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# Anomalous temperature dependence of thermoelectric power of PbTe thin films

V. Damodara Das and K. Seetharama Bhat

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PbTe thin films of thicknesses ranging from 400 to 4000 Å have been prepared by vacuum evaporation at a pressure of  $5 \times 10^{-5}$  Torr on clean glass substrates held at room temperature. The thermoelectromotive force of these films has been measured in the temperature range 300–600 K. It is found that thermoelectric power,  $S_F$  varies anomalously with temperature, being constant at lower temperatures, and rapidly decreasing at higher temperatures.  $S_F$  is found to be positive indicating that the samples are  $p$  type. The anomalous behavior is explained by assuming that at higher temperatures additional donor levels are generated due to creation and ionization of defects in the system.

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## INTRODUCTION

In recent years studies on lead chalcogenides have been very much in progress due to their device applications<sup>1–3</sup> in many fields like IR detectors, photoconductors, thin film transistors, etc. Many works have been reported on the transport properties of these chalcogenides in the bulk state but very little is known about their properties in the thin film state. There has been some work on the thermoelectric power of impurity doped lead telluride films but very little on pure undoped samples in the thin film form. Barisova<sup>4</sup> has measured the thermoelectric power of bulk PbTe doped with Bi, Sb, Cr, and Ag in amounts of 0.1–0.5 at. %. He found that undoped PbTe was  $p$  type whereas those doped with Bi, Sb, and Cr were  $n$  type. However, those doped with excess silver were found to remain  $p$  type. The room temperature value of thermoelectric power,  $S$  for pure undoped PbTe bulk was quoted<sup>4</sup> as around  $300 \mu\text{V}/^\circ\text{K}$ . Gruzinov *et al.*<sup>5</sup> and Mathur *et al.*<sup>6</sup> studied the electrical properties of thallium<sup>5</sup>- and silver<sup>6</sup>-doped PbTe films. The former measured the Hall coefficient in the range 77–700 °K on Tl-doped PbTe films with carrier concentration ranging from  $5 \times 10^{17}$  to  $6 \times 10^{19}/\text{cc}$  at 300 °K. The various band parameters like mobility, effective mass, and population ratio for light and heavy holes were also calculated. In the report from Mathur *et al.*<sup>6</sup>, electrical properties of Ag-doped  $p$ -type PbTe epitaxial films were published and it was found that silver acted as an acceptor in the initial stages of doping but for higher dopant concentrations (more than 0.5 at. %), it acted as a neutral impurity center. Smirnov *et al.*<sup>7</sup> observed departure of thermoelectric power from the theoretical formula in the impurity conduction range (100–400 °K) for both  $n$ - and  $p$ -type PbSe films. The departure was ascribed to the change in effective mass  $m^*$  of the carriers with temperature. Abrahams *et al.*<sup>8</sup> measured the thermoelectric power of single crystal  $p$ -type PbSe and found that the thermoelectric power increased to a maximum value and then decreased rapidly with increasing temperature. They argued that in the two carrier region both electrons and holes diffuse under the influence of the temperature gradient. They also found that thermoelectric power decreased with the increasing carrier

concentration. Bytenskii *et al.*<sup>9</sup> and Gudkin *et al.*<sup>10</sup> have dealt with the influence of potential barriers on the thermoelectric power of lead chalcogenide films. Parameters like  $\sigma$ ,  $S$ , and  $R_H$  were determined in the temperature range 77–350 K. A comparison with bulk values of PbSe (Te, S) revealed that the films were characterized by higher  $S$  and lower  $\sigma$  than in bulk. These differences were attributed to energy selective carrier scattering by potential barriers associated with block boundaries. Scanning electron microscopy studies confirmed that the grain boundaries start from the substrate to the surface, their dimensions almost being equal to the mean-free path of the carriers. The barriers are expected to arise due to strain fields near dislocations and the boundaries.

It is seen from the above that there has been very little study on the thermoelectric behavior of undoped lead telluride thin films. Hence, the present work was carried out. In the present paper, we describe the observations on temperature dependence of thermoelectric power of PbTe films and give possible explanations.

## EXPERIMENT

PbTe alloy was prepared by mixing ultrapure Pb(99.999%) and Te(99.999%) in 1:1 atomic ratio and heating the mixture in vacuum, in a sealed quartz tube, keeping it at 950 °C for about two days and then allowing to cool slowly. The x-ray powder diffraction photograph of the ingot formed showed all the prominent lines for PbTe and the observed relative intensities matched with those of the ASTM card of PbTe. The x-ray diffractograms of the thin film samples were taken and they also showed all the prominent peaks thus confirming the structure and alloy formation even in the thin film state.

Thin films of PbTe varying in thickness from 400 to 4000 Å were obtained by evaporating bulk PbTe onto clean glass plates in a vacuum of  $5 \times 10^{-5}$  Torr using the PbTe alloy as charge. Before evaporation, the glass substrates were cleaned using chromic acid, Teepol detergent, Isopropyl alcohol, and distilled water. The lateral dimensions of the films were  $6 \times 0.5$  cm and the source to substrate distance

was about 25 cm. The thickness was measured *in situ* using a quartz crystal monitor and the deposition conditions were maintained almost the same during all the evaporations to avoid any further effects. The deposition rate was kept constant by allowing the same amount of current to pass through the boat and each time all the material in the boat was completely evaporated to avoid fractionation, if any, of the alloy. The films were annealed before measurements to homogenize the films formed.

The thermoelectric power measurements were done by the integral method, namely, keeping one end of the film at a constant temperature and varying the temperature of the other end. The set up used for such a measurement has been described earlier by Damodara Das *et al.*<sup>11,12</sup> The set up is such that one end of the film can be connected to a heater attachment and the other end to a massive copper block in order to ensure a constant temperature. It was found that the cold end temperature was maintained at room temperature ( $\approx 300$  °K) within  $\pm 0.5$  °K. The temperature of the other end could be varied from 300 to 600 °K. The temperatures of both the ends were measured using copper-constantan thermocouples fixed right on to the film. The thermo emf (electromotive force) developed across the film was measured with respect to copper as a function of hot-end temperature using a high impedance ( $10\text{ M}\Omega$ ) digital millivoltmeter. All

the measurements were made in high vacuum to avoid oxidation of the film or adsorption of gases.

## RESULTS

Figure 1 shows the plot of thermo emf as a function of temperature difference between the hot and cold ends during heating and cooling for a typical PbTe film (thickness 1300 Å). The heating and cooling curves almost coincide, indicating that there is no significant change due to the heat treatment. This was also further confirmed by measuring thermo emf after annealing the films for about 2 h. It was found that thermo emf values were almost the same before and after annealing. Plots of thermo emf versus temperature difference for PbTe films of different thicknesses are displayed in Fig. 2. It is seen that thermo emf increases nonlinearly with increasing temperature difference. Further, the nonlinearity increases as thickness decreases. It is also clear from Fig. 2 that the emf developed for the same temperature difference is higher for higher thickness films indicating that thermoelectric power increases with increasing thickness.

The thermo emf  $S_{AB}$  of PbTe film (B) with respect to copper (A) was found to be negative indicating that the sample is *p* type. ( $S_{AB} = S_A - S_B$ , is  $< 0$ ; but  $S_A = +1.7\ \mu\text{V}/^\circ\text{K}$ <sup>13,14</sup> and hence  $S_B$  is positive, hence *p* type).

Figure 3 shows the plots of thermoelectric power,  $S_F$  against temperature for films of different thicknesses and it is

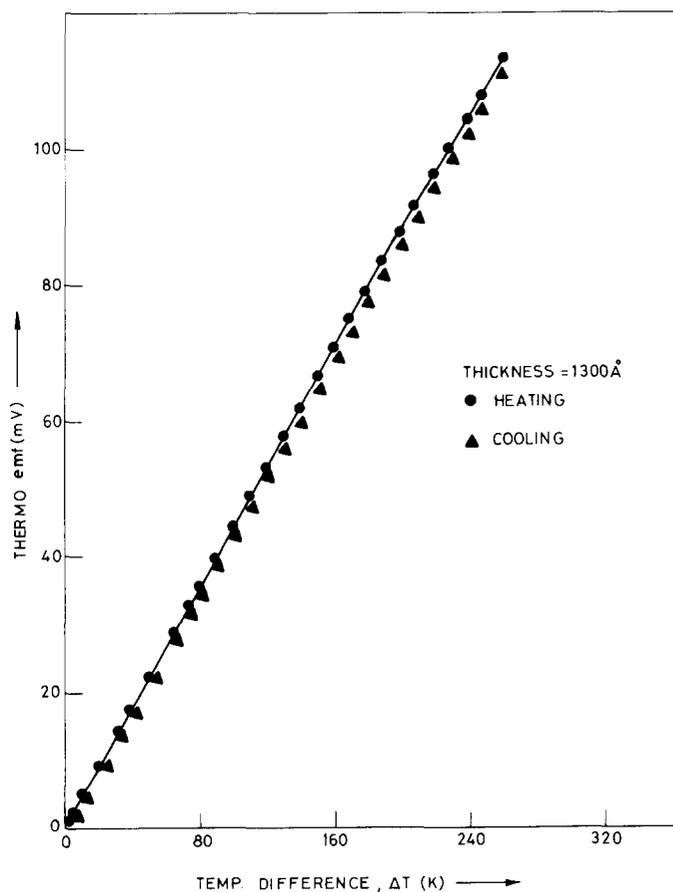


FIG. 1. Plot of thermoelectromotive force vs temperature difference between hot and cold ends for a PbTe thin film of thickness 1300 Å during heating and cooling.

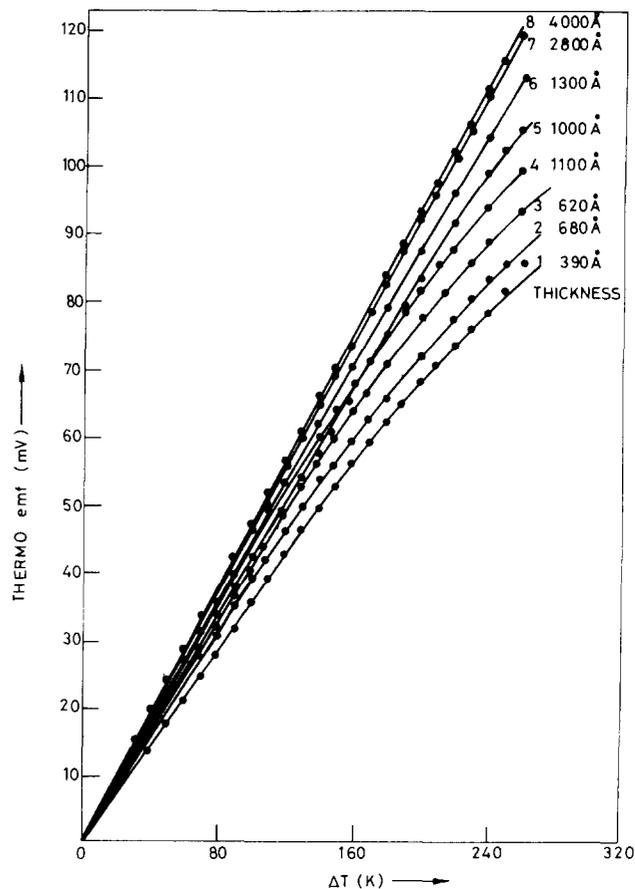


FIG. 2. Plots of thermo emf vs temperature difference between hot and cold ends for PbTe thin films of different thicknesses.

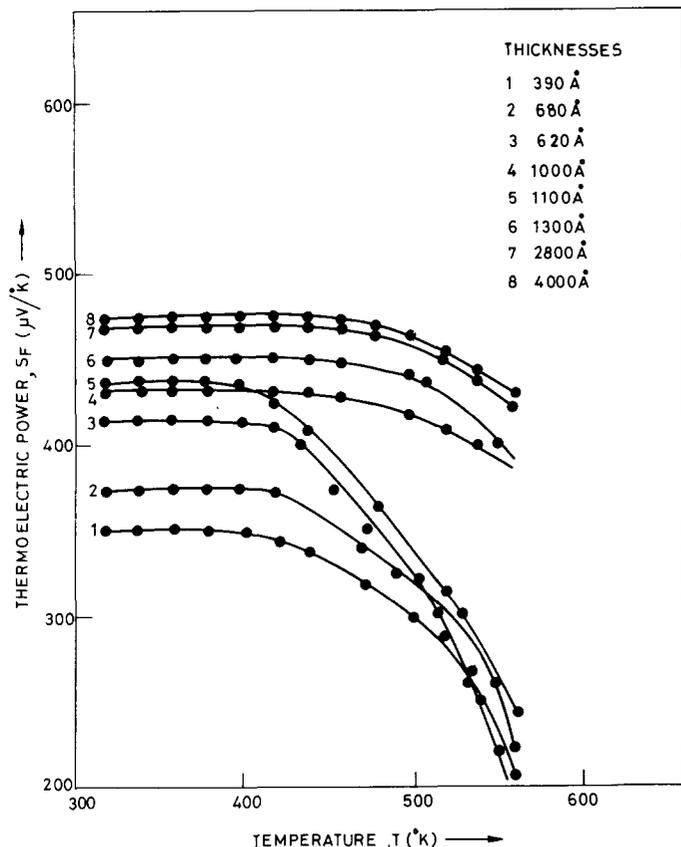


FIG. 3. Thermoelectric power ( $S_F$ ) vs temperature plots for PbTe thin films of different thicknesses.

found that at higher temperatures  $S_F$  decreases rapidly. It is also seen that with increasing thickness, the rapidity of the

decrease of  $S_F$  decreases. However, at lower temperatures  $S_F$  shows very little temperature dependence for all the films. Further, it can also be seen that the thermoelectric power of the thin films is higher than that of the bulk. This variation of  $S_F$  with temperature and the difference in the bulk and thin film values can be explained as detailed below.

## DISCUSSION

In a nondegenerate  $p$ -type semiconductor the thermoelectric power  $S_F$  is given by the expression<sup>12</sup>

$$S_F = + \frac{k}{e} \left( 5/2 + p - \frac{E_F - E_V}{kT} \right) \\ = + \frac{k}{e} \left[ 5/2 + p + \ln \left( \frac{N_V}{n} \right) \right]; N_V = 2 \left( \frac{2\pi m_h^* kT}{h^2} \right)^{3/2}$$

where  $E_F$  is the Fermi energy,  $E_V$  is the energy of the top of the valence band,  $k$  is the Boltzmann's constant,  $e$  is the charge of the electron or hole,  $T$  is the absolute temperature,  $n$  is the hole concentration, and  $p$  is defined by  $\tau(E) = \tau_0 E^p$ , where  $\tau$ , the relaxation time, is considered to be a function of energy and  $\tau_0$  is a constant.  $N_V$  is the effective density of states in the valence band. Since  $N_V > n$ , the expression inside the bracket is positive and hence the sign of the thermoelectric power determines the sign of the carriers. We find that in the case of PbTe films  $S_F$  is positive throughout the temperature range suggesting the sample to be  $p$  type in nature.

However, from the above expression we expect that  $S_F$  should vary as  $1/T$ . But, from the experimental plots of  $S_F$  vs  $1/T$  shown in Fig. 4, we find that  $S_F$  is almost constant at lower temperatures in contrast to the above relation.

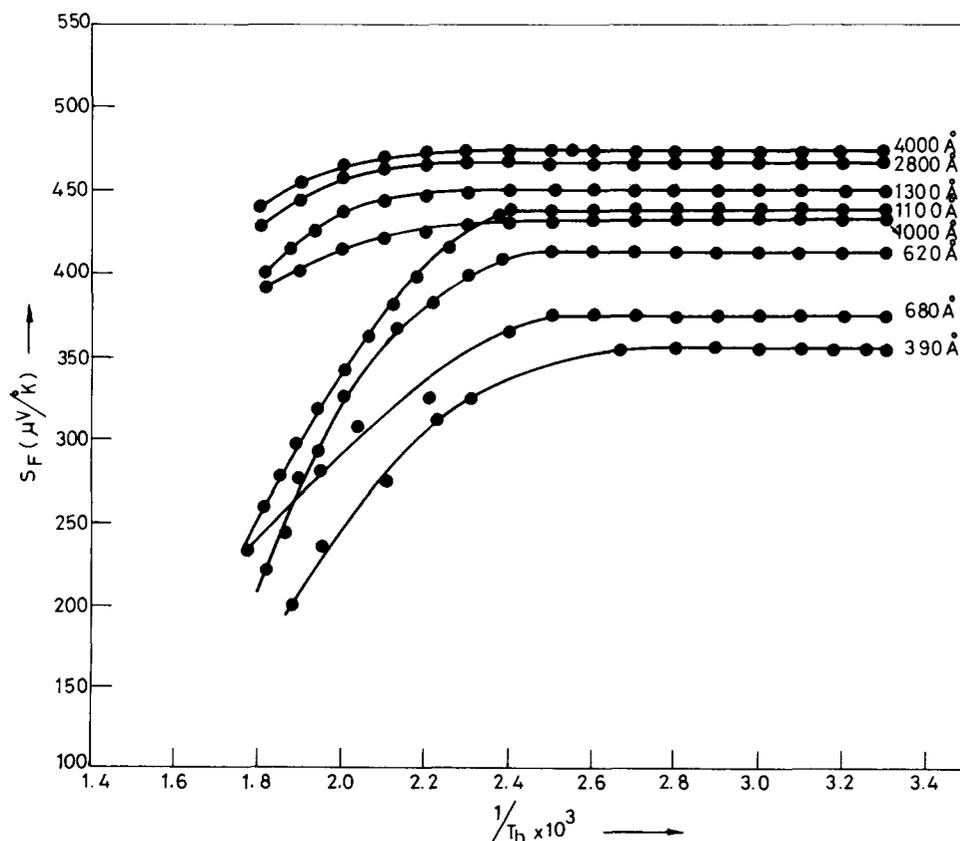


FIG. 4. Thermoelectric power ( $S_F$ ) vs  $1/T$  plots for PbTe thin films of different thicknesses.

Smirnov *et al.*<sup>7</sup> have observed the departure of thermoelectric power from the theoretical formula in the impurity conduction region (100–400 °K) in *n*- and *p*-type PbSe samples. This departure was attributed to the change of effective mass  $m^*$  with temperature ( $S_F$  is a function of  $m^*$  through  $N_V$  as seen above). However, Kolomets *et al.*<sup>15</sup> observed no change in effective mass over a wide temperature range (from 0–450 °C) in PbTe crystals from thermoelectric data. Miller *et al.*<sup>16</sup> also find that the effective masses are constant in the extrinsic range (77–300 °K). Since at lower temperatures in our study (300–400 °K) we are in the intermediate region where the carrier concentration is practically constant, the thermo power is nearly constant in this region.

However, at higher temperatures (> 400 °K) the thermoelectric power decreases suggesting an effective decrease in carrier concentration. Since the PbTe films under investigation are *p* type, the possibility that at higher temperatures electrons are generated by some means should be given a serious thought as that would effectively decrease the carrier (hole) concentration. Smith<sup>17</sup> considered that defects were produced at elevated temperatures primarily as a result of vaporization of tellurium from the specimen. But our results, that the thermo emf values during the heating and the cooling cycles (and subsequently during the second heating and second cooling too) (Fig. 1) are coinciding, rule out this possibility.

Miller *et al.*<sup>16</sup> suggested the possible mechanisms of carriers' generation to be by excitation of electrons from the valence band to the conduction band, and formation of structural defects at elevated temperatures and ionization of their isolated energy levels. Both the mechanisms are under operation at all temperatures, especially at higher temperatures, depending on the activation energy required for the creation of defects. They have shown by quenching experiments on *n*- and *p*-type samples that the defects formed at elevated temperatures contribute significantly to generation of electrons. They have also calculated the activation energies for defect formation to be 0.55 and 0.7 eV for Pb defects in PbTe (Schottky and Frenkel defects, respectively) (Miller *et al.*)<sup>16</sup> Thus, above about 350 to 400 °K one expects the second mechanism to contribute additional electrons. As a consequence, the carrier concentration of *n*-type sample would continuously rise whereas that of a *p*-type sample would begin to fall as the temperature increases. Newman<sup>18</sup> also suggested that in some semiconductors anomalous Seebeck coefficient is to be observed due to the increasing formation of imperfections either donors or acceptors with temperature. In a semiconductor where the band gap does not vary with temperature and which contains a small fixed number of acceptors, the number of donors can be increased with temperature. The phenomenon can be illustrated by the variation of Fermi level with respect to the band edges of the semiconductor due to change in temperature (as in Fig. 5). At temperature  $T_i$ ,  $S_F$  will even change its sign. In fact, Miller *et al.*<sup>16</sup> have observed similar variation of  $S_F$  with temperature in bulk PbTe samples and also a change of sign of  $S_F$  between 500 and 600 °K.

Hence, in *p*-type samples of PbTe films we expect a decrease in thermoelectric power with temperature beyond

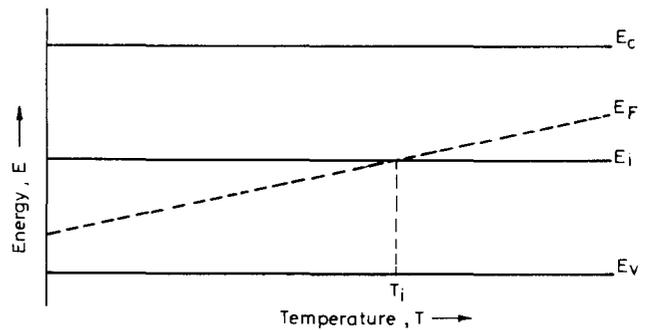


FIG. 5. Variation of Fermi level with temperature in a *p*-type semiconductor due to increasing donor concentration.

about 400 °K, as more number of electrons are generated inside the system. However, we did not observe a change in sign of  $S_F$  up to a temperature about 600 °K. This may be due to smaller concentration of donors in the films and hence a lower rate of change of  $E_F$  with temperature than in the case of bulk. In any case, change of sign should be observed at a higher temperature. We could not go beyond 600 K since the film started agglomerating and to a limited extent evaporating from the substrate, thereby becoming discontinuous.

It is well known<sup>19</sup> that the defect concentration in thin films (point defects, point defect clusters, dislocations, and grain boundaries) is much larger than in the bulk. This concentration is a function of thickness of the films, increasing with increasing thickness up to a certain critical thickness (around 1000–1500 Å, depending upon the material) and then reaching saturation for higher thicknesses. Hence, the concentrations of the carriers that are generated thermally at higher temperatures form a significant fraction of the total number of defects at lower thicknesses while they form a much smaller fraction at higher thicknesses. Hence, the influence of the thermally generated defects will be more at lower thicknesses as compared to that at higher thicknesses. Thus, the increasing nonlinearity of thermo emf versus temperature difference plots (see Fig. 2) and rapid decrease of thermoelectric power (see Fig. 3) for films of lower thicknesses, as compared to films of higher thicknesses, can be qualitatively explained on the above basis. However, quantitative estimation of the extent of the rapidity of decrease of  $S_F$  as a function of thickness cannot be made, as other effects like surface scattering, removal of defects during the measurements, etc., also influence the thermoelectric behavior of the films.

The observation that the thermoelectric power of PbTe films is greater than that of the bulk is in accordance with the results of Gudkin *et al.*<sup>10</sup> in PbTe films. Bytenskii *et al.*<sup>9</sup> also observed similar results in PbSe films. The possible explanation was given in terms of a different scattering mechanism, namely, energy selective carrier scattering by potential barriers associated with block boundaries. It has been reported earlier<sup>10</sup> that single crystal films of PbTe prepared by vacuum evaporation consist of fine blocks with an average distance of about 500 Å between the boundaries. Even at 300 K, this distance is comparable with the mean free path in bulk single crystals. These block boundaries can act as “traps” for the electrons whose filling produces a potential barrier and

prevents further flow of free carriers. Thus the block boundaries can effectively influence the carrier scattering once the carriers become localized at these boundaries. For barrier heights close to the Fermi energy these boundaries should scatter strongly the carriers with energy less than the Fermi level and weakly those with energies above the Fermi level. This results in an extremely strong dispersion of the mean free path near the Fermi level. Hence, the energy in a carrier flux reduces and this increases the thermoelectric power for the same parameters of energy band and structure as compared with the bulk.

## CONCLUSIONS

From the present study, we understand that the reduction of thermoelectric power at higher temperatures in PbTe films is mainly due to the formation of structural defects inside the system which act as donors. The higher value of thermoelectric power of the films as compared to that of the bulk is due to the energy selective carrier scattering taking place near the grain boundaries. Also, the thermoelectric power of the films is thickness dependent, increasing with increasing thickness.

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