Charge Activation Theory of Conduction in Discontinuous Thin Metal Films

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The electrostatic charge activation model of conduction in discontinuous thin metal films is now widely accepted. There are, however, a number of discrepancies between theory and experiment and several aspects which are not well understood. The paper (a) briefly reviews the points of agreement between theory and experiment and surveys the reasons for rejection of other proposed theories, (b) considers the areas of disagreement between theory and experiment, and (c) discusses those aspects of the theory which are insufficiently well established to provide either confirmation or rejection of the theory. In particular, the tunneling parameters are considered in detail. It is decided that the theory, while not yet seriously disputed, does not account for all observations. More accurate determination of film structure is required before any final conclusion is possible.

Introduction

When a metal is evaporated *in vacuo* onto an insulating substrate, the initial nucleation process gives rise to a discontinuous film structure where the metal is confined to small discrete islands.[1] Electrical conduction in such films is an activated process with the form $\sigma=\sigma_0 \exp(-\delta E/kT)$,[2–23] where σ is the film conductance at absolute temperature T, k is Boltzmann's constant, δE is the activation energy, and σ_0 is a constant determined by the materials and film geometry. δE typically lies between $\sim kT$ and ~ 1 eV and decreases with applied field.

Conduction Theories

A number of theories have been proposed to explain the electrical properties of the films. Neugebauer[6] has shown that differential expansion between the islands and substrate can cause a negative TCR but cannot account for observed activation energies. Hartman[7] suggested that the islands might be conveniently represented as potential wells in which case the electron energies would be restricted to narrow permitted levels. Conduction would therefore take place by tunneling between permitted bands and δE would be determined by the band spacing, i.e., by island dimensions. The model does not, however, predict the observed non-Ohmic effects and has not received further attention.

It might be expected that thermionic emission would be a likely mechanism.[2] The barrier height for substrate conduction (i.e., for emission of electrons into the substrate conduction band) is much less than typical metallic work functions[18] and would be reduced by image effects involved in the charge transfer.[21,24] The barrier height in electron volts is then given approximately by $(\phi_0'-5/\epsilon_r d')$, where ϕ_0' is the undisturbed barrier height in electron volts, ϵ_r is the relative dielectric constant, and d' is the gap width in angstroms.[21,24] Reduction of the barrier by an applied field would account for the non-Ohmic properties.[21,24] The gap widths necessary to account for values of δE corresponding to known values of ϕ_0' are generally much smaller than those observed.[21] In addition, it is not possible to obtain consistent agreement of both observed δE and measured field effect using the theory.[2] Furthermore, (a) it has been shown that for typical film geometries tunnel currents will exceed thermionic currents,[2,4,18,19] (b) the effect of air adsorption by the films is inconsistent with thermionic emission,[21,25] and (c) the variation of δE under stress is opposite to that predicted by this model.[21]

Three separate models have been proposed within the classification of impurity conduction. The first (by Hill[8,9]) involves tunneling into substrate trap sites below the Fermi level with subsequent activation to higher energy sites and further tunneling into the next island. Wei's version[10,11] involves a bulk substrate conduction process with an electrostatic activation

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energy similar to that described below. Palatnik *et al.*[12] suggested that the islands might be regarded as impurity sites which modify the substrate surface conduction band. All three models suffer from the same basic problem that a quantitative development of the theory is not available for numerical comparison with experiment. In addition, Hill's model[8] suggests that δE is a function of the substrate alone which is not borne out by experiment.

Charge Activation Theory

The basis of this theory,[3–6,13–23] which appears at present to be the most promising, is that conduction takes place by tunneling between islands. When an electron leaves a given island, however, that island becomes electrostatically charged with a resultant shift in its Fermi level relative to its neighbors. The tunneling electron must therefore possess sufficient energy to surmount this electrostatic "barrier" which gives rise to δE through the Fermi distribution. For oblate spheroid islands (the best available approximation of shape[21,26,27]) of eccentricity l and major axis radius r parallel to the substrate, the electrostatic energy resulting from the loss of an electron across the intervening gap of width d to the next island is[21,28]

$$E=(e^2/4\pi\epsilon_r\epsilon_0 rl)\{\sin^{-1}l-\sin^{-1}[rl/(r+d)]\},$$

where e is the electronic charge and ϵ_0 is the permittivity of free space. The complete expression for the tunnel current density J[19,22] is

$$J=\frac{4\pi me}{h^3B^2}\,\frac{\pi BkT}{\sin\pi BkT}$$
$$\times\exp(-A\bar{\phi}^{\frac{1}{2}})\left(\frac{1-\exp[-B(\delta E+eV)]}{1-\exp[(\delta E+eV)/kT]}\right.$$
$$\left.-\frac{1-\exp[-B(\delta E-eV)]}{1-\exp[(\delta E-eV)/kT]}\right)$$

for $\delta E\gtrless kT$, where m is the electronic rest mass, h is Planck's constant, V is the voltage across the gap, $\bar{\phi}$ is the effective barrier height, $B=A/2\bar{\phi}^{\frac{1}{2}}$, and $A=(4\pi d/h)(2m^*)^{\frac{1}{2}}$, where m^* is an effective reduced electron tunneling mass. No comparison of theory and experiment has been made with this expression. In general, the simplified version for the tunneling conductance/unit area[4,18]

$$\bar{\sigma}=\left(\frac{8\pi me^2}{h^3B^2}\right)\left(\frac{\pi B}{\sin\pi BkT}\right)\exp(-A\bar{\phi}^{\frac{1}{2}})\exp\left(-\frac{\delta E}{kT}\right)$$

is used where it is assumed that $\delta E\gg kT$ and, although it is not usually stated, $\delta E\gg eV$ and $kT\gg eV$. Au–SiO cermet films have been observed where $\delta E\sim kT$[21] but, in general, these restrictions are valid. Differential expansion is also usually neglected.

Activation Energy

Thus far comparison of theory and experiment has been generally restricted to δE. Even here order of magnitude agreement has been considered satisfactory since there are a number of indeterminate parameters involved. In the first place, real films possess distributed geometries and the variation of δE with r and d is nonlinear. Only r is reasonably easy to estimate, d being especially awkward due to island curvatures. Second, the eccentricity l is difficult to determine. (It is hoped that small angle scattering techniques may provide a convenient measurement here.)

The final term in the expression for δE is ϵ_r. Hill states that the appropriate value is the static dielectric constant[18,19] and quotes a figure of 14 for Corning 7059[19] which is clearly high. Intuitively, ϵ_r should be between 1 (air/vacuum) and the substrate value and a comparison of theoretical values of δE (calculated from observed geometries) and experimental values for the two extreme cases of $l=0$, 1 suggests that ϵ_r is between 1.5 and 2.25 with 1 and 3 as outside limits. This result seems to indicate that the high-frequency (optical) value of ϵ_r is applicable. Hill's basis for using the static value is that the island charge remains as a static charge transfer between the islands and the substrate in equilibrium.[18,29] If the transfer is sufficiently fast, then the static charge may be accommodated sufficiently rapidly to account for the small value of ϵ_r. No information is presently available as to the time constant of the transfer.

Annealing and Resistance Variation with Time

One of the original reasons for postulation of the oblate spheroid shape was the resistance increase usually associated with thermal annealing of the films.[26] It is assumed that the islands adopt a more spherical shape and δE increases as σ_0 decreases. The mechanism for this process is not clear. It has been suggested[21] that the oblate spheroid shape is the result of preferential nucleation on substrate charge sites and of the substrate–island charge transfer but in this case there is no apparent reason for change in what would be an equilibrium form. Alternatively, the oblate spheroid form may not be stable at all. The variation of resistance with time and annealing has been alternatively explained on the basis of coalescence.[30] If the change is in fact the result of reductions in l, then the process must be placed on a similar quantitative basis for comparison of theoretical variations in time with experiment.

Similarly, while decreases in film resistance following deposition have been related to the decay of excess film temperatures,[21] the increases occasionally observed[21] have not been satisfactorily explained. No success has been obtained with a coalescence model and a charge transfer relaxation model has been only briefly contemplated.

As yet, no one has related the variation of film resistance during deposition to film growth processes. With highly aggregated films a linear logσ–time relationship[21] is clearly the result of coalescence but it can only be supposed that the more complex relation typical of nearly continuous filamentary films[21] is similar, with the added effect that filamentary linkage bypasses alternative conduction paths.

Switching

A recent patent[31] describes bistable switching characteristics of discontinuous films. Beyond a critical voltage the film resistance switches from a low to a high value and the characteristics are reproducible provided a stabilizing oxide layer is superimposed. Similar irreversible effects have been noted in films with no stabilizing oxide layer[21] and have been attributed to the burning out of filamentary linkages by Joule heating. A fuller investigation of the reversible process is clearly necessary.

Stress

Discontinuous film structures have been used as strain gauges[32,33] yet little theoretical investigation has been made of the effect of stress on the film structure for comparison with changes in the electrical properties. In particular, an obvious series of experiments would be to determine the variation of σ_0 and δE with stress. Those that have attempted this type of test have been plagued with stability problems as structure appears to change in a random fashion.[21,34] Only two films have been sufficiently stable to obtain the reproducible result that σ_0 and δE both decrease with film extension.[21] The decrease in δE is inconsistent with the thermionic model and, while the reduction of σ_0 is in accordance with a tunneling model, the change in δE ($\sim 5\%$) with strain ($\sim 0.05\%$) can only be accounted for by a change in l, which implies that the islands adhere to the substrate over a wide area. An inconsistency arises when it is found that it is also necessary that $l \sim 0.1$, i.e., that the islands are nearly spherical.[21]

SiO Overcoat

The deposition of SiO over a discontinuous Cr film results in an increase in film conductivity attributed to a decreased δE.[35] This variation in δE is believed to be due to island expansion as the surface tension of the islands (assumed spherical) decreases.[35] A similar effect is expected with discontinuous gold films but in fact the opposite is observed (Fig. 1).[21] These results are consistent with a change of island shape to a more spherical form and, since thermal annealing is not a factor,[21] it is believed that the change must be due to relief of the original cause of the oblate shape. With the overcoat the charge transfer previously described is now possible at all island surfaces and it is postulated that the oblate spheroid shape is electrostatically related to this charge transfer.[21]

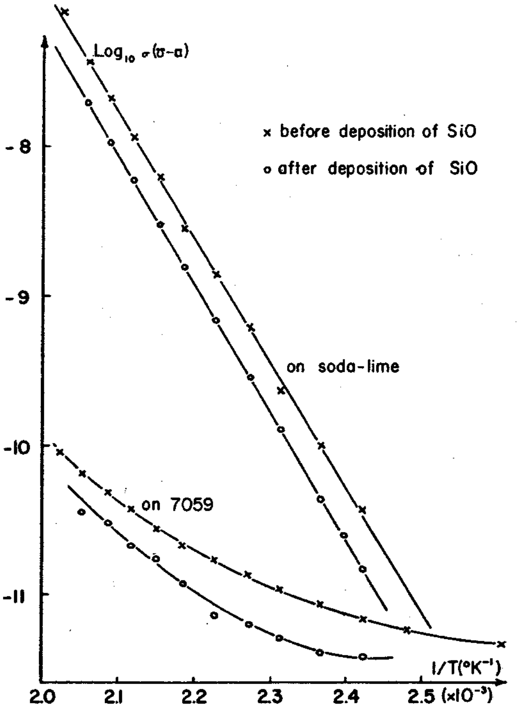

FIGURE 1. The effect of a superimposed SiO layer on film resistances.

Non-Ohmic Effects

The non-Ohmic effects of the tunneling expression and the tunneling barrier are generally overshadowed by the field reduction of δE.[18] In general $\delta E \gg eV$ in accordance with the usual assumption but in some of the author's films eV has approached δE and in some cermet films exceeded it.[21]

δE is given[21] as a function of applied field E_a over the film as

$$\delta E = \frac{e^2}{4\pi\epsilon l r}\left[\sin^{-1} l - \sin^{-1}\left(\frac{lr}{r+x}\right)\right] - \frac{exE_a(2r+d)}{d},$$

where $x = d$ for $0 < E_a < E_{a\,\mathrm{min}}$ and x is the root of

$$(r+x)^2\left((r+x)^2 - l^2r^2\right) = \left[de/4\pi\epsilon E_a(2r+d)\right]^2$$

for $E_{a\,\mathrm{min}} < E_a < E_{a\,\mathrm{max}}$ where

$$E_{a\,\mathrm{min}} = (ed/4\pi\epsilon)(r+d)^{-1}(2r+d)^{-1}((r+d)^2 - l^2r^2)$$

and

$$E_{a\,\mathrm{max}} = (ed/4\pi\epsilon)r^{-2}(2r+d)^{-1}(1-l^2)^{-\frac{1}{2}}.$$

$\delta E = 0$ for $E_a > E_{\mathrm{max}}$.

No comparison of theory and experiment has been made as yet for the general case above. The equivalent expressions have been plotted for spherical islands,[36] however, and do not compare favorably with experiment except in one specific case.[17] Most experimental results indicate that δE decreases linearly with $E_a^{\frac{1}{2}}$ [15,18,21] which is only true for $E_{a\,\mathrm{min}} < E_a < E_{a\,\mathrm{max}}$.[36] Analysis is complicated by nonuniform structures, particularly in nearly continuous filamentary films. In one of the author's experiments δE tended to a constant finite value at high fields instead of to zero.[21]

One implicit assumption above is that there is zero field in the islands themselves which is validated by a comparison of film resistances with that of a continuous layer of similar thickness.[18,21] For zero field in the islands the electron velocity in the islands is isotropic (a necessary assumption in the theory) and is undisturbed by a magnetic field. There is therefore no change in the Fermi distribution or tunneling probability and no magnetoresistance or Hall effect as is observed.[21,37,38]

Tunneling Area

There has been little comparison of theoretical and experimental values for σ_0. Part of the problem is evaluation of the effective electrode area for tunneling in both discontinuous and cermet films. As a first approximation a coplanar electrode configuration is suggested for the discontinuous films.

Tunneling Barrier

Another important aspect of the term σ_0 is the form of the barrier to tunneling. It has been well demonstrated that conduction is via the substrate[8,18,21,25] and the undisturbed barrier height will be the height of the substrate conduction band. The barrier will be modified by the charge transfer considered earlier[18,29] and by image effects.[24] The appropriate value of ϵ_r for the latter modification is generally accepted to be the high-frequency form but if the tunneling time is comparable with the plasma frequency no image reduction of the barrier height will occur.[39] There is ample theoretical evidence that substrate impurities (both ions[40] and neutral absorbates[41]) affect conduction and experimental evidence in discontinuous films includes the effects of substrate bias,[8,18,21] substrate ion drift,[21] and air adsorption.[25] None of these effects is adequately developed in theory as yet. In particular the bias effect with Corning 7740 glass[8] is inadequately explained. The effect of positive ions, as one specific example, is to act as local trap sites in the barrier.[20] There is a dual result in that the barrier height is reduced by imaging and an enhanced tunneling probability due to the exponential dependence on d and a multiple-hop tunneling effect.[20,21] This is accounted for by the reduced mass term in the theory.[20] Clearly the distribution of ions in the gaps will be important in this context. Reasonable values for m^* and $\bar{\phi}$ have been obtained from the high-temperature dependence of tunneling[8] but evaluation from the entire expression for σ_0 has given ridiculous values for cermet films when r^2 is used for the tunneling area.[21]

Conclusions

Clearly the charge activation model is not as conclusively established as might be inferred from the literature. No absolute contradiction has yet come to light, however, and the problems remain essentially those of (a) improvement of experimental accuracy and structural determination, of (b) further theoretical development and, in the more distant future, of (c) determination of charge and ion locations in the tunneling gaps.

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