ELECTRICAL CONDUCTION IN GRANULAR METAL FILMS

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ABSTRACT

In the early 1970's, Abeles et al developed a widely accepted model for electrical conduction in granular metal films based upon an assumed correlation between metal particle size and inter-particle tunneling gap width. The paper critically examines this assumption and other aspects of the theory. No observation of any such correlation has been reported, nor should it be expected, particularly in discontinuous films. The latter point requires separate considerations of the very different structures of discontinuous metal films, granular metals and cermets, using the "granular" term here in a more limited sense than usual.

Other aspects of the theory considered include its implied percolation topology and the field effect. Experimental data are also re-evaluated in terms of other common models. The paper concludes with a brief review of recent work in discontinuous metal films with suggestions for future theoretical and experimental work.

INTRODUCTION

When a metal is deposited *in vacuo* on an insulating substrate such as glass, it does not form a monolayer film. Instead, it aggregates initially into discrete metal islands, forming a *discontinuous metal film*, until these coalesce at some critical thickness into a continuous layer. These islands are typically of nm dimensions and separations. A similar structure in three dimensions is formed with the deposition of a *cermet* (ceramic-metal mixture) of sufficiently low metallic content. Again, discrete metal islands of nm typical diameters are separated by nm gaps, but in this case filled by the dielectric medium.

The term "*granular metal film*" has been applied to both structures in a convention which stresses the similarities in structure and properties, but which unfortunately also serves to minimize the very real and significant distinctions. The issue of structure and terminology is discussed at more length below.

For continuous metal structures, the resistivity is low with a positive temperature coefficient. It is the other side of the insulator transition in which we are interested here, where the temperature coefficient of resistance (TCR) is negative, and where the small but finite conductivity displays non-ohmic effects, high strain-gauge factors, environmental gas sensitivities, and a host of other interesting and (possibly) exploitable phenomena. One thing is certain: that these properties correlate with the observation of a metallic island structure regardless of whether the film is characterized as discontinuous, a cermet or granular metal.

The mechanism of electrical conduction in such films has been a source of interest and controversy for a considerable period of time. The interest stems both from the potential applications mentioned above, (although reproducibility and stability of useful island structures continues to inhibit commercial viability,) and from the immediately intriguing notion of electrical conduction across a sequence of insulating gaps. Some of the controversy has undoubtedly arisen from the variability of experimental data published by different laboratories using different preparatory techniques, but consensus as to the reproducibility of results has generally developed eventually. The problem receiving attention recently has been the application of percolation concepts to an insufficiently characterized real, random structure where, furthermore, the resistive elements would vary continuously over orders of magnitude. In fact, it is not clear that the film can even be modelled as an interconnected array of fixed resistors, since even the most elementary conduction models are field dependent and the microscopic field distributions must be constantly changing as the relatively few free carriers move from island to island through the film.

Following Swann's paper of 1914 [1], which established the link between negative TCR and island structure, Gorter [2] in 1951 and Darmois [3] in 1956 proposed that the electrostatic energy associated with the charging of a very small conducting island by a single electron would produce an activation energy of conduction and the negative TCR. The concept was refined by Neugebauer and Webb [4] who also added the concept of inter-island charge transfer by electron tunneling. These two components (electrostatic activation energy, δE, and tunneling between islands of radius, r, separated by gap, s) form the basis of virtually all contemporary treatments of the problem.

Hill [5] attempted to put the electrostatically activated tunneling model on a more solid theoretical foundation, and also documented some controlled experimental procedures. This work was followed some years later by that of Abeles et al, which is effectively summarized in references [6] to [8]. The essential contribution by Abeles et al was the first attempt at the application of percolation concepts to handle the problem of non-uniform film structure. It followed a growing recognition that the electrical conductivity, σ, at thermodynamic temperature T obeyed a law of the form

$$\sigma = A \exp -(T_o/T)^n \qquad (1)$$

where A and T_o are constants, rather than the simple Arrhenius form

$$\sigma = A \exp -(\delta E/kT) \qquad (2)$$

which had been previously generally accepted. A very wide temperature range is required to make the distinction. It seems that $n = 0.5$ for cermets but that $0.32 < n < 1$ for discontinuous metal films, with $n = 0.5$ still typical. The Abeles model will be described in more detail below, but appears to predict the $n = 0.5$ result successfully.

Only the milestones have been identified above. For more extensive reviews of work performed in the field to this point in the chronology, the reader is referred to Morris and Coutts [9] (whose conclusion was that the detail of the electrostatically activated tunneling model was in need of further development) or Meiksin [10]. For the last ten years, most of the progress in the understanding of the discontinuous film category in particular has been due to Adkins et al [11-19] and has been focussed on the critical examination by innovative experimentation of the postulates of the Abeles model.

ABELES MODEL

The charging energy of a spherical island is assumed to be

$$\delta E = (q^2/4\pi\epsilon)(r^{-1} - (r+s)^{-1}) \qquad (3)$$

in common with other treatments, i.e.

$$s\delta E = (q^2/4\pi\epsilon)((r/s)^{-1} - (1+r/s)^{-1}). \qquad (4)$$

Modeling the island distribution in a 3-D matrix by a simple cubic, the volume fraction of metal, x, is given by

$$x = (4/3)\pi r^3/(2r+s)^3 \qquad (5)$$

i.e.
$$s/r = (4\pi/3x)^{1/3} - 2 \tag{6}$$

so that for a given metallic content, x, the ratio s/r is constant and so is the product $s\delta E$. Within the obvious limitations of the simple square/cubic (or other regular) model, s/r also turns out to be constant for given x for 2-D discontinuous films.

The "gap conductance" is proportional to

$$\exp -(\alpha s + \delta E/kT) = \exp -(\alpha s + \{s\delta E\}/skT) \tag{7}$$

which is a maximum (remembering that $\{s\delta E\}$ is constant) for

$$s^2 = \{s\delta E\}/\alpha kT \tag{8}$$

i.e.
$$\sigma = A \exp -2(\alpha\{s\delta E\}/kT)^{1/2}. \tag{9}$$

The result depends upon the assumption that x remains constant over or through a given film, and that the ratio r/s is also consequently constant.

A similar argument based on the concept of direct field-induced carrier generation leads to the dominant dependence of high field conductance, σ_H, on field ξ,

$$\sigma_H = \sigma_\infty \exp -(\xi_o/\xi) \tag{10}$$

(where σ_∞ and ξ_o are constants,) which also relies upon the assumption of constant $\{s\delta E\}$, i.e. of constant r/s. (There is a more complete form which includes temperature dependence, but the only point at issue here is assumption of the structural relation, so the additional detail is unnecessary.) If there are two adjacent layers of metal islands separated by potential difference $q\Delta V$, then field generation of carriers will occur between islands in opposite layers provided $q\Delta V > \delta E$, i.e. between pairs of islands separated by gaps $s' > \{s\delta E\}/q\Delta V$. Since the smallest possible gaps which meet the criterion should dominate the process, the tunneling probability should be proportional to

$$\exp -\alpha s' = \exp -(\alpha\{s\delta E\}/q\Delta V). \tag{11}$$

STRUCTURES

Briefly stated, one of the principal points to be made in this paper is that the structural correlation assumed in the theory does not exist, i.e. where it has been studied, no correlation has been found, and elsewhere none should be expected. In making this analysis, it is important to distinguish between discontinuous metal films, cermets, and a third category for which we reserve the granular metal film terminology.

Discontinuous metal films

One of the problems which plague basic studies of metal island nucleation on insulating surfaces is the uncertainty in assessing the effective thickness of the film in its very earliest stages of development. As a result of the weak metal-substrate interaction which produces the discontinuous film structure, the atomic sticking coefficient is low, generally unknown, but more significantly here, inclined to vary with the detail of surface condition. What this means is that the uniform average coverage assumption will be invalid to some degree, especially at the very lowest thicknesses.

Even given average uniformity at greater thicknesses, the islands are more satisfactorily modeled as ellipsoids of rotation than as either spheres, hemispheres or discs. The problem is that the axes of rotation appear to fit uncorrelated log-normal distributions [20].

At greater thicknesses, as the islands near coalescence, double-peaked distributions develop, due to secondary nucleation of new islands between the larger aggregates. In this phase, island separations are typically constant and equal to twice the "capture distance" of the islands.

Experimental searches have also confirmed that the necessary correlations between island dimension and gap width do not exist in practice [21, 22].

Cermets

It is in the true 3-D cermet film where the assumptions are expected to hold, but with two provisos. It is widely believed that metal is dispersed within the dielectric in atomic form; the metallic content of the insulating phase must also be constant at a given concentration for the r/s condition to hold. In practice, as for the discontinuous film, gap widths tend to be constant at higher metallic content levels and equal to twice the island capture distance.

To the authors' knowledge, there has been no direct experimental verification of the postulated relationship in cermets. Such a confirmation could be difficult to obtain, since we consider it necessary to have a film of at least ten (say) island/gap "lattice constants" thick in order to qualify as "3-D."

Granular metals

There is a third structure to be considered here, and we append the generic term to it since the discontinuous and cermet structures have already been identified by special features. Most of the experimental data presented by Abeles et al appear to have been obtained on cermet films, i.e. ones which meet the 3-D criterion above, but some, especially those used for demonstrations of structure, were only of the order of one island dimension thick. In this case, electrical conduction might be more akin to that in the 2-D discontinuous film than to that in the cermet.

The island and gap dimensions of several films for which transmission electro-micrographs have been published [6-8] have been analyzed in detail. That the r/s criterion is not met is obvious in many cases by simple visual inspection, but in fact it is also not met in any specific case considered.

PERCOLATION CONCEPTS

The original formulation of the Abeles model used the idea that the regions of optimum σ, or minimum $(2\alpha s + \delta E/kT)$, are interconnected throughout/across the film, so that there is always an optimum path available to the current. This implied in turn that there must be a range of similarly interconnected networks throughout the film, including all the non-optimum ones. For any one of these to establish a continuous percolation path through the film, it must exist in a concentration greater than 0.3 - 0.33 for 3-D films or 0.5 for 2-D (discontinuous) films. Obviously, this is not possible [12]. However, later treatments using critical percolation analysis [23] showed that the interconnection of regions of similar σ is not necessary. The basic objection to the Abeles model is therefore that the required correlation between r and s is not observed.

Adkins and co-workers have also considered other possible sources of the varying activation energy or fractional power law dependence, including reviewing various other published proposals. A particular idea pursued at length is that the scale of structural inhomogeneity in the films might be such as to provide a variety of conduction channels across the film, this element of "choice" being an essential component to such power laws. The regions of inhomogeneity have, in fact, been demonstrated, but the experiments also showed that the fractional n did not correlate with the inhomogeneities in the appropriate way [13].

Current research is focussed on the existence of random potential fluctuations due to island-substrate charge exchange [14-17] which may yield other contributions to energies relevant to charge mobility, and hence affect the choice of optimum path.

CONTACT EFFECTS

It is obvious that in a film with distributed island and gap dimensions, most of the electrical current will be carried by relatively few preferred paths through the film --- but not by just one path. It is also obvious that the preferred paths will change as the temperature and applied field change, as the relative contributions of tunneling probability and carrier generation energy shift. So percolation concepts are undoubtedly vital to a full understanding of the conduction process. But they are equally clearly not the only aspect of the granular film conduction mechanism which is inadequately understood.

In certain experimental configurations, there is clear evidence that contact effects control observed resistances. For example, the observations of Borziak et al [24] make the conclusion that contact injection can play a role inescapable. When the bias polarity is reversed for a film which is known to have dissimilar structures at the two contact ends, the resistance changes. Recent results for the a.c. impedance of such asymmetrical films support the notion of an electrode injection mechanism [25], although more data is required to convert "support" to "confirm." In exceptional cases of extreme asymmetry, a "pseudo-inductive" effect is observed. A model to explain this observation is based on the finite time required to establish a fully conducting film by contact injection of carriers (or space charge.) Under these conditions, detailed processes of carrier generation (and injection) have to be taken into account to explain the results. The role of film contacts, in particular, should be studied in parallel, for there are underlying assumptions in the application of percolation concepts as to the basic carrier generation and transport mechanisms, i.e. in how a perfectly uniform array of islands would behave. (This experiment has been proposed [9], but awaits adequate technology.)

It is clearly essential in designing experiments to explore the conduction mechanism of bulk granular materials in the linear low-field limit, to ensure that contact effects are eliminated. (Genuine four-terminal methods will do this.) Correspondingly, care must be taken to ensure that data interpreted as representative of bulk properties are not, in fact, artefacts of contacts. At the same time, contact effects are of considerable practical importance and merit careful study in their own right, particularly at higher fields, where injected carriers may swamp the thermal background.

CONCLUSIONS

The primary conclusion is that the mechanism of electrical conduction in granular metal films is still not fully understood. The model of Abeles et al is based on assumptions of structural correlation that are not met in any cases investigated. Furthermore, care must be taken in the attribution of experimental data to the bulk composite unless possible contact effects are carefully taken into account.

REFERENCES

1. W.F.G. Swann. Philos. Mag. 28, 467 (1914).

2. C.J. Gorter. Physica 17, 777 (1951).

3. E. Darmois. J. Phys. Radium 17, 210 (1956).

4. C.A. Neugebauer and M.B. Webb. J. Appl. Phys. 33, 74 (1962).

5. R.M. Hill. Pro. Roy. Soc. London Ser. A 309, 375 (1969).

6. B. Abeles, P. Sheng, M.D. Coutts and Y. Arie. Adv. Phys. 24, 407 (1975).

7. B. Abeles. RCA Review 36, 594 (1975).

8. B. Abeles, in Appl. Solid State Sci. vol.6, edited by R. Wolfe (1976).

9. J.E. Morris and T.J. Coutts. Thin Solid Films 47, 1 (1977).

10. Z.H. Meiksin, in Physics of Thin Films vol. 8, edited by G. Hass, M.H. Francombe and R.W. Hoffman (Academic Press, New York, 1975) p. 99.

11. C.J. Adkins, J.M.D. Thomas and M.W. Young. J. Phys. C: Solid State Phys. 13, 3427 (1980).

12. C.J. Adkins. J. Phys. C: Solid State Phys. 15, 7143 (1982).

13. J.D. Benjamin and C.J. Adkins. J. Phys. C: Solid State Phys. 17, 559 (1984).

14. C.J. Adkins, J.D. Benjamin, J.M.D. Thomas, J.W. Gardner and A.J. McGeown. J. Phys. C: Solid State Phys. 17, 4633 (1984).

15. J.W. Gardner and C.J. Adkins. J. Phys. C: Solid State Phys. 18, 6523 (1985).

16. A.J. McGeown and C.J. Adkins. J. Phys. C: Solid State Phys. 19, 1753 (1986).

17. C.J. Adkins. J. Phys. C: Solid State Phys. 20, 235 (1987).

18. C.J. Adkins. J. Phys: Condensed Matter 1, 1253 (1989).

19. J.W. Gardner and C. J. Adkins. Physica 107B, 419 (1981).

20. C.G. Granqvist and R.A. Buhrman. J. Appl. Phys. 47, 5 (1975).

21. J.D. Benjamin. PhD thesis, Cambridge University, 1982.

22. K.D. Leaver. J. Phys. C: Solid State Phys. 10, 249 (1977).

23. J. Heinrichs, A.A. Kumar and N. Kumar, J. Phys. C: Solid State Phys. 9, 3249 (1976).

24. P. Borziak, V. Diukov, A. Kostenko, Yu. Kulyupin and S. Nepijko. Thin Solid Films 36, 21 (1976).

25. J.E. Morris, presented at the 8th Internat. Confer. on Thin Films, San Diego, CA, 1990 (Thin Solid Films, to be published.)