Electrical resistance and the time-dependent oxidation of semicontinuous bismuth films

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We report on the electrical resistance and time-dependent oxidation of thin ($\lesssim 90$ Å) semicontinuous bismuth films. An increase in the room temperature sheet resistance with exposure to air is correlated with the growth of insulating Bi_2O_3 at the surfaces and internal boundaries between bismuth particles. For short oxidation times t, the resistance increases as $R_\square \propto t^{1/2}$, consistent with a parabolic oxide growth law. At longer times the resistance follows the classical percolation law $R_\square \propto |t_c - t|^{-\mu}$, where t_c is a critical exposure time and $\mu \simeq 1.3$ is a critical exponent for two-dimensional systems.

I. INTRODUCTION

The effect of surface oxidation on the electrical resistance of thin metal films is well established in the limits of continuous and discontinuous metal layers. For continuous films the dominant effect, with regard to transport, of a growing insulating oxide layer at the free surface is a reduction in the effective film thickness. If changes in the resistivity of the underlying metal are negligible the increase in resistance with time is then simply related to the oxide growth rate. In discontinuous films, conduction occurs via electron tunneling between isolated particles.[1] The increase in the resistance of such films with exposure to air or oxygen has been interpreted[2,3] as reflecting changes in the metal work function and/or effective particle separation due to the formation of an oxide layer on the particle surfaces. To our knowledge the oxidation resistance in the intermediate thickness regime of semicontinuous films has not been investigated in detail.

In this paper we examine the resistance versus exposure time of semicontinuous bismuth films oxidized at room temperature in air. These films are similar to those on which extensive low temperature transport measurements were performed in a study of localization and charging energy effects.[4,5] The film topology is characterized by transmission electron (TEM) and scanning tunneling (STM) microscopies. We use x-ray photoelectron spectroscopy (XPS) to correlate the resistance increase with the growth of insulating Bi_2O_3 at the granular Bi surfaces. In the early stages of exposure the sheet resistance increases as $R_\square \propto t^{1/2}$, suggesting a parabolic oxide growth law as typically observed in the oxidation of bulk metal[6] and homogeneous film[7,8] surfaces. At later times the resistance diverges rapidly and can be described by a classical percolation relation, $R_\square \propto |t_c - t|^{-\mu}$, where t_c is a critical oxidation time and $\mu \simeq 1.3$ is a critical exponent for two-dimensional systems.

II. EXPERIMENTAL TECHNIQUE

The films were prepared by room temperature evaporation of 99.9999% purity Bi onto glass substrates in an oxygen atmosphere of 50 mTorr. The evaporation rate was maintained at 0.5–1.5 Å/s as determined by a quartz crystal monitor. An aluminum mask defined a four-probe bridge pattern for electrical measurements, with a 10×0.85 mm^2 conduction channel. Following the Bi deposition, an ~250-Å-thick SiO protective layer was deposited over the conduction channel. This layer considerably reduces the oxidation rate and allows for measurements over extended periods in thinner films. The films had postdeposition sheet resistances of $R_\square \sim 1$ kΩ. TEM results indicate that films of nominal thickness $d \lesssim 80$ Å have a semicontinuous island structure as shown in Fig. 1(a) for a 62-Å film. The bismuth particles range in size from 100–1000 Å with nonpercolating voids [lightest regions in Fig. 1(a)] typically 50–100 Å wide. The electron diffraction pattern [Fig. 1(b)] indicates a preferential orientation of rhombohedral crystallites with their trigonal axes perpendicular to the substrate, typical of polycrystalline Bi films.[9] Figure 2 shows STM contour images of the surfaces of 65- and 88-Å films, both of which did not have SiO overlayers. Here we see a clear increase in the surface roughness of the thinner film, with frequent vertical variations comparable to the average thickness. This is consistent with the TEM observation of incomplete substrate coverage for $d \lesssim 80$ Å.

The photoemission data were recorded using a Perkin-Elmer Phi-5400 ESCA system operating at a pressure of $\sim 5 \times 10^{-9}$ Torr, and equipped with an argon-ion mill for depth profiling. The x-ray source was Mg$K\alpha$ radiation (1253.6 eV). The oxidation state of the film surface layer was assessed by scanning the energy region about the most intense Bi photoemission peaks, associated with the $4f_{5/2}$ and $4f_{7/2}$ core levels. These peaks occur in pure Bi as a doublet at binding energies[10] of 162.2 and 156.9 eV, respectively. This doublet is shifted to higher binding energy[11,12] in Bi_2O_3. Two pieces of the 65-Å film studied by STM were examined by XPS on separate occasions, corresponding to different exposure times. This film had a postdeposition $R_\square$ of ~750 Ω. Figure 3(a) shows a sequence of high-resolution XPS scans on this film, oxidized so that $R_\square \simeq 3.8$ kΩ. The uppermost scan shows the spectrum of the top surface. Subsequent scans were recorded following successive 1-min intervals of argon ion sputtering, corresponding to approximately 15–20 Å depth increments. The top surface shows strong Bi_2O_3

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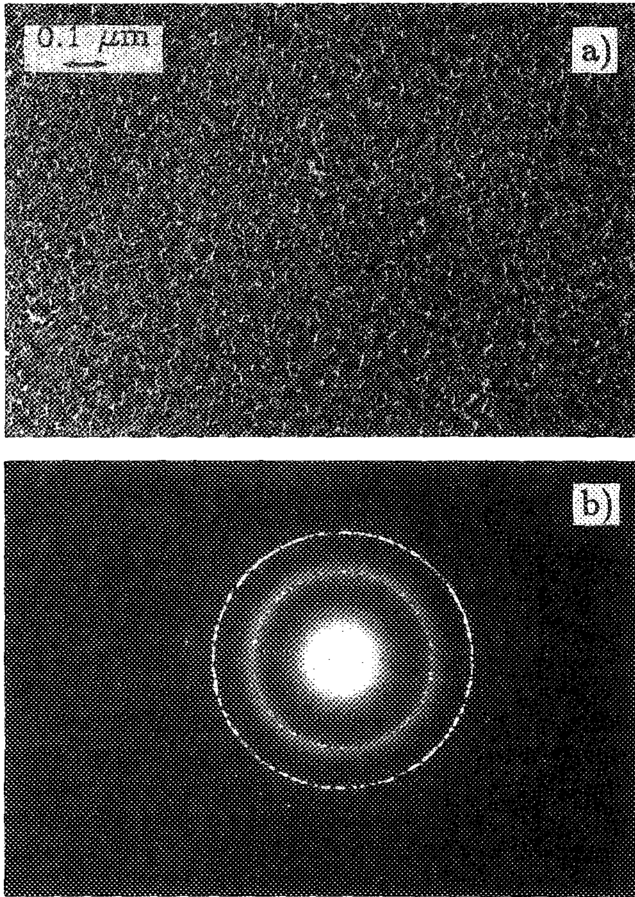

FIG. 1. (a) TEM micrograph of a nominally 62-Å Bi film and (b) electron diffraction pattern.

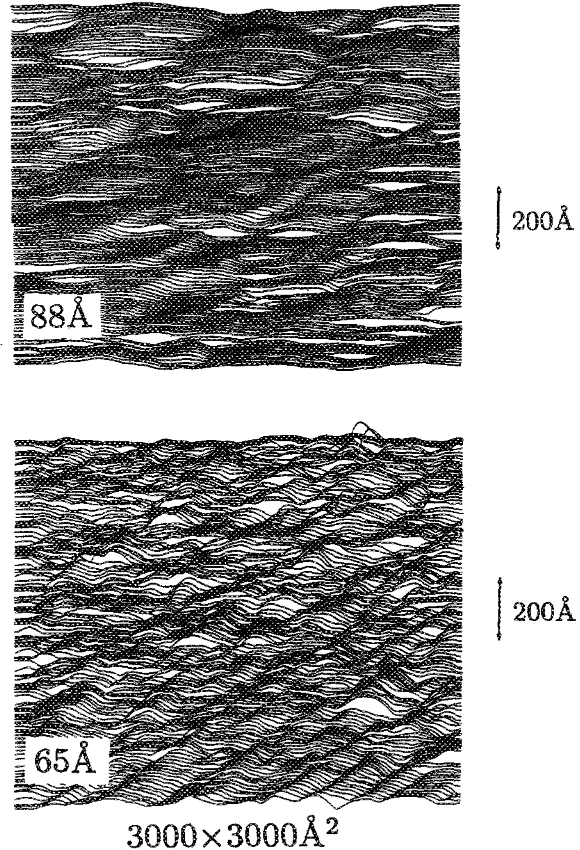

FIG. 2. STM contour images of the surfaces of 88- and 65-Å Bi films. For each film the scanned area is 3000×3000 Å^2 and the vertical scale is defined along a given horizontal trace.

peaks with substantially weaker peaks due to pure Bi, reflecting oxide formation on the unprotected surface layer. Below the top layer the pure Bi peak intensities increase and remain about half the magnitude of those of the oxide down to the substrate. After 3 and 4 min of milling the Bi $4f_{7/2}$ peak becomes partially obscured by a broad Si $2s$ line at a binding energy of ~ 154 eV, presumably associated with photoemission from the silicate glass substrate. Similar scans on a fully oxidized specimen ($R_{\Box} \gtrsim 200$ kΩ) are shown in Fig. 3(b). We see that the surface layer no longer shows the pure Bi peaks and that in the interior of the film these peaks are less prominent than those of Fig. 3(a). These results support a picture of relatively pure Bi particles surrounded by a growing oxide surface layer. This is in agreement with a previous photoemission study[11] which indicates the opening of a band gap of ~ 2 eV in the oxidized surface, consistent with Bi_2O_3 formation.

III. DISCUSSION

The increase in sheet resistance with exposure time is shown in Fig. 4 for 78- and 88-Å films. There are two prominent regimes of oxidation behavior evident in these data. Initially, the resistance increases approximately as $R_{\Box} \propto t^{1/2}$. This can be seen more clearly in the inset of Fig. 4 where the data for the 88-Å specimen have been reproduced on a linear scale. At longer exposure times, $R_{\Box}$ increases very rapidly to values exceeding 100 kΩ. In the crossover regime the resistance is well approximated by an exponential time dependence. These qualitative features hold for many similarly prepared films observed over sufficiently broad time intervals.

We may understand the early stage resistance growth to be a reflection of the parabolic growth law[13] for oxide thickness, $L_{ox} \propto t^{1/2}$. The behavior $R_{\Box} \propto t^{1/2}$ follows if the dominant effect of the initial surface oxidation is an effective reduction in the thickness of the film with little or no change in the resistivity of the underlying metal. We should expect this relation to become inadequate for sufficiently thin semicontinuous films where the geometry of "filamentary" current carrying paths may be sensitive to even the initial oxidation. In this regard we note that the $R_{\Box} \propto t^{1/2}$ regime appears most prominently in the data for the 88-Å specimen and was completely suppressed in a 55-Å film.[5] We may estimate the oxide thickness at the crossover between the $R_{\Box} \propto t^{1/2}$ and $R_{\Box} \propto \exp(t)$ regimes by assuming that the increases in $R_{\Box}$ up to this point are due to a uniform reduction in thickness from initial value d_0: $L_{ox}(t) = d_0[1 - R_{\Box}(0)/R_{\Box}(t)]$. The crossovers for the 78 and 88 Å occur at oxidation times of ~ 100 h and ~ 180 h, respectively, yielding $L_{ox} \sim 20$ and 26 Å. These values are in the range where, in a simplified model of metal oxidation,[14] the oxide growth becomes limited by electron tunnel currents through the oxide layer and a cross-

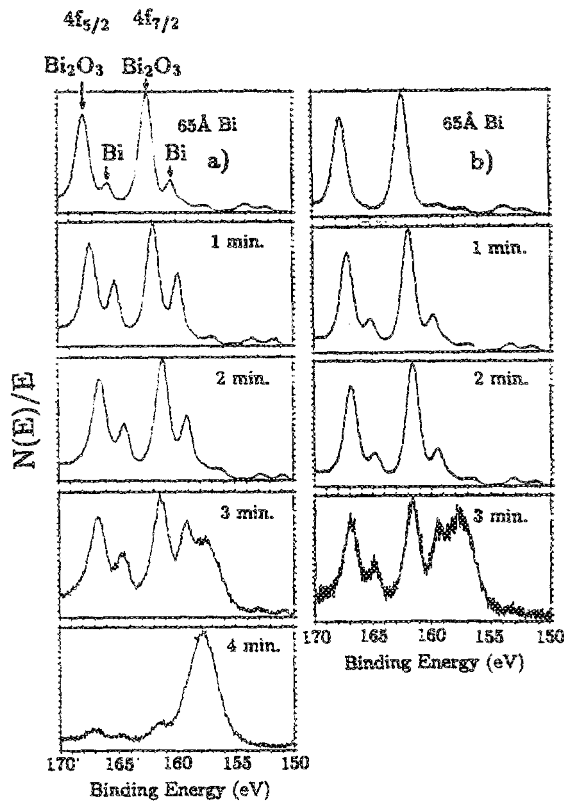

FIG. 3. High-resolution XPS scans of a 65-Å film showing the Bi and Bi_2O_3 $4f_{5/2}$ and $4f_{7/2}$ core levels: (a) when the film has $R_\square = 3.8$ kΩ and (b) after complete oxidation ($R_\square \to \infty$). The sequence of scans from top to bottom were taken following successive 1-min intervals of argon ion milling, corresponding to ablations of 15–20 Å. Note that charging effects have not been subtracted from the data, and hence the peak positions are shifted from their ideal values.

over to $L_{ox} \propto \ln(t)$ behavior is typically observed for bulk[6] and continuous thin-film[8] surfaces. It is not surprising that the rate of resistance increase for our films in this regime is faster than would be expected from a thickness reduction argument based on a logarithmic oxide growth rate. We know from the STM results that the thickness of the 88-Å film is not uniform over the surface, varying by as much as 40 Å. Thus the thinnest regions of the film, i.e, the narrow interparticle connections and grain boundaries, probably become insulating for oxide layers of 20–30 Å. These interparticle oxide barriers will begin to play a prominent role in determining the current-carrying network and hence the total measured resistance. Presumably the $R_\square \propto \exp(t)$ behavior signals that the geometric structure of the film is becoming important. We would expect this regime to be reached for shorter oxidation times in thinner films, and this trend is evident in the data.

The final stage of resistance growth is characterized by a rapidly increasing resistance, faster than exponential. We refer to this as the percolation regime. The relevant conducting portion of the film is the network of granular clusters that defines the current-carrying backbone. It seems likely that the distinction between the exponential and percolation regimes is not due to a difference in the oxidation rate, but rather to a difference in the sensitivity of the resistance to small changes in backbone geometry. According to percolation theory[15] the conductivity of a metal-insulator mixture with metal fraction p should vanish as $\sigma \propto |p - p_c|^\mu$, where p_c is the percolation threshold and μ is a dimensionality-dependent critical exponent expected to be ~ 1.3 in two dimensions. In this oxidation regime we expect there to be, at least in principle, a relation between oxidation time and the relevant variable p. Indeed the resistance increase in this region is "critical" in the sense that $R_\square$ appears to diverge at some finite value of t, which we denote t_c in analogy with the percolation threshold, p_c. Note that the time to reach threshold is reduced substantially when the nominal thickness is decreased from 88 to 78 Å. This is probably a consequence of the incomplete substrate coverage which, as mentioned above, occurs for $d \lesssim 80$ Å.

It has been shown,[16] for evaporated Au films measured *in situ*, that near the critical thickness d_c (the average thickness at which films become electrically continuous during growth) the relation $p - p_c \propto d - d_c$ is valid. This claim is based on indirect evidence and is justified by the fact that log-log plots of σ vs $d - d_c$ yield straight lines with slopes μ in good agreement with theory. More recently Octavio, Gutievrez, and Aponte[17] found similar justification for this relation in ion-milled Ag films. In the same spirit as these studies we propose the relation $p - p_c \propto t_c - t$. This leads us to try the expression $R_\square \propto |t_c - t|^{-\mu}$ to describe the exposure-time data. Values of t_c were found by adjusting t_c until log-log plots of $R_\square$ vs $t_c - t$ gave straight lines. The results for

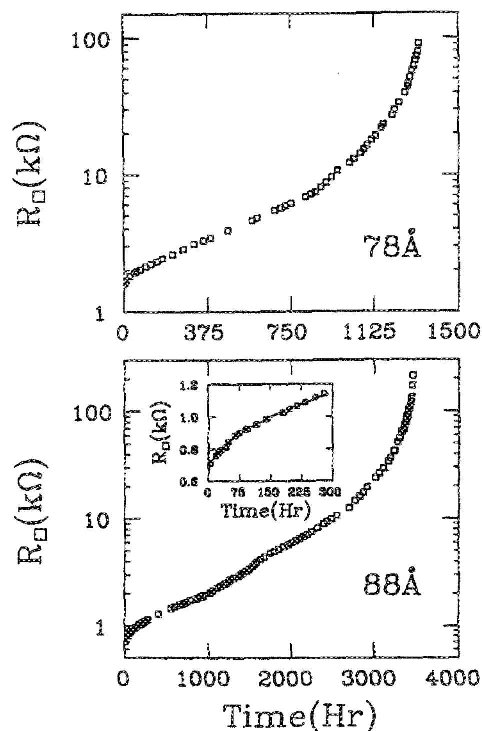

FIG. 4. Sheet resistance vs exposure time for 88- and 78-Å films oxidized in air at room temperature. The inset shows the data for the 88-Å specimen at early times, reproduced on a linear scale. The solid line is a fit to the form $R_\square = R_0 + At^{1/2}$.

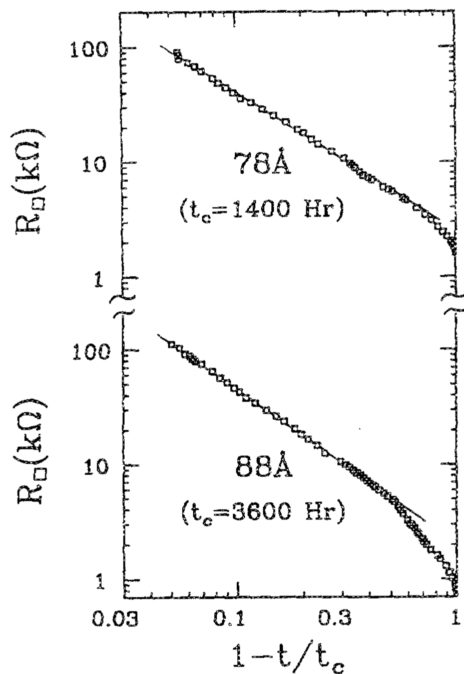

FIG. 5. Log-log plot of $R_\square$ vs relative distance from threshold $1-t/t_c$, for the 88- and 78-Å films.

the 78- and 88-Å films are shown in Fig. 5. The slopes yield $\mu = 1.20$ and 1.34, respectively, in good agreement with theory and the previous experiments.

It is particularly interesting that the onset of percolation behavior occurs consistently for sheet resistances exceeding 4–8 kΩ. We believe that this phenomenon is closely associated with the localization of electrons[18] to individual metal particles, a condition which should be obtained when the average oxide barrier resistance between particles exceeds $\sim \hbar/e^2 = 4.1$ kΩ. A related issue is the onset of a finite charging energy for electron tunneling between particles.[19] We are currently investigating the oxidation behavior of thin films composed of other metals to determine if this behavior is universal.

IV. CONCLUSIONS

In summary, we have presented the results of structural and electrical resistance measurements in a study of the time-dependent oxidation of semicontinuous Bi films. We find that for early stages of oxide growth the resistance increase is consistent with a parabolic oxide growth law. The principal result is that for longer oxidation times the geometric structure of the current-carrying portion of the film becomes sensitive to the continued growth of oxide, apparently defining a classical percolation problem. We find that the onset of two-dimensional percolation behavior occurs for sheet resistances $R_\square \gtrsim 4-8$ kΩ, suggesting that the localization of electrons to individual Bi particles by oxide barriers may be relevant.

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