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Structural and electrical properties of a metallic rough-thin-film system deposited on liquid substrates

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A rough-thin-film system, deposited on silicone oil drop surfaces by a rf-magnetron sputtering method, has been fabricated and its structure as well as I-V characteristics have been studied. A characteristic surface morphology at the micrometer scale is observed. The anomalous deposition rate, which strongly depends on the nominal film thickness, can be interpreted under the assumption of the second evaporating and the penetrating effects. We find $I_c \propto R_0^{-\alpha}$, with $\alpha = 0.52 \pm 0.06$, where R_0 and I_c are the zero power resistance and the breakdown current, respectively. The importance of the liquid substrates is discussed.

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Metallic thin films can be produced in two different forms, flat and rough film systems, which differ in both their structural and their electrical properties.[1–7] The nature of the substrates as well as the deposition method play a significant role in the microstructure and physical properties of the thin-film systems.[6,8] Therefore, considerable effort has recently been expended on investigating the conditions for creating particular microstructures and studying the anomalous physical phenomena.[4–8]

Metallic rough thin films, in which only the up surfaces are roughened, are usually produced by the ion bombardment method, nonequilibrium growth technique, and location-dependent deposition rate method.[7,9,10] By using rough substrates, the bilateral rough films can be fabricated.[6] The experimental results indicate that the crystallinity and surface morphology of the rough films are usually much different from those of the flat systems.[6–8,11] For rough thin films with lower resistivity, the sheet resistance R and the current I satisfy

$$R = R_0 + B_0 I^2, \tag{1}$$

where R_0 and B_0 are the zero-power resistance and the dc third-harmonic coefficient, respectively.[12] This quadratic R-I behavior, which is similar to that of the percolation films deposited on flat substrates,[11,12] is generally interpreted in terms of heating and melting processes of the hot spots (or links) due to the local Joule heating.[12] Above the percolation threshold p_c, the power-law relation between the breakdown current I_c and R_0,

$$I_c \propto R_0^{-\alpha}, \tag{2}$$

which was first found in other systems,[13] still holds in the rough systems.[14] However, the critical exponent α of the rough systems is significantly distinct from those of the systems deposited on flat substrates.[13–16] Therefore, α is generally considered to be nonuniversal and in fact it cannot be predicted theoretically so far.[13]

In this paper, we report the preparation, microstructure, and nonlinear dc I-V characteristics of the metallic rough thin films deposited on silicone oil surfaces. We find that, during the deposition process, a percolation structure appears first. Then the metallic clusters on the oil surface grow gradually and begin to connect each other. Finally a continuous rough thin film with a distinct surface morphology forms. In our experiment, the deposition rate strongly depends on the nominal film thickness, indicating the importance of the liquid surface effect. A discussion of the nonlinear dc I-V characteristics and the power-law behavior of the breakdown current is also presented.

The samples were fabricated by the rf magnetron sputtering method. A small pure silicone oil drop was dripped on a piece of glass. The conductivity of the oil is less than 10^{-10} $(\Omega\ \mathrm{cm})^{-1}$ and its vapor pressure is less than 10^{-6} Pa, which are good enough for our purpose. The metallic atoms were deposited on both the oil drop surface (with diameter $\phi = 2$ mm) and the other area of the glass at the same time. Since d, the thickness of the film deposited on the glass surface, was much bigger than that of the film on the oil surface ($d > 5000$ Å) (the explanation will be given below), then the film on the glass surface was appropriately used as electrodes. The size of each sample was 2.0×0.3 mm^2. The sputtering targets employed were metallic Al (purity 99.95%) and Ag (purity 99.99%) disks. The target-substrate distance was 80 mm. The residual gas pressure before sputtering was about 2×10^{-4} Pa. The films were deposited under Ar gas pressure of 0.2 Pa and at room temperature. The incident rf power was 50 W and the typical deposition rate of the films on glass was 0.8 nm/sec. However, the deposition rate of the films on the oil surfaces could not be measured quantitatively at this stage since it was no longer a constant during the deposition process due to the second evaporating effect and the penetrating effect as well (see the interpretation below). Therefore the nominal thickness of the rough films on the oil surfaces was characterized by the sheet resistance.

An interesting observation is that, when the incident rf power P was lower than 30 W, the deposition rate on the liquid surface is so small that the Ag film cannot be formed (at least in our deposition time interval, i.e., 50 min). However, in the power interval of $P=20$–30 W, the deposition rate of the film on the glass substrate is no less than 0.2 nm/sec. This result indicates that the deposition rate on the oil surface is extremely sensitive to the power P. We propose that, in the case of lower incident rf power (i.e., $P<30$ W), the energy of the Ar ions is lower and the main materials sputtered from the Ag target are independent Ag atoms. When these atoms strike the liquid surface separately, it is not very difficult for them to evaporate again or penetrate the liquid surface. However, if the rf power increases, the energy of the Ar ions would become so powerful that the percentage of the Ag atomic clusters in the sputtering products rises. In this case, the deposition rate would greatly increase because (1) the second evaporation effect would not be very obvious due to the interaction between the Ag atoms in the clusters and (2) it is more difficult for the atomic clusters to penetrate the liquid surface since the mean free path of a cluster is much smaller than that of an independent atom.

Figures 1 and 2 show the scanning electron micrograph (SEM) photographs of the Ag sample surfaces, in which a characteristic structure at the micrometer length scale is observed. In Fig. 1, one finds that, when the incident rf power is fixed (i.e., $P=50$ W), the deposition rate changes sensitively with the film thickness since the film thickness is not proportional to the deposition time t. We propose that, at the early stage of the deposition process, the local temperature of the oil surface would greatly increase due to the strong strike between the liquid surface and the deposition atoms. The high temperature as well as the interaction between the liquid surface and the independent deposition atoms would obviously result in both the second evaporating effect and the penetrating effect. Thus the deposition rate is small. However, as the nominal film thickness increases (i.e., the surface coverage fraction p increases), the liquid surface is gradually covered by the Ag atoms and finally these two effects disappear. Then the deposition rate increases quickly and approaches the value of the deposition rate on glass surfaces.

When the nominal thickness of the film is very small, the film exhibits the percolation structure [Fig. 1(a)]. If the film thickness increases, a characteristic pattern begins to grow around each atomic cluster [see Figs. 1(a) and 1(b)]. Finally, a continuous film with a distinct surface morphology forms [see Figs. 1(c) and 2]. Since the thermal expansive coefficient of the oil is bigger than that of the metallic Ag film, we propose that the anomalous morphology shown in Figs. 1 and 2 is related to the expansion and contraction characteristics of both the Ag film and the oil substrate. The dynamics of the metallic atoms on the liquid surface should also make contributions to the formation of the morphology. The Ag sample mentioned in Fig. 2 was examined by x-ray diffractometry before the electrical measurement. The x-ray diffraction pattern of the sample shows regular Ag peaks (see Fig. 3), providing evidence that the thicker Ag film deposited on the oil substrate still exhibits the polycrystal structure. However, further study on the crystalline mechanism is still needed.

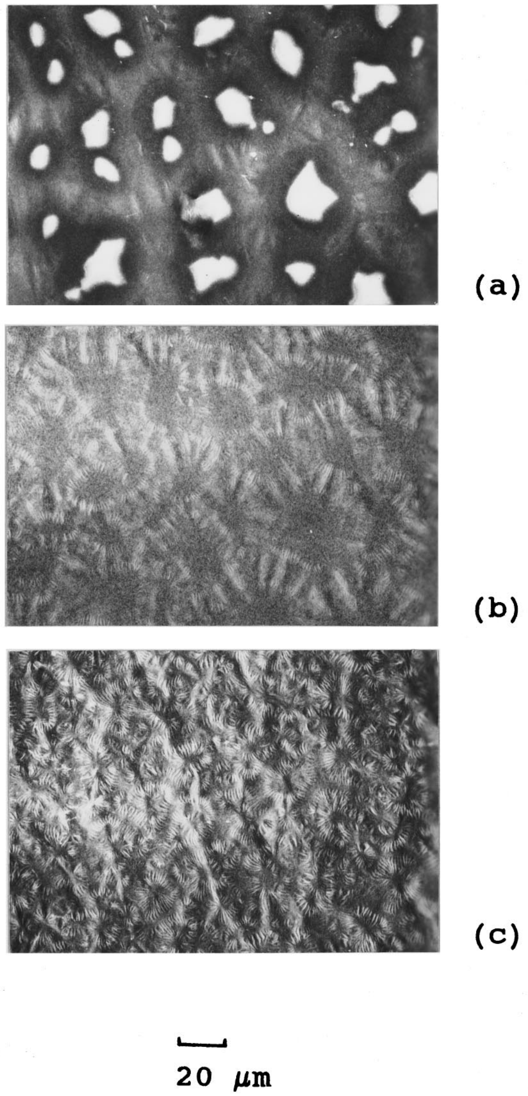

FIG. 1. SEM photograph of the three Ag rough films deposited on the silicone oil drop surfaces. The depositing time is (a) $t=510$ sec; (b) $t=540$ sec; (c) $t=570$ sec.

When the samples with different values of surface coverage were prepared, they were removed from the vacuum system and the dc resistance dependence of the current was measured immediately by the two-probe method at room temperature. As shown in Fig. 4, at low currents the samples show Ohmic behavior; i.e., R is a constant. At higher currents, however, the sheet resistance R increases with the current I, which can be well fitted by Eq. (1). In Fig. 4, one finds the third-harmonic coefficient $B_{0\ \mathrm{Ag}}=2.51\times10^4$ V/A^3 and $B_{0\ \mathrm{Al}}=2.45\times10^4$ V/A^3. The coefficient B_0 is very important since it is closely related to both the $1/f$ noise spectrum and the breakdown current of the system.[11,13] A detailed description of this topic will be published separately. The quadratic nonlinear response, which is similar to those of the other percolation film systems,[11,12] indicates that the local Joule heating effect is still important in the electrical process of the system. This result again provides evidence that the film with a suitable thickness does exhibit the percolationlike structure. When the current further increases and goes beyond the breakdown current I_c (see Fig. 4), the samples undergo a random resistance change in time and finally the resistance becomes infinite. In other words, as soon as the first discon-

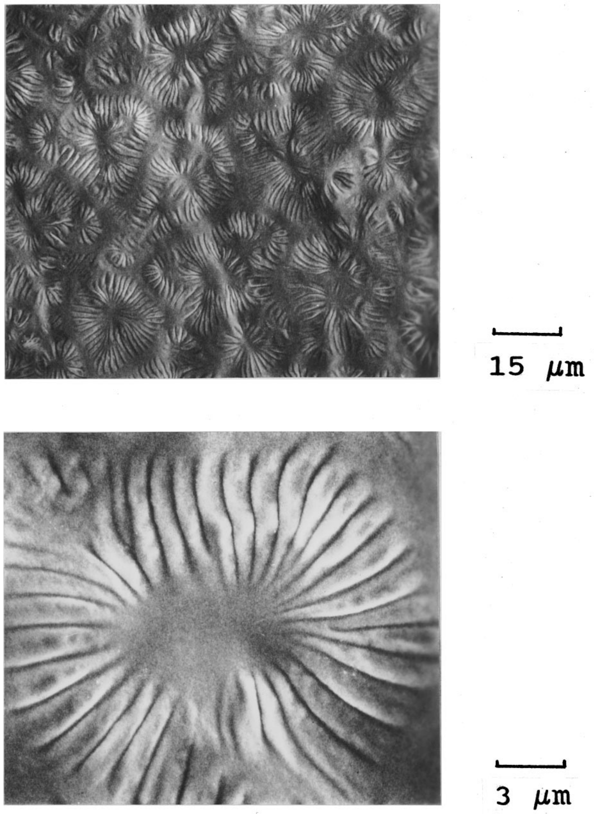

FIG. 2. SEM photograph of a Ag rough sample, in which a characteristic pattern at the micrometer length scale is observed.

tinuity in dR/dI is measured, various irreversible processes (such as the link melting, cluster moving, amalgamating, etc.) take place immediately, which is significantly distinct from those of the other percolation systems.[13] In the resistance span of 10^0–10^2 Ω, the scaling of I_c as a function of R_0 is shown in Fig. 5. For the Ag samples, $I_c \propto R_0^{-\alpha}$, $\alpha = 0.52 \pm 0.06$, which is smaller than those of the systems on flat substrates [both the experimental result ($\alpha \approx 1.75$) and the theoretical prediction ($\alpha \approx 0.85$)],[13,15,16] indicating the importance of the liquid-surface effect. Generally, it is believed that the electrical breakdown process should depend on the microstructure of the system and the exponent α is nonuniversal.[13] The result above supports this proposal.

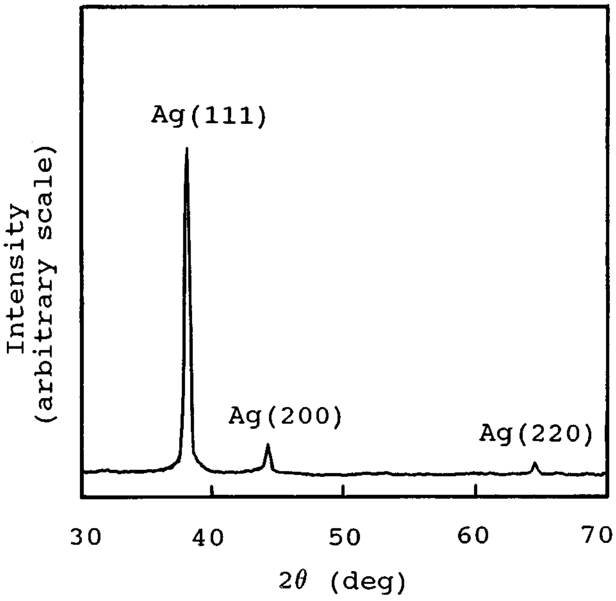

FIG. 3. X-ray diffraction pattern of the sample described in Fig. 2. The regular Ag peaks indicate that the sample still exhibits the polycrystal structure.

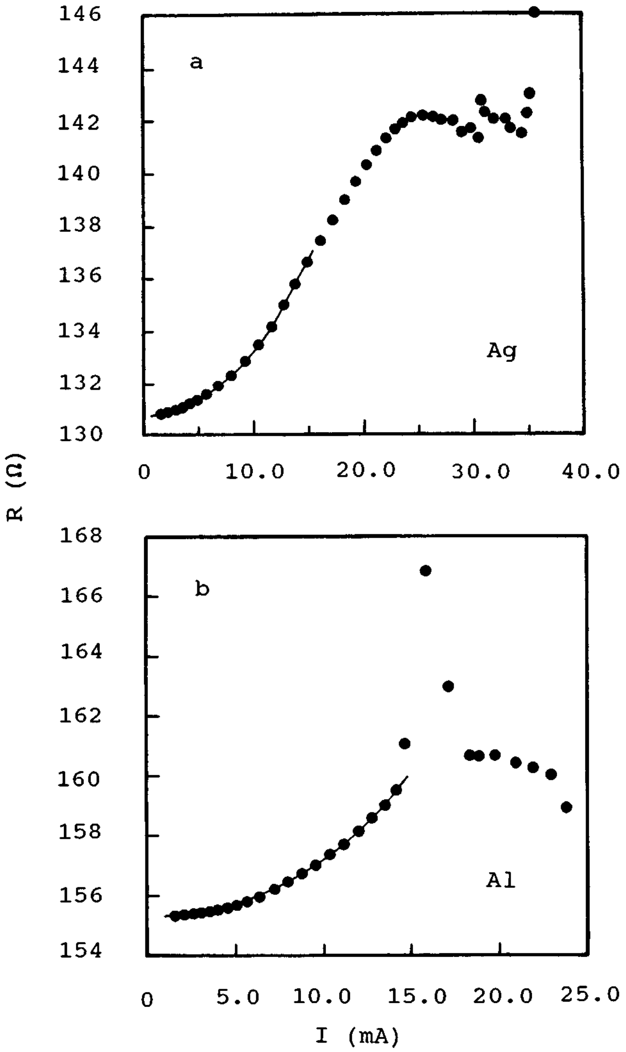

FIG. 4. R-I characteristics of the Ag and Al samples. The random resistance fluctuation is observed when I goes beyond I_c. Dots are the experimental data and the solid lines represent the fit $R = R_0 + B_0 I^2$. (a) $I_c = 27.0$ mA, $B_{0\,\mathrm{Ag}} = 2.51 \times 10^4$ V/A^3; (b) $I_c = 14.5$ mA, $B_{0\,\mathrm{Al}} = 2.45 \times 10^4$ V/A^3.

We propose that the random resistance fluctuation described in Fig. 4 mainly results from both the liquid substrates and the microstructure of the samples since other percolation films do not exhibit such behavior.[13,14] At lower current, the local Joule heating effect is the main contribution to the electrical process, which results in the phenomenon of $dR/dI > 0$.[13] When the current increases and goes beyond I_c, however, a higher current passing through the links and clusters would bring about a large increase of the temperature of the samples. Thus the dynamic viscosity of the liquid substrates decreases and the links in the percola-

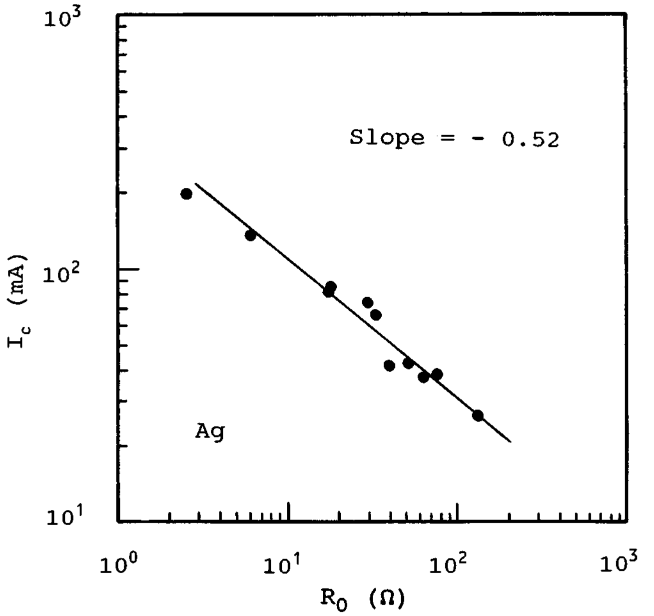

FIG. 5. Scaling of I_c as a function of the Ag film resistance R_0.

tion films begin to melt. Then the unstable shift between the clusters and the substrates takes place, which results in the random resistance fluctuation (see Fig. 4).

In conclusion, we have described a method for preparing a metallic rough-thin-film system, in which the liquid substrates are used. The SEM photographs show that the films exhibit the percolation and characteristic structures, which depend on the nominal thickness of the films. The deposition rate is strongly related to the film thickness mainly due to the second evaporating effect and the penetrating effect. A quadratic R-I behavior is measured and, if the current I goes beyond the breakdown current I_c, the film resistance fluctuates randomly. Therefore, we indicate that the physical mechanism of the electrical breakdown of our samples might be quite different from that of the percolation films deposited on glass substrates. We find that I_c can be well fitted to a power of R_0 with the exponent $\alpha=0.52\pm0.06$ although in our experiment the liquid substrates are used.

The above result presents us with an example that liquid surfaces can also be used as film substrates just as the solid substrate does. We believe that other behaviors of the samples, such as the $1/f$ noise spectrum, localization characteristics, lattice match, crystalline mechanism, etc., will exhibit many physical phenomena. The results presented in this paper are important for two reasons: (1) they will lead to a radically different view of substrates since the nature of the liquid substrate is quite different from that of the solid one, and (2) it is entirely possible to use the liquid substrates in the preparations of other film systems (multilayer films, for instance). Recently, there has been much interest in the formation and microstructure of corrugated films.[17,18] We believe that the liquid surface is a good substrate for corrugated film growth. Both experiments and calculations aimed at determining the microstructure of the films deposited on liquid substrates are now in progress.

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