gy gap.

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Percolation Conductivity in W-Al_2O_3 Granular Metal Films

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The growth of W grains in sputtered W-Al_2O_3 films as a consequence of annealing results in a narrowing of the transition region from metallic to nonmetallic conductivity. The conductivity, σ, as a function of the volume fraction of the metal, x, exhibits a critical behavior given by $\sigma \sim (x - x_c)^p$, where the critical volume fraction of the metal $x_c = 0.47 \pm 0.05$ and the critical exponent $p = 1.9 \pm 0.2$. For $x < 0.47$ the temperature dependence of σ has the form $\ln\sigma \sim -1/\sqrt{T}$ which is characteristic of tunneling between isolated grains.

Granular metals (cermets) fall into the general category of metal-insulator mixtures in which the electrical conductivity is determined by percolation. The electrical properties of such mixtures are of general interest because of their application to problems of conductivity and metal-nonmetal transitions in disordered systems.[1,2] In this Letter we present results of the effect of grain size on the resistivity of granular metals in which the volume fraction of the metal, x, is varied over the range $0.1 < x \leq 1$. By cosputtering the metals W or Mo with the insulators Al_2O_3 or SiO_2, a very finely dispersed grain structure[3] results. With annealing, the size of the metal grains can be varied over a wide range. Unlike the case of Au and Ag cermets,[4,5] the W or Mo does not precipitate out with annealing but remains uniformly dispersed within the insulator.

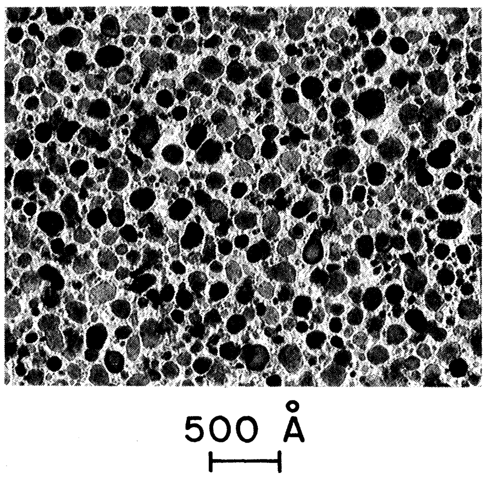

FIG. 1. Electron micrograph of W-Al_2O_3 film after annealing at 1020°K for 10 h. Film thickness is 200 Å; volume fraction of W is $x \simeq 0.53$.

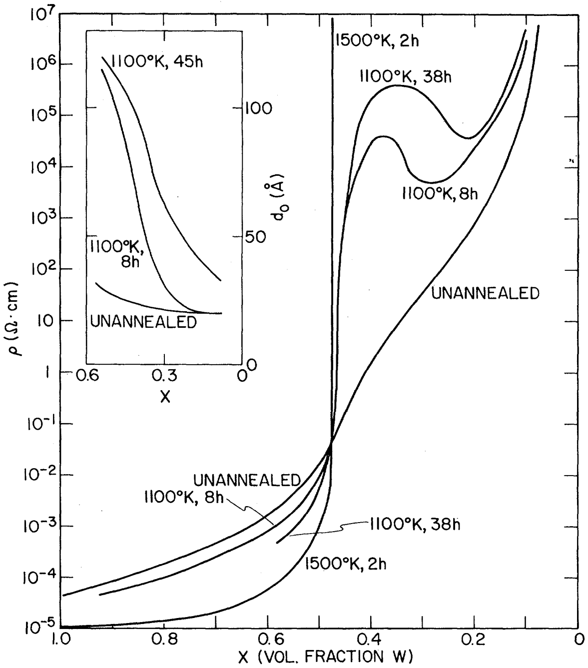

FIG. 2. Resistivity, ρ, of granular W-Al_2O_3 films as a function of volume fraction, x, of W. For the sake of clarity data points are left out and only smoothed curves are shown. The annealing time and temperature are indicated. The inset shows the average W grain size, determined by x-ray diffraction, as a function of x before and after annealing.

The films are of considerable theoretical interest because they allow us to test the validity of percolation-conductivity models.

The films, 0.7 μm thick, were sputtered from composite targets[4,5] of the metal and insulator onto water-cooled alumina (Alsimag 772) substrates, $5\frac{1}{2}$-in. long by $\frac{11}{16}$-in. wide. A continuous variation in composition was obtained along the length of the substrate in a single sputtering run. X-ray and electron microscopy showed that the films consist of crystalline metal grains and amorphous insulator. From chemical and density analysis, the insulator was identified as Al_2O_3 or SiO_2 and the volume fraction of the metal x was determined to an absolute accuracy of about ± 5% and to a relative accuracy of about ±0.5%. The annealing was done in flowing hydrogen gas at 1100–1500°K. Films for transmission electron microscopy were sputtered on copper substrates and lifted off by etching with dilute HNO_3. The annealing was done before the films were lifted off. In the unannealed films, the grains were less than 20 Å in size. A micrograph of an annealed W-Al_2O_3 film is shown in Fig. 1. The grains are rounded and have a wide distribution in sizes.

The resistivity, ρ, as a function of x at 300°K for the case of W-Al_2O_3, is shown in Fig. 2. Similar results were obtained for the other cermets. The three conduction regimes[4,5] of granular metals can be distinguished in Fig. 2: metallic ($x > 0.47$), transition ($x \simeq 0.47$), and dielectric ($x < 0.47$). Annealing affects each of the regimes differently. In the metallic regime the granular metal behaves like a dirty metal; the resistivity is relatively low and the temperature coefficient of resistivity (TCR) is positive. The conductivity is determined by scattering of electrons and by the geometric constraints on the current flow due to the meandering structure of the metal continuum; ρ decreases with annealing because grain growth results in reduced electron scattering and a shortening of the current paths. The resistive transition results from the breaking up of the metal continuum into isolated metal grains. The narrowing of the transition region and the large increase in ρ with annealing are due to the coalescence of touching W grains with the resultant breaking up of the continuous metallic paths. In the dielectric regime the conductivity results from the tunneling of electrons between isolated W grains; the resistivity is high and the TCR negative. The humps in the ρ versus x curves in Fig. 2 develop because the resistivity of the films in the vicinity of $x \simeq 0.47$ increases at a faster rate with annealing then it does for lower values of x. This variation of the rate of increase of ρ with x is attributed to the fact that near $x \simeq 0.47$ the grains are close to one another and therefore their rate of growth is faster then at lower values of x, where the grains are further apart from one another. That the rate of grain growth is a decreasing function of x is seen from the inset of Fig. 2. It is interesting to note that some annealing of the film may already take place while the film is sputtered, as evidenced by the upward curvature of $\rho(x)$ near $x \simeq 0.4$.

The sharp transition from metallic to insulating behavior in the films which were annealed at 1500°K enables us to study percolation threshold behavior in a real physical system. Heretofore most of the work in this field was restricted to computer experiments[2,6] and to idealized systems such as conducting paper prepared with holes,[7] a grid of carbon resistors,[8] and two-dimensional screens with sites removed.[9] According to the plot in Fig. 3, σ can be expressed in the form

$$\sigma \propto (x - x_c)^p, \tag{1}$$

where the critical volume fraction of the metal x_c is 0.47 ± 0.05 and the critical exponent p is 1.9 ± 0.2. Existing percolation theories for metal-insulator mixtures predict considerably lower values for x_c. Simple-cubic lattices yield[2] $x_c = 0.25$ for bond percolation and $x_c = 0.32$ for site percolation. The random-lattice percolation model predicts[6] $x_c = 0.3$; the effective-medium theory,[10] $x_c = 0.33$; and the Cayley-tree networks,[11] $x_c = 0.20-0.33$. The values predicted for p are 1.5–1.6 for the simple-cubic lattices,[2] 1 for the effective-medium theory, and 2 for the Cayley tree networks.[11] The measured value of p in the W-Al_2O_3 granular metals agrees with that of the Cayley-tree network. The large discrepancy between the experimental and theoretical values of x_c needs yet to be explained. Another problem, which we are working on now, is to expand the region near x_c in order to obtain a more accurate value for p.

In the dielectric region we find that the temperature dependence of ρ at low fields has the form $\rho = \rho_0 \exp(\alpha/\sqrt{T})$. This temperature dependence is characteristic of granular metals when transport is due to tunneling between isolated metal grains and when there is a distribution in charging energies[4,12] (energy required to generate a pair of positively and negatively charged grains). As can be seen from Fig. 4, annealing leaves α practically unchanged and the increase in resistivity is reflected as an increase in the preexponential factor ρ_0. The magnitude of α,

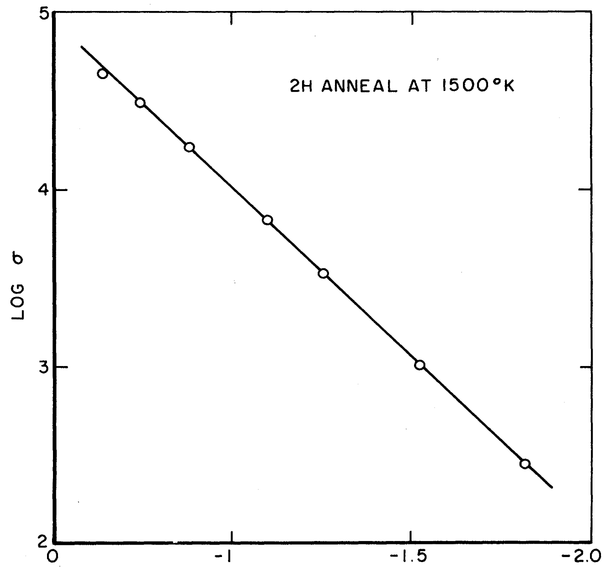

FIG. 3. lnρ versus ln$(x - x_c)$, with $x_c = 0.47$ for the annealed W-Al_2O_3 cermet measured at 300°K. The straight line represents Eq. (1) with $p = 1.9$.

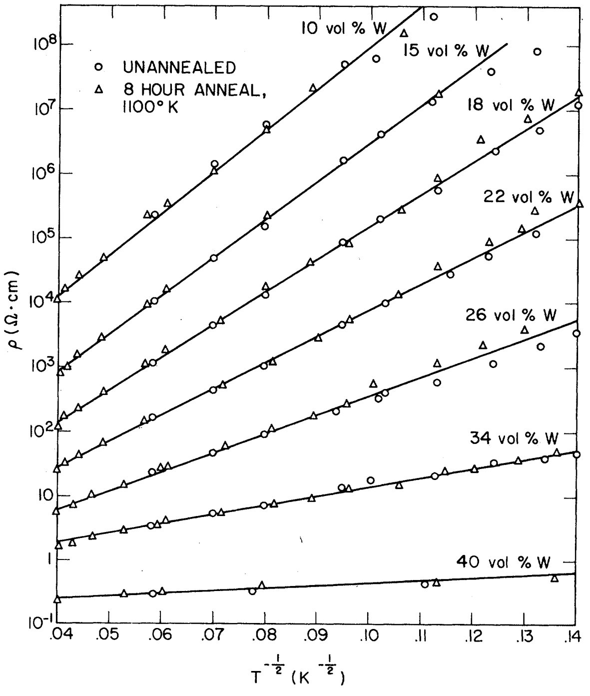

FIG. 4. lnρ versus $1/\sqrt{T}$ for several compositions of W-Al_2O_3, before and after annealing for 8 h at 1100°K. The resistivities of the annealed samples are normalized at 300°K to the resistivity value determined on the same sample before annealing.

its variation with x, and its invariance with grain size are in quantitative agreement with theory.[4] The increase in ρ_0 with annealing is attributed to a decrease in the number density of grains.

Finally we point out that certain device applications require stable, high-resistance films with a low temperature coefficient of resistivity. This combination of properties, unattainable in most materials, is readily achieved in our films for $x \simeq 0.47$.

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Mechanisms That Determine the Electronic Dielectric Constants of Ionic Crystals*

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The very old and widely accepted theory for the electronic dielectric constants of ionic crystals assumes that intra-ionic excitations dominate in the crystal whereby polarizabilities of individual ions may be identified and tabulated. It is shown here that this assumption is unfounded and leads to inconsistencies and unphysical results. In turn I present theoretical and experimental evidence that the mechanism determining the dielectric constants is in fact the extreme opposite, namely strictly interionic excitations, whereby the concept of polarizability of ions in solids is physically meaningless.

The classical picture of an ionic crystal is a collection of positive and negative ions held together by Coulomb forces. Long before the advent of quantum theory, expressions were obtained for the electronic dielectric constants ϵ_∞ of these crystals by taking the ions to be *independently* polarizable. This allows one to write the polarizability of the crystal as the sum of the polarizabilities of the ions, or, equivalently, the susceptibility χ as

$$\chi = N_+\alpha_+ + N_-\alpha_- , \tag{1}$$

where N_+ (N_-) and α_+ (α_-) are the density and polarizability of positive (negative) ions, respectively. The simplest expression for ϵ_∞ is

$$\epsilon_\infty = 1 + 4\pi\chi . \tag{2}$$

When "local fields" are included in the calculation of ϵ_∞, more complicated expressions arise,[1] the simplest of which is the Clausius-Mossotti form

$$(\epsilon_\infty - 1)/(\epsilon_\infty + 2) = \tfrac{4}{3}\pi\chi . \tag{3}$$

By using such expressions, many workers attempted to obtain empirical values for ionic polarizabilities. These attempts have continued until very recent times and by now several "polarizability tables" exist which are used in various problems.[2-4] The details of the approach may be found in most standard textbooks which treat ionic crystals.[5]

Quantum mechanically, the polarizability of a free atom or ion is of course determined by virtual excitations of the ground-state electrons to

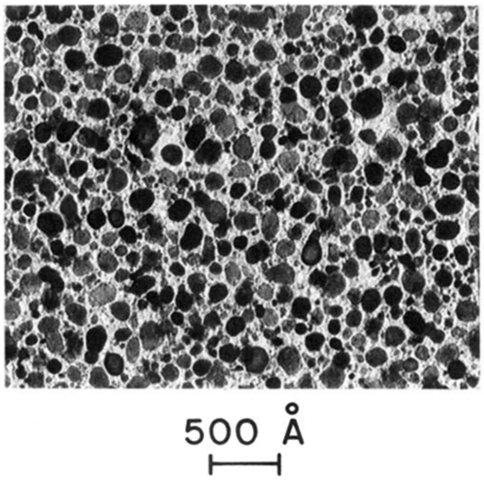

FIG. 1. Electron micrograph of W-Al_2O_3 film after annealing at 1020°K for 10 h. Film thickness is 200 Å; volume fraction of W is $x \simeq 0.53$.