JOURNAL OF MATERIALS SCIENCE 19 (1984) 2396–2400

Some transport properties of palladium films

M. A. ANGADI
Department of Physics, The University of the West Indies, St Augustine, Trinidad
S. M. SHIVAPRASAD*
Department of Physics, Indian Institute of Technology, New Delhi, India

The effect of deposition rate and substrate temperature on the electrical resistivity (ρ), temperature coefficient of resistance (TCR) and thermolelectric power (TEP) of palladium films, in the thickness range 2 to 25 nm, is found to be marked. Higher rates of deposition and substrate temperatures are found to result in larger grains and hence changes in transport properties. The Fuchs– Sondheimer theory is used to explain the size effect in palladium films while the Mayadas–Shatzkes and Meyer relations are employed to study these effects on ρ, TCR and TEP.

1. Introduction

Studies of the "size effect" on the electron transport properties of metal films have caused enormous interest, due to the reduction of the third dimension of the metal. Until recently, thickness dependence studies have given rise to anomalous experimental results for quantities concerning electron transport in metal films. Since the electron scattering centres are formed mainly during the film growth, the deposition parameters that influence the kinetics of the evaporated molecules result in a change in the film microstructure and the electronic properties. Although it is now realized that substrate temperature (T_s), deposition rate, annealing the film in vacuum, and the presence of a d.c. electric field during film growth play an important role in determining the physical properties of transition metal films [1–11], as far as we know an exhaustive and systematic study of the effect of these parameters on the properties of palladium films has not been made. We have already reported on the thickness dependence of electrical resistivity [12], the temperature coefficient of resistance [13], and the thermoelectric power [14] of palladium films. We have also reported on the frequency response of the film resistance [15] and the effect of the presence of a d.c. electric field during film growth [16]. In this paper, we describe our measurements of resistivity (ρ), temperature coefficient of resistance (TCR) and thermoelectric power (TEP) when deposition parameters such as deposition rate and substrate temperature are varied in the thickness range 2 to 25 nm. The experimental results are analysed in the light of some existing theories.

2. Experimental techniques

Palladium of purity 99.9% obtained from Johnson Matthey Ltd UK, was evaporated from a tungsten helix, at a pressure of 10^{-4} Pa, onto glass substrates held at different T_s, i.e. 25° C and 165° C, at different rates of deposition, i.e. 0.03, 0.14 and 0.4 nm sec^{-1}. The substrate, prior to the film deposition, was subjected to chemical, ultra-sonic and ionic bombardment cleaning. The rate of deposition was controlled by the current flowing through the tungsten helix. The substrate was heated to a high temperature by a radiant heater, at a uniform rate of 7° C min^{-1}. The temperature of the film was measured by a chromel–alumel thermocouple held in close contact with the substrate. The thickness and the rate of deposition were monitored during deposition by a quartz crystal thickness monitor. The resistivity and TCR

---

[*] Present address: Department of Physics, University of Sussex, Falmer, Brighton, Sussex, BN1 9RH, UK.

0022–2461/84 $03.00 + .12

measurements were made *in situ*, while the TEP was measured in air after the film resistance had reached a steady value. Films of lead of thickness 150 nm were used as electrodes for measuring the thermoelectric voltage across the film. Lead was selected as the contact material since its thermopower is very small, and it is insensitive to a small impurity content. Hence, the reported values of TEP for palladium are with respect to lead. The temperature of the hot junction was maintained below 75° C to avoid the diffusion of lead into palladium. The thermo-electric e.m.f. was measured by heating one junction gradually to 75° C, while the other junction was kept at room temperature (25° C). The two ends of the film were held rigidly between two brass blocks and were insulated from the blocks and the heating coil by mica sheets. The temperature measurements were done by copper–constantan thermocouples held close to the junctions. The thermoelelectric voltages were measured by a Fluke (Model No. 848AB) high impedance voltmeter and null detector, which can accurately determine voltages as low as 10^{-8} V. The TEP is calculated from plots of thermoelectric e.m.f. against temperature difference. Other experimental details are given elsewhere [17].

3. Theory

A convenient form of the Fuchs–Sondheimer (FS) theory expresses the electrical resistivity and TCR as follows [18],

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

$$\beta = \beta_0\left\{1-\frac{3}{8\lambda}(1-p)\right\} \qquad \lambda > 0.1 \quad (2)$$

where ρ and β are the film resistivity and TCR, ρ_0 and β_0 the resistivity and TCR of an infinitely thick film, respectively. λ is the ratio of the film thickness t, to the electron mean free path l, in the infinitely thick film, and p is the specularity parameter.

It was shown by Mayadas and Shatzkes [19] that the experimentally measured resistivity not only depends on the ordinary Fuch's size effect, but also on the scattering due to the grain boundaries. The approximate expression for film resistivity, based on the Mayadas–Shatzkes (MS) theory may be expressed as [20]:

$$\rho = \rho_0\left\{1+\frac{3}{2}\alpha+\frac{3}{8\lambda}(1-p)\right\} \qquad \text{for small } \alpha \quad (3)$$

where $\alpha = lR/d(1-R)$ and d is the average grain diameter and R the grain boundary reflection coefficient. If Matthiessen's rule is valid in metals, i.e. $\rho\beta = \rho_0\beta_0$, Equation 3 can be conveniently be used for the TCR of the films [21]. Hence, an expression for the TCR based on the MS theory is,

$$\beta = \beta_0\left\{1-\frac{3}{2}\alpha-\frac{3}{8\lambda}(1-p)\right\} \qquad \text{for small } \alpha \quad (4)$$

If we assume the validity of the free electron theory and a spherical Fermi surface, the thermopower of a metal (neglecting the phonon drag contribution) is given by [22],

$$S_0 = -\frac{\pi^2k^2T}{3eE_F}(U+V) \qquad (5)$$

where $U = (\partial \ln l/\partial \ln E)_{E=E_F}$ and $V = (\partial \ln A/\partial \ln E)_{E=E_F}$, E is the electron energy, E_F the Fermi energy, K the Boltzmann constant, T the temperature and A is the area of the Fermi surface. Meyer, considering the FS geometrical theory of size effect has given a simplified relation for TEP as [22],

$$S_F = S_0\left\{1-\frac{3}{8\lambda}(1-p)\frac{U}{1+U}\right\} \qquad \text{for } \lambda > 0.1 \quad (6)$$

where S_F is the TEP of the film and S_0 the TEP of an infinitely thick film, having the same microstructure as that of the film.

4. Experimental results

Fig. 1 shows the thickness dependence of resistivity (ρ) of palladium films in the thickness

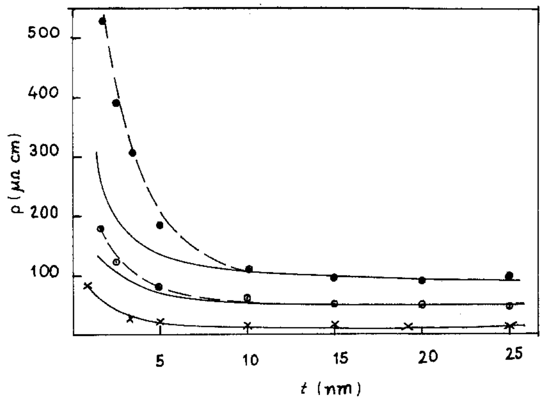

Figure 1 Thickness dependence of resistivity, showing the effect of deposition rate. The FS curve is shown by a continuous line, while the dashed line is the MS plot. The experimental points are shown by •, ⊙, and × for deposition rates, 0.03 nm sec^{-1}, 0.14 nm sec^{-1} and 0.4 nm sec^{-1} respectively.

TABLE I

Deposition parameters		From resistivity data				From TCR data				From TEP data		
R_d (nm sec^{-1})	T_s (°C)	ρ ($\mu\Omega$ cm)	$l(1-p)$ (nm)	p	R	β (X 10^4°C^{-1})	$l(1-p)$ (nm)	p	R	S_0 (μV°C^{-1})	U	V
0.03	25	84	9.2	0	0.3		–	–	–	–	–	–
0.14	25	46	13.3	0.2	0.85	5.5	4.8	0.3	0.05	10.35	1.16	−2.3
0.4	25	10.8	10.2	0.6	0.0	8.4	2.54	0.6	0.047	–	–	–
0.14	165	24	10.6	0.4	0.08	8.1	3.93	0.4	0.048	5.7	2.49	−3.1

R_d = rate of deposition; T_s = substrate temperature.

range 2 to 25 nm, at different rates of deposition. Equation 1 suggests a linear dependence of ρt on t. We have plotted ρt against t (not shown in Fig. 1) for these deposition rates. The intercepts of these graphs on the ordinate axis give $l(1-p)$ and the slopes give ρ_0, the resistivity of an infinitely thick film. Using these values of ρ_0 and $l(1-p)$, we have tried to fit our experimental data, using the FS theory (Equation 1), assuming total diffuse scattering ($p = 0$) of the carriers. FS theory (shown by continuous lines in Fig. 1) fits the experimental data only at greater thicknesses, and the best fit is obtained by giving different values for p (from 0 to 1). Now with the known values of p and $l(1-p)$, the electron mean free path for the infinitely thick film is obtained. The discrepancy between the experimental data and the FS theory at lower thicknesses is explained by the MS theory, to which we have tried to fit our experimental data. The theoretical curves derived from the MS theory are shown by the dashed lines in Fig. 1. With the assumption that the average grain diameter is equal to the thickness of the films [19], we have calculated the values of α and R. The difference between the resistivities of the FS theoretical curves (shown in Fig. 1 by continuous lines) and the experimental data yield $3/2\,(\alpha, \rho_0)$. Using the values of p and l estimated from FS theory, we have estimated the values of the grain boundary reflection coefficient R. All these results are given in Table I.

Similarly, resuts for the effect of substrate temperatures ($T_s = 25°$ C and 165° C) on the resistivity of palladium films grown at 0.14 nm sec^{-1}, are obtained, and are also included in Table I. Fig. 2 is a plot of thickness against resistivity for the two substrate temperatures. Since the Matthiessen rule is found to be valid

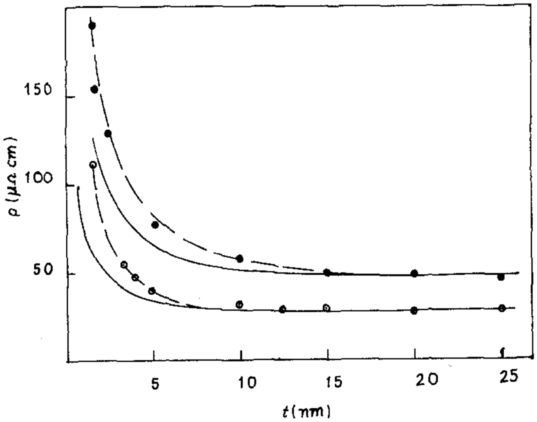

Figure 2 Thickness dependence of resistivity, for different substrate temperatures, 25° C and 165° C, the experimental points shown by • and ⊙ respectively. The theoretical curve due to FS theory is shown by a continuous line.

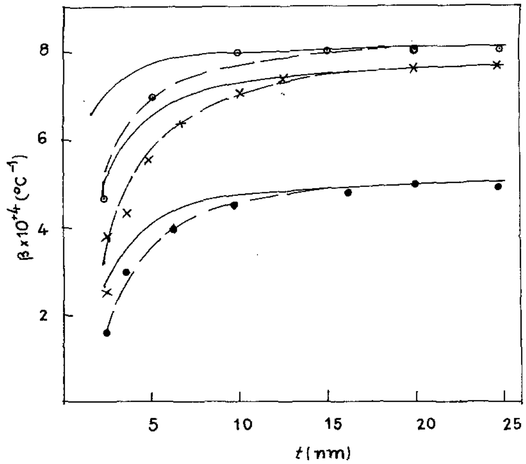

Figure 3 TCR plotted against thickness for palladium films, grown at different rates of deposition and substrate temperatures. The experimental points for films grown at a deposition rate of 0.14 nm sec^{-1} and at $T_s = 25°$ C are shown by solid circles (•). The experimental data for films grown at 0.4 nm sec^{-1} rate and $T_s = 25°$ C are shown by circled points (⊙). Those grown at 165° C with deposition rate 0.14 nm sec^{-1} are shown as crosses (X). Theoretical curves due to FS theory are shown by continuous lines.

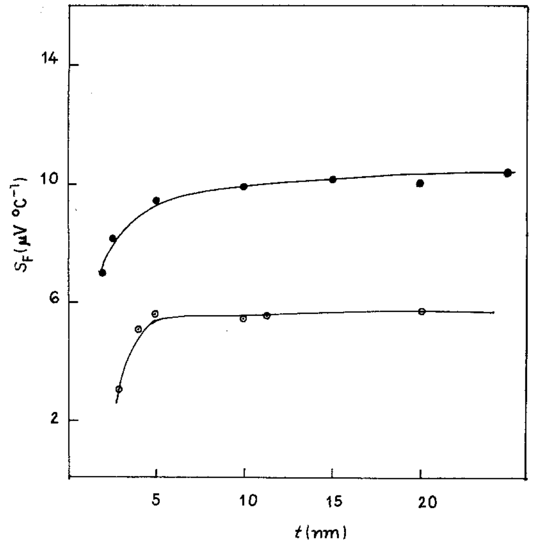

Figure 4 TEP plotted against thickness for thin palladium films deposited at two different substrate temperatures, 25° C and 165° C, shown by ● and ⊙ respectively.

[17] for palladium films over the thickness range studied, Equations 2 and 4 are used to study the effect of the rate of deposition and substrate temperature on the TCR, using both FS and MS theories. Fig. 3 shows how these theories fit our TCR data, and the results are given in Table I.

Fig. 4 shows the thickness dependence of the thermoelectric power for palladium films, grown at room temperature and at high substrate temperatures (165° C). The TEP data for the film deposited at 0.03 nm sec^{-1} is found to be higher than that of the film deposited at 1.4 nm sec^{-1} for all thicknesses, but is not shown in Fig. 4 because of the large scatter of the experimental data. The plot of $S_{\mathrm{F}}t$ against t yields S_0 as the slopes and $l(1-p)U/1+U$ from the intercepts on the ordinate axis. Using the $l(1-p)$ values determined from our resistivity data, we have obtained the values of U, which are given in Table I. Using the thermopower data for bulk palladium as $-9\,\mu$V °C^{-1} [23] in Equation 5, the values of V are obtained (also included in Table I).

5. Discussion

Figs. 1, 2 and 3 shows that initially the values of ρ decrease and β increase with increase in film thickness, and attain constant values after about 12.5 nm thickness. However, it is clear that higher rates of deposition and substrate temperatures result in a considerable reduction in resistivities and increase in the TCR of palladium films. Also, the films seem to attain electrical continuity at lower thicknesses for higher rates of deposition and higher substrate temperatures. The change in the derived infinitely thick film resistivity, with increase in either the deposition rate or the substrate temperature, suggests that higher deposition rates give rise to larger islands and their higher rate of formation [22]. The defect density is much smaller for films deposited at higher rates and at elevated substrate temperatures. Similar results have already been reported for manganese [7, 8], yttrium [24], tin [5] and titanium [25] films. The increase in the island sizes, and hence scattering from the grain boundaries, decreases for higher rates of deposition and substrate temperatures, as is clearly seen by the values of the grain boundary reflection coefficient R, obtained from the respective data (Table I). The increase in the specularity parameter (p) with increase in deposition rate and substrate temperature indicates a more specular reflection of the carriers.

Fig. 4 clearly suggests that the thermoelectric power for palladium films is positive for all thicknesses, while the bulk value [23] and that reported by Wedler *et al.* [26, 27] are negative. We have already reported this discrepancy with theory in our previous communication [14]. Since thermopower is very sensitive to the state and nature of defects in the metal, this discrepancy may be attributed to the structural changes resulting from the change in growth parameters. It is, however, interesting to note that the TEP of palladium films decreases at higher substrate temperature and deposition rates. This suggests that in order to estimate correctly the TEP of supported metal films, one must take into account background, grain boundary and external scattering which are operative simultaneously. In addition, one should take into account the effect of thermal expansion coefficients of the film and the substrate. A few theoretical papers [28, 29] have been published in recent years on TEP of films taking these factors into consideration. It is necessary to interpret our experimental results in the light of these new theoretical developments, in order to derive meaningful conclusions, and these will be published in a future communication.

6. Conclusions

The effect of deposition parameters (in well-defined conditions) on the transport properties of thin palladium films are exhaustively and systematically studied here. Our experiments indicate that the electrical properties of palladium thin films, that is, derived infinitely thick film resistivity, TCR, specularity parameter and thermoelectric power, etc., can conveniently be controlled by a proper choice of the deposition parameters such as the rate of deposition and substrate temperature. Similarly, work can be carried out with other deposition parameters such as the nature of the substrates, the presence of residual gases, residual pressure, etc. This may provide a deeper insight into the transport and structural properties of palladium films, and may prove useful in formulating better theoretical equations for the electrical behaviour of thin metallic films.

Acknowledgements

One of the authors (SMS) gratefully acknowledges the award of a Post-Doctoral Research Fellowship from the Council of Scientific and Industrial Research, New Delhi, India. We are grateful to Dr F. D. Manchester of the University of Toronto, Toronto, Canada, for the supply of pure palladium.

References

1. R. B. BELSER and W. H. HICKLIN, *J. Appl. Phys.* **30** (1959) 313.
2. L. E. MURR, *Thin Solid Films* **7** (1971) 101.
3. M. A. ANGADI and P. V. ASHRIT, *Phys. Status Solidi (a)* **67** (1981) K119.
4. M. A. ANGADI and L. A. UDACHAN, *J. Mater. Sci.* **16** (1981) 1412.
5. *Idem, Thin Solid Films* **78** (1981) 299.
6. M. A. ANGADI and P. V. ASHRIT, *Vacuum* **31** (1981) 161.
7. S. M. SHIVAPRASAD and M. A. ANGADI, *J. Phys. D (Appl. Phys.)* **14** (1981) 1125.
8. *Idem, ibid.* **13** (1980) L157.
9. K. B. SINGH and HATIBARUA, *Ind. J. Pure & Appl. Phys.* **20** (1982) 183.
10. A. BORODZIUK-KULPA, B. STOKECKI and C. WESOLOWSKA, *Thin Solid Films* **85** (1981) 323.
11. *Idem, ibid.* **67** (1980) 21.
12. S. M. SHIVAPRASAD and M. A. ANGADI, *J. Phys. D: Appl. Phys.* **13** (1980) 171.
13. S. M. SHIVAPRASAD, L. A. UDACHAN and M. A. ANGADI, *Phys. Lett. (A)* **78** (1980) 187.
14. M. A. ANGADI and S. M. SHIVAPRASAD, *J. Mater. Sci.* **17** (1982) 65.
15. *Idem, J. Mater. Sci. Lett.* **2** (1983) 207.
16. *Idem, Vacuum* **32** (1982) 51.
17. S. M. SHIVAPRASAD, Ph.D. Thesis, Karnatak University, Dharwad, India (1982).
18. D. LARSON, "Physics of Thin Films", Vol. 6 edited by M. H. Francombe and R. W. Hoffman (Academic Press, New York, 1971) p. 85.
19. A. F. MAYADAS and M. SHATZKES, *Phys. Rev.* **B1** (1970) 1382.
20. A. KAWAZU, Y. SAITO, H. ASAHI and G. TOMINAGA, *Thin Solid Films* **37** (1976) 261.
21. W. F. LEONARD and S. F. LIN, *ibid.* **28** (1975) L9.
22. K. L. CHOPRA, "Thin Film Phenomena" (McGraw Hill, New York, 1970) pp. 200, 420.
23. M. A. VEDERNIKOV, *Adv. Phys.* **16** (1969) 337.
24. M. A. ANGADI and P. V. ASHRIT, *J. Mater. Sci.* **18** (1983) 3177.
25. Y. IGASAKI and H. MITSUHASHI, *Thin Solid Films* **51** (1978) 33.
26. G. WEDLER and G. ALSHORACHI, *ibid.* **74** (1980) 1.
27. G. WEDLER and R. CHANDER, *ibid.* **65** (1980) 53.
28. C. R. PICHARD, A. J. TOSSER and C. R. TELLIER, *J. Mater. Sci.* **17** (1982) 10.
29. N. JAIN and R. SRIVASTAVA, *J. Mater. Sci. Lett.* **1** (1982) 330.

Received 27 June
and accepted 1 November 1983