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Measurements of the electrical mobility of silver over a hot tin oxide surface

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We report on measurements of the drift mobility of silver ions on the surface of tin oxide maintained at temperatures between 400 and 500 °C, in air. Silver contacts are placed on the surface arranged as an inner circular anode and an outer concentric-ring cathode, and by measuring silver advancement outward, mobility can be determined. Measurements were made as a function of temperature, field intensity, surface roughness, and oxygen content of air. Drift-mobility values varied from 10^{-8} to 10^{-5} cm^2/V s. It seems from our results that the dynamic formation of surface oxide (silver oxide is unstable above 300 °C) is important in understanding silver migration.

I. INTRODUCTION

In a letter published two years ago,[1] we presented results showing the rapid migration of metallic silver, as well as silver ions, on surfaces of tin oxide maintained above 300 °C. It was observed that the silver ions were produced at the positive electrode of silver dag contacts placed on the surface. The ions could be made to recondense on the surface in both fractal and dense-packed structures.

We have been unable to find much in the literature on this phenomenon. There is a paper on silver-ion conduction on zinc oxide[2] used as a gas sensor, but the effect was very small and was detected using secondary-ion-mass spectrometry (SIMS). There have been numerous studies on the interstitial diffusion of silver in materials such as glass or ceramics,[3-5] but these are not surface effects. There has also been interest recently in the field-assisted penetration of silver into glass[6] as a means of changing the index of refraction.

II. EXPERIMENTAL DETAILS

The tin oxide films used in these measurements were obtained from a sheet of low-emissivity glass given to us by PPG Canada, Inc. of Thunder Bay. Low-emissivity glass is coated with a transparent conducting film (100 Ω square) of tin oxide.

In preparation for a measurement of silver migration, the films were cleaned with ethanol to remove any surface organic contaminant. Electrode contacts were then painted onto the surface using a colloidal suspension of silver in methyl isobutyl ketone, and the contacts were carefully dried and heated at about 120 °C to remove the organic solvent and leave behind pure silver. The contact geometry consisted of a central dot of approximately 1–1.5-mm radius surrounded by an outer ring contact of 6–7-mm inner radius. Electrical contact was made through gold wires embedded in the silver dag. After this, the substrate could be heated to the temperature of interest for a given experiment.

The surface mobility of silver on sand-blasted surfaces was also measured by the same technique. The films thus treated were cloudy in appearance due to the roughening, with resistances in the tens of kΩ range. The composition of these rough surfaces was primarily that of the glass substrate, as most of the tin oxide was removed by the sand blaster.

After heat treatment, the sample with attached wires was placed on a stainless-steel support inside a small oven. Mounted 60 mm above the oven window was a charge coupled (CCD) video camera with an attached microscopic zoom lens. Using a video recorder and monitor, even small amounts of migration could be measured.

The oven temperature was monitored with a chromel-alumel thermocouple. For the conducting tin oxide film, significant joule heating would occur when higher electric fields were applied across the electrodes, and so the film temperature was monitored independently of oven temperature, using a very small wire thermocouple attached to the center electrode.

Using classical electric-field theory, it can easily be shown that the field (E) on the surface of the tin oxide film for the coaxial geometry used here is

$$E = V/[r \ln(b/a)] , \tag{1}$$

where V is the applied bias, a the inner radius, b the outer radius, and r a point between them. Since all our measurements occur very close to the inner radius, we will set a equal to r. Under the application of an electric bias, silver ions migrate in the direction of the field with a drift velocity $V_m = \mu E$, where μ is the drift mobility. Combining this with Eq. (1), we can write

$$\mu = r\, dr/dt \ln(b/r)/V . \tag{2}$$

Therefore, to measure the drift mobility we need to record the silver-ion front as a function of time as it spreads out from a positive center electrode. Since the ions are normally invisible, we had to develop an experimental trick in order to detect them.

This was done by reversing the electrode bias. Under reverse bias, the silver ions would capture an electron and nucleate in tiny clumps of metallic silver which were easily visible under the microscope. When the bias was returned to normal, the "fog" of silver droplets would quickly redisperse. The time under reverse bias was short compared to the time under forward bias, thus allowing an easy measurement of the drift velocity. The amount of silver involved in the migration had the electrical effect of expanding the radius of the central electrode. Therefore mobility measurements were always near $r = a$, as assumed in the above equation. Eventually the system would short.

III. RESULTS

Figure 1 shows a completed "reverse" bias nucleation of silver ions that have migrated out from the central electrode. In the bottom half of the figure, we can see that the migration has been uniform. The top half shows a dentrite structure that resolves into individual "drops" of silver 2–3 μm in diameter. Higher magnification of the image shows that these drops are composed of smaller features which are sometimes rounded and sometimes faceted.

Video camera images of this process have been recorded and studied. These show that the dentritic structure grows out from nucleation sites on the surface of the central dag when the bias is switched from positive to negative. On film it gives the distinct impression of an outward mass migration, but of course the silver ions are already there on the surface and it is only the ion/metal conversion front that moves outward. When the bias is switched to positive again, "evaporation" proceeds from the outer edge back to the dag, and ionic migration proceeds as before.

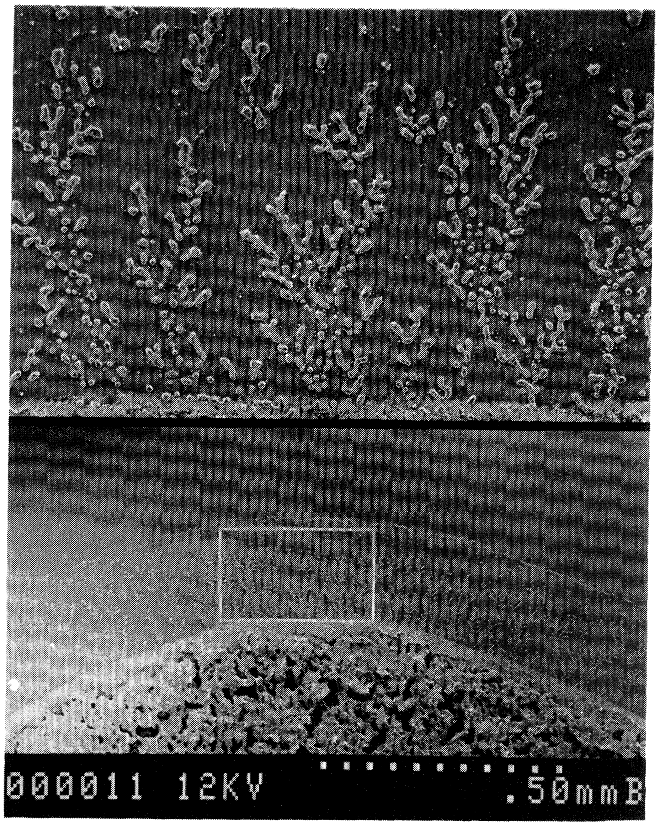

FIG. 1. The scanning electron micrograph of silver nucleation on a smooth conducting film of tin oxide at 430 °C and a field of 13 V/cm near the central positive electrode. The scale shown is 0.50 mm.

At very high temperatures and/or electric fields, silver structures which we might describe as "fingers" or "rivers" burst out from the positive electrode, with no need of a bias reversal. This happens in an uncontrollable fashion, and it is impossible to measure a drift mobility in these cases. The river analogy is apt as the surface of the silver appears to be in constant motion, sending off an occasional flash of light and giving a compelling impression of flow.

Using the technique of bias reversal, measurements of the drift mobility were done on a smooth conducting film of tin oxide. The variation of migration distance versus time for some of these measurements is displayed as Fig. 2, where each data point represents a bias reversal measurement. We see that the silver moves a greater distance at first than it does afterwards. The exception in curve *B* is only apparent since in this experiment the oven was turned off overnight, before resuming the experiment the next day (at 11 000 s on the scale). The calculated mobilities are summarized in Table I, where we have calculated separately an initial mobility versus an average steady-state mobility. We see that the initial mobility is one to two orders of magnitude greater. Of course, the initial mobilities quoted are really averages over times as long as 1 h. In order to obtain a better idea of the initial speed of ion migration, some bias reversals of much shorter duration were done, as shown by line *E* in Fig. 2, which shows a measurement on a smooth film at 450 °C. The mobility rapidly varies from 5×10^{-5} to 1×10^{-5} to 2×10^{-7} cm^2/V s in the first 20 min.

Examining the bias dependence of the mobility, we note in Table I that the initial mobility decreases with an increase in applied field. Because of the difficulty of these measurements, only one significant figure is quoted. The

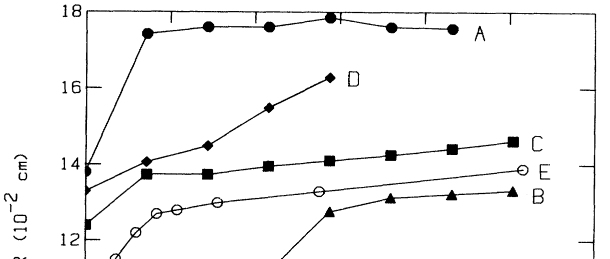

FIG. 2. The migration of silver on a conducting film of tin oxide at 430 °C, showing the distance from the central electrode for successive reverse bias nucleations. The electric field is (*A*) 6, (*B*) 9, (*C*) 13, and (*D*) 30 V/cm. (*E*) shows the fine structure of the initial mobility change at 450 °C and 16 V/cm, where the time scale is expanded by a factor of 20.

TABLE I. Silver mobility on conducting tin oxide and sand-blasted surfaces. The applied electric field varies by a few percent during the measurement due to shielding by the migrated silver. The value given in the table is the initial applied field.

Temperature	Field V/cm	Initial mobility 10^{-8} cm^2/V s	Steady-state mobility 10^{-8} cm^2/V s
	Conducting tin oxide		
430 °C	6	900	6
	9	50	6
	13	30	4
	22	20	8
	30	15	3
	Sand-blasted surface		
510 °C	7	5000	1000
	15	1000	400
	29	200	200

steady-state mobility shows no systematic trend, within about a factor of 2 of experimental error. The temperature dependence of the mobility is difficult to measure although the intensity of the silver-ion transport was seen to increase dramatically with temperature. At temperatures below 400 °C, the intensity is too low for meaningful migration measurements, and above 450 °C it is much too erratic.

Figure 3 shows migration on a surface that has been damaged with a small sand blaster, thereby removing most of the tin oxide film. Changing from forward to reverse bias and back again shows a similar illusion of movement out from the central dag and back again, as was seen for the undamaged surface. If anything, it is more dramatic here. Figure 4 plots radial migration versus time for three different field strengths. The mobility on the damaged surface is much higher than before, but the operating temperature is also much higher. Measurements of more closely spaced bias reversals (Fig. 4, curve *D*) show an initial mobility variation from 7×10^{-6} to 3×10^{-6} cm^2/V s.

Migration can be observed over a temperature range of 450–550 °C on the damaged surface; the intensity of the effect increases over this range as before. In Table I, we note that there is less of a difference between the initial mobility and the steady-state mobility, and that the electric-field dependence is less extreme.

In order to test the importance of oxygen on silver-ion migration, the oven was purged with oxygen-free nitrogen gas. When this was done, migration did not occur, or else immediately stopped if already in progress. Reducing the concentration of oxygen by mixing dry air with nitrogen gas reduced the mobility, as shown in Fig. 5. For 100% dry air, the mobility is 9×10^{-6} cm^2/V s, for 8% dry air it is 5×10^{-6} cm^2/V s, and for 2% dry air it is 4×10^{-7} cm^2/V s.

Attempts were made to detect silver migration on other surfaces. None was seen on mica, copper oxide, or smooth glass or quartz plates.

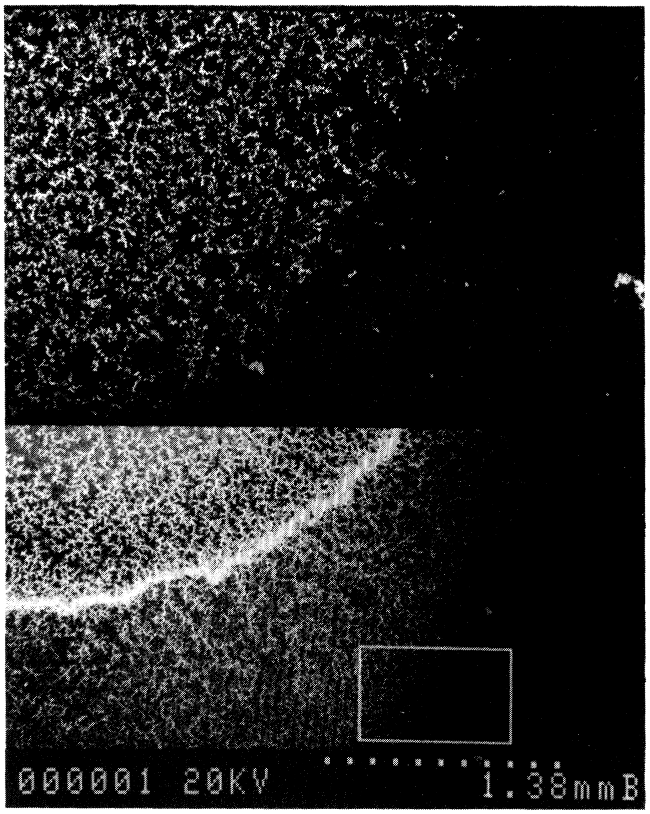

FIG. 3. The scanning electron micrograph of silver nucleation on a sand-blasted surface at 510 °C and a field of 16 V/cm near the central positive electrode. The scale shown is 1.38 mm.

IV. SUMMARY

To summarize the above results, we need a model. We will assume that the silver exists on the tin oxide surface as metal (Ag), as ion (Ag^+), or as oxide (Ag_2O). We will

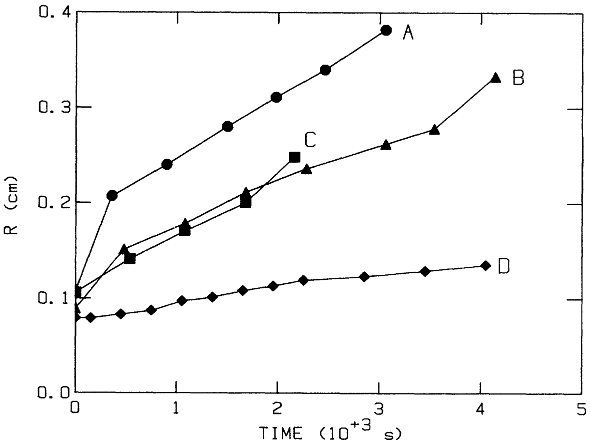

FIG. 4. The migration of silver on a sand-blasted surface at 510 °C, showing the distance from the central electrode for successive reverse bias nucleations. The electric field is (*A*) 7, (*B*) 15, and (*C*) 29 V/cm. (*D*) shows the fine structure of the initial mobility change at 470 °C and 16 V/cm, where the time scale is expanded by a factor of 5.

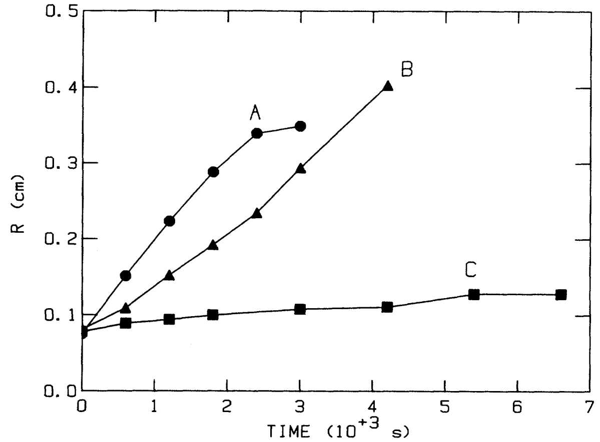

FIG. 5. The effect of the oxygen concentration on silver migration on a sand-blasted surface at 510 °C and 13 V/cm. Dry air is mixed with nitrogen to give (*A*) 100%, (*B*) 8%, and (*C*) 2% air.

further assume that there are two steps in the migration. These are the ejection of silver ions from metal or oxide clusters, and the movement of these same ions on the surface. We finally assume that the ion ejection is the rate-limiting step; that is, silver spends more time in the metal or oxide forms than in the ionic form. Bulk migration then occurs as a short ionic drift or as hops from cluster to cluster. This would give the impression on the macroscopic scale of cluster migration. Whether these clusters are optically visible would depend on the rate of ion production.

From these assumptions we expect that it is easier to eject an ion from a silver oxide positive electrode than the bare metal. The electrode does not have to be solid oxide but can be silver metal with a thick oxide coating. The two reactions involved are

$$\mathrm{Ag_2O} \Rightarrow 2\ \mathrm{Ag^+} + \tfrac{1}{2}\ \mathrm{O_2} + 2e^- , \tag{3}$$

$$\mathrm{Ag(metal)} \Rightarrow \mathrm{Ag^+} + e^- . \tag{4}$$

The first reaction is enhanced since silver oxide is unstable at temperatures above 300 °C (see also Fig. 5). Ionic ejection in the second case has to fight against its own image potential produced by the metal. With bias reversal, Eq. (4) is reversed, and this produces an electrochemical deposition of metal as described in Sec. III and shown clearly in Fig. 1.

We can now understand the high initial mobility as being due to the thick oxide layers existing on silver dag that has recently been heated through the 300 °C decomposition temperature. As migration proceeds, the oxide layer thins or vanishes, producing a lower steady-state mobility.

The temperature dependence of the mobility is very difficult to predict with this model. It is not clear how the reaction of oxygen with silver will vary, above the decomposition temperature of 300 °C, or what the importance of the thermal activity of the tin oxide surface is. We can only observe that mobility measurements can be made over a narrow range of temperature with the technique described.

To explain the low-voltage enhancement of the initial mobility, refer again to Eq. (3). This reaction removes oxide from the silver surface, and higher voltages would do this more quickly. Therefore a thick oxide layer lasts longer for low voltages, giving an enhanced mobility.

A damaged surface will have more nucleation sites for cluster growth. This should reduce the mobility by increasing the number of steps through which the silver ions move. Remember that we have assumed that ion ejection from clusters (the steps) is rate limiting. It is difficult to test this with our data, since the measurements for smooth and damaged surfaces were done using different surface compositions and at different temperatures, and because of the rapidly changing initial mobility of the smooth surface.

It was observed here and in an earlier study[1] that the surface of the silver "fingers" or "rivers" that grow from the positive electrode at high temperatures or under bias reversal is in constant motion. This motion ceases abruptly as soon as the electric field is removed. This constant restructuring of the surface is reminiscent of a similar although much slower effect seen on platinum wires heated to about 800 °C in air.[7] In this case, an originally smooth wire becomes faceted after a few hours. This mass transport is usually ascribed to a dynamic equilibrium between platinum oxide and platinum metal, as the oxide is unstable at 800 °C and has a significant vapor pressure. A definitive study of surface morphology changes of small spheres of platinum, used as an oxidation catalyst, reports similar effects,[8] and the same kind of thermal etching has been seen on silver.[9] Here the effect on silver is greatly enhanced by the electric field, in a manner represented by Eq. (3), but where the ion produced is quickly neutralized by the metal.

ACKNOWLEDGMENTS

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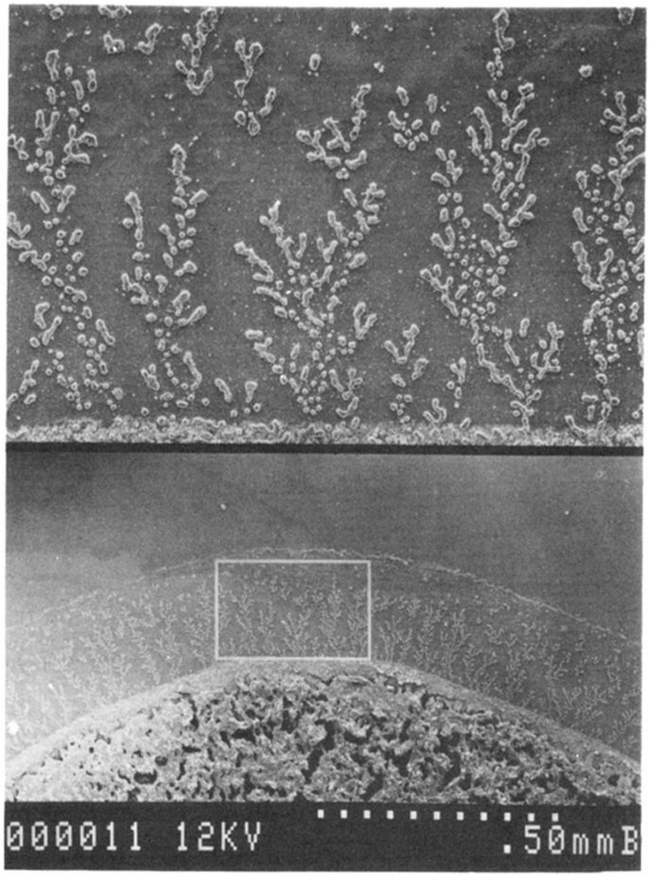

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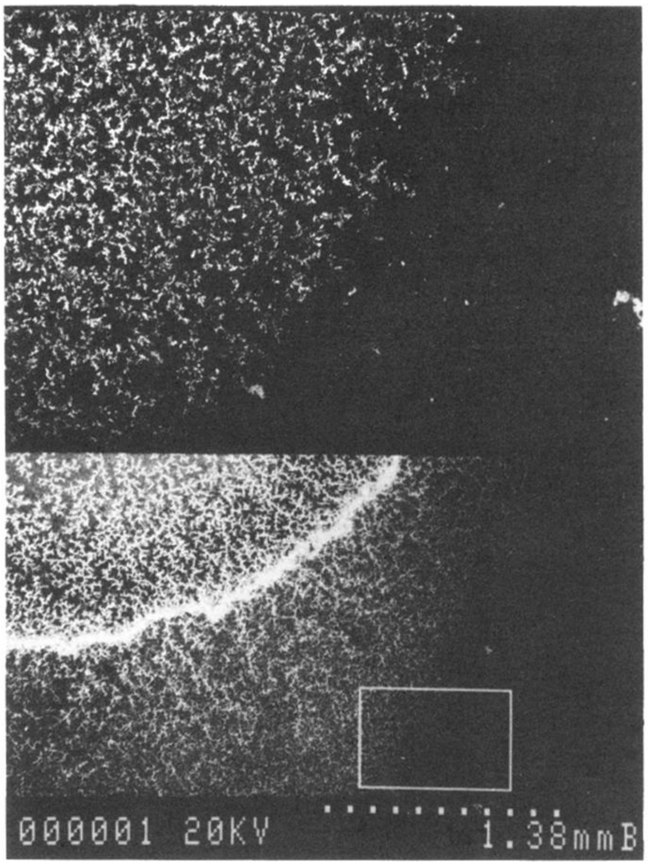

FIG. 3. The scanning electron micrograph of silver nucleation on a sand-blasted surface at 510°C and a field of 16 V/cm near the central positive electrode. The scale shown is 1.38 mm.