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# Anode and anodic interface dependent conduction of silver metaphosphate glass

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**Abstract** The electrical response of an ion-conducting glass to dc biasing was very sensitive to the anode material and anode–glass interface, especially when biasing was made under high electric field at high temperature. The response of the platinum-anoded $AgPO_3$ glass was studied, and was compared with that of the gold-anoded one. Emphasis was laid on the effect of polishing of the glass surface.

## Introduction

When we want to study ion dynamics in an ion-conducting glass, we usually deposit metal electrodes on both sides of a sample, bias it with ac/dc voltage via the electrodes, and measure the electrical response via the electrodes. We cannot escape the electrode phenomena which take place at the electrode–glass interfaces. In truth, the electrical response of a positive ion-conducting glass to dc biasing is very sensitive to the anode material used, especially when biasing is made under high electric field at high temperature. For example, Fig. 1 shows the responses of aluminum [1]-, gold [2]-, or silver [2]-anoded silver metaphosphate ($AgPO_3$) glass, a silver-ion conductor, to biasings with a dc pulse train of 500 V/cm at 140 °C, about 20° below the glass transition temperature. Here, gold was the common cathode material.

It is well known that the silver ions can easily be injected into glass on biasing when silver is used as the anode [3–9]. Therefore, in lieu of silver, gold has frequently been used as the anode material in hopes of obtaining an intrinsic response. Yet, even the gold ions can be injected into glass from the gold anode when the temperature is high and/or when an applied electric field is high [8, 10]. The response of the gold-electroded $AgPO_3$ glass to dc biasing demonstrates that gold, not to mention silver, does not play the role of an ideal ion-blocking anode.

We expected, then, that platinum may be an adequate ion-blocking anode material because of its high chemical inertness. In truth, the platinum metal has long been utilized as the crucibles for glass making. There was a report [11], however, that even the platinum metal can be dissolved into the glass melt. Matushita et al. [12] showed that, when the two platinum plates were immersed into the $(x)$PbO–$(1-x)SiO_2$ glass melt and were dc biased with a constant current, the $Pt^{+2}$ ions conducted as the dominant charge carriers after their dissolution from the platinum anode when $x$ was high.

The purpose of the present study was to check on whether the platinum metal can act as an ion-blocking anode or not. Comparison was made between the platinum-anoded and the gold-anoded $AgPO_3$ glass samples. Another purpose was to check on whether polishing of a glass surface affects the electrical response or not. Although polishing of a glass surface to mirror-flat is believed to be the routine of obtaining a reliable data, is this truly a necessary procedure? The present author has long used the as-quenched glass samples in fear of possible deteriorating effects of polishing.

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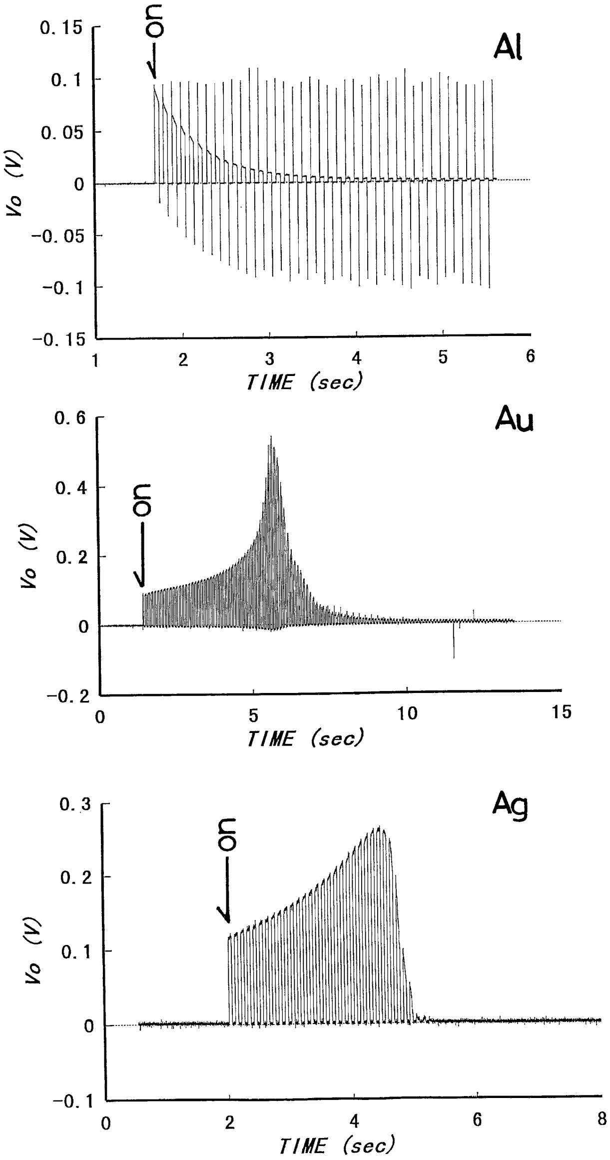

**Fig. 1** Responses of aluminum [1] (Al)-, gold [2] (Au)-, and silver [2] (Ag)-anoded samples to 500 V/cm biasing at 140 °C for 10 s

## Experimental

The samples were made by melting a mixture of appropriate amounts of $NH_4H_2PO_4$ and $AgNO_3$ in a platinum crucible at 500 °C for 1 h, quenching on a carbon plate, and depositing the gold cathode (30–100 nm thick) by evaporation and the platinum anode (~170 nm thick) by sputtering on both sides. The resultant samples, in the configuration $Pt/AgPO_3/Au$, were then dc-biased with 500 V/cm or 250 V/cm at 140 °C in vacuo, of a single pulse for 10 s or 60 s duration or of a pulse train made of pulses of 50 ms duration followed by 50 ms of off biasing. The electrical response was expressed by $V_o$, an output voltage across a reference resistor of 1.18 Ω, as a function of time. Our platinum-anoded samples were labeled Pt-1, Pt-2, etc., and the gold-anoded samples Au-1, etc., respectively. These are the non-polished samples. For the polished samples, labeled Pt(P)-1, etc., polishing of a glass surface to mirror-flat was made first with 200 sandpaper, then with 3 μm-diameter diamond slurry.

After dc runs, the depth profiles of platinum, silver, gold, oxygen, and phosphorus were measured from both sides of a sample with an X-ray photoelectron spectroscopy (XPS), after intermittent etchings of the surface with argon ions. Since the etching rate was different for different compositions and materials as well as experimental settings, the sputtering time rather than the depth was used as the abscissa.

## Results

Figure 2 shows the response curves of samples Pt-1 and Pt-2 to 500 V/cm biasings for 10 s with single (Pt-1) or multiple (Pt-2) pulses, respectively. For both samples the dielectric breakdown took place at the times marked *B*, after some "incubation period" after the initial dominant current ceased flowing. The differences found on biasing with single or multiple pulses are within scatters from sample to sample. For any samples studied to date, irrespective of the anode materials used, the current at the onset of initial biasing corresponded to the dc conductivity of this glass, $2 \times 10^{-4}$ S/cm at 140 °C [10]. It was reported [13] that, even on biasing with an electric field as high as 800 V/cm, the current at the onset of initial biasing was indifferent to the so-called "electrode polarization". It satisfied the Ohm's law.

The response curves of our Pt samples resembled those of the gold-anoded ones (Fig. 1), although the latter samples seldom suffered dielectric breakdown on 500 V/cm biasing at 140 °C [9]. The rise of the charging current to the maximum was ascribed (and was supported by the observation of temperature rise [2]) to joule heating and the accompanying increase in silver conduction. Figure 3 shows the response curve of sample Pt-3 to 250 V/cm biasing with a pulse train for 60 s and, in the bottom, the initial portion of the response. For Pt samples, 250 V/cm biasing induced current rise to a maximum and a fall thereafter. However, for Au samples, 250 V/cm biasing induced steady current decay, as is exemplified in Fig. 4 for sample Au-1.

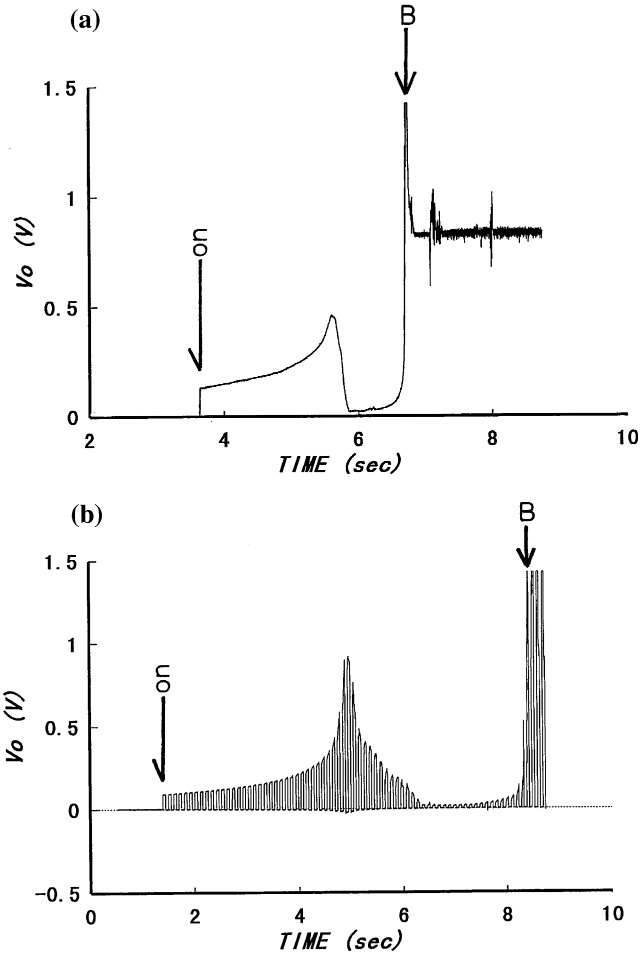

**Fig. 2** Response curves of sample Pt-1 (**a**) to single-pulse biasing with 500 V/cm for 10 s, and sample Pt-2 (**b**) to biasing with a pulse train of 500 V/cm for 10 s. The dielectric breakdown occurred at the time marked *B*. The areas covered by the curves before breakdown are 0.57 C/cm$^2$ for the former and 0.66 C/cm$^2$ for the latter

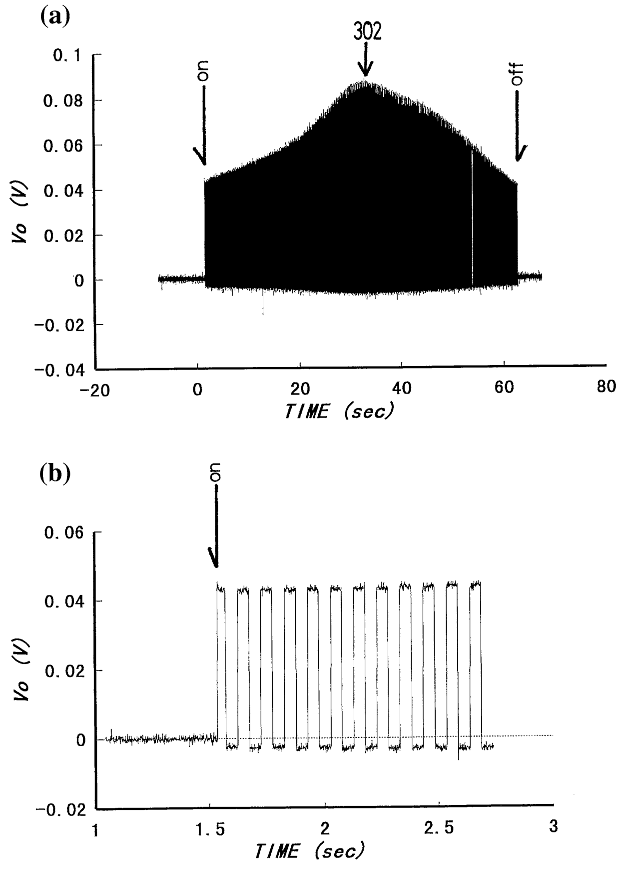

**Fig. 3** (**a**) Response of sample Pt-3 to biasing with 250 V/cm pulse train for 60 s. The area covered by the curve was 2.1 C/cm$^2$. The number 302 marks the cycle of charging/discharging at the maximum charging current. (**b**) Initial portion of the response

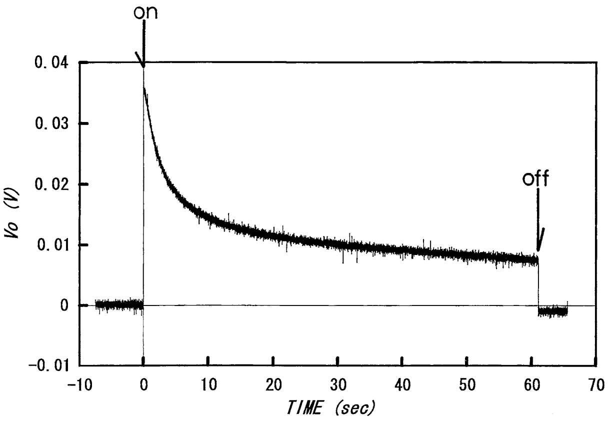

**Fig. 4** Response of sample Au-1 to biasing with 250 V/cm for 60 s. The area covered by the curve was 0.34 C/cm$^2$

For characterizing the electrode phenomena, the depth profiles were measured from the platinum anode side of sample Pt-1, Fig. 5. The depth at the end of the sputtering time was 0.5 μm. The ratios of number of atoms for oxygen-to-phosphorus, O/P, and silver-to-phosphorus, Ag/P, are plotted in the bottom. (As was always the case with depth profilings, the ratio O/P at the plateau was smaller than the nominal value of 3.) In Fig. 5, the XPS measurement was interrupted by gas evolution at the sputtering times of $1.1 \times 10^4$ s, $2.2 \times 10^4$ s, and $5.6 \times 10^4$ s at which discontinuities in data occurred. The position of platinum–glass interface may be located at the sputtering time of $6 \times 10^4$ s at which the concentrations of P and O rose midway to their final plateaus at the right. We found the formation of the positive ion-depleted region (PDR) underneath the anode by conduction of the silver ions, and some penetration of the platinum ions into the glass. For comparison, the depth profiles from both sides of 500 V/cm biased sample Au-2 (the Au sample in Fig. 1) are shown in Fig. 6 [14]. The profiles demonstrate some

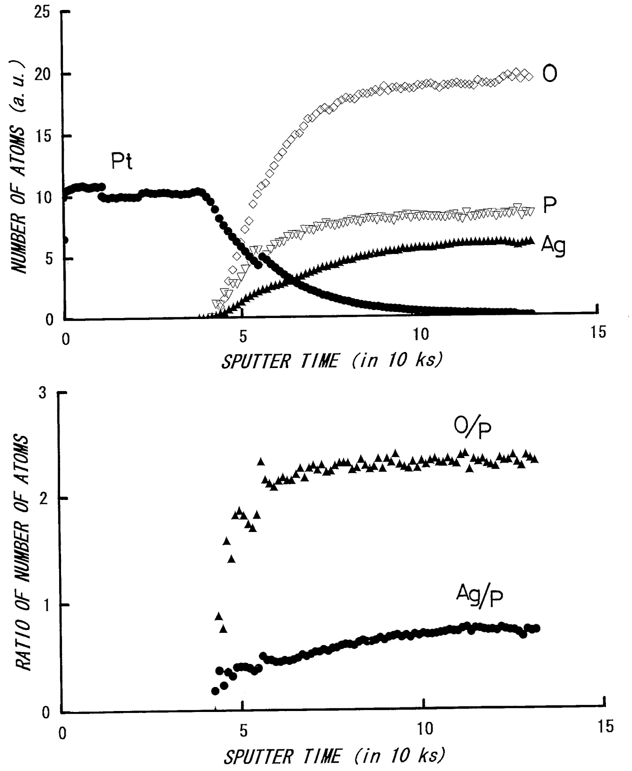

**Fig. 5** (Top) Depth profiles from the platinum anode of sample Pt-1. The XPS measurement was interrupted by gas evolution at the sputtering times of 1.1 × $10^4$ s, 2.2 × $10^4$ s, and 5.6 × $10^4$ s. The depth at the end of the sputtering time was 0.5 μm. (Bottom) The ratios of number of atoms for O/P and Ag/P

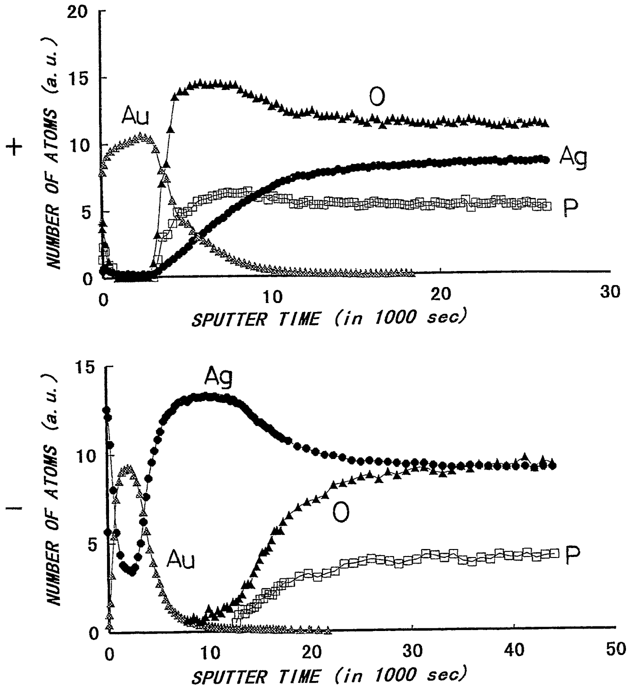

**Fig. 6** Depth profiles from both the anode (+) and the cathode (−) of gold-anoded sample Au-2 after 500 V/cm biasing for 10 s (Fig. 1). The depth at the end of the sputtering time was 0.4–0.6 μm

penetration of the gold ions into glass from the gold anode, some depletion of the silver ions out of the anode region, and accumulation of silver underneath the cathode. The depth profiles on the cathode side of sample Pt-1 (not shown) are similar to those of sample Au-2, showing that the electro-deposited silver underneath the gold cathode pushed up the cathode above the glass. Other morphologies of electro-deposited silver common to both Pt and Au samples are [15] (1) penetration of some silver ions through the gold cathode and their final deposition on the outermost surface of the cathode, (2) the formation of the silver dendrites which oozed out radially on the glass surface from the cathode, and (3) the formation of the silver dendrites which grew from the cathode toward the anode.

Let us now turn to the polishing effects of glass surfaces. Figures 7 and 8 show the responses of samples Pt(P)-1 and Pt(P)-2 (Fig. 7) or of samples Au(P)-1 and Au(P)-2 (Fig. 8) to biasings with 500 V/cm for 10 s, respectively. Although the shapes and magnitudes of the response curves of Pt(P) samples varied a little from sample to sample, with 0.5–0.8 C/$\text{cm}^2$ as the overall charge flowed during biasing, they were similar to those of the non-polished ones. (It is to be noted that the electrode areas for the polished Au and Pt samples were smaller than those of the non-polished ones. Also noted is that polishing of the glass surfaces on the cathode side did not affect the responses.) For Au(P) samples, on the other hand, polishing reduced joule-heating-induced enhancement of silver conduction, to give 0.1–0.3 C/$\text{cm}^2$ as the overall charge flowed on biasing which were lower than ~0.5 C/$\text{cm}^2$ for the non-polished, 500 V/cm-biased Au samples (e.g. Fig. 1) or lower than 0.34 C/$\text{cm}^2$ for the 250 V/cm biased non-polished sample Au-1 (Fig. 4). Besides, we did not see any dielectric breakdown during 10 s of biasing. Although the depth profiles were measured on both sides of samples Au(P)-1 and Pt(P)-1, no particular differences from those of Figs. 5 and 6 were found.

## Discussion

The dominant charge carriers in the $AgPO_3$ glass are the silver ions. When this glass is biased with dc voltage, the silver ions conduct toward the cathode first, leaving the PDR underneath the anode. In a

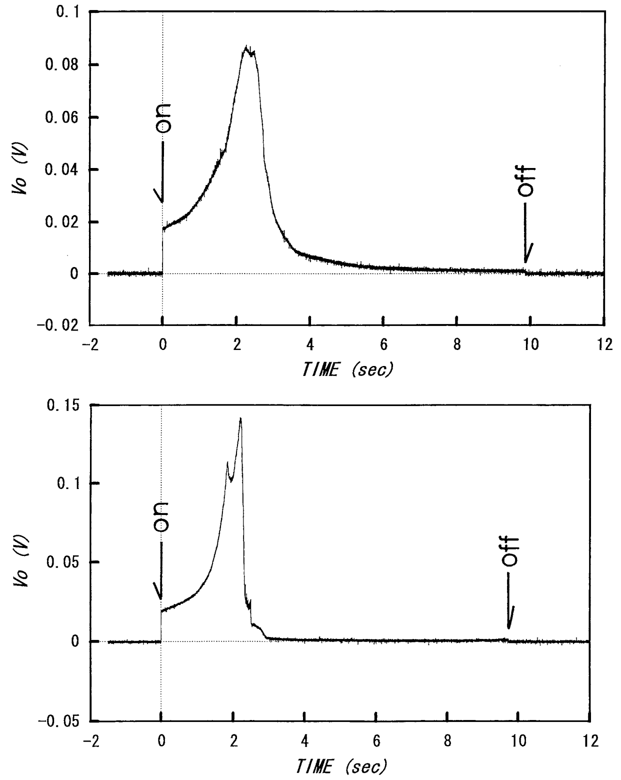

**Fig. 7** Responses of polished Pt samples Pt(P)-1 (above) and Pt(P)-2 (below) to biasings with 500 V/cm for 10 s. The areas covered by the curves are 0.75 C/cm$^2$ for the former and 0.64 C/cm$^2$ for the latter

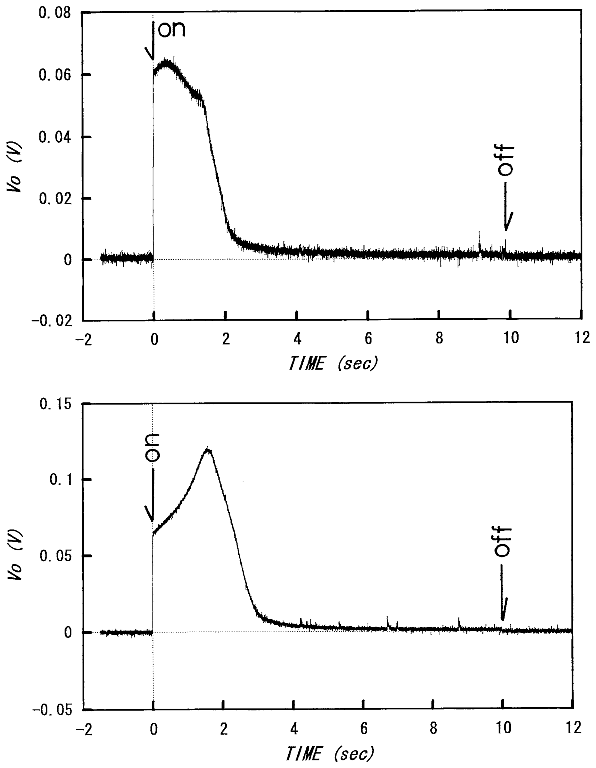

**Fig. 8** Responses of polished Au samples Au(P)-1 (above) and Au(P)-2 (below) to biasings with 500 V/cm for 10 s. The areas covered by the curves are 0.13 C/cm$^2$ for the former and 0.26 C/cm$^2$ for the latter

recent paper [14], it was demonstrated that silver depletion in the PDR was very incomplete, spanning far wider width than that estimated on the assumption that all of the silver ions within the PDR are depleted.

We see the negative current during off biasings of Au and Pt samples (Figs. 1–4). The negative current was ascribed [2] to backdiffusion of the silver ions into the PDR, caused by coulombic attraction of the negative ions within the PDR. (For Ag samples, on the other hand, easy injection of the silver ions from the silver anode would restrict the formation of the PDR, hence no negative current (Fig. 1)). As silver conduction proceeds, the PDR grows in width, to the point where a potential drop across the PDR comes close to the bias voltage and no more silver conduction. A large effective field within the PDR would enable the charge-uncompensated negative ions ($O^-$ or $PO_3^-$?) to conduct toward the anode [1].

Let us discuss biasing of Al samples. For Al samples, because of large affinity for oxidation of aluminum, no sooner the silver ions near the anode are depleted by conduction when the charge-uncompensated negative ions within the PDR would react with the anode and form an oxide layer. The sharp positive and negative current peaks seen at the onsets of biasing and off biasing (Fig. 1) were ascribed [1] to polarization and depolarization of the oxide layer thus formed. This may be the reason for the absence of the negative current in the dc biased Al samples.

For 250 V/cm-biased Pt samples (e.g. Fig. 3), conduction continued for long time without suffering dielectric breakdown, e.g. with 2.1 C/cm$^2$ as the overall charge flowed during 60 s of biasing/off biasing for sample Pt-3. The dielectric breakdown was considered [15] to arise from short-circuiting the electrodes by the silver dendrites which grew from the cathode to the anode. No dendrites were seen for 250 V/cm-biased Pt and Au samples. When the conduction current is low, the growth of the deposited silver underneath the cathode would proceed under thermal equilibrium yielding a dense crystalline layer, rather than yielding a nonequilibrated dendrites. On increasing a bias field, the possibility of dendritic growth increases. Therefore, on 500 V/cm biasing, all the Pt samples investigated so far suffered dielectric breakdown while not so for Au samples. This difference may reflect easier injection of the platinum ions from the platinum anode than the gold ions from the gold anode, and the resultant more easiness in dendritic growth from the cathode. The injected platinum ions may be the $Pt^{+2}$ ions of ionic radius of 0.80 Å which is small as compared to 1.37 Å of the $Au^{+1}$ ions, both in six coordination [16]. A near parallelism in the ratio of O/P (Fig. 5) implies that the injected platinum ions enter into the neutral voids which the disordered structure of glass provides, without disturbing the glass composition [17].

Now turn to the polishing effects of the glass surface. The shapes and magnitudes of the response curves of Pt samples did not change so much on polishing, except suppression of dielectric breakdown (Fig. 7). For Au samples, on the other hand, polishing greatly diminished the overall charge flowed on biasing, although the current density at the onset of initial biasing remained the same (Fig. 8). Such a difference between the polished Pt and the polished Au samples may be explained as follows: Polishing induces damage in the structure of the glass surface, by which the injection of the anode metal ions into glass may be restricted. Less would be the injectability of the large-sized gold ions than the small-sized platinum ions. As a result, the PDR in the Au(P) sample is more liable to become electrically insulating by poorer injectability of the gold ions into the PDR. The formation of an insulating PDR inhibits joule heating, hence no enhancement in silver conduction.

## Conclusion

The electrical responses of the platinum-anoded $AgPO_3$ glass samples to biasings with 500 V/cm or 250 V/cm at 140 °C were studied and were compared with those of the gold-anoded ones. Emphasis was laid on the effects of polishing of the glass surfaces on the responses of platinum- or gold-anoded samples. It was found that the responses were very sensitive to the anode materials used, and to the anode–glass interfaces.

Roughly speaking, the responses of Pt and Au samples were very similar to each other. However, it is suggested that the platinum ions are easier to be injected into glass on biasing than the gold ions because of smaller ionic radius. Continuous injection of the anode metal ions keeps the PDR from electrically insulating. As a result, rapid dendritic growth of the deposited silver and the resultant dielectric breakdown are more liable to occur in Pt samples than in Au samples. Polishing, however, destructs the surface structure of glass, and reduces injectability of the anode metal ions into glass. The overall charge flowed on biasing is therefore reduced by polishing, especially for Au samples as compared to Pt-anoded ones.

From the above result, it is suggested that the technique of maintaining a current as long time as possible and obtaining a charge flowed on biasing as large as possible is (1) by adjusting a bias voltage to an appropriately high value not to make the PDR electrically insulating by continuous injection of the anode metal ions into the PDR, but (2) by adjusting a bias voltage to a low conduction current level not to yield dendritic growth of the deposited silver from the cathode. That is, a compromise seems to be inevitable.

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