JOURNAL OF MATERIALS SCIENCE 22 (1987) 1971–1974

Optical properties of manganese films

M. A. ANGADI, K. NALLAMSHETTY
Department of Physics, University of the West Indies, St Augustine, Trinidad

The optical properties of thin manganese films in the thickness range 40 to 1200 nm are reported for UV, visible and near infrared regions. The reflectance and absorbance of annealed and unannealed manganese films is measured from film side and substrate side, in the wavelength range 190 to 900 nm, and for normal incidence of light. These measurements are used to calculate the refractive index (n), extinction coefficient (k), and the imaginary part of the dielectric constant (ε).

1. Introduction

There is very little experimental work published on the physical properties of manganese films [1]. In recent years some attempt has been made to study the transport properties of these films [2–8] which exhibit very interesting electrical properties [7]. To the best of our knowledge, there is very little published data on the optical properties of manganese films [9–11]. Sabine [9] was the first researcher to report on the optical reflectance of manganese films in the wavelength range from 40 to 450 nm, at an angle of incidence of 18°. Bueche [10] has reported on the reflectivity of evaporated films for five angles of incidence in the visible and near infrared (NIR) region and the data was used to determine the dielectric constant of the metal. More recently, Atkinson [11] has reported on the variation of the optical constants with wavelength in the visible region (400 to 600 nm). So far no attempt has been made to study the absorbance in these films. A systematic study on the optical reflectance and absorbance may provide useful information on the possible application of manganese films in optical devices.

Previously published work does not report the thickness and other deposition conditions which influence the optical properties of thin metallic films. In this paper, we report on the optical reflectance and absorbance in the wavelength range 190 to 900 nm at normal incidence of light. The data for normal incidence is used to calculate the refractive index (n), extinction coefficient (k) and the imaginary part of the dielectric constant (ε). The effect of annealing on the optical properties is studied for UV, visible and NIR regions.

2. Experimental method

Manganese of purity 99.999% (obtained from Good-Fellow Metals, Cambridge, UK) was evaporated at a pressure of 10^{-4} Pa onto a glass substrate held at 22° C. The films of different thicknesses were deposited by electron beam evaporation process using Edwards High Vacuum System (Model E306). The thickness and the rate of deposition of film was monitored by a quartz crystal thickness meter with an accuracy of ±0.1 nm. The films were deposited at a uniform rate in the range 0.2 to 0.5 nm sec^{-1}. The films were annealed in vacuum using a radiant heater soon after film deposition for about 2 h at 150° C.

The optical reflectance and absorbance measurements were carried out using a specular reflectance accessory and Philips UV/Visible/NIR Spectrophotometer (Model PU8800) in the wavelength range 190 to 900 nm. The reflectance and absorbance data of freshly deposited manganese films was recorded on a chart recorder.

3. Theory

Metallic films are characterized optically by their optical constants, i.e. the extinction coefficient and refractive index. The extinction coefficient k is the imaginary part of the complex refractive index $N = n + ik$. Knowledge of n and k is required to calculate the reflectance of a metal surface at various angles of incidence, the effect of surface films on the reflectance, and the phase change on reflection. The contribution of light scattering to optical losses (L) is given by

$$L = A + S, \qquad 1 = R + T + L \qquad (1)$$

where A is absorption, S is scattering, and T is transmittance. If several films of different thickness are made and if the thicknesses are determined independently then use may be made of the fact that, for thicknesses large enough for multiple reflection to be ignored, the transmittance of the film is given by [12] the following equation,

$$T = \frac{16 n_0 n_1 (n^2 + k^2)}{[(n + n_1)^2 + k^2][(n_0 + n)^2 + k^2]} \times \exp(-4\pi k t/\lambda) \qquad (2)$$

where n is the refractive index of the film, t is the film thickness, n_1 is the refractive index of substrate, n_0 is the refractive index of incident medium and k is the extinction coefficient of the film. A measurement of the reflectance for a thick film enables n to be found from the measured k values since, for normal incidence,

$$R = \frac{(n - n_0)^2 + k^2}{(n + n_0)^2 + k^2} \qquad (3)$$

It is reported that the absorptive part of the dielectric constant (ε) of a thin film can be determined directly

0022-2461/87 $03.00 + .12

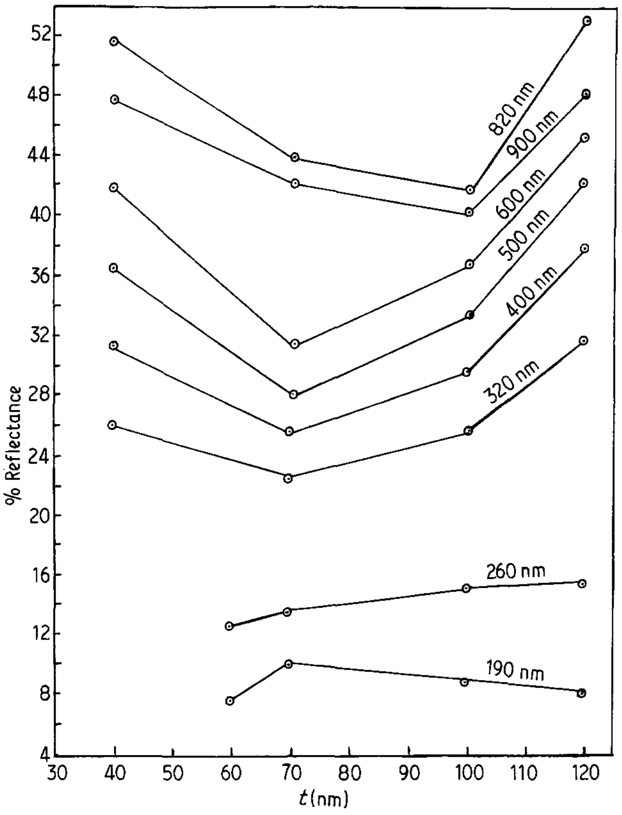

Figure 1 Percentage reflectance against thickness for different wavelengths of light incident normally on unannealed films.

by the following equation [13, 14],

$$n\eta t = \frac{1 - \mathscr{R}' - \mathscr{T}}{\mathscr{T}} = (2\pi\varepsilon/\lambda)t \qquad (4)$$

where η is the absorption coefficient of the film, $\mathscr{R}'$ is the reflectance from the substrate side, and $\mathscr{T}$ is the transmittance of the film substrate assembly. The Equation 4 is valid for $nt \ll \lambda$, where λ is the wavelength of the incident light.

4. Experimental results and discussion

Fig. 1 shows the variation of percentage of reflectance against thickness for different wavelengths of incident light for unannealed manganese films. The reflectance is high in the NIR region for all thicknesses. The reflectance is very low in the UV region (320 to 190 nm). The percentage reflectance is minimum at 70 nm thickness for all wavelengths except for the UV region. Fig. 2 shows the variation of percentage reflectance against thickness for different wavelengths of incident light for annealed manganese films. The reflectance is generally higher for all thicknesses by about 4 to 6% compared to unannealed films. This is expected in view of the formation of larger grains after annealing. A decrease in the electrical resistivity of manganese films has also been reported on annealing for a few hours [3]. The reflectance is again found to be a minimum for 70 nm thick films. It is not clear to us why reflectance is minimal for 70 nm thickness. Fig. 3 shows the variation of absorbance against thickness for different wavelengths. Here the absorbance data is for unannealed films and for normal incidence. The absorbance shows a maximum at 70 nm thickness and is maximum for all thicknesses in the UV region. For

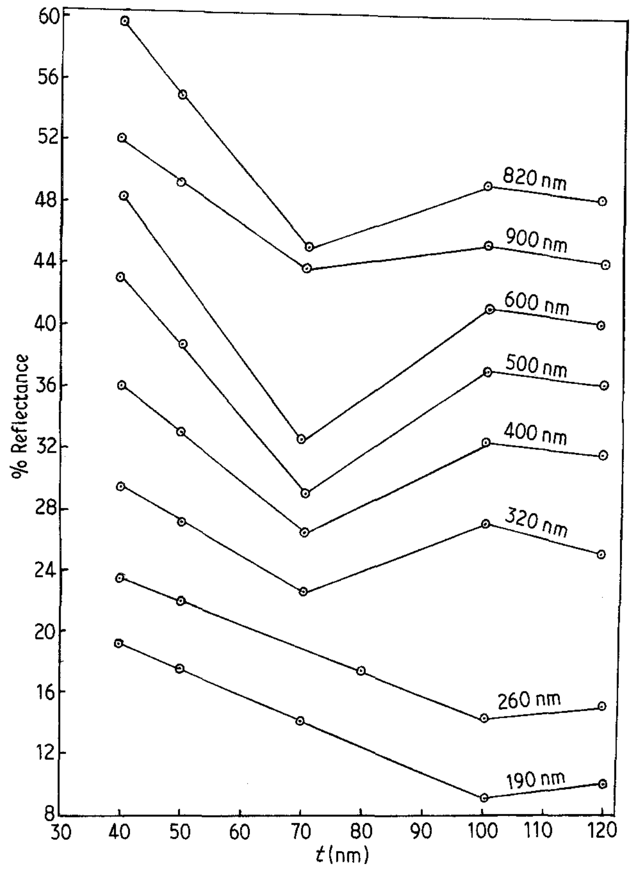

Figure 2 Percentage reflectance against thickness for different wavelengths of light incident normally on annealed films.

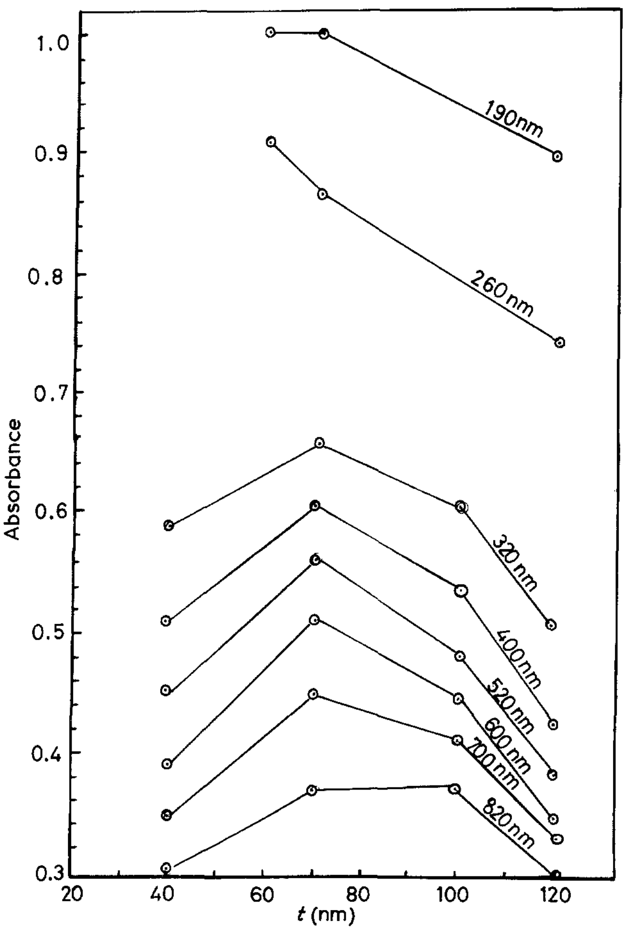

Figure 3 Absorbance against thickness for different wavelengths of light incident normally on unannealed films.

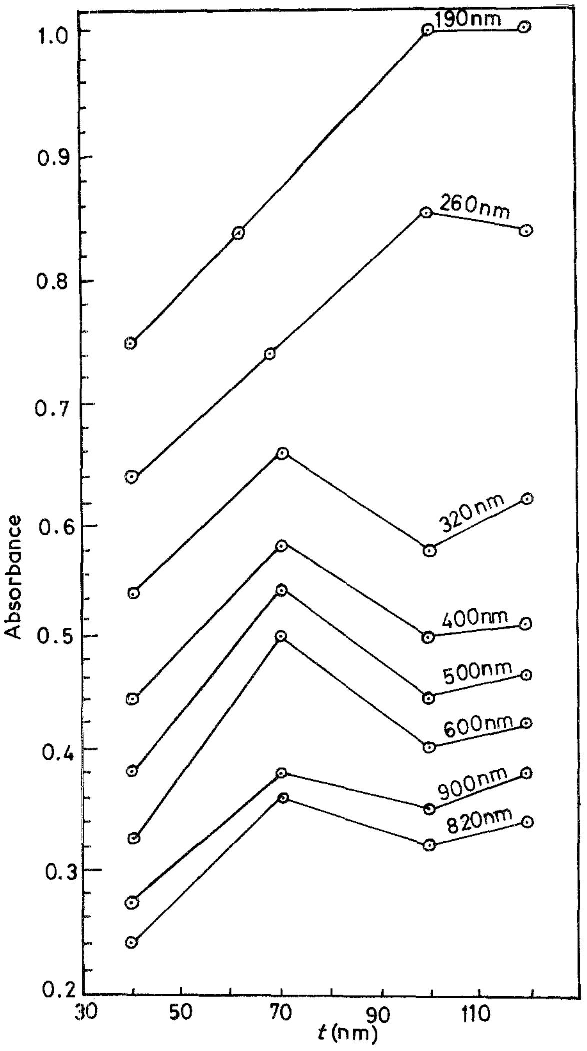

Figure 4 Absorbance against thickness graphs for different wavelengths of light incident normally on annealed films.

annealed films (Fig. 4) however, the absorbance is less compared to unannealed films for all thicknesses.

Equation 2 can be used to plot a graph of log T against thickness (t). The slope of this graph is used to calculate the extinction coefficient k for different wavelengths. For normal incidence, Equation 3 can be used to calculate the refractive index of films for different wavelengths. Fig. 5 shows the variation of the refractive index with changes in wavelength of the incident light for unannealed films. The changes in the refractive index values are quite large near the infrared region compared to those in the visible region. Fig. 6 shows the graph of refractive index against wavelength for different thicknesses of annealed films. The variation of refractive index against wavelength is approximately linear for annealed films. Fig. 7 shows the thickness dependence of the refractive index for fixed wavelength for unannealed films. In the NIR region, the refractive index reaches a maximum for 70 nm film and diminishes at higher thicknesses. However, for annealed films (Fig. 8), the changes in n are small compared to unannealed films. Fig. 9 shows the absorption ($n\eta$ versus ν) for different thicknesses. This plot is used to determine the imaginary part of the dielectric constant (ε).

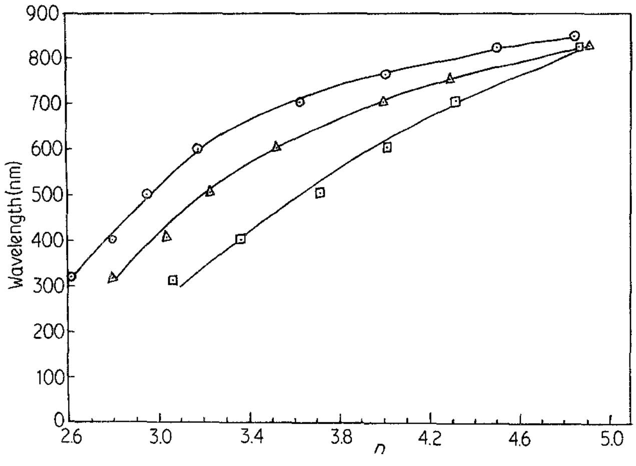

Figure 5 The variation of refractive index against wavelength for different thicknesses of unannealed films. Film thickness (□) 100 nm, (△) 70 nm, (⊙) 60 nm.

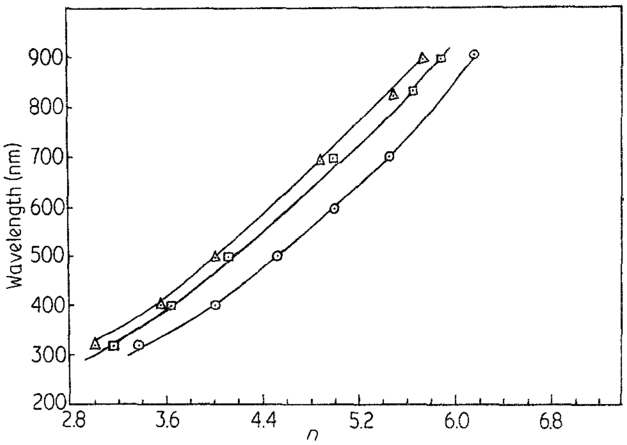

Figure 6 The variation of refractive index against wavelength for different thicknesses of annealed films. Film thickness (△) 120 nm, (□) 100 nm, (⊙) 40 nm.

It is important to note that Equations 2 and 3 are approximate and valid only for large thicknesses. Therefore, the accuracy of the values of n and k are dependent on the accuracy in the measurement of film thickness and surface conditions. Our values of n are much higher compared to those reported by Atkinson [11] and Bueche [10] for the visible region. The optical constants of films are dependent on the method of film formation and deposition conditions [12]. This might be the main contributing factor for the discrepancy among the published experimental data on the optical constants of manganese films. The error due to any

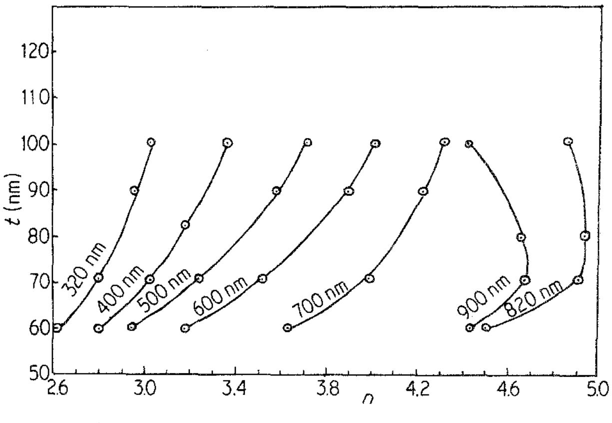

Figure 7 The thickness dependence of refractive index for a constant wavelength for unannealed films.

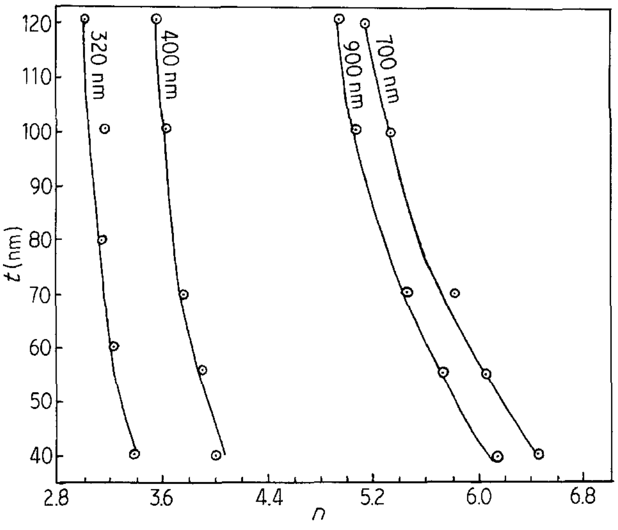

Figure 8 The thickness dependence of refractive index for a constant wavelength for annealed films.

contaminating layer on the surface is considered to be small since all our data was taken immediately after the evaporation. Although the uncertainties in our experimental data due to the changes in the deposition conditions are difficult to estimate, we expect that the n and k values are accurate within $\pm 5\%$.

5. Conclusions

We have reported on the optical constants of manganese films in the thickness range 40 to 120 nm. These constants are determined in the wavelength range 190 to 900 nm for annealed and unannealed films. The absorbance and reflectance measurements on the film and substrate side are utilized to determine the imaginary part of the dielectric constant (ε). We find manganese films to be highly absorbing for the entire wavelength range (900 to 190 nm) studied in our investigation. In view of this, manganese films are being used to develop a spectrally selective surface using a multilayered thin film structure [15]. We have also measured the optical reflectance and absorbance of these films for variable angles of incident light. The analysis of these experimental results is far more complex than reported here for normal incidence and these results will be published in a future communication. The reflectance and absorbance of manganese films depends also on the various deposition parameters such as, deposition rate, substrate temperature, the type of substrate and the pressure inside the vacuum chamber. Experimental work on this aspect of the investigation is currently underway and will be reported in due course.

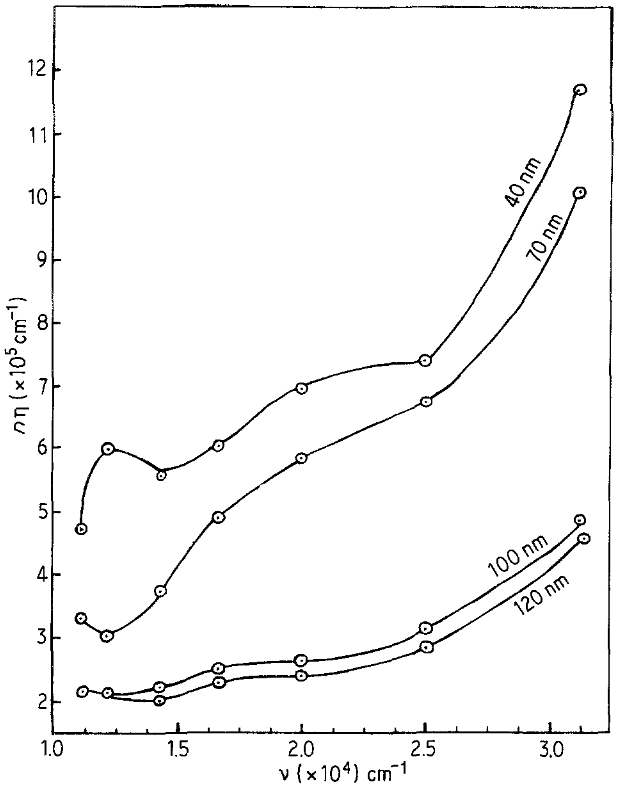

Figure 9 $n\eta$ against wavenumber (ν) for different thicknesses of manganese films.

Acknowledgements

The authors are grateful to the Campus Research Fund Committee of the University of the West Indies, St Augustine, Trinidad for financial support.

References

1. M. A. ANGADI, *J. Mater. Sci.* **20** (1985) 761.
2. M. A. ANGADI, S. M. SHIVAPRASAD and P. V. ASHRIT, *Phys. Status Solidi* (*a*) **60** (1980) K159.
3. M. A. ANGADI, S. M. SHIVAPRASAD and L. A. UDACHAN, *Thin Solid Films* **71** (1980) L1.
4. M. A. ANGADI and S. M. SHIVAPRASAD, *J. Phys. D* (*Appl. Phys.*) **13** (1980) L157.
5. *Idem, ibid.* **14** (1981) 1125.
6. *Idem, Vacuum* **32** (1982) 51.
7. *Idem, J. Mater. Sci. Lett.* **3** (1984) 739.
8. *Idem, ibid.* **5** (1986) 405.
9. G. E. SABINE, *Phys. Rev.* **55** (1939) 1064.
10. F. BUECHE, *J. Opt. Soc. Amer.* **38** (1948) 806.
11. R. ATKINSON, *Thin Solid Films* **37** (1976) 195.
12. O. S. HEAVENS, in "Physics of Thin Films", Vol. 2, edited by G. Hass and R. E. Thun (Academic Press, New York, 1964) p. 193.
13. H. J. TRODAHL, *J. Phys. E* **17** (1984) 27.
14. S. G. TOMLIN, *Brit. J. Appl. Phys.* **1** (1968) 1667.
15. M. A. ANGADI and K. NALLAMSHETTY, *Phys. Status Solidi* (*a*) in press.

Received 16 June 1986
and accepted 15 January 1987