

Letter

Contact angle contribution to the negative TCR of discontinuous metal films

J. E. MORRIS

Physics Department, Victoria University of Wellington, Private Bag, Wellington
(New Zealand)

(Received July 8, 1975; accepted July 16, 1975)

In a recent note¹ it was shown that contact angle changes would alter the tunnelling distance between the metal islands of a discontinuous metal film and hence modify the film conductance. The purposes of this communication are: (a) to show that the island-substrate contact angle will vary with temperature; (b) to show that this variation will contribute to the measured negative temperature coefficient of resistance (TCR); (c) to attempt a quantitative evaluation of the effect; and (d) to explore some of its consequences.

The contact angle θ of the islands is given classically²⁻⁴ by

$$\cos \theta = -1 + \frac{\gamma_s + |\Delta F_{ad}|}{\gamma_i}$$

where γ_s and γ_i are the surface energies of substrate and island, respectively, and ΔF_{ad} is the island-substrate binding energy. The example which will be considered is that of gold on glass. The bulk surface energy of gold varies with absolute temperature T as $\gamma_i = 1.267 - 10^{-4} T \text{ J m}^{-2}$ (ref. 4). A typical value of γ_s is about 0.3 J m^{-2} (ref. 4) which, in the absence of any contrary information⁴⁻⁶, is assumed to be independent of temperature. With $\Delta F_{ad} \approx 0$ (gold-glass binding weak), $\theta \approx 139^\circ$, which seems reasonable^{2,3,6-8}. Even with $|\Delta F_{ad}| = 0.854 \text{ J m}^{-2}$ (ref. 9) the final result is affected by less than 1%, provided that it is also regarded as being constant with temperature.

θ , then, decreases with increasing temperature and for a "spherical" island of radius r and constant volume $(4/3)\pi r_0^3$

$$r = r_0 \{4/(2 - 3 \cos \theta + \cos^3 \theta)\}^{1/3} = r_0 F(\theta)$$

and the tunnelling distance between two identical islands of centre separation R is $d = R - 2r \sin \theta$. The zero field conductance σ of a single gap (or a square of film with regular geometry) is¹⁰

$$\sigma \approx \frac{8\pi m e^2 \Delta}{\pi B k T} \{1 - \exp(-B\delta E)\} \exp(-A\phi^{1/2}) \exp\left(-\frac{\delta E}{\dots}\right)$$

where Δ is the effective tunnelling area of the gap and the other symbols have the usual meanings. It will be assumed, for simplicity, that $1 - \exp(-B\delta E) \approx 1$ and that the temperature effects will be dominated by the other exponential terms. Writing

$$\sigma = K \exp \left\{ -\frac{4\pi d}{h} (2m^* \phi)^{1/2} \right\} \exp \left(-\frac{\delta E}{kT} \right)$$

an "apparent" activation energy δE_a can be evaluated as

$$\frac{\delta E_a}{k} = \frac{\partial(\ln \sigma)}{\partial(1/T)} = \frac{\delta E}{k} - \frac{8\pi r_0}{h} (2m^* \phi)^{1/2} \frac{\partial\{(\sin\theta)F(\theta)\}}{\partial(1/T)}$$

For m^* equal to the electronic rest mass, $\phi = 1$ eV and the surface energies quoted, $\delta E_a \approx \delta E + 5.8k(10^{10}r)$ at 300 K. The variation of $(\sin\theta)F(\theta)$ is shown in Fig. 1. While the plot is not linear, the curvature over the temperature range 300 - 500 K is small.

Most of the research effort into determining the conduction mechanism in discontinuous metal films has been expended on comparison of theoretical and observed activation energies. Some authors¹¹⁻¹³ have obtained remarkably good agreement based on the widely accepted electrostatic model using the low frequency dielectric constant of the substrate. Others¹³⁻¹⁵ either have required the use of a high frequency value to explain otherwise anomalously large δE measurements, or have assumed disc-shaped islands¹⁶. The present theory offers a consistent explanation for these differences. The predicted increase in apparent δE is negligible for small islands where the electrostatic δE is largest, and only becomes comparable with the electrostatic contribution for large island sizes. It is therefore worth noting that films for which the electrostatic theory predicts low δE values (assuming static dielectric constants) are highly agglomerated, *i.e.* tunnelling takes place between a small island and a large aggregate. (See, for example, Figs. 5 and 6 in ref. 2, Fig. 1 in ref. 17, and ref. 18.) Under these conditions δE_a will be made up of an electrostatic contribution (small island) plus the contact angle effect (aggregate).

The non-ohmic property of discontinuous metal films is wellknown. As the applied voltage is increased δE decreases to zero. The author has previously reported the observation of a conductance increase to a limiting high field value with a non-zero activation energy^{16,18}. Once again, the anomalous effect is observed in highly aggregated films and is consistent with the present model where only the electrostatic contribution is subject to field reduction.

In Table I the limiting value of the high field activation energy δE_m is compared with the discrepancy between the extrapolated zero field value δE_e and the theoretical value δE_0 (calculated by Hill's formula¹¹ with $\epsilon_r = 6$) for previously reported films¹⁶. Agreement is reasonable, in support of the theory, but is taken over a very limited sample.

Most workers have avoided any comparison of experimental with theoretical values for σ_0 (where $\sigma = \sigma_0 \exp(-\delta E/kT)$) owing to the

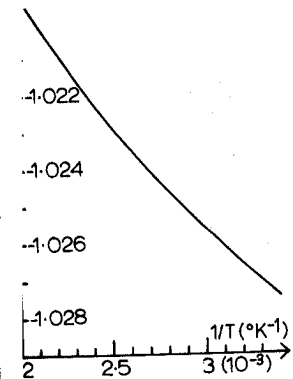


Fig. 1. Variation of $(\sin\theta)F(\theta)$ with temperature.

TABLE I

Comparison of low field activation energy δE_e , theoretical value δE_0 and minimum high field value δE_m (all in eV)

Film	δE_e	δE_0	$\delta E_e - \delta E_0$	δE_m
2	0.91	0.10	0.81	< 0.83
5	0.79	0.17	0.62	< 0.69
7	1.06	0.34	0.72	0.81
14	> 0.82	0.19	> 0.63	0.85

problems of estimating tunnelling area etc. According to this model, however, the apparent experimental figure should exceed theory owing to the increased slope of $\log \sigma$ versus T^{-1} .

One other anomalous observation made on aggregated discontinuous films is that of a decrease in δE with film strain^{14,19}. This might tentatively be attributed to a small reduction in the radius of curvature of the aggregate edge (*i.e.* in the aggregate thickness) with lineal extension in the substrate plane.

Clearly, the quantitative treatment (as far as it goes) makes several unwarranted assumptions. (1) The value of γ_i used and its variation with temperature were evaluated at much higher temperatures than those used here. (2) It is unlikely that bulk values will be appropriate to islands of about 1 nm dimension. (3) While the absolute value of $\gamma_s + |\Delta F_{ad}|$ is not critical in evaluation of the TCR, any thermal variation will be. The application of a similar approach to that above to the Al-sapphire system predicts a contact angle variation of only a tenth that observed⁷.

It has been shown that the contact angle of islands in a discontinuous metal film varies with temperature to produce a negative TCR by changing inter-island tunnelling distances. On a more speculative level, the effect has

been offered as a possible explanation for anomalous observations in aggregated discontinuous metal films. There are too many uncertainties to attempt a realistic quantitative prediction of the effect. Direct observation would be the most effective way to confirm the theory and to obtain a numerical estimate of its magnitude. Such an experiment will be attempted shortly and reported separately.

References

- 1 J. E. Morris, *Thin Solid Films*, 28 (1975) L21.
- 2 J. E. Morris, *Metallography*, 5, (1972) 41.
- 3 H. K. Livingston and C. S. Swingley, *Surf. Sci.*, 24 (1971) 625.
- 4 C. A. Neugebauer, in L. Maissel and R. Glang (eds.), *Handbook of Thin Film Technology*, McGraw-Hill, New York, 1970.
- 5 L. Holland, *The Properties of Glass Surfaces*, Chapman and Hall, London, 1964.
- 6 *Handbook of Chemistry and Physics*, 52nd edn., Chemical Rubber Co., Cleveland, Ohio, 1971-2.
- 7 K. Prabripataloong and M. R. Piggott, *Surf. Sci.*, 44 (1974) 585.
- 8 R. Faure, A. Carlan, J. Crebassa, G. Desrousseaux and B. Robrieux, *Thin Solid Films*, 9 (1972) 329.
- 9 H. von Harrach, *Thin Solid Films*, 22 (1974) 305.
- 10 A. Barr and R. D. Finney, *Thin Solid Films*, 24 (1974) 511.
- 11 R. M. Hill, *Proc. R. Soc. London, Ser. A*, 309 (1969) 377; 397.
- 12 P. A. Tick and F. P. Fehlner, *J. Appl. Phys.*, 43 (1972) 362.
- 13 D. S. Herman and T. N. Rhodin, *J. Appl. Phys.*, 37 (1966) 1594.
- 14 J. E. Morris, *J. Vac. Sci. Technol.*, 9 (1972) 437.
- 15 L. L. Kazmerski and D. M. Racine, *J. Appl. Phys.*, 46 (1975) 791.
- 16 J. E. Morris, *Thin Solid Films*, 11 (1972) 81.
- 17 J. E. Morris, *Thin Solid Films*, 5 (1970) 339.
- 18 J. E. Morris, *Ph.D. Thesis*, University of Saskatchewan, Canada, 1971.
- 19 J. E. Morris, *Thin Solid Films*, 11 (1972) 259.