Hysteresis like behaviour in Thin Films with heating-cooling cycle.

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The expression of temperature distribution along a film thickness is derived and distribution of temperature in the film as the substrate is heated is shown. The variation of film resistance with different substrate temperature is calculated and the existence of temperature gradient along the film thickness with finite thermal conductivity leads to hysteresis like behaviour on heating-cooling the film.

PACS numbers: 73.61; 73.61.G; 81.40.C

I. INTRODUCTION

The electrical conductivity measurements are important in characterising conducting or semiconducting materials, both in their thin film and bulk state. It is routinely carried out for various materials. The temperature dependence of resistivity yields information about intrinsic band gap of the material, the activation energy for conduction in films due to grain boundary barrier height or impurity activation energy etc. For the above estimation, the resistance measurement are taken either in the heating or cooling direction of temperature variation. If the system is heated or cooled very slowly, i.e. with same rate of change of temperature, both the heating and cooling cycles coincide. However, considerable difference has been observed when an amorphous film is heated above crystalline transition temperature and cooled back to room temperature. This can be understood as due to structural changes\cite{1,2,3}. In such cases after cooling, most of the films do not regain their initial resistance. However some did regain their initial resistance, thus enclosing an area as in hysteresis loops. Hysteresis have been observed in bismuth films even without structural changes\cite{4} where the heating and cooling rates were kept different. This is interesting and since no attempt is made to explain this variation, in this manuscript we attempt to explain the appearance of hysteresis due to non-equilibrium state of the film.

II. THEORY

We consider the film to be kept on a copper block which is heated by a heating coil embedded in it. The heating rate is varied by the voltage applied to the heating coil, such that the whole surface of the copper block is having uniform temperature. The film is kept on this copper block resulting in heating from the substrate side (fig 1). The temperature varies along the film thickness with time. The variation of temperature with time and spatial co-ordinates...
is given by

$$c_v \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2}$$

(1)

where $\lambda$ is the thermal conductivity of the film and $c_v$ is the specific heat of the film. A solution of this partial differential equation depends on the initial and boundary conditions of the problem. Depending on the initial and boundary conditions solution would be different. The initial condition for the film of thickness ‘d’ being heated from the substrate side would be given as

$$T(x = 0, t = 0) = T_{sub}$$

(2)

$$T(x = d, t = 0) = T_{sur}$$

(3)

while after a long time the film would be uniformly heated, with the surface attaining the same temperature as that of the substrate, i.e.

$$T(x, \infty) = T_{sub}$$

From the given conditions, we search for a solution of the form

$$T(x, t) = g(x)h(t)$$

Or in other words the variables are separable and thus, solving equation (1) by separable variable method we have

$$T(x, t) = a + b \sin \left( \frac{\pi x}{2d} \right) e^{-\frac{\pi^2 D t}{4d^2}}$$

(4)

where $D$ is the thermal diffusivity, $\lambda/c_v$. Applying the conditions stated in (2) and (3) the above solution may be written as

$$T(x, t) = T_{sub} - (T_{sub} - T_{sur}) \sin \left( \frac{\pi x}{2d} \right) e^{-\frac{\pi^2 D t}{4d^2}}$$

(5)

Under experimental conditions, where resistivity or resistance is measured as a function of temperature, the substrate temperature would be continuously changing with time i.e. would be time dependent. Hence the above equation cannot be used as it is. Numerically, first the surface temperature is calculated for a given substrate temperature at a given instant, along with temperatures along the thickness of the film. The new surface temperature can be plugged back into the expression along with the new substrate temperature. This scenario is valid for film’s with moderate thermal conductivity. To carry out such a numerical calculation we assume the substrate temperature to vary with time during the heating cycle as

$$T_{sub}(t) = P(1 - e^{-Qt}) + R$$
where 'R' is the room temperature. We have numerically determined the distribution of temperature along the thickness of 1000Å films of varying diffusivity, as described in the last section. Figure 2 shows the variation of temperature along the thickness of three different diffusivities (a) \(5 \times 10^{-3}\text{Å}^2/\text{sec}\), (b) \(5 \times 10^{2}\text{Å}^2/\text{sec}\) and (c) \(5 \times 10^{3}\text{Å}^2/\text{sec}\). Diffusivity, as already stated is the ratio of thermal conductivity to the specific heat of the material. Comparing three different diffusivity of same thickness implies different materials of same thickness is being studied. If we assume there is not much variation in specific heat, the comparative study is being done for materials of varying thermal conductivity (1). For numerical computation we assume the values of the constants of equation (1) to be 360°C, 0.00039sec\(^{-1}\) and 14.5°C for P, Q and R respectively. The saturation temperature that can be attained would be \(\sim 380\)°C, which would be very high. Hence, we assume the heater is switched off after 800sec, by which time, the copper block would be at \(\sim 110\)°C. The family of curves show the spatial distribution of temperature at various time, namely after (i) 0 sec, (ii) 200sec, (iii) 400sec, (iv) 600sec and (v) 800 sec of heating. As is evident from figure 2(a) the surface remains at room temperature since heat does not spread to the surface though the substrate is getting hotter with time. This is due to the poor thermal conductivity of the film. This difference in surface and substrate temperature decreases with time as can be understood from fig 2(b) and (c).

If the heating and cooling is done in vacuum the cooling of the film, i.e. loss of heat can take place by IR radiation losses or by conduction through the substrate side. After the heater is switched off, since the process is in vacuum, the substrate temperature remains constant for an appreciably long time before it starts falling. We assume that the fall in substrate temperature takes place after 200sec from instant that the heater is switched off. Due to the temperature gradient present along the thickness of the film, the surface tends to attain the same temperature as the substrate. Figure 3 shows the temperature along the thickness of the film at various time, between the instant when the heater was switched off to 200 sec after it was switched off. It can be seen from figure 3 (a), the spatial distribution of temperature remains the same even after 200 sec due to the poor thermal conductivity of the film. However, as can be seen from fig 3(b) and (c), with improving thermal conductivity, the film eventually attains equilibrium with time.

The variation of the substrates temperature with time is taken as

\[ T_{sub} = Se^{-ut} + R \]

where S is the maximum temperature that the substrate had reached in the heating cycle, before the onset of cooling. For computation of the temperature distribution, to maintain assumption that the rate of cooling is very different from the heating rate, 'u' is taken as 0.00012sec\(^{-1}\). Figure 4 shows the temperature distribution along the length of the film at regular intervals after the onset of cooling. For the film of low thermal conductivity (fig 4 a), the distribution profile is very similar to that of heating cycle as shown in fig 3 (a). However, as exhibited by figure 4 (b) and (c), the profile is different for films with better thermal conductivity, where in some cases (4c, ii-v), the surface is seen to at a higher temperature then the substrate. This immediately suggests there would be some difference in film properties, such as resistance, during heating and cooling cycle.
III. FILM RESISTANCE

The film can be thought of as numerous infinitesimal identical thin layers, one on top of the other. All the layers acting as resistive elements with the net resistance of the film being the effect of these resistance appearing in parallel combination. Since the layers are identical, at room temperature all of them have equal value. However, due to the metallic/semiconducting nature of the film, the resistance of these layers vary with temperature. The variation of resistance with temperature is given as

\[ R = R_o (1 + \alpha T) \]

where \( \alpha \) and \( R_o \) are the temperature coefficient of temperature (TCR) and the resistance of the identical layer. For the case \( T = 0^\circ C \), the film’s resistance would be given as

\[ \frac{1}{R} = \frac{1}{R_o} \sum_{i=1}^{n} \frac{1}{R_o} = \frac{n}{R_o} \]  \hspace{1cm} (6)

The TCR is positive for metal while it is negative for semiconductors. Since, spatial distribution of temperature was calculated for various substrate temperatures at various instant, the film’s resistance can be trivially calculated as a function of substrate temperature and time.

Figures 5-7 were plotted with data generated assuming the 1000 Å thick film to be made up of 10 resistive layers in parallel combination, with each layer to have a room temperature resistance of 170KΩ and \( \alpha = -0.80^{-30^oC^{-1}} \). These numerical values are taken from our previous study on Sb₂Te₃ films [7]. Figure 5 shows the variation of resistance with substrate temperature. As can be seen films with moderate thermal conductivity and those with good thermal conductivity enclose very small area. However, films with intermediate diffusivity enclose large area due to aggravated difference between the heating and cooling cycle.

Figure 7 is of interest. The TCR or the variation of resistance with temperature has been calculated for various diffusivity. It is evident that the TCR of good thermally conducting films match the TCR of it’s constituent infinitesimal thin layer of which the film is made of. For a mathematical analysis consider the film to be made up of infinite strips of layer, such that each neighbouring layer has a slightly different temperature and in turn a slightly different resistance. The summation sign of equation (6) may then be replaced by an integration sign, hence the net resistance of the film would be given as

\[ \frac{1}{R} = \frac{1}{R_o} \int_{i=0}^{n=d/a} \frac{di}{(1 + \alpha T)} \]

At an given instant the temperature is given by equation (5), hence the above equation can be re-written as

\[ \frac{R_o}{R} = \int_{0}^{n} \frac{di}{(1 + \alpha T_{sub}) - \alpha(T_{sub} - T_{sur})e^{-\frac{d}{4\alpha T_{sur}}} sin \left( \frac{\pi i}{2n} \right)} \]  \hspace{1cm} (7)
For solving the above equation, we substitute
\[
A = 1 + \alpha T_{\text{sub}} \\
B = \alpha(T_{\text{sub}} - T_{\text{sur}})e^{-\frac{\alpha T_{\text{sub}}}{4T}} \\
x = \frac{\pi}{2n}i
\]
Thus, equation (7) can be written as
\[
\frac{\pi R_0}{2nR} = \int_{0}^{\pi/2} \frac{di}{A - B\sin\left(\frac{\pi}{2n}i\right)}
\]
\[
\frac{\pi R_0}{2nR} = \frac{1}{\sqrt{A^2 - B^2}} \tan^{-1}\left(\frac{A + B}{A - B}\right)
\]
As the film’s diffusivity increases, the term B becomes smaller and smaller, i.e. tends to zero. The above equation then reduces to
\[
\frac{\pi R_0}{2nR} = \frac{1}{A} \tan^{-1}(1) = \frac{\pi}{2A}
\]
or
\[
\frac{nR}{R_0} = 1 + \alpha T
\]
on re-arranging
\[
R = \frac{R_0}{n}(1 + \alpha T)
\]
using the equation showing rise in temperature with time, we have
\[
\frac{dR}{dt} = \frac{R_0}{n}(\alpha PQe^{-Qt})
\]
and
\[
\frac{dT}{dt} = PQe^{-Qt}
\]
Thus the film’s TCR works out as
\[
TCR_{\text{film}} = \frac{n}{R_0} \frac{dR}{dT} = \alpha
\]
The mathematics show that not only does a good thermally conducting film’s TCR match that of the infinitesimal thin layer of which the film is made of, it is also independent of the rate of heating/cooling. It can be inferred that the TCR of the film’s with lower thermal conductivity would show dependence on the rate of heating and cooling.
This can be seen from figure 8. Figure 8 shows the effect the rate of heating would have on the slope, and in turn the TCR. The data was calculated in the same manner as discussed in the previous sections. While Figure 8A exhibits the variation of resistance with temperature for a poor thermally conducting film (D=500Å/sec), Figure 8B is for a good conducting film (D=5000Å/sec). Three curves are present in both figures, each for different heating rates, namely (i) \(3.6 \times 10^{-3}\)°C/sec, (ii) 72°C/sec and (iii) 216°C/sec. All three curves coincide for the conducting film. However, in the figure 8A, where a low thermal conducting film the curves do not coincide and their slopes are different. Thus, the TCR values would depend on the rate of heating and cooling. An interesting feature is that the resistances at various temperatures of a poor conducting film measured at very low heating rates match those of a good conducting film being heated rapidly.

### IV. CONCLUSIONS

The electrical studies of thin films are usually done by heating the sample and measuring resistance/resistivity with temperature. Though, the measurements are to be done after the film has attained a steady temperature, usually the measurement is done as the film is being heated or cooled. As discussed in the article, if the film has a finite thermal conductivity (i.e. it is not metallic), one essentially is making measurement in non-equilibrium conditions. Thus, parameters like TCR etc. computed is not only material dependent but depends on conditions of the experiment, e.g. the rate of heating or cooling. It is essentially due to this non-equilibrium measurement that leads to a loop like formation due to the heating-cooling cycle.

### Acknowledgments

The authors would like to acknowledge the contributions of Prof. S. R. Choudhury, Pankaj Tyagi and Naveen Gaur.
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FIG. 1: Direction of heat flow and initial condition of temperature on both surfaces of the film.
FIG. 2: Variation of temperature along the thickness of a 1000Å thick film of different diffusivity (a) $5 \times 10^{-3}$ Å/sec, (b) $5 \times 10^2$ Å/sec and (c) $5 \times 10^3$ Å/sec after (i) 0 sec, (ii) 200 sec, (iii) 400 sec, (iv) 600 sec and (v) 800 seconds of substrate heating.
FIG. 3: Variation of temperature along the thickness of a 1000Å thick film of different diffusivity (a) $5 \times 10^{-3}$Å/sec, (b) $5 \times 10^2$Å/sec and (c) $5 \times 10^3$Å/sec after (i) 0 sec, (ii) 40 sec, (iii) 80 sec, (iv) 120 sec, (v) 160 sec and (vi) 200 seconds after the source of heating was switched off.
FIG. 4: Variation of temperature along the thickness of a 1000Å thick film of different diffusivity (a) $5 \times 10^{-3}$ Å/sec, (b) $5 \times 10^2$ Å/sec and (c) $5 \times 10^3$ Å/sec after (i) 8000 sec, (ii) 16000 sec, (iii) 24000 sec, (iv) 32000 sec and (v) 40000 seconds after the setting in of the film’s cooling.
FIG. 5: Hysteresis loops formed in film resistance with the heating-cooling cycle. The calculations were done for film thickness of 1000 Å and diffusivity (i) $5 \times 10^{-3} \text{Å}^2/\text{sec}$, (ii) $50 \text{Å}^2/\text{sec}$, (iii) $5 \times 10^2 \text{Å}^2/\text{sec}$ and (iv) $5 \times 10^3 \text{Å}^2/\text{sec}$.
FIG. 6: The variation in the area enclosed by loops formed during the resistance variation with temperature during heating-cooling cycles. The variation is due to the difference in the films diffusivity.
FIG. 7: Computed TCR for films of different diffusivity, where the films are assumed to be of same thickness and made up of numerous layers, with all the layers having the same TCR.
Figure 8: Figure exhibits the change of resistance with temperature for (A) a poor thermal conducting film and (D = 5 × 10^2 A/sec) (B) a good thermally conducting film (D = 5 × 10^3 A/sec). The heating rates were maintained different (i) 3.6 × 10^{-3}°C/sec, (ii) 72°C/sec and (iii) 216°C/sec.