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GENERAL ELECTRIC

Research Laboratory

Final Report

THE TEMPERATURE COEFFICIENT OF RESISTANCE IN ULTRATHIN, EVAPORATED METAL FILMS (INVESTIGATION OF METAL THIN FILM FORMATION AND STRUCTURE)

C. A. Neugebauer

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C. A. Neugebauer

Research Laboratory
GENERAL ELECTRIC COMPANY
Schenectady, New York

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ABSTRACT

It is known that some of the abnormal magnetic properties of ultrathin metal films, and their electrical conduction mechanism, can be explained on the basis of their "island" structure. It can be shown that the electrical conductivity and the temperature coefficient of resistance are controlled principally by the radius of the islands and the distances between them. By suitably adjusting these structural parameters, both of which enter the relation for the film conductivity exponentially, one can be made to predominate over the other. Thus, if the islands and the distances between them are small, very large negative temperature coefficients are observed. On the other hand, if the islands are very large or the thermal expansion coefficient of the substrate is unusually high, positive temperature coefficients can be observed, often several times larger than even the bulk values, even for films of resistances as high as 10^6 Ω/square or higher.

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THE TEMPERATURE COEFFICIENT OF RESISTANCE IN ULTRATHIN, EVAPORATED METAL FILMS (INVESTIGATION OF METAL THIN FILM FORMATION AND STRUCTURE)

C. A. Neugebauer

INTRODUCTION

It has been known for many years that a thin film may exhibit properties quite different from the bulk material. In general, the deviations from bulk behavior become more and more severe as the film thickness decreases. In the "ultrathin" thickness range from a few to 100 A the abnormal behavior of films is quite marked; on the other hand, it is still possible to apply conventional techniques to them, such as electron microscopy and diffraction, x-ray fluorescence, magnetic balances, and simple electrical measurements. It is thus an appropriate thickness range to explore in order to explain the role which the decreasing thickness dimension plays in causing deviations from the bulk behavior.

These deviations are apparent in many ways. Thus, even the appearance of the films is often quite different from the bulk. Metal films which have a silvery luster when thick often appear to be dull black when ultrathin. Ultrathin gold films display a pink color when ultrathin, and ultrathin silver films often have a yellow color.

Experiments designed to test the magnetic properties of ultrathin films of ferromagnatic[1-15] have shown that, at least for films in the 20 A thickness range or thinner, the magnetic moment appears to be lower than that expected if it behaved like the bulk material. Often such a decrease can be found even for films thicker than 20 A, depending on the conditions of preparation.

Also, measurements of the electrical resistivity of ultrathin metal films[16-25] have revealed that not only is the resistivity greatly increased, as one might expect, but also that the temperature coefficient of resistance (TCR), which is normally positive for metals, is negative. Actually it is possible to get positive TCR's in such films, sometimes even many times larger than the TCR of the bulk material Thus a wide range of behavior, deviating strongly from the bulk behavior, has to be explained.

It was the purpose of the work under this contract to determine the cause for the abnormal behavior displayed by ultrathin metal films.

It has long been suspected that the abnormal behavior was due to a film structure quite different from that normally encountered in bulk metals. It turns out that, almost regardless of the mode of preparation, an ultrathin metal film is usually not a uniform, continuous film, but will consist of many small, discrete islands entirely separated from each other,[26-29] and that most of the abnormal behavior, and certainly that pointed out above, can be explained on the basis of this island structure. An electron micrograph of an ultrathin gold film evaporated on rocksalt exhibiting this island is shown in Fig. 1. It has been found[14,15,30,31] that the important parameters which control the properties of such a film are the size of the islands and the distances between them.

The decrease in magnetic moment which is observed for ultrathin ferromagnetic films can be explained if it is realized that these small particles or islands of which they in reality consist are in the superparamagnetic size range. Since the magnetization vector of these

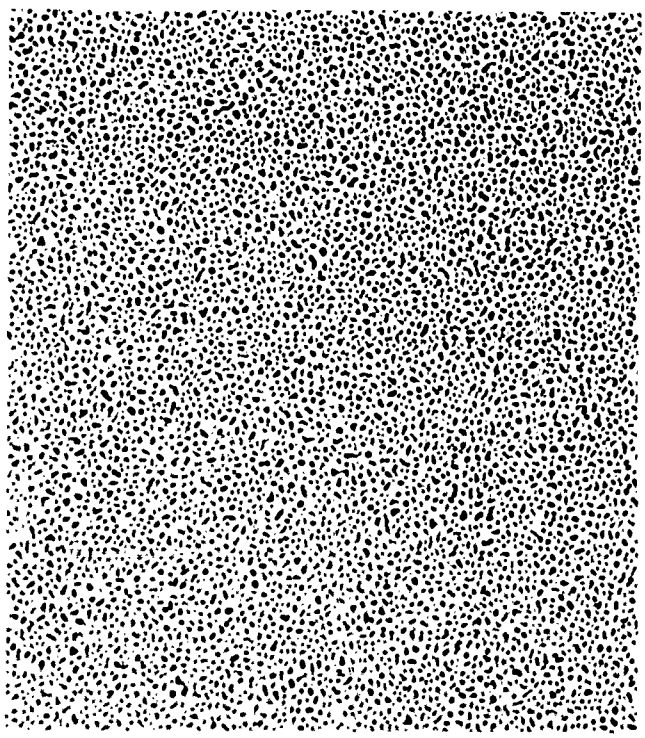


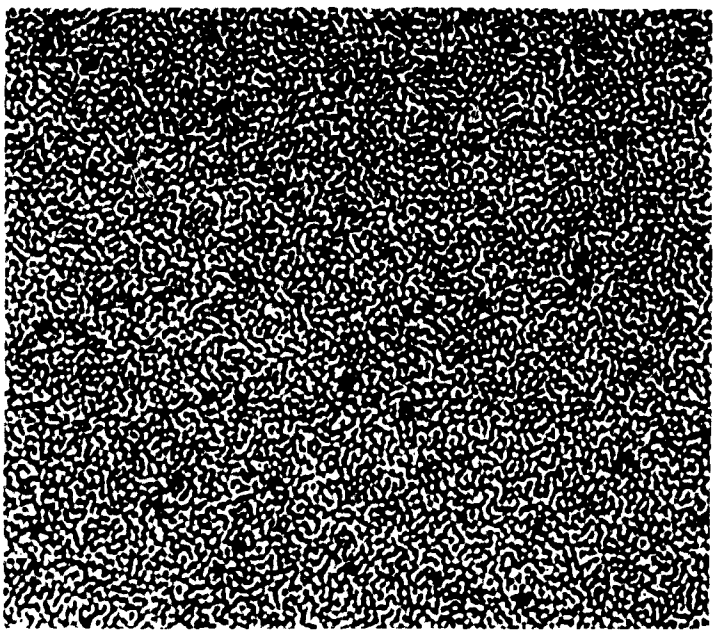
Fig. 1 Electron micrograph of ultrathin gold film on rocksalt exhibiting island structure. 100,000X

islands therefore fluctuates thermally,[32] the total magnetic moment of this collection of islands will appear to be less than that expected on the basis of the bulk material, unless relatively much higher fields are applied. The smaller the islands, and the further apart they are, the greater the apparent decrease in magnetic moment. This has been investigated and reported earlier,[14, 15, 31] partially under this contract.

Similarly, the electrical conduction mechanism can be explained on the basis of the island structure of an ultrathin film. This, too, was investigated under this contract and reported earlier.[30] Basically, the conduction mechanism is thought to consist of, first, a thermally activated charge carrier creation process, involving the removal of an electron from an initially neutral island leaving it positively charged and, second, the drifting of these "free" charges downfield by electron tunneling through the gaps between islands. From this model it follows that the conductivity must obey an Arrhenius type relation, i. e., its logarithm is proportional to the reciprocal temperature. The smaller the size of the islands, the greater the activation energy; and the larger the distance between islands, the lower the tunneling probability, and thus, the lower the conductivity. Experimentally the agreement with this theory is excellent.

The above illustrates the importance of island size and distance between them in determining the film properties. It is thus of interest to discuss the ways in which these two structural parameters depend on various experimental factors commonly encountered in thin film preparation, namely the temperature of the substrate, the film thickness, and the chemical nature of the metal and substrate.

Probably the biggest factor controlling island sizes and gap lengths is the temperature of the substrate, either during deposition of the film or later If the temperature of the substrate during deposition is high, the impinging metal atoms, if indeed they do not re-evaporate, will have a higher surface mobility over the surface of the substrate, and can thus generally look for a position on the surface where they have a lower potential energy than at the low substrate temperatures. If the metal atoms bind to each other more tightly than to the substrate (glass),and this is the case for most metals other than perhaps the most reactive, such as the alkali metals, then the lowest energy configuration will be a single sphere of these metal atoms, since here each atom has as many nearest neighbors as possible. A single sphere is never found on the substrate, but, if given enough mobility, the impinging metal atoms will form patches as large as possible and containing as few surface atoms



(a)

(b)

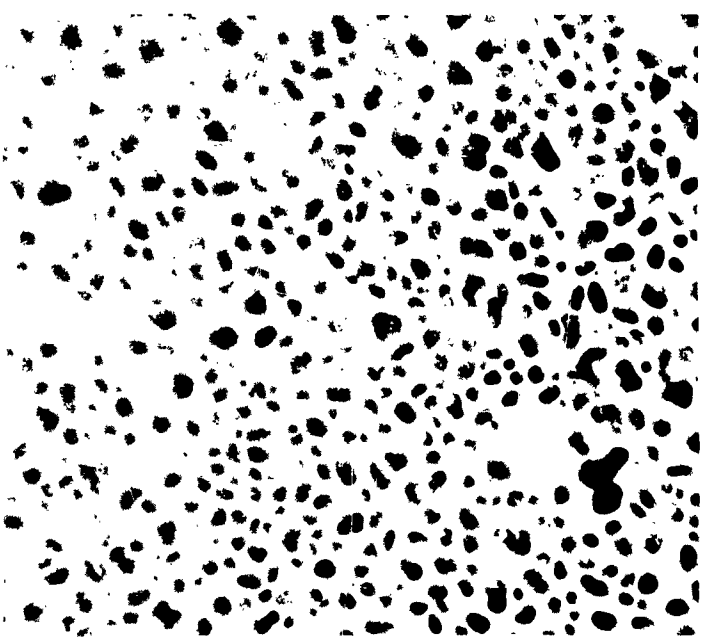


Fig. 2 Electron micrograph of ultrathin nickel film evaporated on rock-salt at (a) 200°C (200,000X) and (b) 400°C (20,000X).

as possible. This will naturally also lead to relatively larger distances between the islands. Experimentally this tendency to form larger islands at higher substrate temperatures has often been observed and is illustrated in Fig. 2, where electromicrographs of an ultrathin nickel film evaporated on rocksalt at a low (~200°C) and a high (~400°C) substrate temperature (a and b, respectively) are shown. The tendency to agglomerate into larger islands and the larger distances between them at the higher substrate temperatures is evident.

Another factor controlling island sizes and the distances between them is the film thickness. If all other factors remain the same, the island size will increase with increasing film thickness (here the "average" thickness is meant which would result if the film did not consist of islands but were completely uniform and continuous), while the distances between the islands will slowly decrease until they eventually touch to produce a continuous film, which will always happen in the later stages of film growth. This has been experimentally observed. (29, 30)

A third factor important in controlling island sizes and the distances between them is the nature of the metal and the substrate. As a very rough rule of thumb, the lower the melting point of the metal, the higher its surface mobility on the substrate, provided no reaction occurs between them. Thus, a nickel film on glass will consist of much smaller islands than a silver film of the same thickness, if prepared under otherwise equal conditions. Similarly, large differences in film structure are encountered for different substrate materials. An organic substrate such as Teflon, for instance, is much more inert toward impinging metal atoms than even glass or rocksalt. This means that the metal atoms bind even less tightly to Teflon than on glass, and this results in much higher surface mobility and larger islands and larger distances between them. Even the sticking probability of most metals on Teflon is observed to be considerably lower than that on glass since many of the impinging metal atoms re-evaporate again, illustrating the very loose binding between metal and substrate. The high mobility and poor sticking of metal atoms on organics also explains the structural inhomogeneities observed for films evaporated on substrates which have not been carefully cleaned Figures 3 and 4 illustrate this for gold films evaporated on top of "dirty" rocksalt crystals. The film structure is seen to be quite different on different areas of the substrate In some areas big agglomerates are found, and other areas are not covered at all by the gold, although they were exposed to the same vapor beam. This indicates regions of vastly different sticking probability or surface mobility on the substrate, presumably the gold sticks or stays much less on the contaminated regions.

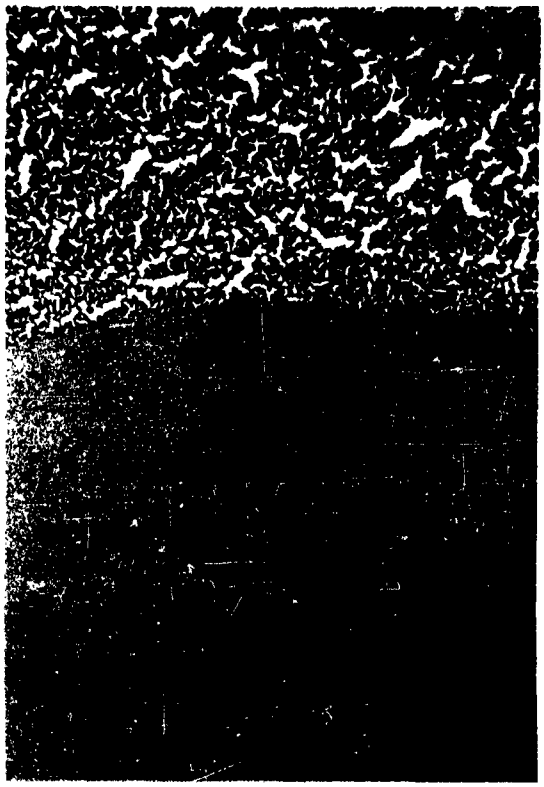


Fig. 3 Electron micrograph of ultrathin gold film evaporated on "dirty" rocksalt, showing two regions of different metal-substrate binding. 10,000X

Fig. 4 Electron micrograph of ultrathin gold film evaporated on "dirty" rocksalt, showing three regions of different metal-substrate binding. 20,000X

The role of the island structure of ultrathin films in determining magnetic properties and the electrical conduction mechanism has been discussed in earlier reports under this contract. There remains one film property which is very sensitively affected by changes in the film structure, and that is the temperature coefficient of resistance. A large body of literature exists on the subject, [16-25, 33] but a satisfactory explanation for the very often diverse results has not yet been put forward. In this report the dependence of the TCR is discussed as a function of film structure, and experimental results are given. Under discussion will be the negative TCR in ultrathin metal films, the effect of film annealing on the TCR, the role of the temperature coefficient of thermal expansion in thin film conduction and the TCR, abnormally high positive TCR's in ultrathin films, and the simultaneous appearance of positive and negative TCR's in ultrathin metal films on Teflon substrates.

THE NEGATIVE TCR IN ULTRATHIN METAL FILMS

As reported earlier, [30] the conductivity of an "island structure" metal film depends on the distance d between islands and their radius r in the following way:

$$\sigma = \frac{A\sqrt{2m\phi}}{h^2 d} \exp\left(-\frac{4\pi d}{h}\sqrt{2m\phi}\right) \cdot B \exp\left(-\frac{e^2/\kappa r}{kT}\right) \Omega^{-1}\ \mathrm{cm}^{-1} \qquad (1)$$

where A and B are constants

ϕ is the potential barrier between islands and can roughly be approximated by the work function of the metal

e is the electronic charge

m is the electronic mass

κ is the dielectric constant of the substrate.

The tunneling transmission coefficient expressed as

$$D = \frac{\sqrt{2m\phi}}{h^2 d} \exp\left(-\frac{4\pi d}{h}\sqrt{2m\phi}\right)$$

in Eq (1) is only a simple approximation to express the dependency of σ on d. Equation (1) should therefore not be expected to give exact quantitative agreement with experiment, but the fundamental dependencies

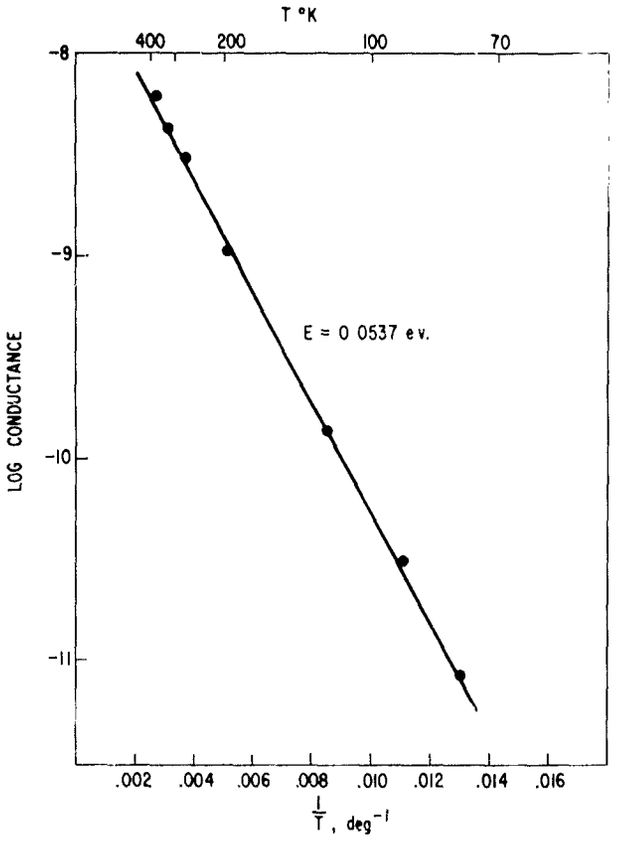


Fig. 5 Log conductance vs reciprocal temperature for an ultrathin platinum film on a glass substrate, demonstrating that Eq. (2) is obeyed.

should be correct. If the variations in d with temperature (caused by thermal expansion) are negligible in comparison with the term

$$\frac{e^2/\kappa r}{kT}$$

in Eq. (1), it can be neglected and for this case Eq. (1) can be rewritten

$$\sigma = C \exp\left(-\frac{e^2/\kappa r}{kT}\right) \qquad (2)$$

where C is a constant.

This equation is usually applicable for films consisting of very small islands in the few to 100 A radius range on substrates possessing only moderate thermal expansion coefficients. An illustration of this activated conductivity is shown in Fig. 5 for a platinum film on glass. This type of conduction is the most often encountered experimental situation

for ultrathin films, and has been discussed in detail in Ref. 30 The change in resistivity with temperature is given by, differentiating Eq. (2):

$$\frac{d \ln \rho}{dT} = - \frac{e^2/\kappa r}{kT^2}$$

Thus the TCR is negative and strongly temperature dependent.

THE EFFECT OF FILM ANNEALING ON THE TCR

It was pointed out above than an increased substrate temperature during deposition should result in larger island sizes. A similar result can be obtained by annealing a film at a higher temperature than that of the substrate during deposition. From Eq. (1) an increased island size would make itself felt by a now reduced activation energy for conduction. This is indeed realized experimentally and is illustrated in Fig. 6 where the log

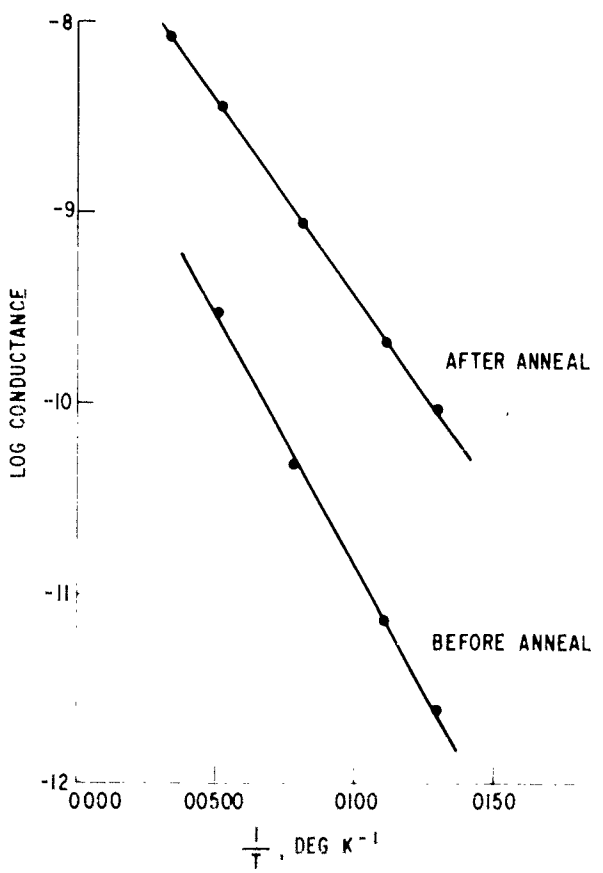


Fig. 6 Log conductance vs reciprocal temperature for an ultrathin gold film on glass before and after annealing, showing the change in the activation energy.

conductance is plotted against reciprocal temperature for a gold film on glass before and after annealing. This film was originally prepared at a substrate temperature of 195°K (lower curve) and then annealed at room temperature (upper curve). The activation energy of the annealed film is found to be only 2/3 that of the original one, and this is consistent with the postulated increase in island size on annealing.

It may be noted that in the example shown in Fig. 6 the conductivity of the annealed film increased on annealing. This is just what one expects from Eq. (1) for a larger value of r in the exponent. However, in films thinner than the gold film under discussion one usually observes decreases in the conductivity on annealing. This apparently contradictory result can be understood if one realizes that if the islands get larger, average distances between them must get larger also at the same film thickness. This then would greatly lower the tunneling probability which is exponentially dependent on the distance between islands, and this would tend to lower the conductivity. It turns out that in thicker films the conductivity generally is observed to increase on annealing, while for thinner films it decreases. It should also be borne in mind that the current will always flow through the least resistant path in the film. Extensive rearrangement of the metal film on the substrate on annealing may well create a less resistive path than was available before.

Lowered activation energies on annealing are also demonstrated in Table I for a Pt film. With a higher annealing temperature the activation energy goes down, as predicted.

TABLE I

Activation Energy of a Thin Platinum Film as a Function of Annealing Temperatures

Temperature of Anneal (°C)	Activation Energy (ev)
25	0.177
100	.165
190	.115

THE ROLE OF THE TEMPERATURE COEFFICIENT OF THERMAL EXPANSION IN THIN FILM CONDUCTION AND THE TCR

In addition to the activation energy of conduction, the conductivity of an "island structure" film is very sensitively dependent on the distance between islands, d. One can thus easily visualize how thermal expansion of the substrate and film can change the conductivity of the film.

First, if one assumes that the metal islands are only loosely bound to the substrate, then increasing the temperature leads to a decrease in d since the metal usually has a higher thermal expansion coefficient than most substrates, such as glass, and the islands are assumed to be free to expand or contract without experiencing any constraint from the substrate. This decrease in the distance d between islands would then give a higher transmission probability, and thus an increased conductivity.

On the other hand, if one assumes that the metal islands are tightly bound to the substrate, the transmission coefficient will decrease with increasing temperature, since now the metal islands cannot expand freely, but are restrained by the substrate. The distance between islands will therefore increase with increasing temperature, giving a smaller transmission coefficient, and a lower conductivity. The resulting stress in the film, if higher than the elastic limit, could be relieved by plastic deformation.

The magnitude of the thermal expansion effect on the film conductivity can be estimated for these two extremes. For the first case, the nonrestrained metal islands, one can express the temperature dependence of the distance between islands as

$$d = d_0 - \alpha \ell_0 \Delta T \quad , \tag{3}$$

where d_0 = original distance

ℓ_0 = original linear dimension of island

α = difference between thermal expansion coefficients of metal and glass $\sim 5 \cdot 10^{-6}/^\circ C$

ΔT = temperature differential.

This expression will be valid as long as $d_0 < \ell_0$. Substituting in the expression for the transmission coefficient, and ignoring the relatively small pre-exponential dependence on d:

$$D_{(T)} = A \exp \left[- \frac{4\pi}{h} \sqrt{2m\phi} \, (d_0 - \alpha \ell_0 \Delta T) \right] \quad . \tag{4}$$

Since $\frac{4\pi}{h} \sqrt{2m\phi}\, \alpha \ell_0 \Delta T$ is small,

$$\exp\left(\frac{4\pi}{h} \sqrt{2m\phi}\, \alpha \ell_0 \Delta T\right) = 1 + \frac{4\phi\sqrt{2m\phi}}{h} \alpha \ell_0 \Delta T \quad .$$

Equation (4) then becomes

$$D_{(T)} = A\left(1 + \frac{4\pi\sqrt{2m\phi}}{h}\,\alpha\,\ell_0\,\Delta T\right)\exp\left(-\frac{4\pi\sqrt{2m\phi}\;d_0}{h}\right) \qquad (5)$$

or

$$\frac{D_{(T)}}{D_{(0)}} = 1 + \frac{4\pi\sqrt{2m\phi}}{h}\;\alpha\,\ell_0\Delta T \quad . \qquad (6)$$

This expression gives the ratio of the tunneling transmission probabilities at two different temperatures, one ΔT higher than the other, for an island structure thin film. For a typical film with $\ell_0 = 100\,A$, $\phi = 5$ ev, and $\alpha = 5 \cdot 10^{-6}/°C$

$$\frac{D(T)}{D(0)} = 1.12 \text{ for } \Delta T = 100°C$$

and

$$\frac{D(T)}{D(0)} = 1.41 \text{ for } \Delta T = 300°C \quad .$$

If, therefore, this were the only dependence of film conductivity on temperature, one would expect a slow increase in conductivity with temperature, and thus a negative TCR. However, for films on most substrates, the change in conductivity with temperature due to the activation term

$$\exp\left(-\frac{e^2/r}{kT}\right)$$

in Eq. (1) is so large over such a temperature range, usually amounting to three or more orders of magnitude, that it completely predominates over the thermal expansion effect which is usually lost

The same can be said for the second extreme, where the metal islands are assumed to be under constraint and the distance between them is determined by the thermal expansion of the substrate alone. Here

$$d = d_0\,(1 + \alpha_S\,\Delta T) \qquad (7)$$

where α_S = thermal expansion coefficient of substrate.

Again substituting in the transmission coefficient,

$$D_{(T)} = A \exp\left(-\frac{4\pi}{h}\sqrt{2m\phi}\right)(d_0 + d_0\ \alpha_s\ \Delta T) \quad .$$

Again, since $\frac{4\pi}{h}\sqrt{2m\phi}\ d_0\alpha_s\ \Delta T$ is small, this reduces to

$$\frac{D(T)}{D(0)} = 1 - \frac{4\pi\sqrt{2m\phi}}{h}\alpha_s\ d_0\ \Delta T \quad . \tag{8}$$

This gives the ratio of the tunneling transmission probabilities at two different temperatures for a film in which the metal islands are constrained by the substrate, and where only the thermal expansion of the substrate has to be taken into account. For a film with $d_0 = 10$ A, $\phi = 5$ ev, and $\alpha_s = 5 \cdot 10^{-6}/°C$ (glass);

$$\frac{D(T)}{D(0)} = 0.9885 \text{ for } \Delta T = 100°C$$
$$= 0\ 954 \text{ for } \Delta T = 300°C.$$

This again illustrates that for relatively small island dimensions and the relatively small thermal expansion coefficients of most substrates, such as glass, the contribution to the TCR by the thermal expansion of substrate and film is usually negligible in comparison to the contribution made by the activation energy.

ABNORMALLY HIGH POSITIVE TEMPERATURE COEFFICIENTS OF RESISTANCE IN ULTRATHIN METAL FILMS

It is reported,[33] when the resistivity of thin metal films in the 500 to 1000 Ω/square region are investigated, that such films not only display negative TCR's, but often positive ones, approaching or perhaps even exceeding that of the bulk metal. In most cases this can probably be explained in terms of the film structure. A film of a resistance in the 1000 Ω/square region has a structure which is intermediate between the pure island structure films exclusively investigated here ($R > 10^4$ Ω/square), and an ideal continuous film ($R \sim 50$ Ω/square for a 10 A film, making a simple correction for mean free path effects).

Thus it might conceivably consist of large islands just about to grow together, some filamentary paths relatively uninterrupted by gaps, and many more or less isolated patches of metal. Such films have, for instance, been described by Ehrlich.[34] It is apparent that for such a situation the resistance is entirely determined by a rather well defined narrow path which happens to have the lowest resistance. Even in this path the resistance will be concentrated in some few bottlenecks, such as gaps. Since for such a film the "island" sizes are much larger than in the high resistance films, the contribution to the temperature dependence due to the activation term in Eq. (1) will be minimized, and it is thus easy to see that if the gaps widen due to thermal expansion of the substrate on heating, as discussed above, large positive TCR's might result. This should be even more true if the thermal expansion coefficient of the substrate is quite large. Teflon is an example of such a substrate, having an expansion coefficient of $10 \cdot 10^{-5}/^{\circ}C$, which is 10 times larger than that of a typical metal, and a factor of 20 to 50 times bigger than that of glass. In fact, it is possible to see positive temperature coefficients even for relatively high resistance films on Teflon substrates. There is another reason for this, besides the high expansion coefficient. Metals are in general not bound very tightly to Teflon, as is evidenced by the fact that the sticking probability of gold atoms, when impinging on Teflon at room temperature, is much smaller than on glass or rocksalt since a much higher metal beam pressure is necessary before condensation begins. As explained above, this loose binding to the substrate will discourage smaller nuclei from forming, since they get no assist in the form of greater stability by tight binding to the substrate, and thus relatively few but large nuclei or islands will grow during the first or ultrathin stage of film formation. Since the negative temperature coefficient of resistance normally observed in films with an island structure becomes smaller with increasing island dimensions, only a small decrease in conductivity on lowering the temperature should be expected from this source. This is equivalent to saying that the contribution to the temperature dependence of the conductivity due to the activation term in Eq. (1) can become negligible in comparison to that of the transmission probability. Thus, assuming that the islands are so large, and therefore the activation energy for conduction so small, that practically all the temperature dependence of the film conductivity is due to the thermal expansion of the substrate, then the conductivity is given by, from Eq. (1):

$$\sigma = A \frac{\sqrt{2m\phi}}{h^2 d} \exp\left(-\frac{4\pi d}{h}\sqrt{2m\phi}\right)$$

The temperature dependence is introduced by

$$d = d_0 (1 + \alpha_S T)$$

where α_S is the thermal expansion coefficient of the substrate, and much larger than that of the metal, $\alpha_S >> \alpha_m$.

Then

$$\sigma = \frac{A \sqrt{2m\phi}}{h^2 d_0 (1 + \alpha_S T)} \exp \left[- \frac{4 \pi d_0}{h} (1 + \alpha_S T) \sqrt{2m\phi} \right] \qquad (9)$$

For such a film one would thus expect the conductivity to vary exponentially with temperature, since the small pre-exponential dependence is negligible. This situation is realized experimentally quite easily for very thin silver or gold films evaporated on Teflon substrates. Both of these metals have a high surface mobility and easily agglorerate into large islands on Teflon. Figure 7 shows the linear relation which one obtains for a plot of log conductance vs T, as predicted by Eq. (9). Note that the TCR for this gold film is positive and several times larger (0.008/°C at 100°K) than that for bulk gold (0.003/°C). It should be pointed out here that the resistance of this film is very high, $10^6 \Omega$/square, roughly corresponding to a resistivity of 1 Ω-cm, and it is inconceivable that the large positive TCR observed could be due to the normal TCR of the bulk material.

From Eq. (9) the slope of the curve in Fig. 7 is (again ignoring the pre-exponential temperature dependence)

$$\frac{d \ln \sigma}{dT} = - \frac{4 \pi d_0 \sqrt{2m\phi}}{h} \alpha_S \quad .$$

Taking $\phi = 4$ ev and $\alpha_S = 9 \cdot 10^{-5}$/°C, one finds that $d_0 = 23$ A. The distance between islands in the gold film given in Fig. 7 is therefore of the order of 20 A. This is in satisfactory agreement with the value one would expect for the distance between islands, considering the very approximate nature of the equations used.

It is interesting to calculate the island size required to just offset this positive TCR to give no temperature dependence at all, at a particular temperature.

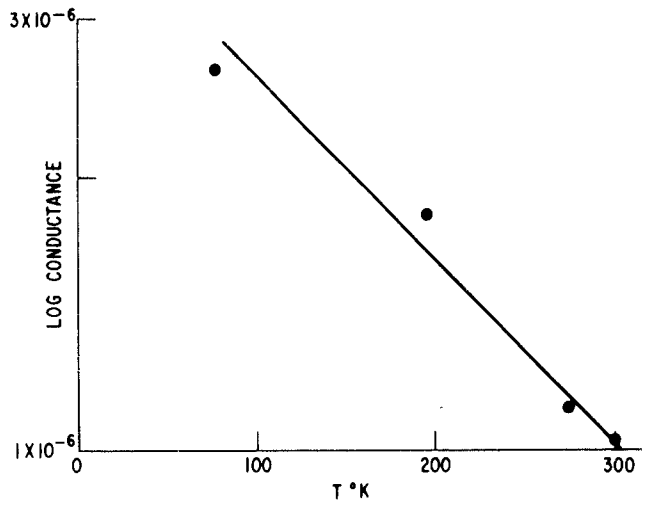


Fig. 7 Log conductance vs temperature for an ultrathin gold film on Teflon exhibiting behavior according to Eq. (9).

Equation (1) can be rewritten as

$$I = \frac{A\sqrt{2m\phi}}{h^2 d} \exp\left(-\frac{4\pi d}{h}\sqrt{2m\phi}\right) \cdot B \exp\left(-\frac{e^2/\kappa r}{kT}\right) \quad .$$

Ignoring the pre-exponential dependence and assuming $\alpha_s >> \alpha_m$

$$\frac{d \ln I}{dT} = -\frac{4\pi}{h}\sqrt{2m\phi}\ \alpha_s d_0 + \frac{e^2/\kappa r}{kT^2} \quad . \tag{10}$$

Solving for r if $d\ \ell nI/dT = 0$, and taking

$\phi = 4$ ev

$d_0 = 25$ A

$\alpha_s = 10^{-4}/°C$

$\kappa = 2$

one obtains

$$r = 180 \text{ A at } 300°K \quad .$$

Thus one should expect that for islands larger than about 200 A in radius the TCR of a metal film on Teflon will be positive, and negative for radii smaller than that. Again this is to be considered only an order of magnitude estimate.

THE SIMULTANEOUS APPEARANCE OF POSITIVE AND NEGATIVE TCR's IN ULTRATHIN METAL FILMS ON TEFLON SUBSTRATES

Judging from the calculations in the last section it is conceivable that one should be able to observe temperature coefficients of resistance of both signs for metal films on substrates possessing high thermal expansion coefficients, depending on the details of their structure. Thus, if the size of the islands making up the film is very small, and the distances between them are also small, a negative TCR is observed, particularly at the lower temperatures. However, for large islands, large distances between them, and at higher temperatures, the positive TCR is observed. By controlling the film thickness and substrate temperature during film formation, one can obtain a range of island sizes and distances between them, such that one can make the same film fall into both ranges. This has been carried out experimentally for several films, and is illustrated in Fig. 8 for a gold film of progressive thickness on Teflon. The very

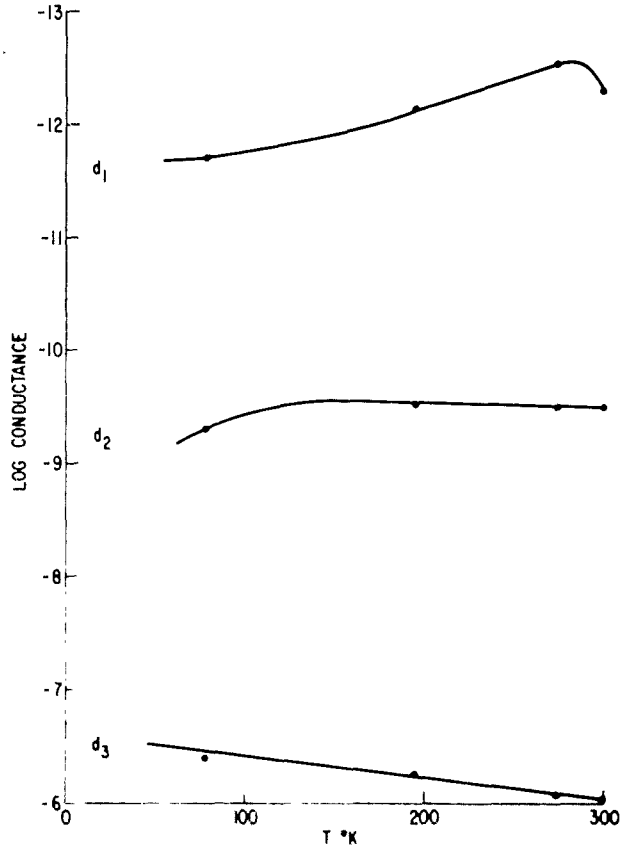


Fig. 8 Log conductance vs temperature for gold films on Teflon demonstrating positive and negative temperature coefficients of resistance as a function of temperature and film thickness.

thinnest film, of thickness d_1, exhibits the negative TCR, at least at lower temperatures. When made thicker to give film d_2 by depositing more gold, the TCR was found to have both signs, depending on the temperature. A still thicker film, d_3, prepared by evaporating still more gold, finally exhibits a positive TCR over the entire temperature range investigated. This is exactly the behavior expected from the above discussion, and can be simply explained by the fact that both, the thermal expansion and the activation controlled conduction mechanism, are applicable, but one predominates over the other at different temperatures.

It is relatively easy to prepare films of gold or silver on Teflon with island radii large enough to show the positive TCR. Other metals, such as nickel, have lower surface mobilities on Teflon, and much smaller islands can be expected under the same growth conditions. However, even for nickel films on Teflon it was found that, while exhibiting the negative TCR when thin, thicker films show the positive TCR. This is illustrated in Table II below, where the TCR at 0°C is given as a function of film resistance (or thickness).

TABLE II

The TCR at 0°C of Increasingly Thicker Metal Films on Teflon

Film	Conductance at 0°C (Ω)	$\frac{dR/dT}{R}$
d_1	$9.8 \cdot 10^{-12}$	-0.017
d_2	$2.4 \cdot 10^{-11}$	- .014
d_3	$5.2 \cdot 10^{-10}$	- .011
d_4	$3.1 \cdot 10^{-9}$	- .0065
d_5	$5.4 \cdot 10^{-8}$	- .0019
d_6	$6.7 \cdot 10^{-7}$	.000
d_7	$7.4 \cdot 10^{-6}$	+ .0012

It should be noted that the resistivity of even the thickest film, d_7, is still about a million times higher than that of bulk nickel, and the positive TCR for that film could not have been simply due to the normal TCR of the bulk material. On annealing R always increases, but the TCR tends to become more positive, as expected, since the island sizes increase.

SUMMARY

The very wide range of values of the TCR of ultrathin, metal films on inert substrates can be explained in terms of the island structure of such films. It was postulated and it was demonstrated electron-microscopically that films showing negative TCR's consist of many small metal islands separated by distances in the few angstroms range. The negative TCR comes about because of an activation energy for conduction which involves, first, a charge carrier creation process involving the removal of an electron from an initially neutral island and, second, the tunneling of this charge from island to island in the applied field. On film annealing, larger island sizes result, leading to lower activation energies. If the island sizes are much larger than about 200 A, the contribution to the temperature dependence made by the now very small activation energy may become negligible compared to that made by the tunneling transmission probability, which contains the distance between islands, which in turn is subject to variations with temperature because of the thermal expansion of substrate and film. Abnormally high TCR's found in ultrathin films, sometimes even higher than that of the bulk metal, particularly if the substrate possesses a very high thermal expansion coefficient, can be explained on the basis of the thermal expansion of the substrate alone. If the contribution of the activation energy and the thermal expansion of the substrate are comparable, an ultrathin metal film may display both, negative and positive TCR's, within a relatively short temperature interval.

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