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Electrical conductivity of thin metallic manganese films

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Thin metallic Mn films of various thicknesses were thermally vapour-deposited on glass substrates at room temperature in a high vacuum. The electrical conductivity of these Mn films was measured *in situ* as a function of film thickness and annealing temperature. The experimental results indicate that the electrical resistivity decreases as the film thickness and annealing temperature increase. The calculated values of the activation energy for electric conduction decrease as the film thickness increases. The mean free path and mobility for charge carriers, and the electrical resistivity of infinitely thick films, were calculated as a function of temperature; they are in good agreement with the theoretical relationships.

1. Introduction

Thin manganese films exhibit large resistivity, a very low temperature coefficient of resistivity (TCR), very low thermoelectric power (TEP), very low noise level, accurate control of resistivity, stability under operating conditions and finally low cost. All these characteristics make manganese thin films very suitable for use in the fabrication of thin-film resistors (TFR) and/or as a reference material in the fabrication of thin-film thermoelectric junctions [1]. Several transition metals such as Cr, Ti, W, Mo and Ta satisfy some of the previously mentioned characteristics of Mn films [2]. Although Ta exhibits a large resistivity, Ta films are not suitable for the fabrication as TFR due to the large variations in both TCR and TEP and because the technology for Ta as TFR is further complicated [3].

The electrical resistivity ρ_f has been studied for thin Mn films deposited on glass substrates [2, 4–8] and deposited on to unheated carbon–mica substrates prepared in the presence of an applied electric field [9]. The electrical conductivity was studied for pure Mn films and Mn–SiO cermet of various compositions deposited on glass substrates [10–12] and for pure Mn films and Mn–MgF_2 cermets of various compositions [13–15]. The low-temperature dependence of the electrical conductivity was studied for Mn films deposited on glass substrates [16–18]. The behaviour was similar to that observed for bulk Mn-alloyed transition elements [19].

The aim of the present work was to study the effect of film thickness and annealing temperature on the electrical conductivity of thin metallic Mn films deposited on glass substrates. The activation energy for electric conduction was studied as a function of film thickness. The mean free path and mobility for the charge carriers and the resistivity of infinitely thick films are studied as a function of temperature.

2. Experimental procedure

Manganese of purity 99.99% from Balzers was thermally evaporated from an Mo boat and deposited on glass substrates at room temperature (297 K) in a vacuum of 10^{-3} Pa with deposition rate 0.7 nm s^{-1}. The film thickness and deposition rate were controlled and measured using a quartz crystal thickness monitor. The temperatures of the substrate and the deposited films were measured using Ni–NiCr thermocouples attached to the substrates. Four indium electrodes were welded to the substrates for electrical measurements. Mn films of thickness 85–380 nm were deposited and the electrical resistivity was measured *in situ* directly after deposition as a function of film thickness at the deposition temperature (297 K). The deposited films were annealed *in vacuo* in the temperature range 323–393 K for 30 min, then the electrical resistivity was measured as a function of annealing temperature for each thickness. This experimental work was carried out at Minia University using an Edwards coating unit type E 306 A.

3. Results and discussion

The variation of the electrical resistivity ρ_f with film thickness t for Mn films is shown Fig. 1. It is quite evident that the electrical resistivity decreases as the film thickness increases. Films of metals with high melting points (1518 K for Mn) have an island structure instead of a continuous structure [20] even at fairly high thicknesses. The higher value of resistivity for thinner films is attributed mainly to the presence of an island structure with a large density of defect sites. The islands increase in size as the film thickness increases and become attached to each other. This leads to the disappearance of the island structure or the formation of a continuous film where the density of the defect

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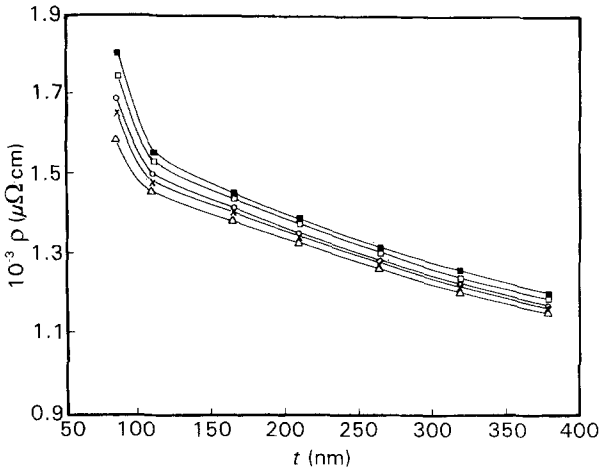

Figure 1 Thickness dependence of the electrical resistivity for Mn films: (■) 297k, (□) 323k, (○) 353k, (×) 373k, (△) 393k.

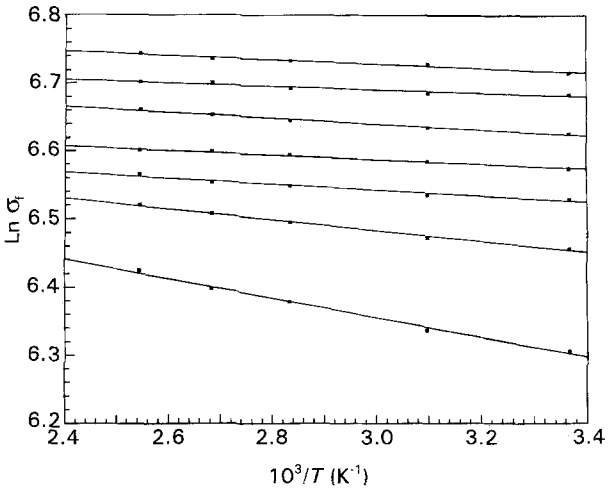

Figure 3 Relation between electrical conductivity ln σ_f and $1/T$ for thin Mn films.

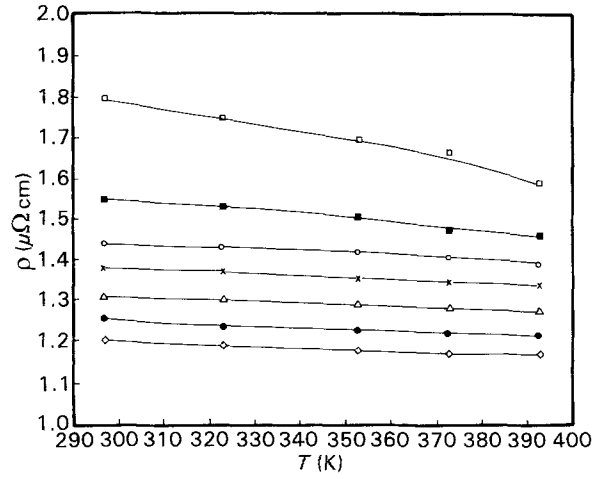

Figure 2 Effect of annealing temperature on electrical resistivity: thickness (□) 65 nm, (■) 110 nm, (○) 165 nm, (×) 210 nm, (△) 265 nm, (●) 320 nm, (◇) 380 nm.

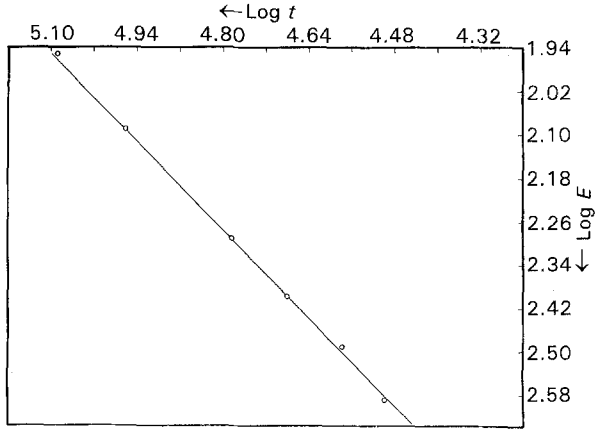

Figure 4 Activation energy for electrical conduction as a function of Mn film thickness.

sites will markedly decrease. As a result the electrical resistivity decreases as the film thickness increases.

The temperature dependence of the electrical resistivity ρ_f is presented in Fig. 2. This indicates that the electrical resistivity decreases as the annealing temperature increases. The decrease is sharp for thinner films (85 nm) and becomes very small for thicker films. As the annealing temperature increases, the small islands in the film can be arranged or moved to minimize the number and size of the channels between them, and on the other hand the adsorbed adatoms of impurities can be liberated from the film. As a result the electrical resistivity decreases as the annealing temperature increases. This decrease is very sharp for thinner films, which are thus strongly affected by increasing the annealing temperature.

The logarithmic relation between the film electrical conductivity σ_f and the annealing temperature T for thin Mn films is illustrated in Fig. 3. The relations represent straight lines with negative slopes, controlled by the expression

$$\sigma_f = \sigma_0 \exp(-E/kT) \quad (1)$$

where σ_0 is constant, k is Boltzmann's constant and E is the activation energy (eV) for electric conduction. The activation energy for electric conduction can be calculated from the slopes of the lines in Fig. 3 for each thickness. E was found to be in the range 0.011–0.0019 eV with the film thickness in the range 85–380 nm. The calculated values of activation energy were found to decrease as the film thickness increases. The number of scattering centres for charge carriers decreases as the film thickness increases, leading to greater decrease in the values of the resistivity and consequently the activation energy for electric conduction.

The logarithmic relation between E and t was drawn as shown in Fig. 4 to identify the shape of the theoretical expression controlling them. The logarithmic relation in Fig. 4 represents a straight line with a negative slope equal to 1.03. This means that E is inversely proportional to t, or in general one can write this dependence as

$$E = A + \frac{B}{t} \quad (2)$$

where A is a constant which has the units of energy (eV) and B is another constant which has the units of

eV cm. The relation between E and $1/t$ for the experimental results of this study represents a straight line passing through the origin ($t \rightarrow \infty$). This proves that the constant $A = 0$, and on the other hand verifies that the activation energy for electric conduction of the bulk Mn equals zero. Therefore the final expression which controls the variation of E with t can be suggested to be in the form

$$E = B/t \tag{3}$$

This equation must be applied to other thin metallic films to test its generality and validity.

According to the well-known Fuchs–Sondheimer theory for electrical conduction [22, 23], the electrical resistivity ρ_f of thin metallic films can be written in the form

$$\rho_f/\rho_0 = 1 + \frac{3}{8}\frac{(\lambda_0)}{t}(1 - P) \tag{4}$$

where ρ_0 is the electrical resisitivity of an infinitely thick film, λ_0 the mean free path for the charge carriers and P the specularity parameter. When the relation between $\rho_f t$ and t is drawn for each temperature, a straight line will result with slope equal to ρ_0 and an intercept on the vertical axis equal to $(3/8)\rho_0\lambda_0(1 - P)$ according to Equation 4. The best value of P which approaches the experimental and the theoretically calculated values of resistivity (ρ_f–t curves) was found to be 0.6 for Mn thin films in this study. Using the value of $P = 0.6$ and the value of ρ_0 from the slopes, the mean free path λ_0 can be calculated for each temperature T. The values of λ_0 and the corresponding temperatures in this study are in the range 476–118 nm and 323–393 K, respectively: for example λ_0 in this study is 476 nm at 297 K, which is higher than the published value 96.7 nm [2, 4, 5]. This may be related to the lower value of vacuum (10^{-3} Pa) and higher deposition rate (0.7 nm s^{-1}) as compared with the corresponding published values of 10^{-4} Pa and 0.2 nm s^{-1} [2, 4, 5]. The deposition conditions in this study are very suitable to minimize the size of the islands forming a large number of scattering centres for charge carriers, and consequently this increases the value of the mean free path.

The logarithmic relation between λ_0 and T is presented in Fig. 5, which represents a straight line with a negative slope equal to 4.96; this is in good agreement with our previous work for Al thin films [24]. At temperatures lower than the Debye temperature T_D, the temperature dependence of the mean free path is controlled by the following equation [25]:

$$\lambda_0 = AT^{-5} \tag{5}$$

where A is a constant.

The calculated value of the slope from Fig. 5 (-4.96) agrees well with the theoretical value (-5) according to Equation 5; this is because the studied range of temperatures 323–393 K is still lower than the Debye temperature T_D which is 410 K [26].

The drift mobility μ of the charge carriers can be calculated at each temperature from the values of λ_0 using the following expression [27] which was based on the Lorentz–Sommerfeld theory:

$$\mu = \frac{\lambda_0 e}{225(2\pi m^* KT)^{1/2}} \tag{6}$$

where e and m^* are the charge and effective mass of the electron, respectively. The calculated values of the drift mobility are in the range 6.7–1.4 $cm^2 V^{-1} s^{-1}$ for temperatures in the range 297–393 K. The calculated values of mobility μ are presented in Fig. 6 as a function of temperature. According to Equation 6 and Fig. 6, the drift mobility decreases as the temperature increases. Since λ_0 decreases exponentially as T increases, the collisions between charge carriers occur at shorter free paths leading to a decrease in their mobilities.

The calculated values of the electrical resistivity of infinitely thick films ρ_∞ in Fig. 4 (as calculated from the slopes of the lines) are presented in Fig. 7 as a function of temperature. It is clear that ρ_∞ increases as the temperature increases, which is contrary to the behaviour of thin films; this is the natural character of the bulk metals. The values of ρ_∞ in this study are higher than those published, for example ρ_∞ in this study at 297 K is 1108 $\mu\Omega$ cm which is higher than the 376 $\mu\Omega$ cm reported for Mn thin films [2, 4, 5]. The values of ρ_∞ in this study and those previously published [2, 4, 5] are all higher than the value of 185 $\mu\Omega$ cm for bulk Mn metal [28]. This large deviation between the resistivity of the infinitely thick films and the bulk is a typical characteristic of many transition metallic films [2]. The higher values of ρ_∞ for

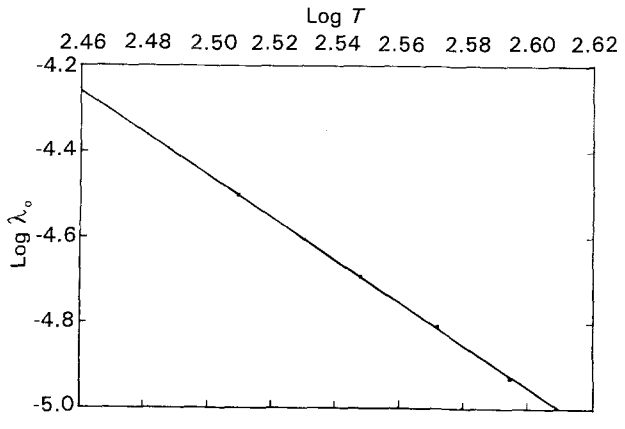

Figure 5 Temperature dependence of the mean free path.

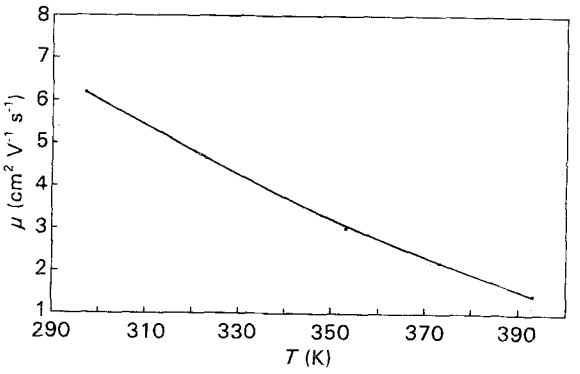

Figure 6 Mobility as a function of temperature.

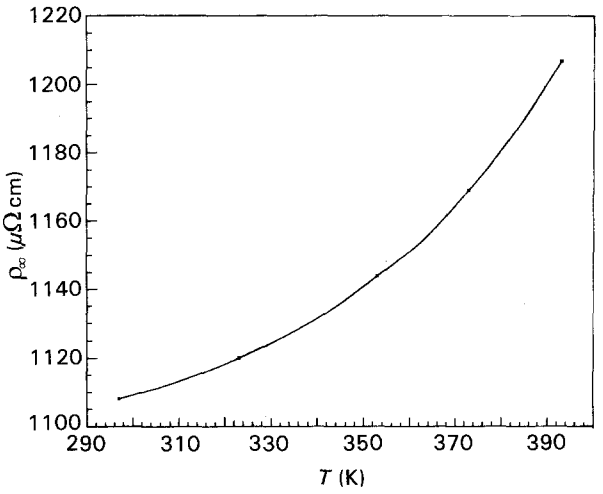

Figure 7 Variation of the electrical resistivity of infinitely thick Mn films with temperature.

Mn films are attributed to the inherent defects incorporated into the film structure during its growth [29], especially when the substrate temperature is low (297 K) and the deposition rate is high (0.7 nm s^{-1}) as in this study. It can be attributed to contamination of the substrate before and during the film growth, especially at the lower vacuum used in this study (10^{-3} Pa). Experimentally it is possible to minimize the discrepancy between the bulk and infinitely thick film resistivities by proper selection of the deposition rate [3] and substrate temperature [5], and by depositing a protective thin insulating layer of SiO on Mn films to minimize the oxidation process [6].

4. Conclusion

The results of this study can be summarized as follows:

1. The electrical resistivity of thin metallic Mn films decreases as the film thickness and annealing temperature increase.
2. The activation energy for electric conduction decreases as the film thickness increases. An empirical formula is suggested to represent the thickness dependence of the activation energy.
3. The Fuchs–Sondheimer theory for electric conduction proved to be applicable to Mn thin films.
4. The mean free path and the drift mobility of the charge carriers decrease as the temperature increases.
5. The calculated values of ρ_∞ have the same character as that of the bulk Mn, increasing with increasing temperature.
6. The values of ρ_f, ρ_∞ and λ_0 are higher than the published values.

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