

Note on the Anisotropy of the Conductivity in Thin Amorphous Films*

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We present a new interpretation of the anisotropy of the conductivity in thin films of amorphous Ge and Si. The interpretation is based on a transition from percolation conduction to Miller and Abrahams's conduction at small film thickness. A simple theory, together with experimental data, is presented. The comparison between them is found to be good.

Recently one of us reported observations of an anisotropy in the conductivity of thin films of amorphous germanium.¹ The anisotropy was tentatively interpreted as arising from voids. We present here an alternative explanation.

Qualitatively, an anisotropy similar to the one observed had been predicted by one of the authors² as arising from a transition in thin amorphous films from conduction along critical percolation paths to conduction along paths more similar to those proposed by Miller and Abrahams³ (MA). An alternative way to understand this transition is to realize that as a result of fluctuations, relatively large regions have a conductance much higher than the bulk. Such regions will constitute shorts across thin enough films and dominate the transverse conductance.

We present here a simple theory for the anisotropy caused by such a transition, and compare it with experimental data in *a*-Ge and *a*-Si films (*a* for amorphous). For germanium we use the parameter recently obtained from measurements on the longitudinal conductance in thin films.⁴ The agreement between the experimental results and the simple theory will be shown to be reasonable.

We summarize briefly the theoretical cause for the anisotropy in the conductivity discussed in Ref. 2. The reason why the MA theory does not normally work is that it restricts conduction to very specific paths, formed by making every step through the smallest impedance in the forward direction.⁵ The probability that every such step is smaller than a certain value is the product of the probabilities that each individual step is smaller than this value. Since the probability for each step is smaller than unity, the product must go to zero for a very large number of steps.

However, the approach to zero with increasing number of steps *N* is not rapid. If the number of steps is not very large, as is the case in transverse conductivity through thin films, the MA paths are not ruled out. In fact, the conductance through the MA paths is, up to a certain thickness, larger than the conductance through percolation paths. In the following we shall assume that when this happens the conductivity of the films is well described by the MA paths. When the opposite happens, the percolation theory will be assumed to describe the conduction. Clearly there is an intermediate region when other, more complicated, paths must be important, but these will not be considered here.

We begin with the expression for the probability $P_N(Z)$ that, starting at some site at one electrode, an *N*-step-long path has all impedances less than *Z*. The probability that each step is less than *Z* is given by the Poisson distribution and is⁶

$$p_1(Z) = 1 - \exp(-\pi\nu a^3 kT \xi^4 / 28.5) \equiv 1 - e^{-\alpha\xi^4}, \quad (1)$$

where

$$Z \propto \exp(2r/a + E/kT) \equiv \exp\xi,$$

ν is the density of states, *a* is the radius of the localized wave function, *r* is the length of the pair to which the impedance *Z* relates, and *E* is an energy equal to the difference between the site energies if the two sites are on the opposite sides of the Fermi energy. Otherwise *E* is the larger of the two distances from the Fermi energy.^{2,7} Thus

$$P_N(Z) = (1 - e^{-\alpha\xi^4})^N. \quad (2)$$

The probability $P_N(Z)$ is clearly proportional to the density of paths characterized by *Z* per unit area. Thus the conductivity due to these paths

characterized by Z is proportional to $P_N(Z)/Z$. We shall approximate the conductivity by the maximum value of this expression. This is given by the equation

$$4\alpha N(\alpha\xi)^3 = e^{(\alpha\xi)^4} - 1. \quad (3)$$

The solution of this equation gives the value of ξ as a function of N , which depends on the thickness t . The relation between N and the thickness is

$$N \approx t / \langle r \cos\theta \rangle, \quad (4)$$

where r is the hop distance and θ the angle between the hop direction and the direction of the normal to the film surface. If r and θ are uncorrelated,⁶ $\langle r \cos\theta \rangle = \langle r \rangle \langle \cos\theta \rangle = \frac{1}{2}(0.17\xi a)$, and

$$N = 11.6t / \xi a. \quad (5)$$

The steps have been restricted here to the forward hemisphere, as in MA. The relation between ξ and t then is

$$46.4\alpha^2(t/a)(\alpha\xi)^2 \equiv K(\alpha\xi)^2 = e^{(\alpha\xi)^4} - 1. \quad (6)$$

This relation is plotted in Fig. 1. From this plotted function we can calculate the conductance per unit area $P_N(Z)/Z$, and its dependence on the thickness of the film, provided that we know the density of states ν and the radius of the wave function a . These are known for a -Ge from previous experiments on the longitudinal conduc-

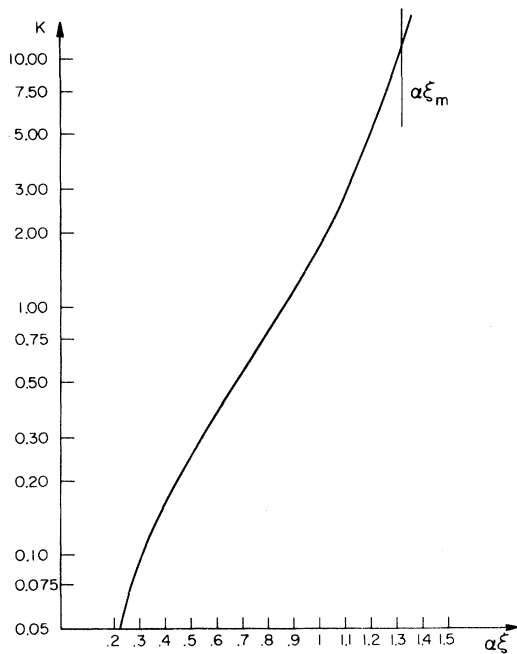


FIG. 1. A plot of Eq. (6).

tance of thin films.⁴ The values are $\nu \approx 10^{18} \text{ cm}^{-3} \text{ eV}^{-1}$ and $a = 10 \text{ \AA}$. With these values, the results for the conductivity as a function of temperature and of thickness are plotted in Fig. 2. The heavy curve is the percolation limit. Of the various critical percolation values^{2,7,8} for Z_m , we chose the value obtained from computer calculations,⁸ since it is likely to be the most reliable. Also needed is the density of percolation paths, i.e., the analog of $P_N(Z)$. A precise calculation is difficult, but as the scale in Fig. 2 shows, an inaccuracy by a factor 2 is relatively unimportant. For a site to be on a percolation path, at least two impedances must be connected to it with values less than the critical percolation impedance. The number of such sites can be calculated with the methods of Ref. 2. Clearly not all such sites are on a percolation path. We estimate that the fractional number which are is $\frac{1}{3}$.

The experimental results for a -Ge are shown in Fig. 3. It is observed that there is good qualitative agreement between the experimental and the theoretical results. The value of T_0 decreases with decreasing thickness. The curves are convex on a $T^{-1/4}$ plot. The latter point is qualitatively obvious, since the hopping distance, and

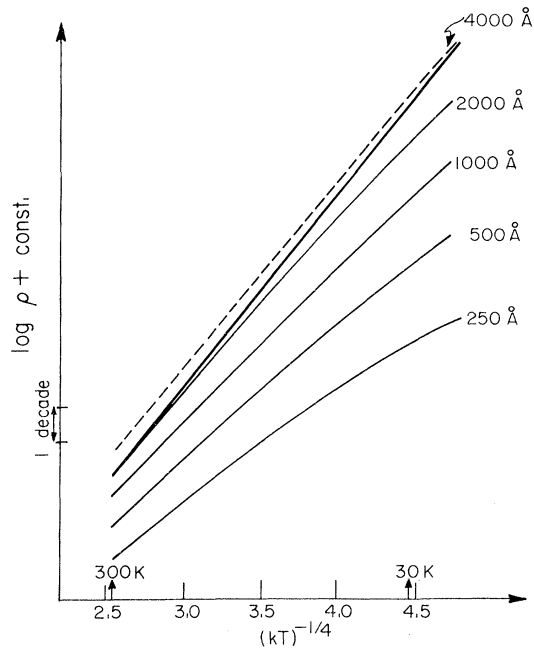


FIG. 2. Theoretical dependence of the conductivity on film thickness and temperature for a -Ge. Heavy line, the percolation limit; dashed line, a case where the MA paths give a larger impedance than the percolation paths.

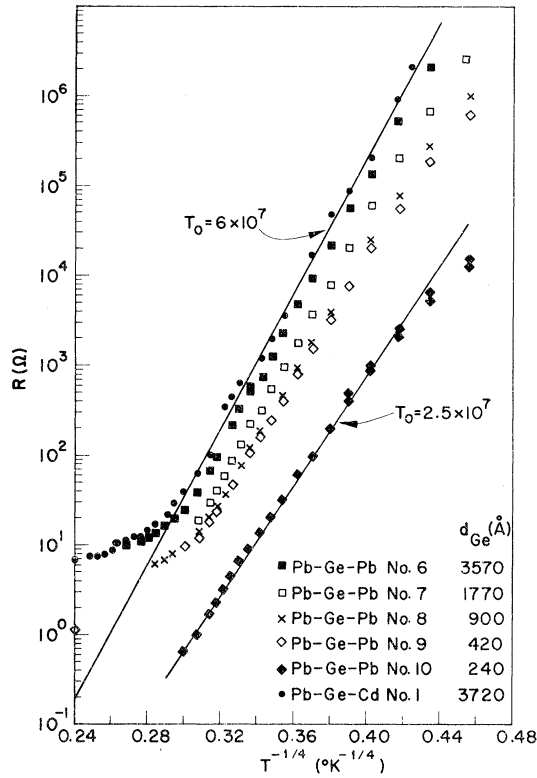


FIG. 3. Experimental dependence of resistance on film thickness and temperature for *a*-Ge.

thus the ratio of the hopping distance to the thickness, increases with decreasing temperature.

The onset of the anisotropy occurs at about the correct thickness. The experimental onset occurs at¹ about 4000 Å, while the theoretical occurs about 3000 Å. However, this thickness can be expected to be pushed somewhat higher by the more complex paths, which must be important in the transition, but which are not considered here.

The quantitative agreement is reasonable, and is shown in Table I where we compare the experimental and the theoretical values of $T_0/(T_0)_{\text{perc}} \cdot T_0^{-1/4}$, as defined in Ref. 1, is the tangent of the plot of $\ln \rho$ versus $T^{-1/4}$ at $T \approx 150$ K. $(T_0)_{\text{perc}}$ is the value of T_0 for bulk.

In Fig. 4 we plot the experimental results for *a*-Si. These are qualitatively similar to those of *a*-Ge. Since the quantities *a* and ν are, so far, unknown for *a*-Si, a comparison with theory is not possible. From the fact that the onset of the anisotropy occurs in *a*-Si at smaller thickness, we would conclude that either the value of *a* is smaller than in *a*-Ge, or the value of ν larger, or both.

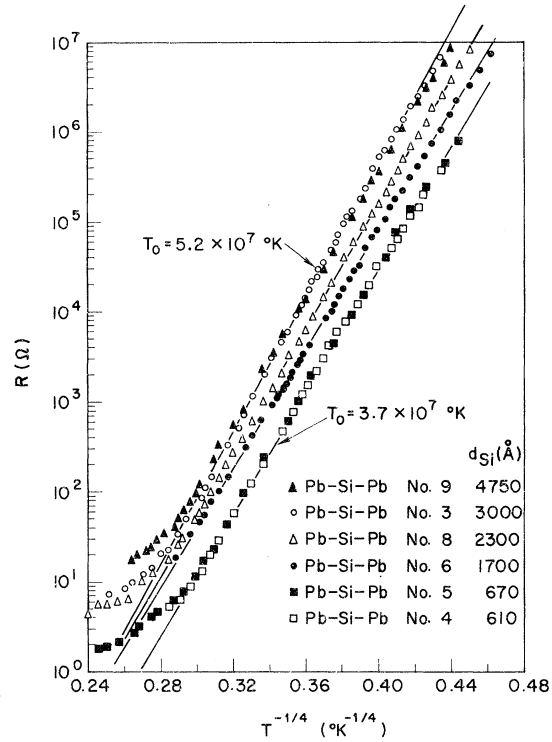


FIG. 4. Experimental dependence of resistance on film thickness and temperature for *a*-Si.

It is appropriate to summarize the approximations implicit in our simple theory: (1) Replacing the conductance by the maximum value of $P_N(Z)/Z$ constitutes an approximation. (2) A unique value of *N* for a given thickness has been assumed, while in fact there must be a distribution of *N* for any given thickness. (3) Paths which

TABLE I. A comparison between the theoretical and the experimental values of $T_0/(T_0)_{\text{perc}}$ for *a*-Ge. $T_0^{-1/4}$ is the slope of the plot of $\ln \rho$ versus $T^{-1/4}$ at ~ 150 K; $(T_0)_{\text{perc}}$ is the value of T_0 for thick films.

<i>d</i> (Å)	$T_0/(T_0)_{\text{perc}}$	
	Experiment	Theory
3720	0.60	
3570	0.58	
2000		0.61
1770	0.51	
1000		0.41
900	0.41	
500		0.25
450	0.36	
420	0.33	
250		0.16
240	0.32 to 0.11	

include other than the smallest impedance steps must contribute to the conductivity, particularly at thicknesses approaching the percolation limit. (4) The assumption of the directional constraint to the forward hemisphere, while justified in some detail by MA, is not exact.

The uncertainties in the experimental results are discussed in Ref. 1.

Considering the above approximations and uncertainties, we feel that the comparison between our experiments and our simple theory support the interpretation of the anisotropy in terms of a transition from percolation paths to MA paths at small thicknesses.

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⁵Actually, in the MA theory, a few steps are allowed in the backward direction, but this has no appreciable effect on the discussion which follows.

⁶This result includes the correlation between adjacent impedances discussed in Ref. 2.

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Point-Charge-Cluster Calculation of Adsorbate Ionization Energies for "Ionic" Metal-Adsorbate Systems*

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Adsorbate ionization energies (energy levels) have been calculated for a number of metal-adsorbate systems that have been studied recently by ultraviolet photoelectron spectroscopy. The method, which is only applicable to highly "ionic" metal-adsorbate systems, is based on a point-charge-cluster approximation to the metal-adsorbate system. Values of the adsorbate ionization energies calculated by this method agree with experiment within at least 10% for the metal-adsorbate systems investigated.

Measurements of the energy levels of various gases adsorbed on metal surfaces by electron spectroscopy have appeared in the literature within the last two years or so.¹⁻⁶ There are at present, however, no quantitative theoretical calculations available that provide values for the observed electronic energy levels.

In this Letter we describe a calculation of adsorbate electronic energy levels for a very special class of adsorbate-substrate systems: those for which the adsorbate-substrate interaction is strongly ionic. We believe this to be the first quantitative calculation of adsorbate energy levels with no adjustable parameters. The method employs an appropriate point-charge cluster to approximate the "ionic" adsorbate-substrate system.

The goal of this work was to find a *simple* method of calculating the electron ionization energies of adsorbates. To this end we have at-

tempted to obtain a good estimate without resorting to detailed calculations with a number of adjustable parameters. In the formalism to be presented, terms in the energy equation have been separated so that parameters with known values, e.g., electron affinities, work functions, etc., can be used; terms which are very difficult to calculate are grouped so as to minimize their sum.

Metal-adsorbate systems to which this calculation can be applied are those which typically form highly ionic bulk compounds. The restriction of this method to these systems is due to the necessity of treating the adsorbate as a point-charge impurity so that overlap between the adsorbate anion wave function and the wave function of the surrounding metal can be neglected. The calculation described gives the energy position of this δ function with respect to the vacuum level, which is the electron ionization energy of the adsorbate