Anomalous electrical conductivity of a gold thin film percolation system

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A gold thin film percolation system, deposited on a glass surface by the vapor deposition method, has been fabricated. By using the expansive and mobile properties of the silicone oil drop, a characteristic wedge-shaped film system with a slope of $\sim 10^{-5}$ naturally forms during deposition. The electrical conductivity of the bandlike film, i.e., the uniform part of the wedge-shaped film with a fixed thickness, is measured with the four-probe method. It is found that the hopping and tunneling effects of the films are stronger than those of the other films. The dependence between the dc sheet resistance R_0 and temperature T shows that the samples exhibit a negative coefficient dR_0/dT below the temperature T^*. According to our experiment, it is suggested that all the anomalous behaviors of the system should be related to the characteristic microstructure of the samples, which results from the immediate quench processes by the oil drop during deposition. The experiment indicates that the relaxation period of the microstructure of the samples may be longer than 30 min.

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I. INTRODUCTION

The microstructure of thin films plays a crucial role in a wide variety of physical processes. There is clear evidence that many physical properties of a thin film vary dramatically as its microstructure changes.[1] For instance, rough substrates can be used to fabricate a bilateral rough film system with a specific surface morphology, and its electrical transport properties are much different from those of the flat system. In other words, deviations of thin film surfaces/interfaces from flatness have a strong influence on their electrical transport properties, since they induce additional electronic scattering.[2–4] In addition, growth methods also strongly influence the conductivity of the films.[5] Therefore, it is expected that the microstructure of films can be well controlled or designed in more efficient ways so that the films can exhibit desirable properties.

The microgeometry of a percolation film can be considered as a random resistance network with total sheet resistance R, carrying a current I, made up of elements of resistance R_α carrying current i_α. Theoretical analysis on the random resistor network (RRN) model has yielded the relation[6–8]

$$B = R_0^{2+w}, \tag{1}$$

where R_0 is the zero-power sheet resistance, w is a critical exponent, and B is the normalized third-harmonic coefficient, which is related directly to the resistance fluctuation. The coefficient B_0, which equals the value of B when the frequency of the current, i.e., ω, approaches zero, is obtained from the dc $R-I$ relation

$$R = R_0 + B_0 I^2. \tag{2}$$

It should be noted that the quadratic $R-I$ behavior in Eq. (2) is interpreted in terms of the rise in the temperature of the hot spots (or links) in films due to the local Joule heating while the microstructure of the percolation film remains unchanged in this process.

It has been proved that, if $\omega \to 0$, the value of B obtained by ac measurement will approach the dc value B_0 and, furthermore, that the critical exponent w is independent of the frequency ω although the coefficient B depend on the frequency.[8,9] Therefore, using Eq. (2) to measure the critical exponent w is an ideal method for its simplicity and accuracy.

According to the RRN model,[6,7] above the percolation threshold p_c, the power-law relation between the breakdown current I_c and R_0, is

$$I_c \propto R_0^{-\gamma}. \tag{3}$$

Since the critical exponent γ of the rough systems is significantly distinct from those of the systems deposited on flat substrates, γ is generally considered to be nonuniversal, and in fact has not been predicated theoretically so far.[6,7]

In this paper, we report the preparation and measurements of the nonlinear $R-I$ behavior of a metallic film percolation system deposited on glass surfaces by using the expansive and mobile characteristics of silicon oil drops. It is observed that hopping and tunneling effects in the films are much stronger than that of the other film systems. The dependence between the sheet resistance R_0 and temperature T is measured and an evident crossover of dR_0/dT at zero magnetic filed is observed experimentally.

II. EXPERIMENT

The samples used in this study were prepared by thermal evaporation of 99.999% pure gold at pressure of 5×10^{-4} Pa. A drop of pure silicone oil (Dow Corning 705 Diffusion Pump Fluid with a vapor pressure below 10^{-8} Pa at room temperature) with a diameter $\phi = 2$–4 mm was dripped on a piece of glass. The oil drop here was used to quench the gold film deposited on the glass surface during deposition (for details see the following description). The substrate, i.e., the piece of glass, was levelly fixed 200 mm above the evaporating filament (tungsten). The deposition rate f and the nominal film thickness d were controlled by a quartz-crystal thickness monitor which was located just beside the substrate. The deposition rate f for all samples was 0.01 nm/s. The most interesting phenomenon in our experiment is that the radius of the oil drop expanded steadily

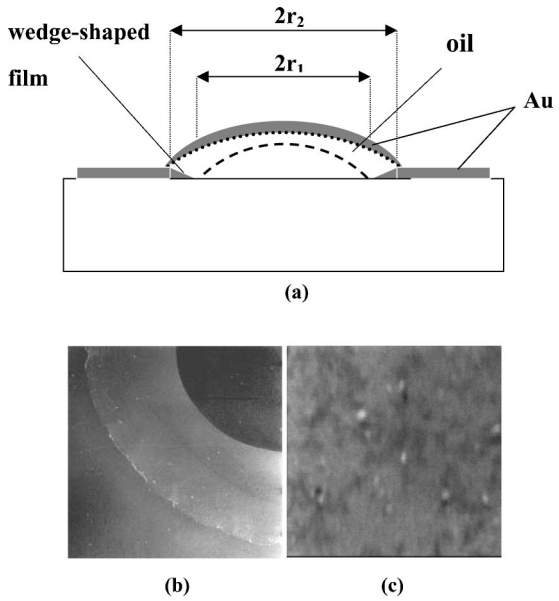

FIG. 1. (a) Schematic view of the gold films deposited on the glass and oil surfaces. The shaped parts are the Au films. The dashed and dotted curves denote the outlines of the oil drop before and after deposition, respectively. (b) Photograph of the ring-shaped film on a glass surface (2.0×2.0 cm^2). (c) SEM image taken at the central area of the ring-shaped film. (2.0×2.0 μm^2).

mainly due to the heating of the filament and the bombardment of the deposition atoms, which is the key characteristic of the liquid drop used for our samples (see the details below). After deposition, the sample was removed from the vacuum chamber. With the four-probe method, the temperature dependence of R_0 was then measured and the dc sheet resistance R of the samples as a function of the dc current I was measured at room temperature. The effective size of all samples is 1.5×0.5 mm^2.

III. RESULTS AND DISCUSSION

After the samples were ready, the oil drops on the glass surfaces as well as the gold films on the oil surfaces were cleaned with acetone. The schematic view of the gold film deposited on the glass surface is shown in Fig. 1. For each sample, there is a ring-shaped film on the glass surface: the inner and outer circles of the ring-shaped film are the marks of the oil drop before and after the deposition, respectively. Obviously, there is no film in the area of the inner circle, since it was always covered with the oil during the deposition. The thickness of the gold film in the area outside the ring-shaped film should equal the nominal thickness d detected by the quartz-crystal thickness monitor since it was always uncovered. With an optic microscope, we found that the thickness of the ring-shaped gold film on the glass surface increases linearly from the inner radius r_1 to the outer radius r_2 of the ring-shaped film approximately, indicating that the oil drop expands and its radius r increases uniformly during the deposition. Consequently the slope of the ring-shaped film (or the wedge-shaped film) can be determined as $\theta=d/(r_2-r_1)$. The slope θ of our samples is of the order of $\sim10^{-5}$ rad.

During the deposition, our thermocouple detected the accumulated temperature increment on the glass surface was around 0.5 K, and changed with the filament temperature and the deposition time. Therefore, we believe that the expansive phenomenon of the oil drop is mainly resulted from the local temperature rise of the oil drop surface during deposition because of both the thermal radiation from the filament and the strike by the deposited gold atoms.

According to the experimental observation above, we therefore propose that, during the deposition, when the oil drop has been covered with several layers of gold atoms, the volume of the oil drop increases and its surface tension decreases due to the local temperature rise. Then the radius r increases and the expanding oil breaks the connection between the gold film on the oil surface and the gold film on the glass surface. Therefore, the gold atomic layer on the glass surface and near the oil drop will be covered gradually with the oil. This process repeats during the deposition and finally a metallic wedge-shaped (ring-shaped) film forms, as shown in Fig. 1. After the gold atomic layer is covered with oil during the deposition, the kinetic energy of the gold atoms will be dissipated and the oil molecules will block the thermal diffusion of the gold atoms as well. Thus, due to such a quick quenching process, a huge number of defects and a characteristic percolation structure form naturally in the gold film. If the qualitative growth model described above is correct, a characteristic microstructure of the sample is expected and therefore the dc conductivity behavior of the samples should be quite different from those of the other film systems.

Figure 1(c) presents the typical scanning electron microscope (SEM) image for the ring-shaped film. One finds that no obvious crystalline structure is observed in Fig. 1(c) at this length scale, and the ring-shaped film exhibits an characteristic structure. The structure shown in Fig. 1(c) should be resulted from the quick quenching process (see the description above) since the gold film outside the ring-shaped film exhibits a very smooth surface morphology at the same length scale.

In order to measure the $R-I$ behavior of the sample, the ring-shaped film on a glass surface was carefully carved and shaped with a small knife along the circumference of the ring-shaped film so that bandlike films of width b were obtained, as shown in Fig. 2. Our samples were carved from the wedge-shaped (ring-shaped) film with $\theta=10^{-5}$ rad, $d=20$ nm, and $\Delta r=r_2-r_1=10.0$ mm. Since the thickness of the gold film on the glass surface increases linearly from the inner radius to the outer radius, the thickness of the bandlike film can be determined as $d'\approx[d/(r_2-r_1)]\times(r-r_1)$. In other words, the thickness of the bandlike film can be selected by choosing the areas at different radii in the ring-shaped film. In our experiment, the width of the bandlike film was very narrow (~0.5 mm), the maximum relative thickness difference, i.e., $\Delta d'/d'$, in different regions of each bandlike film in Fig. 3 was less than 10%. In this sense, each band-like film can be viewed as homogenous film approximately because of small thickness fluctuation.

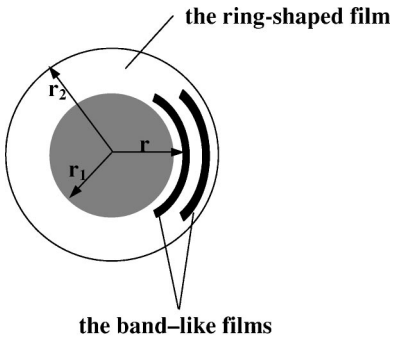

FIG. 2. Schematic view of the bandlike film carved from the ring-shaped film.

The dc current dependence of the resistance of the bandlike gold film is plotted in Fig. 3. By varying applied current I from 0 to 30 mA, it can be seen in Fig. 3 that the sheet resistance increases gradually with current at low current intensity and the value of the slope, i.e., dR/dI is positive. This $R-I$ behavior can be well fitted by the quadratic relation [Eq. (2)]. When I equals the crossover current I_m, however, R reaches its maximum value and then starts to drop quickly with the current, which is quite different from those of the other film systems.[6–11] On the other hand, in Fig. 3, both R and dR/dI behaviors remain almost unchanged after the first measurement and furthermore there is approximately no remark difference between the result measured in air and that in vacuum condition. Therefore, the $R-I$ behavior in Fig. 3 is almost reversible and it should be related to the microstructure of the film.

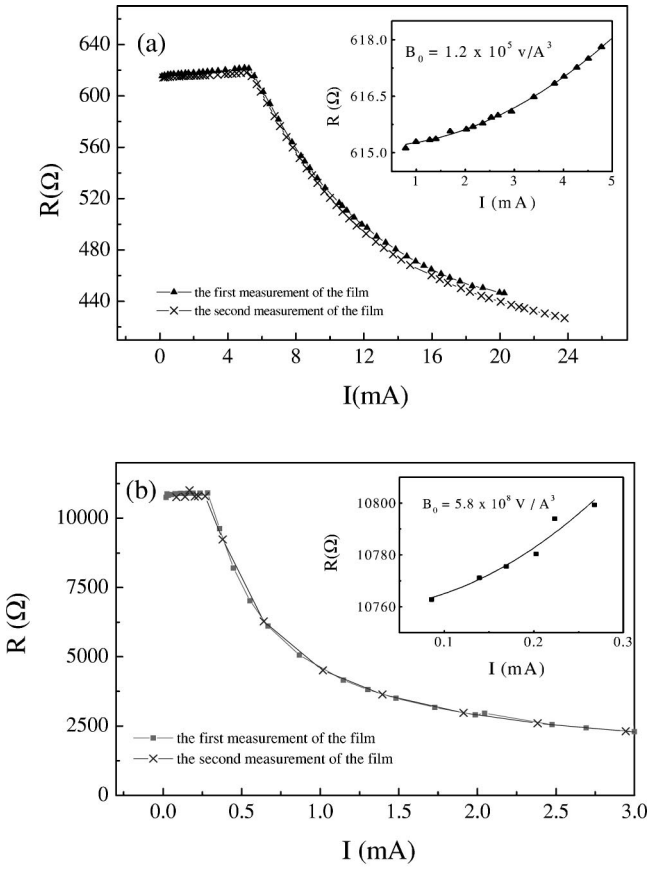

FIG. 3. $R-I$ characteristics of the bandlike gold film. The two insets show the $I-R$ characteristics of the bandlike film when $I<I_m$: up triangles and squares are the experimental data and the solid lines represent the fit $R=R_0+B_0I^2$. (a) $d'=9.0\pm1.0$ nm, $B_0=1.2\times10^5$ V/A^3. (b) $d'=4.0\pm1.0$ nm, $B_0=5.8\times10^8$ V/A^3.

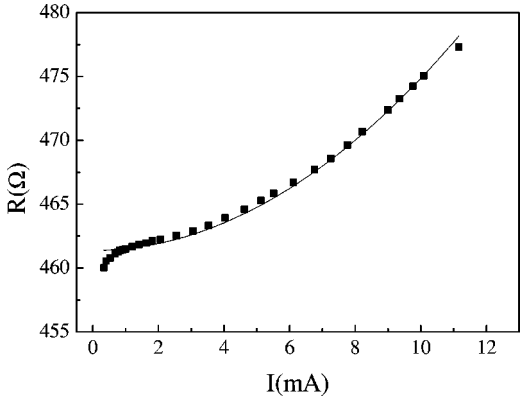

FIG. 4. dc current I vs the resistance R of bandlike gold film deposited on a glass surface, $d'=15.0$ nm. Squares are the experimental data and the solid line represents the fit $R=R_0+B_0I^2$, $B_0=1.1\times10^5$ V/A^3.

In viewing this, we propose that the nonlinear $R-I$ behaviors illustrated in Fig. 3 mainly resulted from the characteristic microstructure of the films since other film systems do not exhibit such behaviors.[6–11] Because of the immediate quench process of the oil drop, a huge number of defects and a characteristic percolation structure would exist in the film. Therefore, many weak links, just as various metal-insulator-metal (MIM) tunneling junctions, are constructed in the band-like film. When a high current passes through a weak link, the local temperature change is sufficient to excite local hopping and breakdown of the MIM tunneling junction. Both the hopping and tunnelling effects would reduce the current density in the link and therefore the sheet resistance. The higher the current is, the more the amount of the resistance will be reduced. In this sense we ascribe the phenomenon of $dR/dI<0$ mainly to hopping and tunneling effects.[6]

We note that the crossover current I_m in Fig. 3(a) is larger than that in Fig. 3(b). The present experiment showed that, as the thickness $d'\rightarrow d$, the current I_m increases rapidly and the film exhibits the quadratic $R-I$ behavior in a very large current range (see Fig. 4), which is similar to the phenomenon observed in other systems.[6–11] Obviously, as the thickness of the bandlike gold film increases, more gold atoms can be deposited on the glass surface before the atomic layer is covered with the oil drop. Thus the influence on the properties of the bandlike films by the immediate quench process should be reduced as the film thickness increases and the nature of the thick bandlike films should be similar to those of the normal films on glass surfaces. Therefore the $R-I$ behavior of the bandlike film near the edge of the ring-shaped film should be close to that of the normal gold films deposited on glass surfaces.

A power law of w provides a further evidence that the local hopping and tunneling effects relate to the microstruc-

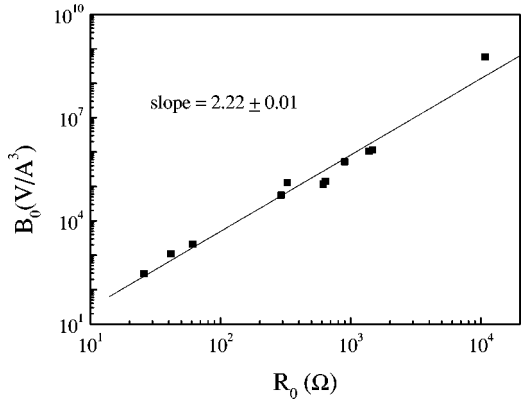

FIG. 5. Scaling of B_0 as a function of the bandlike film resistance R_0.

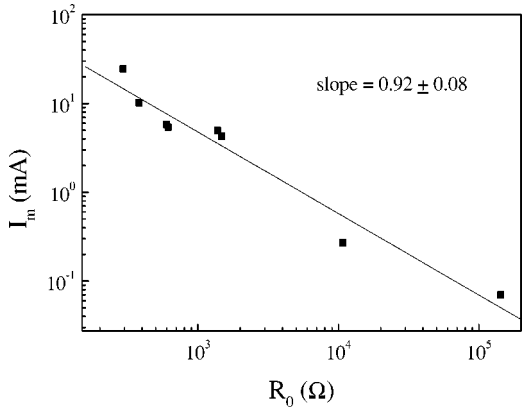

FIG. 6. Scaling of I_m as a function of the bandlike film resistance R_0.

ture of the films. It has been proved that the critical exponent w is nonuniversal and closely related to the microstructure of the system.[8] Fitting the experimental data in Fig. 3(a) by Eq. (2) for $I<I_m$, one finds $B_0=1.2\times10^5$ (V/A^3). By using this method, the coefficient B_0 of different samples with different sheet resistances are obtained and the scaling law of B_0 as a function of the sheet resistance R_0 is shown in Fig. 5. According to Eq. (1), the value of critical exponent w is determined to be 0.22 ± 0.01, which is much smaller than those of the other film systems and the theoretical predictions in two-dimensional system.[8,12–16] We propose that the lower critical exponent w may be resulted from the local hopping and tunnelling effects of the bandlike films. As motioned above, both the hopping and tunnelling effects would reduce the current density in the various links and then the sheet resistance. The higher the current is, the more the amount of the resistance will be reduced, which causes a weaker third-harmonic coefficient B_0 [see Eq. (2)], and hence the critical exponent w becomes smaller. According to this analysis, the experimental phenomenon shown in Fig. 5 indicates that the hopping and tunnelling effects in the bandlike films are much stronger than those of the flat films. This conclusion is reasonable since the weak links (or tunneling junctions) in the bandlike films are much more plentiful than that in the normal flat systems due to the immediate quench process.

It is difficult to obtain the power-law relation between the breakdown current I_c (Refs. 6 and 7) and the sheet resistance R_0 of the samples from the curve of $I-R$ because the sheet resistance has been reduced due to the anomalous hopping and tunnelling effects for $I<I_c$. However, the R_0-I_m behavior of the bandlike gold films can be measured in experiment and plotted in Fig. 6. A power-law behavior

$$I_m \propto R_0^{-\alpha} \tag{4}$$

is observed, and the deduced exponent α for the bandlike film is about 0.92 ± 0.08, which is quite different from the exponent γ.[6,7] This result indicates that the I_c is not related to I_m intrinsically. In fact, I_m is the current when the resistance R reaches its maximum value, which is the crossover from the local Joule heating effect to hoping and tunneling effects, and I_c is the breakdown current. In the vicinity of I_m, the increment of the resistance due to the Joule heating effect is equal to the decrement of the resistance due to the hopping and tunneling effects, i.e., those two effects compensate for one another. We believe that the crossover current I_m on the $R-I$ curve should depend on the microstructure of the system and the exponent α is nonuniversal. The small exponents w and α can be viewed as evidence of the existence of a considerable amount of characteristic defects in the bandlike film, resulting from such a special deposition process.

The temperature dependence of the resistance of the bandlike gold films is plotted in Fig. 7. At high temperature, the resistance decreases monotonically as the temperature decreases, and R can be well described by positive linear coefficient. For temperatures just below the temperature T^*, the sample resistance exhibits a nonmonotonic behavior: the resistance slowly increases with the decreasing of the temperature, and dR_0/dT becomes negative. The resistance R_0 was found to obey the Arrhenius law

$$R_0(T)=R_0'\exp(-\beta T), \tag{5}$$

where the prefactor R_0' is expected to be temperature independent. On the other hand, the temperature dependence of the resistance R_0 of the sample is approximately unchanged as the temperature various direction changes during the measurement. It is noted that similar experimental phenomena was observed in a previous electrical transport measurement on single-wall carbon nanotubes.[17] Therefore, we believe that the unusual R_0-T behavior are related to the microstructure of the films.

The experimental result presented above is really unexpected. The experimental results suggest that the proximity of the metal-insulator transition is due to the presence of localized states at the Fermi level E_F. However, until now the question of the origin of such localized states, whether they are due to the long-range quasiperiodicity or to the local structural environment or to some kind of structural disorder, has not been fully answered yet.[18] A detailed study on this topic is beyond the scope of this paper. However, we believe that the characteristic R_0-T behavior described in Fig. 7 might result mainly from the characteristic microstructure of the samples, since the immediate quenching process may re-

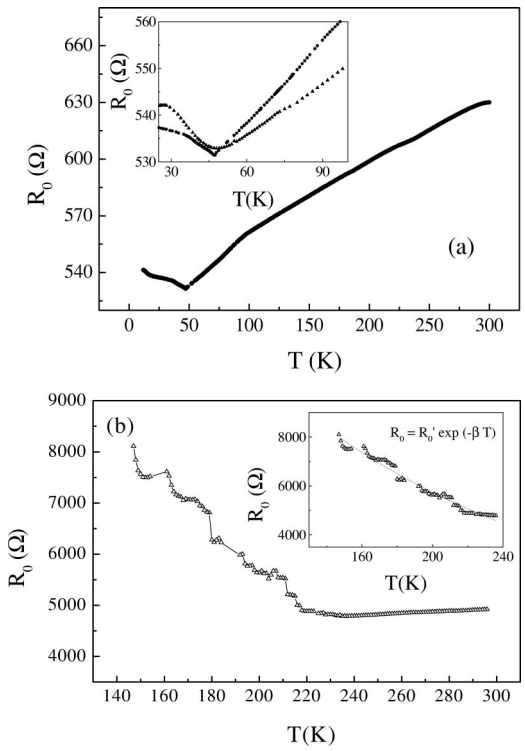

FIG. 7. Temperature dependence of the dc sheet resistance of the bandlike gold films, at the measurement current $I=30$ mA. (a) $d'=9.0\pm1.0$ nm. The inset shows the R_0-T characteristic of the bandlike film when $T<100$ K. Dots are the experimental data measured as the temperature decreases and the up triangles are the experimental data measured as the temperature increases. (b) $d'=4.0\pm1.0$ nm. The inset shows the R_0-T characteristic of the bandlike film when $T<T^*$. Up triangles are the experimental data, and the solid line represents the fit $R_0=R_0'\exp(-\beta T)$.

sult in a huge number of defects in the samples and therefore the film would exhibit a characteristic percolation structure for the suitable film thicknesses d'.

Figure 8 shows the dependence between the crossover temperature T^* and the resistance R_0 of the bandlike films. One finds that T^* is strongly dependent on R_0, i.e., T^* increases with R_0. At the moment, a consistent theory for this phenomenon is still lacking. However, we propose here that the phenomena should be related to the characteristic defects and disorders in the films, which are strongly dependent on the film thickness d'. The thinner the film thickness is, the more amount of the defects will be exist in the film. For thick bandlike gold films, more gold atoms can be deposited on the glass surface before it is covered with the oil drop. Thus if the thickness of the bandlike film is great enough, the influence on the properties of the sample by the immediate

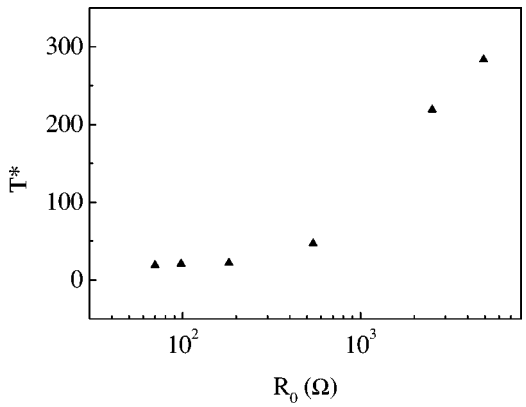

FIG. 8. Crossover temperature T^* vs the dc sheet resistance R_0 of bandlike films deposited on glass surfaces.

quench process should be very small so that it could not be detected in our experiment. Therefore, for the thick bandlike films, all the physical properties should be similar to those of the other films deposited on glass surfaces and T^* approaches zero, as shown in Fig. 8. Considering the small deposition rate and the film thickness of the samples, Fig. 8 implies that the relaxation period of the microstructure of the film may be longer than 30 min.

IV. CONCLUSION

In summary, we have fabricated a wedge-shaped gold thin film system with a slope of $\sim10^{-5}$ and a characteristic percolation structure by a vapor deposition method. The immediate quench process by the oil drop is the main reason which results in the characteristic microstructure. The $I-R$ characteristics of the bandlike films have been studied. Both the anomalous $R-I$ behavior and the small exponents w and α indicate that the bandlike films contain a huge number of characteristic defects due to the special deposition process. A crossover of the coefficient dR_0/dT is observed from R_0-T measurements for the bandlike films. The crossover temperature T^* is found to be dependent on the film resistance. It is proposed that those anomalous behaviors should be closely related to the quench process by the oil drop during deposition. Furthermore, it is proved that the relaxation period of the microstructure of the samples may be longer than 30 min.

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