing  $\tau_B$  by  $\tau_g$  and other bulk parameters  $\rho_B$ ,  $\beta_B$ , and  $S_B$  by the “grain boundary” parameters  $\rho_g$ ,  $\beta_g$  and  $S_g$ . The “grain boundary” parameters are the parameters of an “infinitely thick polycrystalline film” implying that these correspond to a bulk sample having the same grain structure as that of a polycrystalline film.

They obtain an expression for the thin film thermoelectric power as<sup>16</sup>

$$S_F = \frac{-\pi^2 k^2 T}{3 e E_F} \left\{ V + U \left[ \frac{\sigma_g}{\sigma_B} - \frac{3}{8}(1-p) \frac{\lambda_B}{t} \left( \frac{\sigma_g}{\sigma_B} \right)^2 \right] \right\} \dots \quad (2)$$

using the approximation  $\beta_g/\beta_B = \sigma_g/\sigma_B$ .<sup>19</sup> Here  $\sigma_g$  and  $\beta_g$  are the “grain boundary” conductivity and “grain boundary” TCR, and  $\sigma_B$  and  $\beta_B$  are the respective bulk values. Other symbols have the same meaning as in Eq. (1). This equation is valid for polycrystalline films.

It is seen from the above two equations that  $S_F$  is a linear function of reciprocal thickness, if it is assumed that  $p$  is independent of thickness. Hence a plot of  $S_F$  vs  $1/t$  will be a straight line in either case. The intercept on the  $y$  axis gives (i) according to Eq. (2),<sup>16</sup> the “grain boundary” thermoelectric power  $S_g$ , and (ii) according to Eq. (1) the bulk thermoelectric power  $S_B$ . The slope is equal to<sup>16</sup>  $[3(1-p)\lambda_B U/8](\sigma_g/\sigma_B)^2$  [according to Eq. (2)] or  $[3(1-p)\lambda_B/8](U/1+U)$  in the two cases, respectively.

As the films under present study were not monocrystalline, strictly speaking we have to use Eq. (2) which takes into account grain boundary scattering. As mentioned earlier, the plot of  $S_F$  vs  $1/t$  was found to be linear (Fig. 5) and hence  $\beta$ -tin films obey the inverse thickness dependence predicted by either of the size effect theories. The  $y$  intercept of the plot gives the value of the grain boundary thermoelectric power of  $\beta$  tin with respect to copper as  $3.48 \mu\text{V}/^\circ\text{K}$  and its absolute value as  $-1.65 \mu\text{V}/^\circ\text{K}$  as stated before [cf., Eq. (2)].

Andrew<sup>20</sup> and Niebuhr<sup>21</sup> have shown that surface scattering is diffuse in the case of tin foils and tin thin films deposited above  $200^\circ\text{K}$ . Hence we can take the specularly parameter,  $p = 0$ .  $U$ , as mentioned earlier, has a value 2 for

$\lambda_B \propto E^2$ . If we use the expression for the slope  $[3(1-p)\lambda_B/8](U/1+U)$  (i.e., use Eq. (1) instead of Eq. (2) which should be strictly used) the substitution of the values of  $U$  and  $p$  gives the mean free path  $\lambda_B$  to be 530 Å which is in good agreement with that obtained for tin films by Niebuhr<sup>21</sup> (550 Å). This suggests that the use of Eq. (1) instead of Eq. (2) does not lead to significant error. This is possibly due to a much less grain boundary scattering effect than the surface scattering effect. This may be due to the fact that even though the films studied were polycrystalline, they had a fibrous structure, with (100) planes of all the grains being parallel to the substrate (normal to thickness). Therefore, if we take absolute  $S_g = -1.65 \mu\text{V}/^\circ\text{K} \approx S_B$ , there would not be significant error in the calculations of Fermi energy. The Fermi energy value obtained taking  $-1.65 \mu\text{V}/^\circ\text{K}$  as  $S_B$ ;  $U = 2$ ,  $V = 1$  using the relation for  $S_B$  given earlier is 13.36 eV. This value is about twice that of noble metals.

It may be mentioned here that it is not possible to use Eq. (2) for the evaluation of  $U$  and  $V$ , even if  $\sigma_g$ ,  $\beta_g$ , and  $\lambda_B(1-p)$  are evaluated from resistivity and TCR data by equations suggested by Tellier *et al.*,<sup>16</sup> if the value of the Fermi energy is not independently known, which is the case in the case of tin.

## CONCLUSIONS

It is found from the present study that the thermoelectric power of  $\beta$ -tin thin films in the thickness range 500–7000 Å obeys the size effect theories and that the thermoelectric power is independent of temperature in the range 300–425 °K. The electronic mean free path is evaluated to be 530 Å at room temperature and the Fermi energy to be 13.36 eV using  $S_g \approx S_B$ .

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- <sup>1</sup>Toshizo Fujita, Suguru Kobayashi, and Taiuhiro Ohtsuka, *J. Phys. Soc. Jpn.* **44**, 544 (1978).
- <sup>2</sup>N. V. Zavaritskii and A. A. Altukhov, *Sov. Phys. JETP* **43**, 969 (1976).
- <sup>3</sup>A. A. Altukhov and N. V. Zavaritskii, *Sov. Phys. JETP Lett.* **20**, 10 (1974).
- <sup>4</sup>R. E. Fryer, C. C. Lee, V. Rowe, and P. A. Schroeder, *Physica* **31**, 149 (1965).
- <sup>5</sup>A. R. De Vroomen, thesis, Peideu (1959).
- <sup>6</sup>G. T. Pullan, *Proc. R. Soc. Ser. A* **217**, 280 (1953).
- <sup>7</sup>C. Van Baarle, A. J. Cuelenacre, G. J. Roest, and M. K. Young, *Physica* **30**, 244 (1964).
- <sup>8</sup>K. K. Zhilik, *Phys. Met. Metallogr. (USSR)* **23**, 195 (1967).
- <sup>9</sup>A. R. Patel and D. V. Mysorewala, *Mater. Res. Bull.* **5**, 1031 (1970).
- <sup>10</sup>N. Cusack and P. Kendall, *Proc. Phys. Soc. London* **72**, 898 (1958).
- <sup>11</sup>K. Fuchs, *Proc. Cambridge Philos. Soc.* **34**, 100 (1938).
- <sup>12</sup>E. H. Sondheimer, *Phys. Rev.* **80**, 401 (1950).
- <sup>13</sup>E. H. Sondheimer, *Adv. Phys.* **1**, 1 (1952).
- <sup>14</sup>H. Mayer, *Physik dünner Schichten*, Vol. 2 (Wissenschaftliche Verlag, Stuttgart, West Germany, 1955).
- <sup>15</sup>J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, 1962), p. 397.
- <sup>16</sup>C. R. Pichard, C. R. Tellier, and A. J. Tosser, *J. Phys. F* **10**, 2009 (1980).
- <sup>17</sup>C. R. Tellier, *Thin Solid Films* **51**, 311 (1978).
- <sup>18</sup>A. F. Mayadas and M. Shatzkes, *Phys. Rev. B* **1**, 1382 (1970).
- <sup>19</sup>C. R. Tellier, *Thin Solid Films* **44**, 201 (1977).
- <sup>20</sup>E. R. Andrews, *Proc. Phys. Soc. London Sec. A* **62**, 77 (1949).
- <sup>21</sup>J. Niebuhr, *Z. Phys.* **132**, 468 (1952).