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Dendrites creating in silver metaphosphate glass treated by direct current of high density

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Applying high voltage to an ion-conducting glass at high temperature is equivalent to electrolyse a glass. We observed several morphologies of electro-deposited silver and other conducting ions on dc biasing of silver metaphosphate glass. One of the findings is that electro-deposited silver underneath the gold cathode pushed up the cathode.

1. Introduction

Many glasses such as window glass are ion-conducting. How an ion-conducting glass responds to an electrical voltage has been the subject of researches for more than one century. The study has usually been made by depositing metal electrodes on both sides of a sample, applying ac voltage, and measuring the response in terms of an admittance, Y^* ($= G + jB$, where G and B are the in-phase and 90° out-of-phase components of the response to an applied voltage). This ac technique is believed to have a merit that we can draw an intrinsic response of a glass by escaping "electrode polarization" (a generic term for irreversible phenomena taking place at the electrode-glass interfaces) by selecting an appropriate frequency window.

However, as we know, ionic conduction of glass is an electrolysis of glass, by neutralization of conducting ions at the electrode(s). We cannot escape interfacial phenomena. For a given frequency window, ionic conduction is enhanced by raising the temperature and/or the bias voltage. In the ac technique, the polarity of an electrode changes sign in each half-cycle, acting the cathode in one half-cycle but acting the anode in the next half-cycle. Therefore, in order to discriminate interfacial phenomena on both sides, the dc technique is more preferable [1–4].

The purpose of the present study was to dc bias the gold-electroded silver metaphosphate ($AgPO_3$) glass, a silver-ion conductor, and to know the interfacial phenomena which occurred on both sides. This is an extension of the previous work [4].

2. Experimental

The sample was made by melting a mixture of appropriate amounts of $NH_4H_2PO_4$ and $AgNO_3$ in a platinum crucible at 700°C for 2 h, quenching on a carbon plate, and depositing gold (400–1400 Å thick) on both sides. The sample was then dc-biased with 50 V (400–600 V/cm) for 10 sec at 148 ± 2°C *in vacuo*.

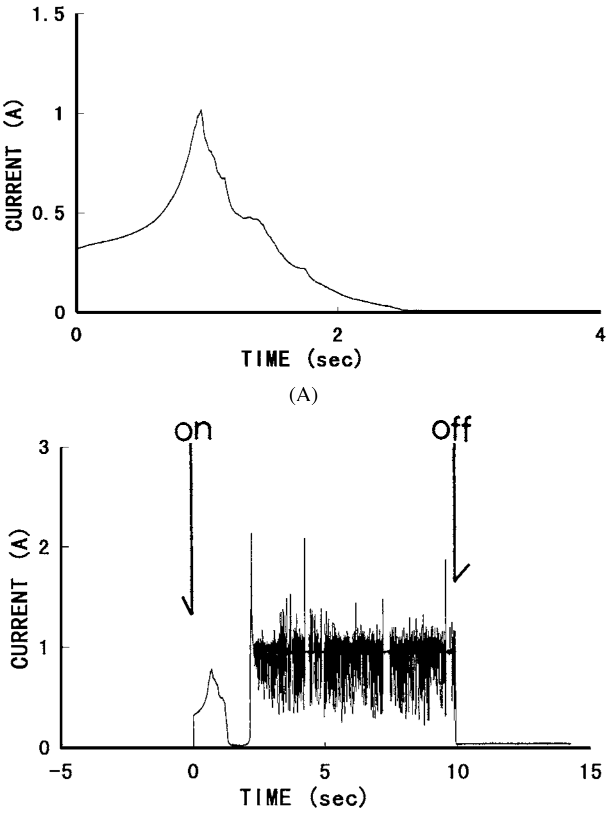
After dc runs, the depth profiles of gold, silver, oxygen, and phosphorus were measured from the electrode surfaces with an X-ray photoelectron spectroscopy (XPS), after intermittent etchings of the surface with argon ions. The photoelectrons came from the Au 4f bands at 84.5 and 88.1 eV, the Ag 3d bands at 368.3 and 372.5 eV, the O 1s bands at 531.2 and 533.1 eV, and the P 2p band at 134.2 eV, respectively. Because of the difficulty in quantitative analyses, only the raw data were presented. Since the etching rate was different for different materials/compositions, as 0.08 Å/s for gold, sputtering time rather than the depth was used as the abscissa.

After dc runs we observed visually the silver dendrites growing radially on the glass surface from the circular gold cathode. Besides, several dendrites grew within the glass from the cathode towards the anode, especially from the rim of the cathode. Finally, the black layer was found underneath the gold anode. The dendrites on the glass surface were studied with a scanning electron microscope (SEM), an Auger-electron spectroscopy (AES), and an atomic force microscope (AFM) in the contact mode. The Auger electrons came from silver by the *MNN* transitions at 351 eV. The dendrites within the glass were photographed using an optical microscope.

3. Results and discussion

The current with total charge of 0.4–1.0 C/cm^2 flowed on 50 V biasing for 10 sec. On dc biasing, some samples suffered dielectric breakdown while some others did not (Fig. 1). Fig. 2 shows the depth profiles, on the anode side, of the dielectrically non-broken (A) and broken (B′) samples, as well as the profiles for the sample heated in a similar fashion without dc biasing (C). Fig. 3 compares in particular the depth profiles of oxygen and phosphorus in sample B′. The interface between glass and the anode may correspond to the sputtering time at which silver, oxygen, and phosphorus rose abruptly from their low levels.

For a silver-anoded glass, silver ions in the silver anode were easily injected into glass on dc biasing so that the anode was easily exhausted [4]. When gold in



(A)

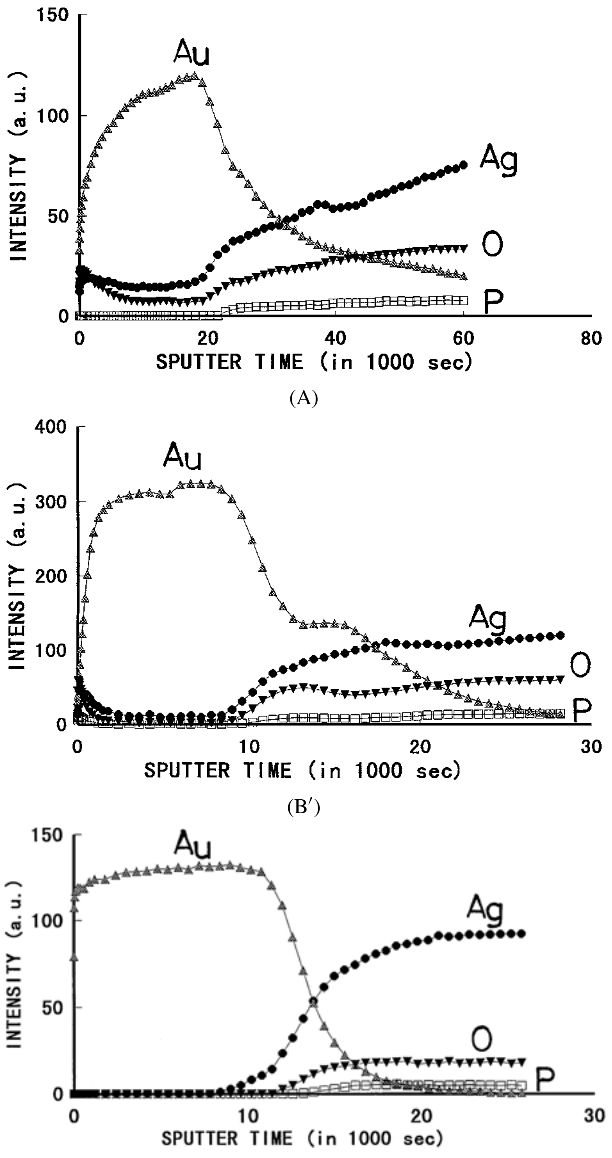
(B)

Figure 1 The current as a function of time on 50 V biasing for 10 sec. Sample B suffered dielectric breakdown while sample A did not.

place of silver was used as the anode, the depth profile showed that even the gold atoms (hereinafter we call the species "atoms" since XPS cannot discriminate atoms and ions) were injected into glass. The profile of the gold anode was distorted from the trapezoid on dc biasing. For sample B′, the biasing time before the onset of dielectric breakdown was too short (0.7 sec) as compared to sample A so that penetration of gold into glass was small.

Since our glass is a silver-ion conductor, the silver-depleted region (SDR) was generated beneath the gold anode by conduction of silver ions towards the cathode [3]. A gradual rise in silver with sputtering time implies large width in the SDR by incomplete depletion of silver. This may be related to the micro-heterogeneous structure of glass, by which those silver ions residing in the conduction paths can conduct easily while those residing in the localized regions cannot.

The black layer underneath the anode was thick, as ~10 μm or more. From the study with SEM, it is suggested that some crystalline phase was generated below the anode. For some samples the depth profiles of oxygen, silver, gold, and phosphorus showed the hills underneath the anode-glass interface. It is possible that those hills correspond to the unknown crystal. We cannot identify this phase. More precise study about the black layer is under way.



(A)

(B′)

(C)

Figure 2 Depth profiles, on the anode side, of dielectrically non-broken (A) or broken (B′) samples, as well as the profiles for the sample heated in a similar fashion without dc biasing (C).

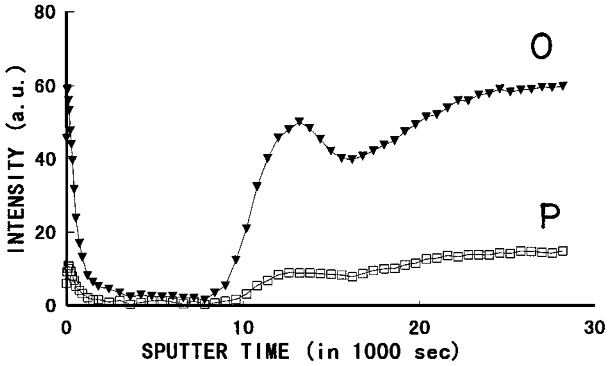


Figure 3 Depth profiles of oxygen and phosphorus on the anode side of sample B′, enlarged from Fig. 2.

Another finding is the penetrations of silver, oxygen, and phosphorus into the gold anode. It is plausible that the charge-uncompensated oxygen ions in the SDR conduct towards the anode and penetrate into it. But, why can those positive ions as silver and phosphorus have the profiles similar to that of oxygen? One possible explanation is that conduction of silver and phosphorus ions towards and through the anode would take place at high temperature *after* dc biasing, caused by coulombic attraction of the oxygen ions residing within the anode.

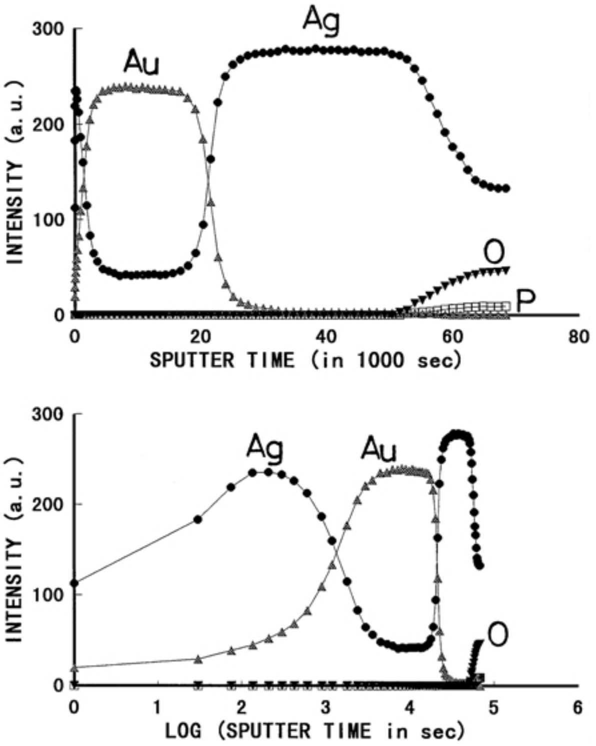


Figure 4 Depth profiles, on the cathode side, of sample A in Fig. 2, plotted in the semilogarithmic as well as in the normal scales.

Fig. 4 shows the depth profiles of sample A on the cathode side, plotted in the semilogarithmic as well as in the normal scales. We found large accumulations of silver both on the outermost surface of and underneath the gold cathode. The total charge flowed on dc biasing (Fig. 1A), 0.46 C/cm^2, corresponds to the silver thickness of 5000 Å provided the charge is carried solely by conducting silver ions. This roughly fits the observation (Fig. 4). Close inspection of the depth profiles for oxygen and phosphorus demonstrates that they emerged out of the noise level at the terminal of the silver layer developed underneath the gold cathode. It is suggested, therefore, that those silver ions which were neutralized at the cathode

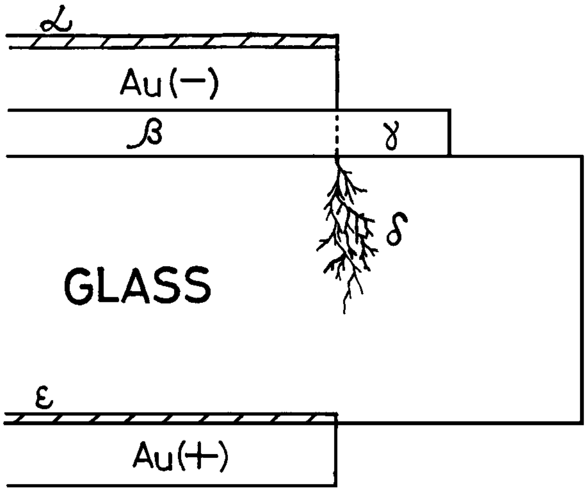


Figure 5 Schematic illustration of morphologies of electro-deposited silver, piling up beneath the gold cathode (β), within or on the outermost surface of the cathode (α), or in the forms of dendrites oozed out on the glass surface (γ), or within the glass (δ). On the anode side, the black layer was seen beneath the gold anode (ε).

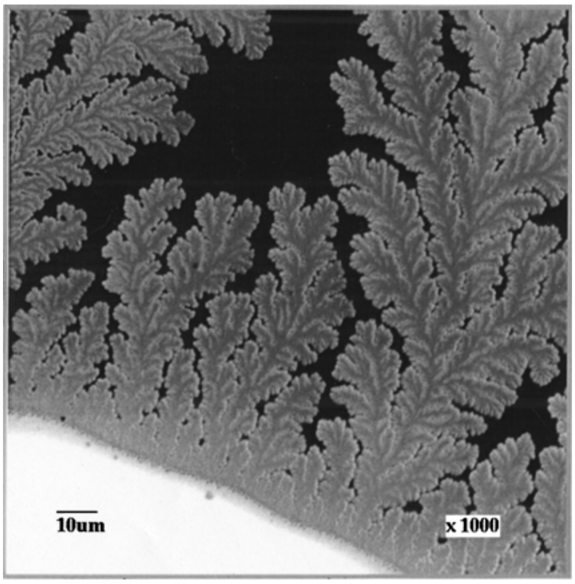


Figure 6 SEM image of dendrites which grew on the glass surface from the gold cathode (the white region at the bottom).

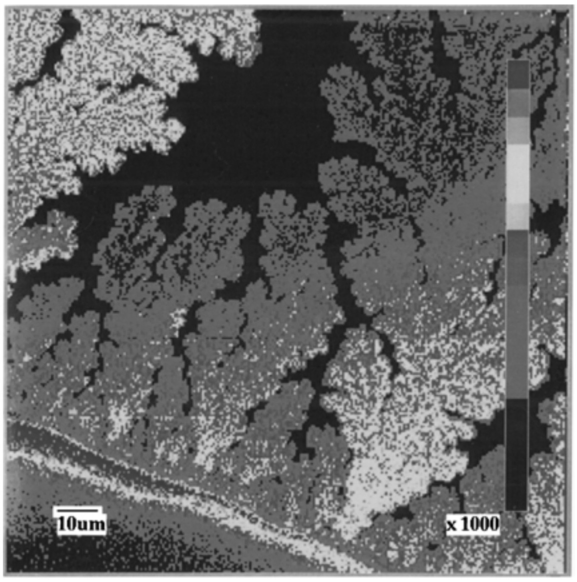


Figure 7 AES image of silver in the same frame as in Fig. 6. The bright spots are more rich in silver than the dark spots.

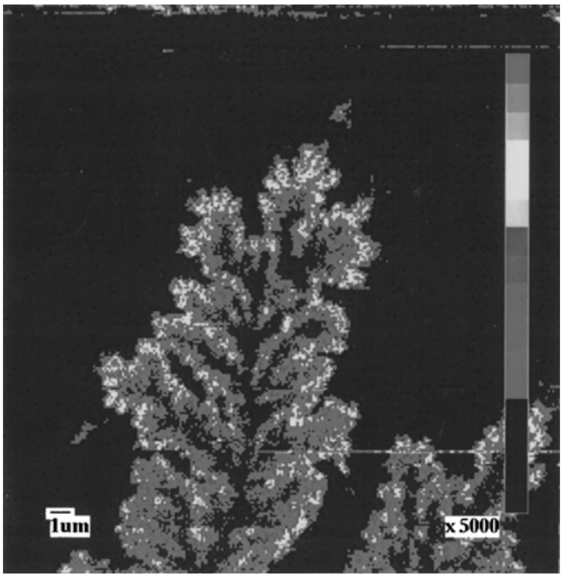


Figure 8 AES image of silver at the extremities of the dendrites. The bright spots are more rich in silver than the dark spots.

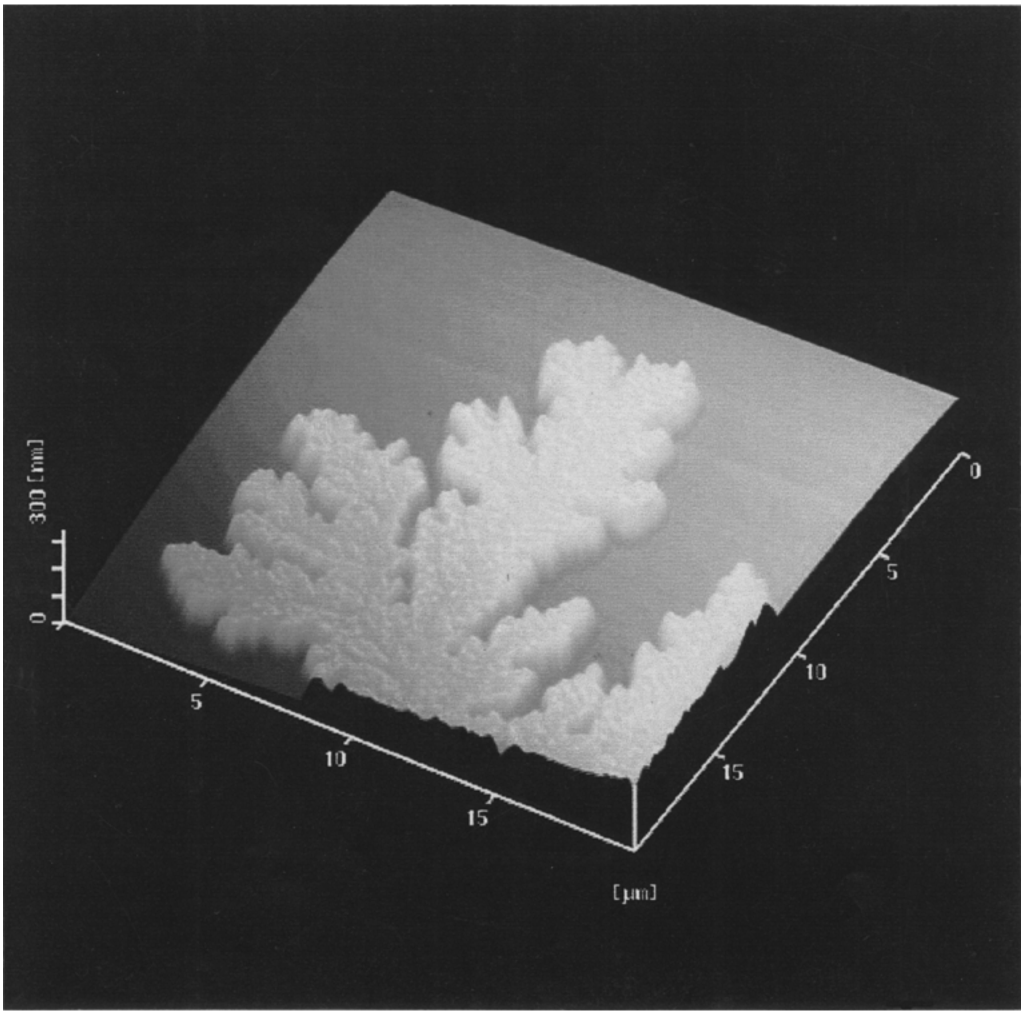


Figure 9 AFM image of dendrites which grew on the glass surface from the gold cathode, plotted in the scale of 20 μm × 20 μm × 300 nm.

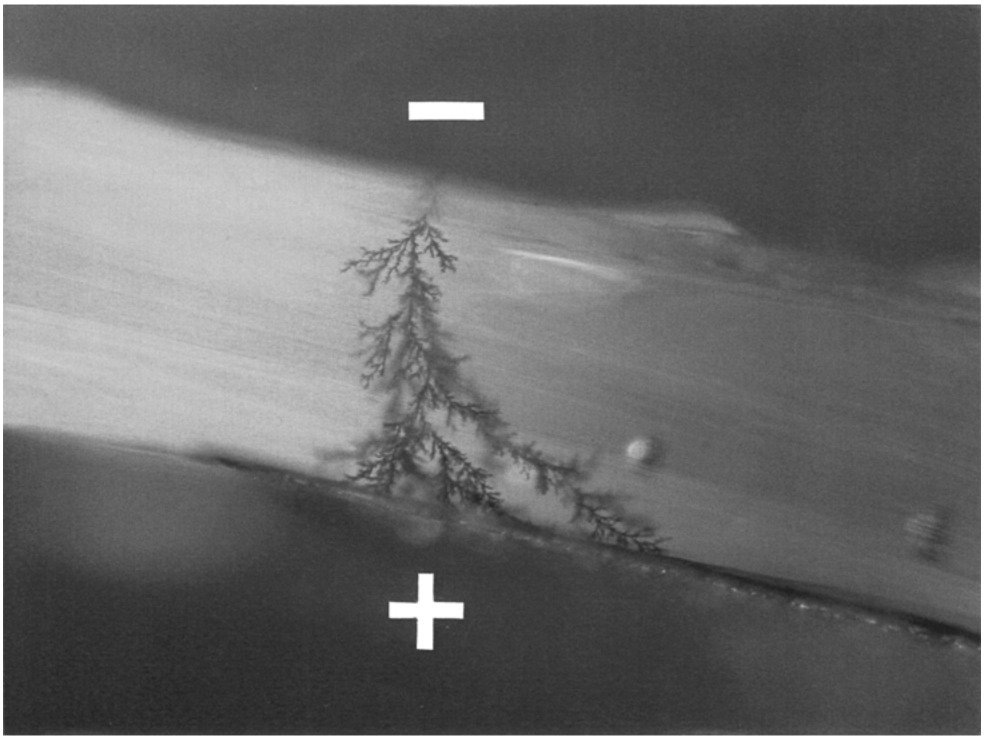


Figure 10 A typical dendrite grown from the cathode towards the anode, seen sideways. The dendrite almost reached the black layer formed underneath the anode.

pushed up the cathode above the glass, as illustrated in Fig. 5.

As suggested previously [4, 5], some of the silver ions which reach the cathode by conduction escape neutralization and conduct as ions through the cathode until their final neutralization at the outermost surface. The excess electrons (which give rise to an applied voltage) stay not only on the cathode-glass interface but also on the outermost surface of the cathode. Suppose the density of excess electrons is higher on the latter than on the former. An internal electric field thus generated within the gold cathode would induce conduction of the silver ions through the cathode until their neutralization and subsequent coagulation on the outermost surface.

Visually, the silver dendrites grew radially on the glass surface from the circlular gold cathode. The observed SEM image (Fig. 6) satisfies the model of diffusion-limited aggregation [6]. Figs 7 and 8 show AES images of silver at the roots, near the cathode, and at the extremities of the dendrites, respectively. Roughly speaking, the silver atoms were rich near the cathode and near the edges of the leaves, but poor in the veins. The topographic imaging of the dendrites by AFM (Fig. 9) substantiated this, showing that the thicknesses of the dendrites were $\sim$1000 Å but were $\sim$100 Å less at the veins. It is suggested that the silver atoms, after their neutralization at the gold cathode, oozed out radially on the glass surface, with the rate-determining step for dendritic growth being at the front. Of course, we cannot deny a possibility that the atoms came from the outside, directly from the glass, as well as from underneath the cathode.

Besides the dendrites on the glass surface, we saw the dendrites which grew from the cathode to the anode, especially from the rim of the cathode. Fig. 10 shows a typical dendrite, seen sideways, almost reaching the black layer underneath the anode. For dielectrically broken samples, one of the dendrites would reach the anode and the yellowish brown-colored deposit was seen on the anode surface, at the exit of this particular dendrite. We observed temperature rises in several degrees when the samples suffered dielectric breakdown.

4. Conclusions

Applying high dc/ac voltage to an ion-conducting glass at high temperature is equivalent to electrolyse a glass. Since our glass is a silver-ion conductor, electrodeposition of silver occurred in several morphologies; (1) Silver accumulated underneath the gold cathode and pushed up the electrode above the glass. (2) Some of the silver atoms underneath the cathode oozed out radially on the glass surface and formed the dendrites. (3) The silver dendrites grew within the glass from the cathode towards the anode and dielectric breakdown occurred when the dendrites reached the anode. And (4), some of the silver ions which reached the cathode on dc biasing were not neutralized there, but penetrated through the cathode as ions until their final neutralization on the outermost surface of the cathode.

On the anode side, we observed (1) the silver-depleted region (SDR) by conduction of the silver ions towards the cathode, (2) penetration of the gold ions deep into glass from the gold anode, and (3) conduction of the oxygen ions in the SDR (and the accompanying conduction of silver and phosphorus ions occurring, possibly, during off-biasing) towards and through the anode.

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