Silver-island films deposited on a substrate above its softening temperature

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In this paper we report the results of investigations carried out on the electrical properties of silver-island films deposited onto polymethylmethacrylate-coated substrates heated to 423 K, well above the softening temperature of the polymer. For films with initial resistances less than 4.1 $M\Omega/\square$, a sharp fall in resistance was observed which may be due to the formation of a close-packed subsurface structure. This fall in resistance occurred after a time interval of 180 s following deposition. For films with initial resistance greater than 4.1 $M\Omega/\square$, the resistance increased enormously, marking this resistance range as a possible transition region. A film deposited at room temperature and heated behaved similarly to the silver-island films on glass substrates.

INTRODUCTION

Discontinuous metal films exhibit attractive properties such as high sheet resistance and high gauge factor which can be exploited for device applications. But the inherent instability in their physical properties is a major hurdle against using them in devices. Several reasons are given for the instability in discontinuous metal films.[1-3] It is generally accepted that mobility coalescence of islands is responsible for the post-deposition resistance increase, which is supported by electron microscopy studies.[3] There were attempts to reduce this instability which were not very successful.[4-6] Recently it was reported that when inorganic evaporants are deposited on an organic substrate heated to beyond the glass transition temperature of the organic polymer substrate, a subsurface particulate structure is formed.[7-10] These structures are similar to discontinuous films formed on rigid substrates. It is expected that such a structure would be stable while retaining the attractive properties of discontinuous films. However, the electrical properties of such structures are as yet unexplored.

In this paper the results of the study on the electrical properties of island silver films deposited on softened polymethylmethacrylate (PMMA) -coated substrates are presented.

EXPERIMENTAL DETAILS

Discontinuous silver films of initial resistances (resistance immediately after the end of deposition) R_o in the range 1–10 $M\Omega/\square$ were deposited on glass substrates coated with PMMA held at 423 K in a vacuum of 1×10^{-5} Torr. Thick silver contacts were predeposited with a 2.5×2.5 cm^2 gap at the center. In this gap PMMA was solution coated and thin cooper wires were soldered to the contacts for resistance monitoring with a Keithley electrometer. The four-probe method was not employed for resistance measurements since the contact resistance was found to be very small when compared to the film resistance and it was not varying with time and temperature. The source to substrate distance was main-

tained at 20 cm. A copper-Constantan thermocouple was used to measure the temperature by clamping it to the substrate surface holding the film. The deposition rate was 4–6 Å/sec. A manually operated shutter was used to stop the deposition at the required resistance. The polymer had a softening temperature at around 378 K (T_g), in agreement with the reported value.[11] The substrates were held at 423 K during deposition for all the films. Films were annealed for 1 h at this temperature before they were cooled to room temperature. After bringing the films to room temperature they were exposed to atmosphere. The film resistance in atmosphere was monitored. One film of $R_0=0.5$ $M\Omega/\square$ was deposited at room temperature and aged for 1 h. This was then heated to 350 K.

RESULTS AND DISCUSSION

Figure 1 shows the typical variation of resistance with time after the deposition is stopped. For films with $R_o<4.1$ $M\Omega/\square$ resistance remained in the $M\Omega$ region followed by a sharp fall in resistance to a few hundred ohms within a period of 180 s. The time variation of resistance after this fall is shown in the inset. It can be seen that in this region the variation of resistance is not very significant. All the films with initial resistance greater than 4.1 $M\Omega/\square$ showed a three-order increase in resistance within 10 min of deposition. In the figure, variation of resistance with time for one such film is shown. Figure 2 shows the variation of resistance with temperature when the films are cooled to room temperature. The variation is linear with a very small slope. Figure 3 shows the scanning electron micrograph (SEM) for a film of $R_0=1.5$ $M\Omega/\square$ at a magnification of 10 000. Figure 4 shows the SEM picture for a film of $R_0=1.9$ $M\Omega/\square$ at a magnification of 5000. The structure is that of a continuous film consisting of very fine grains. Table I gives data on the time taken for the resistance to fall to the lowest value, the resistance after the fall, and the temperature coefficient of resistance (TCR). The films deposited at room temperature on PMMA and heated after aging for 1 h exhibited a behavior similar to island films on
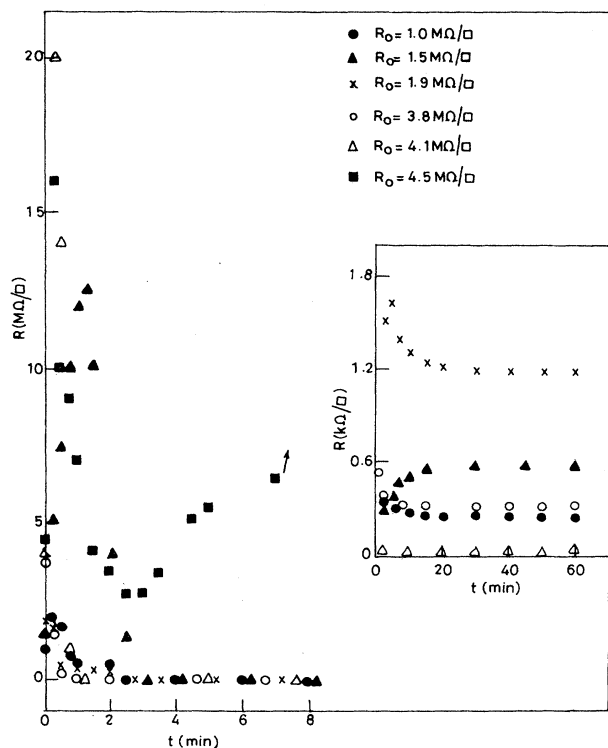
FIG. 1. Variation of film resistance with time at 423 K after the deposition is stopped.
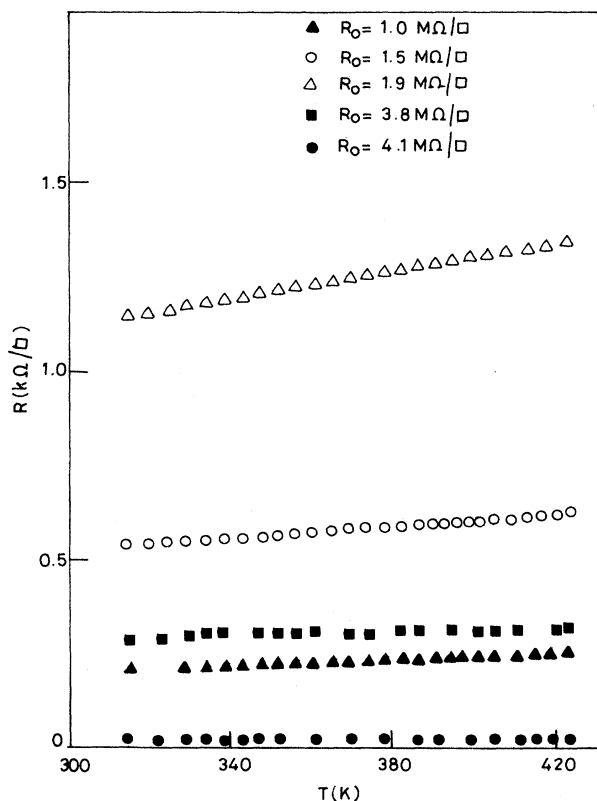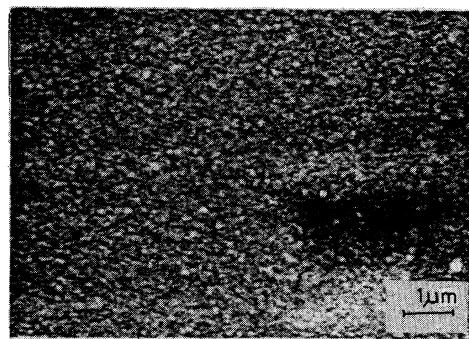

FIG. 2. Variation of film resistance with temperature.

FIG. 3. SEM picture for a film of $R_0 = 1.5$ MΩ/$\square$.

a glass substrate. Figure 5 shows the variation of resistance with time for a typical film of $R_0 = 0.5$ MΩ/$\square$ at room temperature. The interisland spacings calculated according to a scheme adopted earlier[12] at the beginning of aging and after aging for 1 h were 20.11 and 23.27 Å, respectively, for the film of $R_0 = 0.5$ MΩ/$\square$ at room temperature. The coalescence rate defined as the change in interisland spacing per minute calculated over a time span of 60 min is 0.0526 Å/min. Figure 6 shows the temperature variation of resistance for this film. An initial fall in resistance with temperature followed by a rapid increase at a temperature of 340 K is clearly seen.

When inorganic materials are vacuum evaporated onto softened polymer substrates, a subsurface particulate monolayer structure is thermodynamically preferred.[7] The favorable condition for formation of such a structure is given by

$$\gamma_1 > \gamma_2 + \gamma_{12} \, ,$$

arrived at by considering the surface free energies of the system,[8] where γ_1 and γ_2 are surface tensions of the evaporant and substrate materials, respectively. γ_{12} is the interfacial tension. This inequality generally holds for most inorganic evaporant and organic polymer combinations.[9] Silver, when deposited on hexylmethacrylate copolymer held at 120 °C, formed tightly packed particles about 25 nm in size below the surface.[7] The structure was very close to that of a continuous film. In our case also such a structure might have been formed with a metallic conduction path being established between the con-

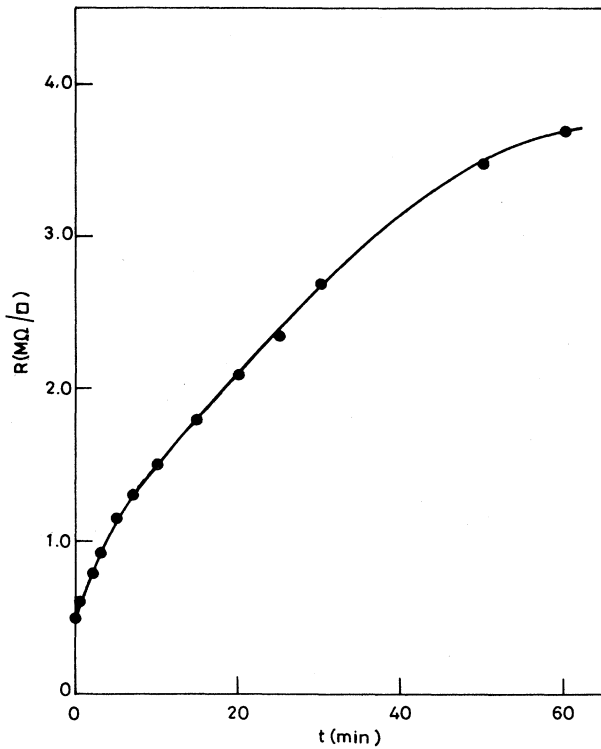FIG. 4. SEM picture for a film of $R_0 = 1.9$ MΩ/$\square$.

FIG. 5. Variation of film resistance with time at room temperature for a film of $R_0 = 0.5$ MΩ/$\square$.

FIG. 6. Variation of film resistance with temperature for a film of $R_0 = 0.5$ MΩ/$\square$ at room temperature.

tacts. Very low electrical resistance and low positive TCR, characteristic of continuous or semicontinuous metallic films, are exhibited by the films with $R_0 < 4.1$ MΩ/$\square$ which showed a sharp fall in resistance (Figs. 1 and 2, and Table I). SEM pictures also show that a close-packed structure has been formed (Figs. 3 and 4). The above observations suggest that a close-packed subsurface structure might have been formed. When the films are exposed to atmosphere there was no change in resistance with time. This is due to two facts. If the film is formed beneath the surface, the film will be expected to be insensitive to the interaction of atmospheric gases. Secondly, if the film itself is continuous, its sensitivity to atmospheric gases will be much less than discontinuous films. In atmosphere the films were stable up to 48–72 h. After 72 h their resistance started increasing slowly with time. This is to be contrasted with the findings of a film
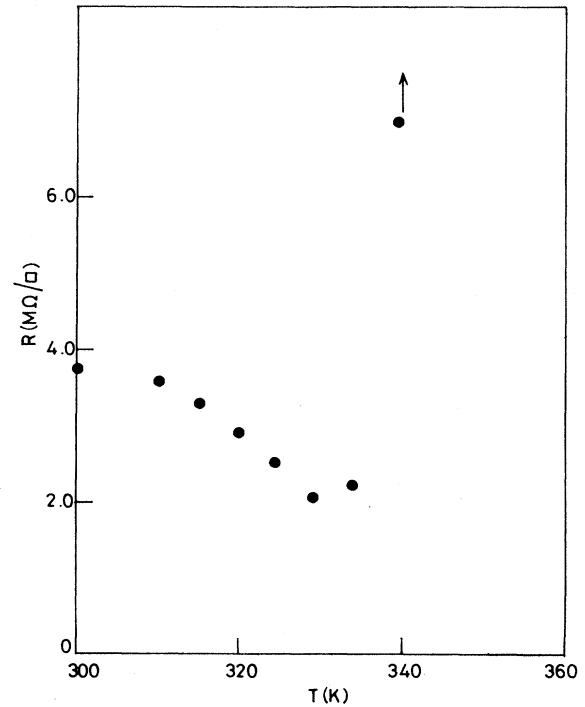
preserved in a dehydrated dessicator, which showed no resistance drift up to and beyond 300 h. It is clear that the film degradation is due to the attack by water vapor in the atmosphere. The continuous nature of the films is strengthened by the linear I-V behavior with a very low voltage drop existing across the film.

From Fig. 1 it is clear that the fall in resistance occurs only for films with $R_0 < 4.1$ MΩ/$\square$. Also, there is a time interval between the end of deposition and the fall in resistance. From Table I it can be seen that for films with R_0 below 1.9 MΩ/$\square$ this time is about 180 s, whereas for films with $R_0 = 3.8$ and 4.1 MΩ/$\square$ it is only 60 s. Initially islands are formed on the polymer surface accounting for the high resistance. It is energetically favorable for the particles to sink into the polymer. Once the particles sink and rearrange themselves to form a close-packed structure, the resistance falls to a small value. The time taken for the rearrangement is greater for lower-

TABLE I. Time for the resistance to fall to a lowest value, the resistance after the fall, TCR, and room-temperature resistance.

R_0 (MΩ/$\square$)	Time taken for the resistance to fall to a lowest value (s)	Resistance after the fall (Ω/$\square$)	TCR (ppm/K)	Resistance at room temp. (Ω/$\square$)
1.0	150	350	1836	207
1.5	180	313	1476	538
1.9	150	1500	1430	1243
3.8	60	450	1153	286
4.1	60	35	1470	23

resistance films (higher-thickness films) and lower for higher-resistance films (lower-thickness films). However, there does not appear to be any correlation between the initial resistance and the resistance after the fall. The slight changes in resistances after the fall may be due to local reordering of the film. The TCR values which are almost equal (Table I) indicate that the structure of the films is also identical.

For the films with $R_0 > 4.1$ M$\Omega/\square$, the resistance was of the order of MΩ for a few minutes after deposition and a very sharp increase in resistance was observed within 10 min of deposition (Fig. 1). Large discontinuities in the film were visible for such films. The material deposited may not be sufficient to form a close-packed subsurface structure with a metallic conduction path between the electrodes. Instead, a close-packed structure with very large islands separated by very large separations is formed and hence a very high resistance (of the order of substrate resistance) is attained. The distribution of the metal in the PMMA matrix could not be controlled by just varying the amount of silver deposited.

A film of $R_0 = 0.5$ M$\Omega/\square$ deposited at room temperature behaved similar to the island films deposited on glass substrates (Fig. 5). When this film was heated an initial negative TCR was observed, characteristic of an island film. At about 330 K the resistance started increasing, attaining a very high value at 340 K (Fig. 6). Similar R-T characteristics were observed in the case of island Cu films[13,14] and silver films[15] both above and below room temperature. We believe the same physical explanation to hold in this case also.[13] It should be noted that the temperature at which the resistance starts increasing is much below the softening temperature of the polymer and hence resistance changes due to the changes in substrate properties are ruled out.

The "subsurface" silver films are much more stable than the normal on-top discontinuous metal films, when exposed to atmosphere. Normal on-top films with and without overlayers showed a sharp increase in resistance at a well-defined pressure range of 5×10^{-2} Torr when exposed to atmosphere and the film resistance continued to change until a few hundred hours in atmosphere.[15] Contrary to this, subsurface films showed no drift in resistance during exposure to atmosphere and in atmosphere for nearly 72 h. Though the stability is improved, the discontinuous nature of the film is not retained.

A high-resistance subsurface film with structure similar to those obtained in cermets may be obtained by depositing films onto substrate at higher temperature by using a suitable polymer which can withstand such a high temperature without degradiation.

CONCLUSIONS

From the study of electrical properties of silver deposited on a softened substrate we arrive at the following conclusions.

(1) Variation of resistance with time, TCR, and I-V behavior, and SEM photographs suggest that Ag films form a close-packed subsurface structure analogous to a continuous film.

(2) Films deposited at room temperature exhibit a behavior similar to island films deposited on glass at room temperature.

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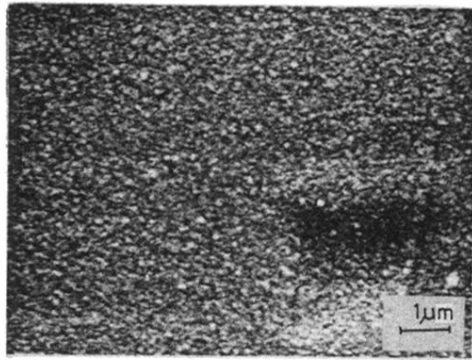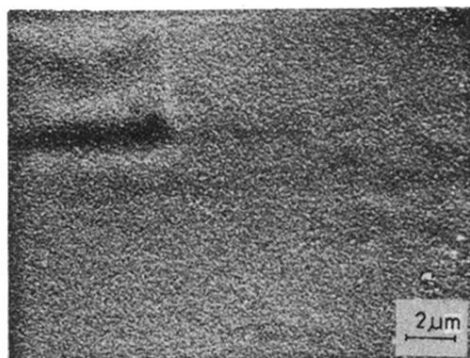FIG. 3. SEM picture for a film of $R_0 = 1.5$ MΩ/□.

FIG. 4. SEM picture for a film of $R_0 = 1.9$ MΩ/$\square$.