

RESISTANCE CHANGES OF DISCONTINUOUS GOLD FILMS IN AIR

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SUMMARY

Increases in the resistance of discontinuous thin gold films in air are analysed as functions of time and temperature. The increases are reversible, if the film is returned to vacuum, and the conductivity activation energy is not affected. Diffusion of air into the substrate gives rise to negative ions in the tunnelling barriers between metal aggregates and increases the effective barrier height and hence the film resistance.

INTRODUCTION

A very thin metal film (typically $< 100 \text{ \AA}$) consists of discrete metal particles which increase in size as the film grows and finally coalesce, forming a continuous layer¹. This early island structure results from the initial nucleation processes of film formation on an insulating substrate². Though there is no continuous metal path through such films, there may be significant electronic conductivity, the mechanism of which has been the source of considerable discussion in recent years²⁻¹⁹. Early efforts to explain observed conductivities have been reviewed by Neugebauer and Wilson⁸, and a detailed analysis of the present theory has been presented by Hill¹⁶⁻¹⁸. Electronic current passes from island to island by quantum mechanical tunnelling through the inter-island potential barriers, and the electrostatic energy involved in the charge transfer between islands gives rise to an activation energy. The film resistance, R , can therefore be expressed approximately for low applied voltages as:

$$R = A \cdot \exp as\phi^{\frac{1}{2}} \cdot \exp \psi/kT \quad (1)$$

where ϕ and s are the effective height and width of the potential barrier, ψ is the electrostatic activation energy, k is Boltzmann's constant, A and a are constants

for a given island spacing and T is the absolute temperature. A is weakly dependent on T and is also proportional to ϕ/s^2 , which is similarly a weak dependence in comparison with the exponential term and is neglected in the discussion below. ψ is a sensitive function of the film geometry. Implicit in eqn. (1) is the requirement that $\psi > kT$ (ref. 16).

It has been observed in this laboratory that the resistance of thin gold films with an activated conductivity invariably increases when the films are removed from the vacuum system, typically by an order of magnitude over extended periods. This paper will describe a simple series of experiments that show that the effect is due to the increased inter-island potential barrier heights produced by absorption of air into the substrate.

DEPOSITION AND STRUCTURE

Thin gold films 2.5 cm. long by 2.0 cm. wide were deposited on Corning 7059 substrates in an oil diffusion vacuum system at rates around 0.2 Å/sec and pressures in the range $2-5 \times 10^{-6}$ torr. The substrates were cleaned by wiping with lens paper and air blasting in accordance with the manufacturer's recommendations. Heating the films above deposition temperature may produce resistance changes by island movement and coalescence²⁰. To avoid this possibility, the substrate temperature is held at about 200 °C during the deposition, and subsequent temperature cycling is limited to about 20 °C below this value. As a result of the high substrate temperature, the onset of measurable conductivity occurs later (when the film has reached a few hundred Å in thickness) than previously indicated. In anticipation of resistance increases in air, and since subsequent testing will be at lower temperatures, deposition is continued to film thicknesses around 550 Å and resistances in the MΩ range. All resistance measurements were made directly with a Keithley electrometer.

Transmission electron microscopy of the films shows that the structure is not the very discrete island formation assumed in the simple theory. The films are typically polycrystalline with some of the more prominent crystallites up to 3000 Å in diameter, but broadening of X-ray diffraction peaks gives a typical mean crystallite diameter of about 200 Å. There are discontinuities (about 100 Å wide) between large aggregates of many microcrystals, and the overall structure appears best described as filamentary. Careful examination of electron micrographs of suitably low magnification shows that there is no continuous conduction path through the film and that the filamentary aggregates are still discrete. An electron-micrograph of film 1 is shown as an example in Fig. 1. A detailed correlation of film structure and conductivity will be presented elsewhere.

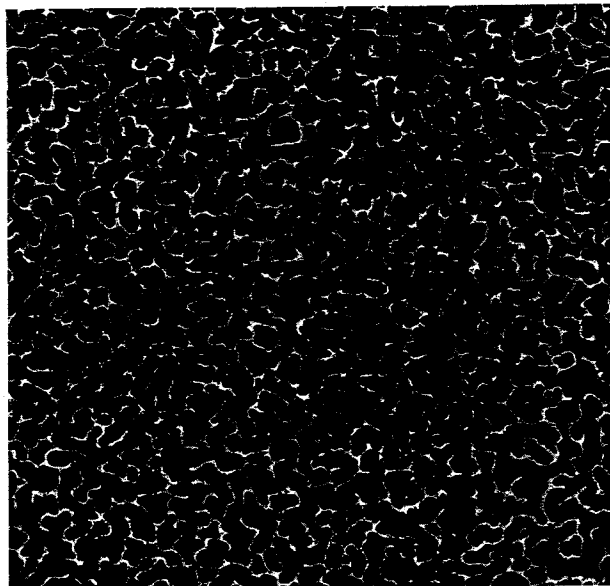


Fig. 1. Electronmicrograph of film 1 ($6 \text{ cm} = 10^5 \text{ \AA}$).

PRELIMINARY EXPERIMENTS

It is noted that continuous films (which have the positive temperature coefficient of resistance typical of metals) do not measurably increase in resistance upon exposure to air, and that observed increases in the resistivity of discontinuous films are due to the fundamentally different conduction process.

Figure 2 demonstrates the reversibility of the resistance changes and hence rules out structural reorganisation as the origin. Film resistance rises upon admission of air to the vacuum system, but decreases to the original value when the system is pumped out again. It is noted that system pressure rises to full scale on a thermocouple gauge instantaneously when the system is opened to atmosphere, and to atmospheric (estimated by audible hissing) in a matter of seconds. While pumping down is a slower process overall, the drop under roughing is rapid and the faster change under pumpdown (Fig. 2) shows that most of the change occurs in this high pressure region. Nevertheless, resistance changes with time described below are obtained by admission of air, since the rate of pressure rise is identical between runs.

Both curves show a sudden initial change at $t = 0$, and there is a small increase with time in the equilibrium resistance under vacuum. These effects are caused by observed temperature changes and complicate the interpretation of quantitative results. Under vacuum, for example, a certain equilibrium temperature is measured for a given power dissipation in the substrate heater. The heater is

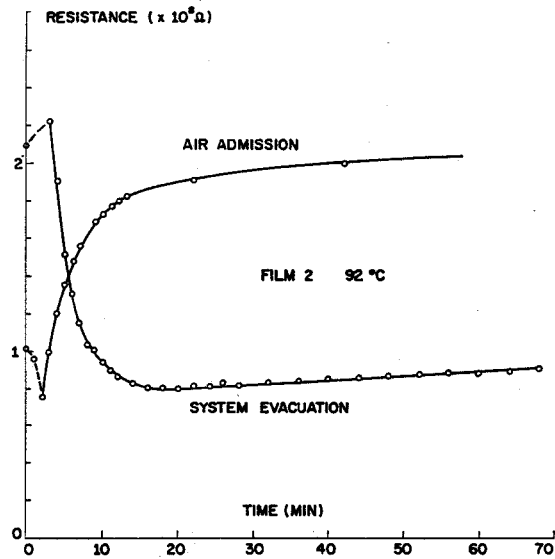


Fig. 2. Resistance change with admission of air and chamber evacuation (film 2, 92 °C).

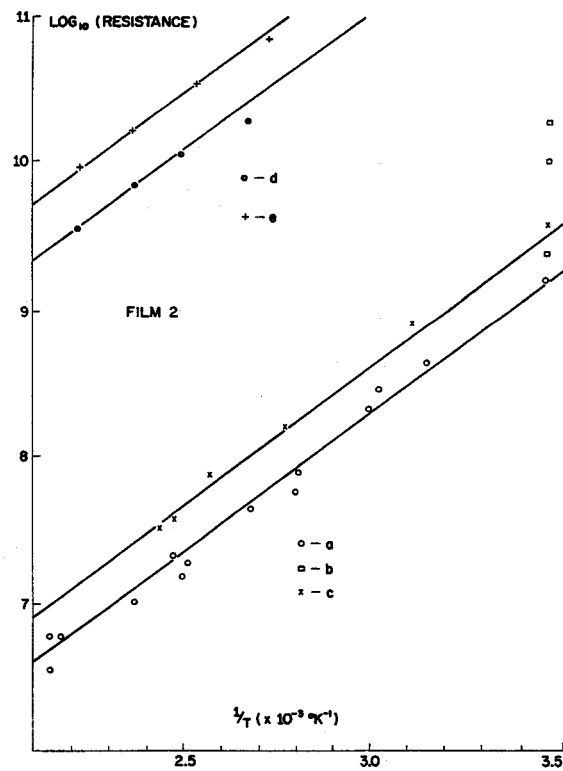


Fig. 3. Activation energy *in vacuo* and in air (film 2).

behind the substrate and delivers heat to the film by substrate conduction. When air is admitted to the system, an immediate temperature rise is observed at the film surface as extra heat is delivered by convection. This temperature rapidly decays to approximately the original value, small differences being due to heater operation in a new environment.

No change is observed in the activation energy of the films, as is demonstrated in Fig. 3 (*i.e.*, the resistance change is not attributable to any minor activation energy changes). The line (a) is obtained under vacuum immediately after deposition. Air is admitted when the substrate has cooled to ambient temperature, and resistance increases to $2.5 \times 10^9 \Omega$ and $1.6 \times 10^{10} \Omega$ in periods of half an hour and $2\frac{1}{2}$ days respectively (b). Resistance drops rapidly to $1.05 \times 10^{10} \Omega$ when the system is re-evacuated and the activation energy is remeasured (c). Curves (d) and (e) are measured several days later after prolonged heating in air. The result that the activation energy is constant is consistent with the conclusion that there is no structural change. Note that the activation energy (in this case 0.34 eV) is much greater than kT , as eqn. (1) requires (despite large particle sizes), due to the plate-like nature of the aggregates¹¹.

THEORY

The resistance expression is very sensitive to the barrier height through the exponential dependence of the tunnelling probability. Resistance increases in very thin zirconium films have been found to be due to increases in both work function by initial monolayer formation and in effective island spacings by subsequent oxidation of the metal islands²¹. Resistance increases in gold films have been previously reported briefly and attributed to increases in the work function of gold when exposed to oxygen¹². The analysis of the results for both gold and zirconium assume that tunnelling is direct from island to island through air or vacuum. Theory and experiment show, however, that since the barrier to tunnelling through the substrate is determined by the insulator conduction band, it will be necessarily lower than that for direct tunnelling through vacuum^{6,16}. Under these circumstances it is initially postulated that the source of resistance increase is an increase in the height of the substrate tunnelling barrier.

Equation (1) is now rewritten as:

$$R(T, t) = A \exp \psi/kT \exp as(\phi_0 + \Delta\phi(T, t))^{\frac{1}{2}} \quad (2)$$

where $R(T, t)$ is the film resistance (now a function of temperature T and time t), ϕ_0 is the initial barrier height and $\Delta\phi(T, t)$ is the change in the barrier height which, it is assumed, will vary with time and temperature upon exposure of the film to air. It is known that the formation of an ionic layer on a metal surface modifies the work function²². In the case of singly charged negative ions, a retarding field is set

up and ϕ increases by an amount:

$$\Delta\phi(T, t) = N(T, t) \cdot ed/\epsilon \quad (3)$$

where e is the electric charge, ϵ is the dielectric constant, d is the separation of the ionic layer of surface density $N(T, t)$ and the induced surface charge in the metal, and $\Delta\phi(T, t)$ is in eV. The modified resistance expression (2) reduces to:

$$R(T, t) = A \cdot \exp \psi/kT \cdot \exp as\phi_0^{\frac{1}{2}}(1 + \Delta\phi(T, t)/2\phi_0) \quad (4)$$

for small changes $\Delta\phi(T, t)$, *i.e.* to:

$$R(T, t) = R_0(T) \exp bN(T, t) \quad (5)$$

where:

$$R_0(T) = A \exp as\phi_0^{\frac{1}{2}} \exp \psi/kT$$

and:

$$b = ase d/2\epsilon\phi_0^{\frac{1}{2}}$$

The volume of air $V(T, t)$ desorbed by glass at constant pressure is given by the diffusion relation:

$$V(T, t) = P't^{\frac{1}{2}} \cdot \exp -p/T + M(T) \quad (6)$$

where p and P' are constants for a given glass and $M(T)$ represents initial monolayer desorption^{23,24}. Adopting the expression for the reverse process of absorption and neglecting $M(T)$, eqn. (5) becomes:

$$R(T, t) = R_0(T) \exp (bPt^{\frac{1}{2}} \exp -p/T) \quad (7)$$

where it has been assumed that diffusion of air into the substrate gives rise to an ion density at the island substrate interface related to the volume absorbed by:

$$N(T, t) = (P/P') \cdot V(T, t)$$

Use of the barrier height modification by ions at the metal surface requires qualification. The presence of ions at any position in the barrier will change the effective height of the barrier as a result of image effects. Effective increases in barrier height due to negative ions depend on the ion positions^{16,25}, but at a given position the relationship between total effective increase and ion density is linear²⁵. To extend the above theory to the general case of ions at any position in the gap it is only necessary to specify that the relative distribution of ions along the tunnelling path remains constant. In this case the linear dependence of $\Delta\phi(T, t)$ on $N(T, t)$ will hold with the constant b now indeterminate. Even when this requirement is not rigidly adhered to, the averaging effects of many gaps in the conduction paths and of time variations should prove adequate for comparison of theory and experiment. The barrier width s is also modified by the presence of ions, but with a

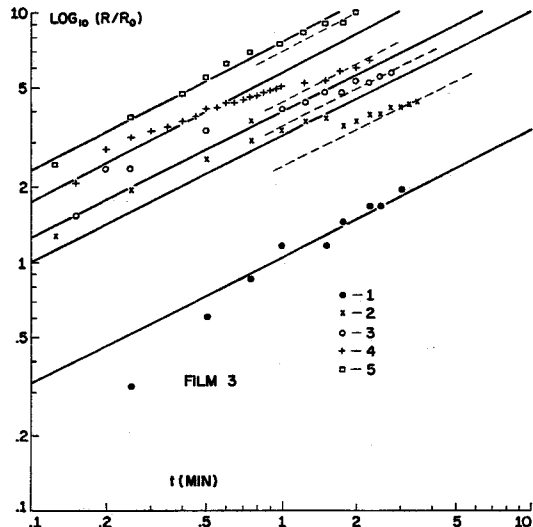


Fig. 5. Log-log plot of $\log (R(t)/R_0)$ vs. time for different temperatures (film 3). Solid lines, estimated average slope; broken lines, initial slope.

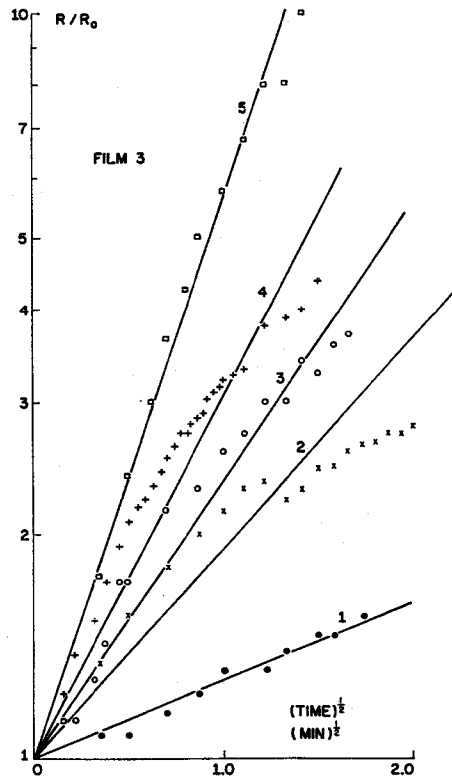


Fig. 6. $\text{LOG} (R(t)/R_0)$ vs. square root of time (film 3).

non-linear relationship. However, the changes in s are small relative to changes in ϕ^{25} , and are neglected. Note that the above discussion relates to shape changes in the static or equilibrium barrier. An important factor in the magnitude of the tunnelling current is the modification of the static to the dynamic barrier by the multiple image effects of the tunnelling electron itself. The height of the dynamic barrier at a position x equals the height of the static barrier minus an image correction term which is a function of x only if s is constant. The barrier height modification described above may therefore be considered as a change in the dynamic height. Once again there is a variation in s resulting from the ions and dynamic image effects which is not a linear function of ion density, but which can be neglected because it is small.

Trapnell has shown that oxygen and nitrogen are immeasurably absorbed by thin gold films²⁶. The possibility of increasing barrier width resulting from diffusion of air into the surface of the islands themselves is therefore eliminated as a source of resistance change for both substrate conduction and direct tunnelling through air or vacuum. In the case of direct tunnelling through air or vacuum, monolayer formation on the islands would be expected to raise the metallic work function and hence the barrier height. Monolayer formation on the substrate between islands could conceivably give rise to ions in the gap. Monolayers are, however, ruled out as the agents of change in the experiments described below. Only two mechanisms are left to explain the resistance increases. One is the ion diffusion process which is described above, the other is a process of metallic work function modification by oxygen atoms (as distinct from ions) at the island-substrate interface. This latter process may also be dominated by substrate diffusion and may give similar results to those described below. Note that work function modification by oxygen is usually attributed to the formation of ionic surface layers²², in which case the process is equivalent to that assumed above. However, published results imply that oxygen can form direct bonds with the surface molecules of gold, but in this case the work function increases in discrete jumps²⁷. It is also difficult to extend the concept to observed resistance decreases in water vapour¹² without reverting to ionic arguments. At first glance it appears that the substrate barrier height would be independent of the metal work function, anyway, and equal to the energy difference between the insulator Fermi level and conduction band. The process of Fermi level alignment, however, introduces charge into the dielectric which causes band-bending at the interface and effectively increases the barrier height. The amount of charge transferred is directly proportional to the work function of the metal¹⁶. It is clear, therefore, that while metallic work function increases affect the barrier height, they do so indirectly and by a mechanism which is equivalent to the introduction of surface ions and can be treated as such. Treatment of resistance increases in terms of ions in the tunnelling barrier is therefore valid.

TIME AND TEMPERATURE

$\log R(T, t)$ is plotted in Fig. 4 as a function of time for five set temperatures *in vacuo*. Maximum observed temperature rises referred to previously are noted in brackets. The curves come close to a $Q_0 + Q(1 - \exp - qt)$ form indicative of mono-

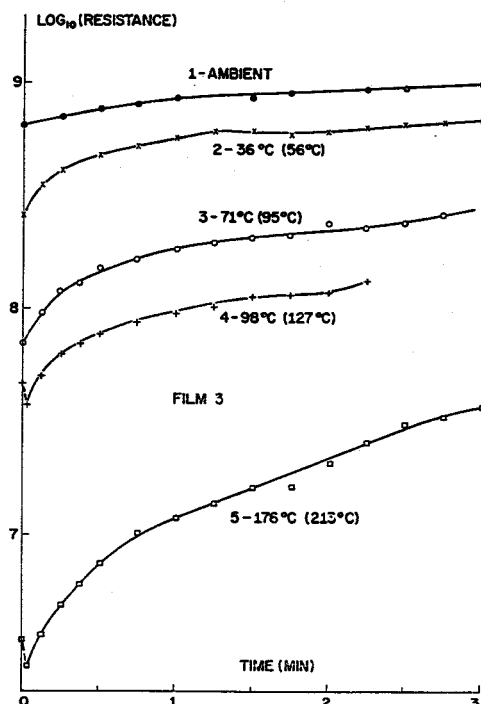


Fig. 4. Change of resistance in air with time at different temperatures (film 3).

layer growth²³, but Q (corresponding to an equilibrium value of $N(T, t)$) increases with increasing temperature, which is contrary to monolayer properties. In Figs. 5 and 6 the same data are plotted as $\log(\log(R(T, t)/R_0(T)))$ against $\log t$ and as $\log(R(T, t)/R_0(T))$ against $t^{\frac{1}{2}}$ respectively. $R_0(T)$ is taken as the initial resistance *in vacuo* except for 4 and 5, where considerable temperature rises and resistance decreases were observed. Estimated reduced values of $3 \times 10^7 \Omega$ and $2 \times 10^6 \Omega$ respectively were used in these cases.

According to the theory, the experimental points for each temperature (Fig. 5) should lie on straight lines of slope equal to one-half. Lines with this slope have been drawn in for comparison. In Fig. 6 the points should fall on straight lines through the origin. Agreement with theory does not appear promising, but it is remembered that some deviation is to be expected as a result of the temperature

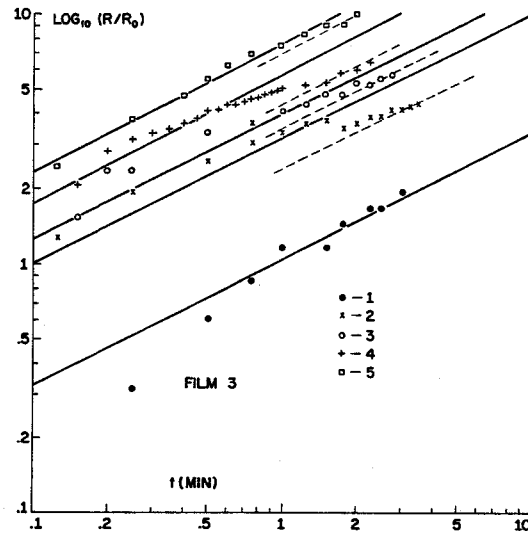


Fig. 5. Log-log plot of $\log (R(t)/R_0)$ vs. time for different temperatures (film 3). Solid lines, estimated average slope; broken lines, initial slope.

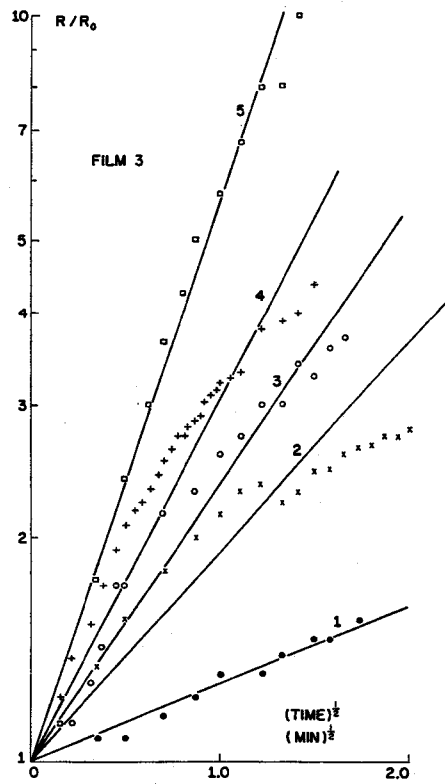


Fig. 6. $\text{Log} (R(t)/R_0)$ vs. square root of time (film 3).

fluctuations. Figure 7 shows the validity of the $t^{\frac{1}{2}}$ relationship at ambient temperature and over an extended period.

Values of p are available for various types of glasses. Typical figures range between 4000 and 8000 °K. None have been found for Corning 7059, but other borosilicate glasses have values around 4000 °K^{23,24}. According to the theory, p can be found from the slopes of the lines in Fig. 6, and the intercepts at $t = 1$ in Fig. 5. A plot of $(bP/2.3) \exp -p/T$ against $1/T$ is presented in Fig. 8, where a

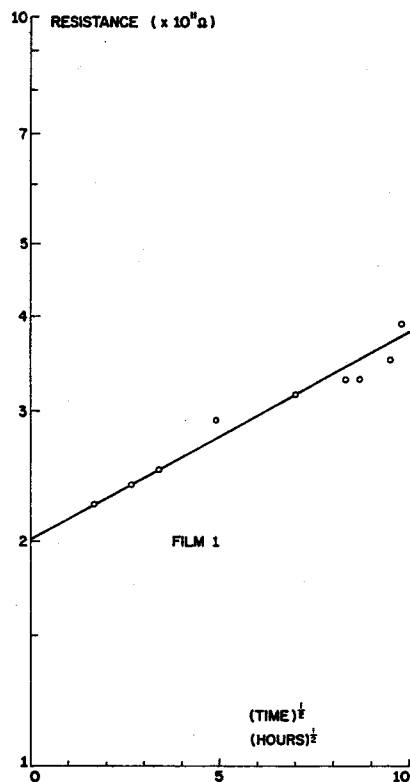


Fig. 7. Long-term resistance increase (film 1).

number of different slope or intercept combinations with set and maximum temperatures have been used (as indicated on the diagram) in an effort to minimise errors introduced by temperature fluctuations. (The factor 2.3 arises with the use of base 10 logarithms.) A line has been drawn through one set of points only, but the slope, which is the feature of interest, appears to be quite typical of the others. This line gives a value of p equal to 1050 °K, which is in order of magnitude agreement with typical figures for borosilicate glasses.

Efforts to improve the accuracy of determination of p are continuing. If the

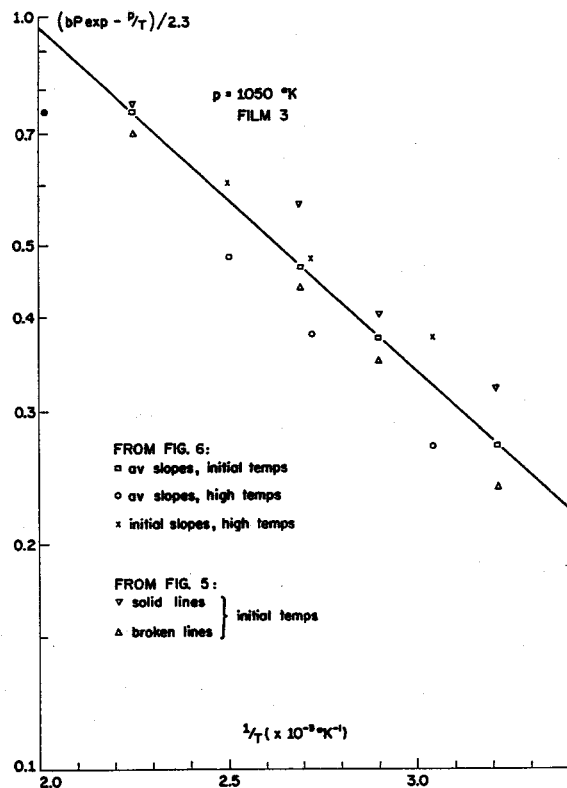


Fig. 8. Activation energy of diffusion (film 3).

variation in $R_0(T)$ with time is introduced into the theory, eqn. (7) becomes:

$$\log_{10} R(T, t) = \log_{10} R_0(T, t) + (bP/2.3)t^{\frac{1}{2}} \exp -p/T$$

where $R_0(T)$ has been replaced by $R_0(T, t)$. Differentiation with respect to $t^{\frac{1}{2}}$ gives:

$$\frac{\partial \log_{10} R(T, t)}{\partial (t^{\frac{1}{2}})} = \frac{bP}{2.3} \exp -p/T + \left(\frac{1}{T^2}\right) \left(\frac{\partial T}{\partial (t^{\frac{1}{2}})}\right) \left(p \log_{10} \frac{R(T, t)}{R_0(T, t)} - \frac{\psi}{2.3 k}\right)$$

At $t = 0$, the slope of the $\log_{10} R(T, t) - t^{\frac{1}{2}}$ plot may therefore be negative if $\psi > 2.3 kp$, since $R(T, 0) \approx R_0(T, 0)$. In general, after this region, the correction term is positive and negative respectively for increasing and decreasing temperature. The correction term is zero at two distinct times when $\partial T/\partial t^{\frac{1}{2}}$ is zero, i.e. when temperature reaches a maximum and begins decaying and when it reaches its final value. Two values of the slope are obtained by this method at two distinct temperatures. Resistance and temperature variation upon admission of air are plotted as functions of $t^{\frac{1}{2}}$ in Fig. 9 for one set substrate temperature. A diffusion activation constant is obtained by four such experiments, the results of which are shown in Fig. 10. The

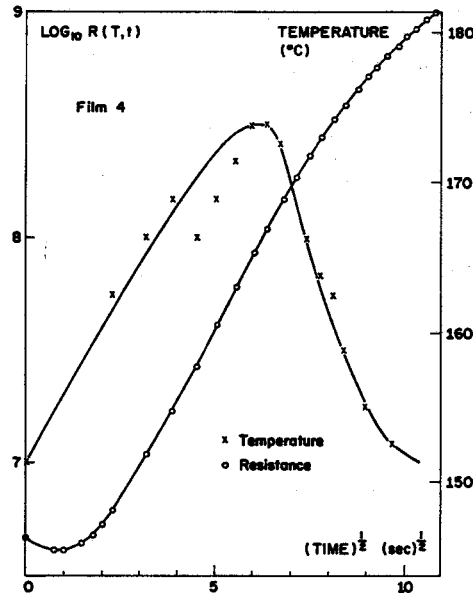


Fig. 9. $\text{Log}(R(t)/R_0)$ and T vs. square root of time (film 4).

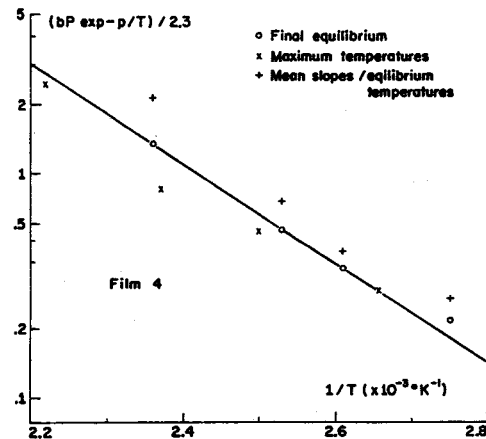


Fig. 10. Activation energy of diffusion (film 4).

method of temperature measurement introduces an uncertainty in the value of the maximum reached. Actual film temperatures equal the measured values at equilibrium, but will always be less than the measured values in the transient stage. Points are also indicated which correspond to mean slopes and equilibrium temperatures for a comparison with the more approximate method previously used. The activation constant obtained is $5100 \text{ }^\circ\text{K}$ and the error roughly estimated from the spread of the points is about 20%. A value reached by the mean slope method

would only be in error by approximately this amount. Values of p obtained for different samples show order of magnitude consistency only.

The long-term linearity of the log of resistance with the square root of time at constant temperature, the existence of well-defined activation energies of diffusion as demonstrated in Figs. 8 and 10, and the agreement of numerical values with typical figures for similar glasses are considered sufficient evidence for the conclusion that the resistance increases are caused by diffusion of air into the substrate.

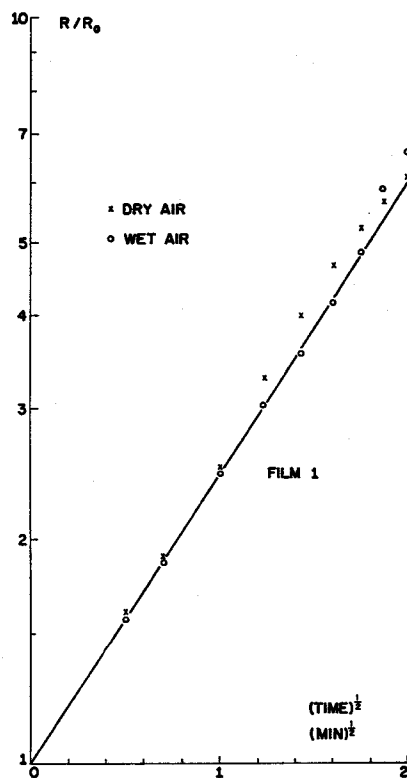


Fig. 11. Resistance increase with dried and undried air (film 1).

DRY AIR

Weitzenkamp and Bashara have previously reported increases in the resistivity of discontinuous gold films in oxygen, and decreases in water vapour¹². These results are consistent with the above theory, since it is reasonable that oxygen will give rise to negative ions and that hydrogen ions introduced by water vapour will dominate the diffusion process. In general, the principal component of ab-

sorbed gases in glass is water vapour^{23,24}. A brief comparison (Fig. 9) of resistance increases with direct admission of air and with drying the air by passing it through activated alumina shows the humidity of normal air has no significance in this laboratory. Tests in areas with more humid climates may give very different results. No other component of air has been considered, and the attribution of the effect to oxygen is based solely on the observation of the effect in oxygen atmospheres¹².

It is noted that the concept of ions influencing barrier heights in discontinuous thin films has been proposed before as a partial explanation of the substrate bias effect, where a positive (negative) potential applied to the rear of the substrate increases (decreases) film conductivity by migration of substrate ions into the film gaps^{6,16,17}. The effect is not generally observable in 7059 substrates, and, unfortunately, consistent results have not been achieved in this laboratory for films on soda-lime substrates. It is expected, however, that experiments performed in air will show a much less pronounced effect than those *in vacuo* if the gaps are saturated with negative ions.

CONCLUSIONS

When the resistance increases of discontinuous gold films in air were first noted, it was assumed that for some reason the metal aggregates, while stable in vacuum, became unstable in air, perhaps due to the metal-air surface energy being different to that of the metal-vacuum surface². The reversibility of the change (Fig. 2) and the constant activation energy (Fig. 3) showed, however, that structure is not changed and that the tunnelling probability is reduced in air. With the assumption of substrate tunnelling, a theory was developed around the diffusion of air into the substrate. It was postulated that the air gives rise to negative ions which increase the barrier height. A linear relationship between barrier height change $\Delta\phi(T, t)$ and ion density $N(T, t)$ was justified and substituted in the resistance expression with $N(T, t)$ given by a diffusion relation. The diffusion mechanism is subsequently justified by the long-term variation of resistance and by a diffusion activation energy in good agreement with typical values.

ACKNOWLEDGEMENTS

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