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The effect of substrate temperature, deposition rate and annealing on the electrical resistivity of thin yttrium films

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The effect of substrate temperature, deposition rate and annealing on the electrical resistivity of thin yttrium films in the thickness range 10 to 80 nm is reported. The resistivity of films decreases at higher deposition rates and substrate temperatures. These experimental results are analysed using the Fuchs–Sondheimer and Mayadas–Shatzkes theories. The annealing behaviour of yttrium films is in agreement with the Vand theory.

1. Introduction

The majority of the physical properties of thin films utilized in practical application depend to a great extent on the structure of the film. It is, therefore, important to know how the deposition parameters influence the structure of the film during its growth. It is reported [1–7] that the deposition parameters such as substrate temperature, deposition rate, d.c. electric field and substrates affect the structural and the electrical properties of many rare earth metal films. In addition to these deposition parameters, annealing films in a very high vacuum for a sufficiently long time also influences the structure of the films and hence their electrical properties. It is well known that a large number of point, linear and planar defects are frozen in during the atomic condensation process in the vapour deposition of a metallic film [8]. The nature and the concentration of the structural defects in each crystallite of a polycrystalline film depend on the deposition conditions and the film thickness. Prolonged annealing, in vacuum, reduces the film resistance, due to the elimination of the various defects incorporated in the film structure during growth. The effect of annealing on the electrical resistivity of rare earth films is quite complicated since these films are quite susceptible to oxidation. In this paper we report on the effect of substrate temperature, deposition rate and annealing on yttrium films in the thickness range 10 to 80 nm. We have already reported on the electrical resistivity [9] and temperature coefficient of resistance [7] of thin yttrium films.

2. Experimental details

Yttrium of purity 99.95% (obtained from Leico Industries, New York, USA) was evaporated from a tungsten basket at a pressure of 10^{-6} torr onto optically flat glass substrates. These substrates prior to the film deposition, were subjected to ultrasonic, chemical and ionic bombardment cleaning.

The thickness measurements were done using a quartz crystal thickness meter and later verified by a gravimetric method for higher film thicknesses. The electrical measurements were done *in situ* using the standard four-probe technique. A chromel–alumel thermocouple held close to the substrate was used to monitor the substrate temperature. The *in situ* annealing of the film was carried out by heating the film to a required temperature and then maintaining it at that temperature for several hours. Other experimental details are given elsewhere [10].

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3. Theory

The electrical resistivity of thin films, according to the Fuchs–Sondheimer (FS) theory can be expressed as [11],

$$\rho = \rho_0\left[1+\frac{3}{8\lambda}(1-p)\right] \qquad \lambda > 0.1 \quad (1)$$

where ρ is the resistivity of the film, ρ_0 that of an infinitely thick film, λ is the ratio of the film thickness t, to the mean free path l of the bulk and p is the specularity parameter. Our experimental data can be interpreted using FS theory only at higher film thicknesses but there is a considerable discrepancy between theory and experimental data at lower thicknesses.

This discrepancy can be accounted for if the Mayadas–Shatzkes (MS) theory [12] is used to analyse the experimental data at lower film thicknesses. Mayadas and Shatzkes [12] have shown that the thickness dependence of the electrical resistivity is not only due to the Fuchs size effect but also due to the grain boundary scattering of the conduction electrons. The simple expression for the total resistivity of the film based on the MS theory is,

$$\rho = \rho_0\left[1+\tfrac{3}{2}\beta+\frac{3}{8\lambda}(1-p)\right] \qquad (2)$$

where $\beta = (l/D)[R/(1-R)]$, l is the mean free path of the electrons in the bulk, D is the average grain diameter and R is the grain boundary reflection coefficient.

Taking surface correction into account Falkovsky [13], modified Equation 2, as follows:

$$\rho = \rho_0\left\{\left[\frac{3}{8\lambda}\left(\frac{3R+1}{1-R}\right)(1-p)\right] + \left(3\lambda\left[\frac{1+2\lambda}{(2\lambda)^{1/2}}\tan^{-1}\left(\frac{1}{2\lambda}\right)^{1/2}-1\right]\right)^{-1}\right\} \qquad (3)$$

According to Matthiessen's rule the resistance of the film is given by,

$$R' = R_t + R_i \qquad (4)$$

where R_t and R_i are resistances due to electron–phonon interaction and defects in the lattice, respectively. For analysing the resistance behaviour with temperature, Vand [14] considered three types of defects (i) lattice vacancies (ii) interstitial atoms and (iii) combined vacancies and interstitials. The first two types of defects need a high activation energy since their elimination is by long range displacement to the surface. If the defects are of the combined type they would annihilate by short range diffusion, thus requiring a lower activation energy. The activation energy for such processes can be calculated by using relation,

$$R' = R_0 \exp(E/2kT) \qquad (5)$$

where R' is the resistance of the sample at temperature T and R_0 is a constant. Hence a plot of $\log R'$ against $1/T$ gives the value of the activation energy E.

Thin films during their deposition, in general, contain a host of structural defects. This represents a considerable departure from equilibrium and hence some of these defects will anneal out of the film on the application of a mild heat treatment. In many cases this leads to a decrease in the film resistivity. In certain instances, however, annealing in vacuum leads to an increase in resistivity becasue of the effects of oxidation and/or agglomeration. The density of defects in a film is a function of the thermal history, i.e. the previous highest temperature attained by the film above the temperature of its deposition. The changes brought about in the resistance of the film can be represented by the curve shown in Fig. 1 due to Vand [14]. Along the region AB, the resistance shows a linear behaviour. The actual elimination of defects starts at the temperature, at B, which is roughly the temperature at which the film is deposited. After point B, the change in resistance is irreversible, i.e. if the temperature is reduced, the resistance does not trace back through the previous path but reduces along the straight line CG, parallel to AB. Hence at this point G, the resistance is given by R_i, the resistance due to the defects. If the heating is carried on further, the removal of defects takes place till point F, after which the film starts melting. If the film is completely exhausted of defects at a point, say D (annealing temperature), then the resistance is only the R_t part, arising due to the scattering of electrons from the thermal oscillations of the lattice. Hence at absolute zero, this part reduces to zero.

4. Experimental results

Fig. 2 shows the thickness dependence of the resistivity curves of yttrium films in the thickness range 10 to 80 nm for three substrate temperatures, 22, 100 and 160° C. All these films were deposited at the same rate of 0.5 nm sec^{-1}. It is

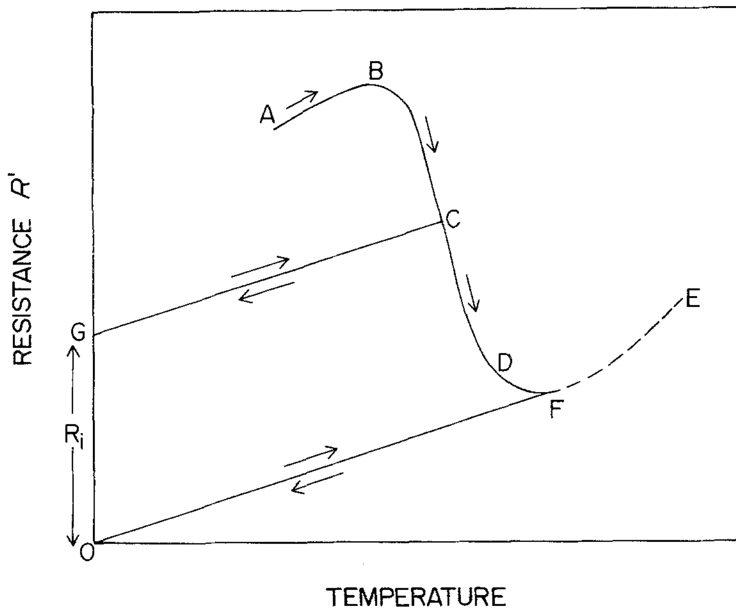

Figure 1 The temperature dependence of resistance in metallic films.

interesting to note from this figure that the resistivity is independent of the substrate temperature at higher film thicknesses (> 65 nm). However, at lower thicknesses, the films deposited at higher substrate temperatures show a lower resistivity than those deposited at room temperature (22° C). The resistivity of the films deposited at the substrate temperatures 100 and 160° C are comparable in magnitude.

Fig. 3 shows resistivity against the inverse of thickness. This plot according to Equation 1 yields ρ_0 as 175 $\mu\Omega$cm, and $l(1-p)$ as 95.2 nm. Using these values, Equation 1 has been plotted for different values of p, assuming total diffuse scattering. The films deposited at higher substrate temperatures show a resistivity behaviour in good agreement with the FS theory (curve b, Fig. 2) for a p value of 0.25. However, the films deposited at room temperature, although they deviate from the FS theory at lower thicknesses, show good agreement with it at higher thicknesses (> 65 nm). Using the same values of $l(1-p)$ and the specularity parameter p, Equation 3 was plotted for different values of the grain boundary reflection coefficient, R, to see whether the higher values of the electrical resistivity of the films deposited at room temperature (22° C) can be explained by the grain boundary scattering of the conduction elec-

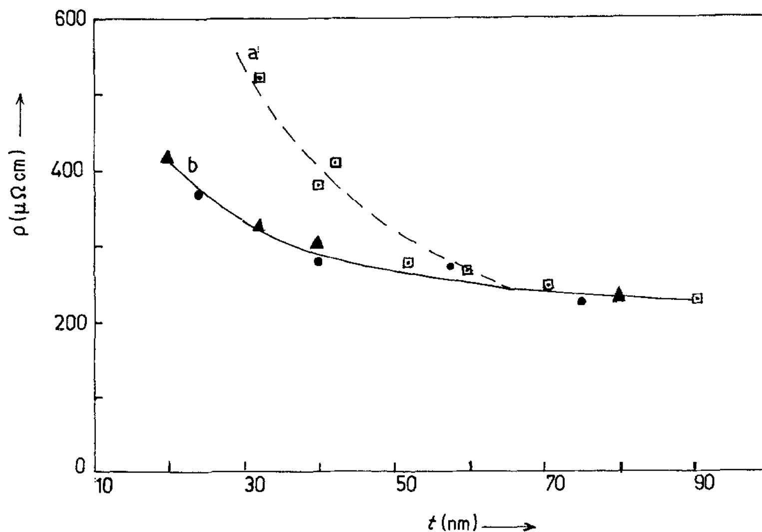

Figure 2 Thickness dependence of resistivity curves of yttrium films for different substrate temperatures. The experimental points are shown by ⊡, • and ▲ for the substrate temperatures, 22, 100 and 160° C, respectively. The continuous line b shows FS theoretical curve and dashed line a shows MS theoretical curve.

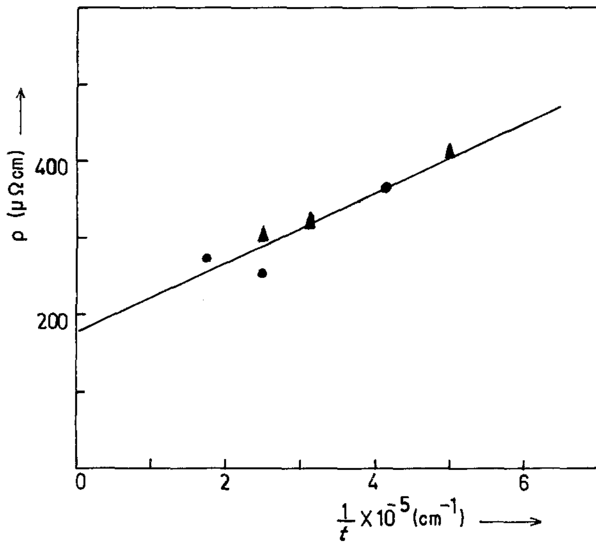

Figure 3 ρ against $1/t$ plot for yttrium films deposited at higher substrate temperatures, 100 and 160° C. The experimental points are shown by • and ▲ for 100 and 160° C, respectively.

trons. We find that the modified MS Equation 3, is indeed in good agreement with our experimental data for a R value of 0.28.

Fig. 4 shows the thickness dependence of resistivity for yttrium films grown with deposition rates of 0.5 and 1.5 nm sec^{-1}. The films deposited at a lower rate (0.5 nm sec^{-1}) have much higher resistivities compared to those deposited at 1.5 nm sec^{-1}. The resistivity data of yttrium films deposited at 1.5 nm sec^{-1} is in good agreement with the FS theory (for $p = 0.5$) while the data for the lower deposition rate is in agreement with the MS theory (Equation 3) for an R value of 0.28 and a p value of 0.5.

The annealing behaviour of yttrium films of thickness 50 and 70 nm is shown in Fig. 5. In case of the 50 nm thickness film, the film resistance initially increases along the curve A′B′. This increase is a reversible one. At point B′, the resistance starts decreasing along the region B′C′D′. However, after reaching the point D′, this film exhibits a peculiar behaviour. After reaching the minimum resistance value at D′, the resistance starts increasing either with an increase or decrease in temperature. This change is shown along the dashed lines D′E′ and D′F′. The change in resistance after point D′ is irreversible in the case of yttrium film of thickness 50 nm. Film of 70 nm thickness shows a similar behaviour in the initial stages. The film resistance increases along AB which is again a reversible region. The resistance then starts decreasing along BCD. With a further increase in temperature, the resistance increases along DE. However, with a decrease in tempera-

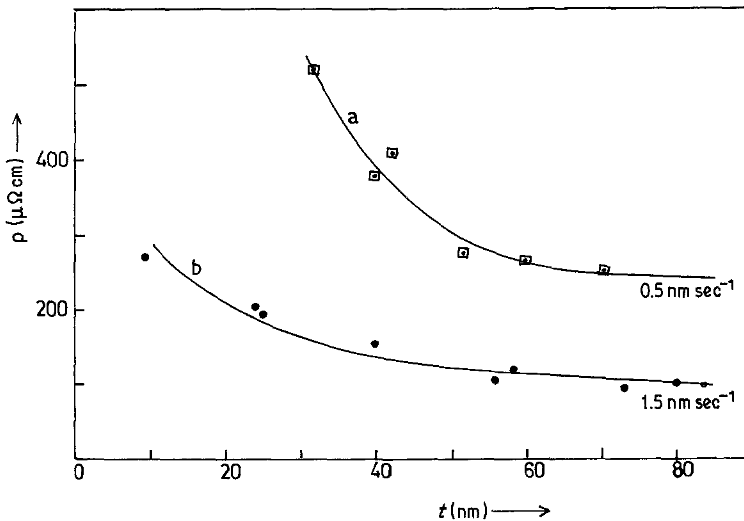

Figure 4 Thickness dependence of resistivity curves of yttrium films for different deposition rates. The experimental points are shown by ⊡ and • for the deposition rates, 0.5 and 1.5 nm sec^{-1}, respectively. Curve a, shows MS theoretical curve and curve b, shows FS theoretical curve for the deposition rates 0.5 and 1.5 nm sec^{-1}, respectively.

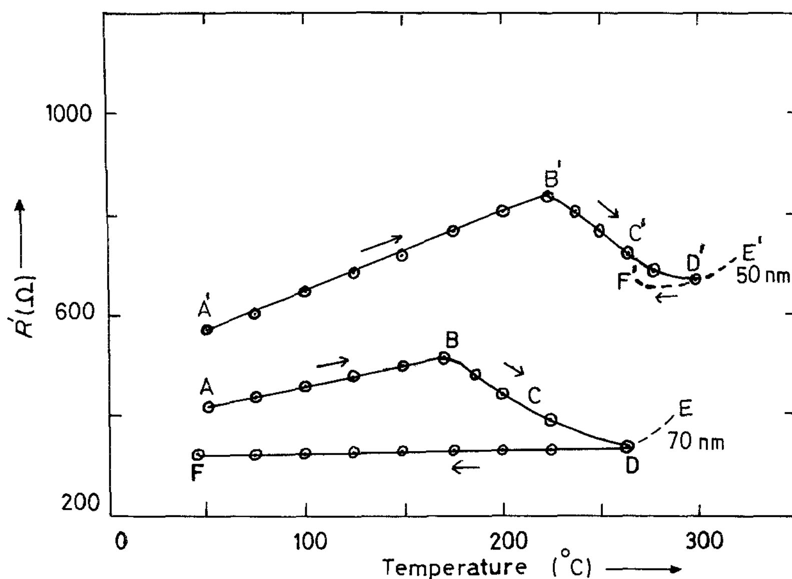

Figure 5 Variation of film resistance (R') with temperature for yttrium films of thicknesses, 50 and 70 nm.

ture, the resistance decreases along DF. But this decrease in resistance is extremely small compared to other regions of this plot.

The activation energies involved in the elimination of defects have been calculated in two yttrium films using Equation 5. The activation energies are 0.18 and 0.19 eV for the films of thickness 50 and 70 nm, respectively.

We have studied the effect of d.c. electric field up to 150 V cm^{-1} applied during the film deposition, on the electrical resistivity of yttrium films. We have not noticed any change in resistance for all film thicknesses.

5. Discussion of experimental results

The substrate temperature has considerable effect on the electrical resistivity at lower thicknesses (< 60 nm) while it has no effect at higher thicknesses. The effect of substrate temperature on the electrical resistivity may be attributed to two competing factors, (a) the decrease of the resistivity due to the increase in mobility of atoms and (b) the increase in the resistivity due to the persistance of an island or grain-like structure for a sufficiently long time before the formation of continuous film. Therefore, the net result of the effect, depends on which of the two factors dominate the process. The fact that the resistivity of yttrium films greater than 60 nm is not affected by the substrate temperature suggests that these two competing factors cancel each other. The decrease in resistivity at lower thicknesses for higher substrate temperature has also been reported for manganese [15] and palladium [16]. The increase in resistivity at the higher substrate temperature has also been reported for many metallic films [17–21]. It has been reported that the increase in resistivity at the higher substrate temperature occurs in only those films which exhibit a large formation of a grain-like structure at lower thicknesses. In view of this, most of these films also exhibit a negative temperature coefficient of resistance at lower thicknesses [22–24]. Yttrium films do not show a grain-like structure at low thicknesses and hence its resistivity data can be explained by the FS theory over the entire thickness range [9]. Hence, in the case of yttrium films the higher substrate temperature may not promote the formation of islands but it only affects the mobility of the adsorbed atoms. The increased mobility of these atoms leads to the decrease in the electrical resistivity at the higher substrate temperature.

The films deposited at the rate of 1.5 nm sec^{-1}, exhibit much lower resistivity compared to those deposited at 0.5 nm sec^{-1}. The experimental curve for the deposition rate 1.5 nm sec^{-1} is in agreement with the FS theory for all film thicknesses. Increasing the deposition rate increases the rate of the formation of smaller islands in the initial stage of film growth, resulting in a continuous film. Higher deposition rates also result in the incorporation of a small number of defects in the film and hence give rise to smaller film resistivity. The decrease in resistivity at higher deposition rates has also been reported for many metallic films [24, 25].

The yttrium films show a good agreement with

the Vand theory of defects. As seen in case of other metallic films [26, 27], yttrium films show an initial increase in resistivity with temperature and then the elimination of defects starts. This is marked by the decrease in the resistivity with increase in annealing temperature. After a further increase in temperature, the yttrium film of thickness 50 nm shows an increase in resistivity either with an increase or decrease in temperature. This is an indication of the fact that at higher temperatures, the rare earth metallic films tend to become oxidized and hence show irreversible increases in resistivity. The yttrium film of thickness 70 nm shows a perfect behaviour as expected from the theory of defects. Initially it shows an increase, similar to that for the 50 nm film. However, it differs in the fact that after reaching the minimum value of the resistance, with a decrease in temperature the resistance decreases. This decrease in resistance is very small compared to the intial decrease in resistance, occurring due to the elimination of defects.

According to Vand's theory, after the elimination of defects, the reversible changes in resistance with temperature, should be of high order. Further, the theory predicts the resistance value to become zero at absolute zero temperature. However, this is not the case in yttrium films, as the resistance change along the reversible region is very small. This may be due to the oxidation of the film, after annealing is stopped. Hence, the resulting resistance observed is the net effect of the elimination of defects and the oxidation of the film. In case of the yttrium film of 70 nm thickness, the oxidation effect is comparatively less than that of 50 nm one. The value of the activation energies calculated in both cases are of the same order of magnitude and suggest that the defects are of the combined type, since these would require smaller activation energies to migrate and annihilate each other. The defect densities could not be calculated because of this oxidation effect.

6. Conclusions

Although electrical resistivity of metallic films is generally much higher than the bulk materials, it is, however, possible to control the film resistivity by proper choice of the deposition parameters such as substrate temperature, deposition rate, d.c. electric field and annealing temperature. It is also clear from our experimental study on yttrium films that a higher substrate temperature leads to a decrease in the resistivity for films which do not exhibit a grain-like structure. It may be interesting to confirm these experimental facts from structural studies of rare earth films grown under ultrahigh vacuum conditions.

References

1. M. A. ANGADI and P. V. ASHRIT, *Vacuum* **31** (1981) 161.
2. *Idem, Phys. Status Solidi (a)* **67** (1981) K119.
3. *Idem, Vacuum* **32** (1982) 99.
4. *Idem, J. Mater. Sci.* **16** (1981) 3513.
5. *Idem, Phys. Status Solidi (a)* **77** (1983) in press.
6. *Idem,* Proceedings of the Solid State Physics Nuclear Physics Symposium organised by the department of Atomic Energy, Govt. of India at the Indian Institute of Technology, New Delhi, India, **23C**, (1980).
7. *Idem, J. Less-Common Met.* **75** (1980) 147.
8. K. L. CHOPRA, "Thin Film Phenomena" (McGraw Hill, New York, 1969).
9. M. A. ANGADI and P. V. ASHRIT, *Thin Solid Films* **72** (1980) L5.
10. P. V. ASHRIT, PhD thesis (unpublished) Karnatak University, India (1983).
11. D. LARSON, "Physics of Thin Films" Vol. 6, edited by M. Francomb and R. W. Hoffman (Academic Press, New York, 1971) p. 65.
12. A. F. MAYADAS and M. SHATZKES, *Phys. Rev.* **B1** (1970) 1382.
13. L. A. FALKOVSKY, *J. Expt. Theor. Phys.* **64** (1973) 1855.
14. V. VAND, *Proc. Phys. Soc.* **55** (1943) 222.
15. S. M. SHIVAPRASAD and M. A. ANGADI, *J. Phys. D (Appl. Phys.)* **14** (1981) 1125.
16. S. M. SHIVAPRASAD, PhD thesis (unpublished) Karnatak University Dharwad 580 003, India (1982).
17. M. A. ANGADI and L. A. UDACHAN, *J. Mater. Sci.* **16** (1981) 1412.
18. M. A. ANGADI and P. V. ASHRIT, *Vacuum* **31** (1981) 161.
19. *Idem, ibid.* submitted for publication.
20. A. BORODZIUK-KUPLA, B. STOLECKI and C. WESOLOWSKA, *Thin Solid Films* **85** (1981) 323.
21. B. STOLECKI, A. BORODZIUK-KULPA and C. WESOLOWSKA, *ibid.* **56** (1979) 299.
22. L. A. UDACHAN, S. M. SHIVAPRASAD, P. V. ASHRIT and M. A. ANGADI, *Phys. Status Solidi (a)* **60** (1980) K191.
23. P. V. ASHRIT and M. A. ANGADI, *ibid.* **63** (1981) K77.
24. S. M. SHIVAPRASAD and M. A. ANGADI, *J. Phys. D (Appl. Phys.)* **13** (1980) L157.
24. M. A. ANGADI and L. A. UDACHAN, *Thin Solid Films* 78 (1981) 299.
26. K. NARAYANDAS, M. RADHAKRISHNAN and C. BALASUBRAMANIAN, *ibid.* **67** (1980) 357.
27. K. L. CHOPRA, R. SURRI and A. P. THAKOOR, *J. Appl. Phys.* **48** (1977) 538.

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