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Effect of annealing on aging characteristics of MgO-CaO film as a protective layer for AC PDP

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The present generation of AC plasma display panels (AC PDP) requires further improvement because of poor voltage characteristics and high production cost. The voltage characteristics of AC PDPs are greatly affected by a protective layer because it is directly exposed to the gas plasma. To replace the conventional MgO protective layer in order to improve the voltage characteristics, panels with various protective layers of an MgO-CaO system were prepared by an e-beam evaporation method. Among the oxides of various composition of the MgO-CaO system, a panel with an $Mg_{0.9}Ca_{0.1}O$ protective layer had the lowest firing and sustaining voltages. But, it exhibited poor aging characteristics, compared to the conventional MgO protective layer. A post annealing process was introduced so as to improve the surface properties and aging characteristics of the $Mg_{0.9}Ca_{0.1}O$ protective layer in this work. The annealing process was performed in nitrogen gas as a function of holding time at 400 °C. From XRD analyses, the (111) orientation formed in the as-deposited $Mg_{0.9}Ca_{0.1}O$ thin film remained unchanged after the annealing process. However, the surface morphology of the $Mg_{0.9}Ca_{0.1}O$ protective layer, which is closely related to its aging characteristics was greatly affected by the annealing conditions. The refractive index of the $Mg_{0.9}Ca_{0.1}O$ thin film was increased by the annealing process at 400 °C for 5 h, which is probably due to an increase in film density. The sustaining voltage of the annealed $Mg_{0.9}Ca_{0.1}O$ film is lower in the initial aging period but higher than that of the as-deposited $Mg_{0.9}Ca_{0.1}O$ film after obtaining a stable voltage. However, the annealing in nitrogen gas made the aging process much shorter, compared to that of the as-deposited $Mg_{0.9}Ca_{0.1}O$ film. The aging characteristic of the $Mg_{0.9}Ca_{0.1}O$ protective layer was found to be greatly improved by the annealing process in nitrogen gas at 400 °C for 5 h.

1. Introduction

Large plasma display panels (PDP) are already competing effectively against cathode-ray-tubes (CRT) and liquid crystal (LC) projectors for presentation and entertainment applications, in spite of their high price range. Furthermore, larger panels with higher resolution are currently under development. However, the PDP technology still needs further improvements in production cost and display quality to be competitive. There are three major strategies for reducing the cost of PDP: lower operating voltage, lower peak current, and a reduced number of high-voltage drivers [1]. Among these, the operating voltage of a PDP is highly affected by the protective layer materials because the operation mechanism of the AC PDP is based on the gas discharge phenomenon through the protective layer that covers the dielectric layer. Therefore, the protective layer plays an important role in the discharge characteristics because it is directly adjacent to the gas [2]. The prospective MgO-CaO protective material, which is expected to replace the conventional pure MgO protective layer, was reported in our earlier study [3]. It was found to have better voltage characteristics and a higher secondary electron emission coefficient than those of the MgO protective layer. It, however, has to be examined with respect to the stability of the sustaining voltage for a long time, which is closely connected with its life span, in order to be reliably applied to the protective layer of the AC PDP in place of the MgO.

Generally, many processes such as sealing, outgassing, and aging are needed to be carried out for the production of the PDP. Particularly, the long aging process to get a stable voltage characteristic by activating the protective layer is one of the main reasons for the increase in the production cost of the PDP due to its excessive power consumption and processing time. Therefore, to cut down the production cost of the PDP to the level of the CRT, the time consumed in the

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aging process has to be minimized. In this work, the aging characteristic of the MgO-CaO protective layer that showed better electrical performance is compared with that of the conventional MgO protective layer and the annealing process in nitrogen gas is introduced to improve the aging characteristics of the MgO-CaO films.

2. Experimental details

The process to fabricate evaporation sources was reported elsewhere [3]. An e-beam evaporation chamber was pumped by an oil-diffusion pump to a base pressure of 5×10^{-4} Pa. The input power of an electron-gun was 1.2 kW, a high-voltage 180° bent-beam electron gun was used, and the accelerating high-voltage was fixed constantly at 4 kV. Substrates were not heated and oxygen gases were not introduced in the chamber. The film thickness was controlled by evaporation time and was later measured by using a surface profilometer. The microstructure of the layers was obtained by a thin film X-ray diffractometer (XRD) with a Cu target at 40 kV and 120 mA. The surface topograghy of the films was obtained by a field emission scanning electron microscopy (FESEM). The refractive index of the evaporated films was evaluated by an AutoEL-II automatic ellipsometry with a wavelength of 670 nm and then the film density was calculated by using the Lorentz-Lorentz relationship from the measured refractive index values [4]. Composition of the $Mg_{0.9}Ca_{0.1}O$ films before and after annealing was analyzed by a Auger electron spectroscopy (AES). To determine the voltage characteristics of the panels, the dielectric layers were printed on soda-lime glass substrates, followed by a printing of the silver electrodes which had a line width and gap of 200 μm and 100 μm, respectively. The protective materials with 300-nm thickness were deposited by the electron beam evaporation method on the dielectric layers. The voltage characteristics of the panels were then evaluated in a specially designed chamber filled with He gases at 300 Torr [3]. The heat treatment to improve the aging characteristics of the MgO-CaO protective layer was performed in nitrogen gases with the heating rate of 4 °C/min up to 400 °C as a function of the holding time. A number of measurements mentioned above, such as the XRD, AES, SEM and ellipsometry were performed before and after the annealing process so that we could inspect the effect of the annealing process on the physical and electrical properties of the MgO-CaO films.

3. Results and discussion

Fig. 1 shows the firing voltage (V_f) and the memory coefficient (MC) as a function of the [CaO/(MgO + CaO)] ratio in the starting powder materials. The memory coefficient (MC) for the MgO-CaO system was determined by using the following equation [5].

$$MC = 2 \times (V_f - V_s)/(V_f)$$

where V_f and V_s are firing voltage and sustaining voltage, respectively.

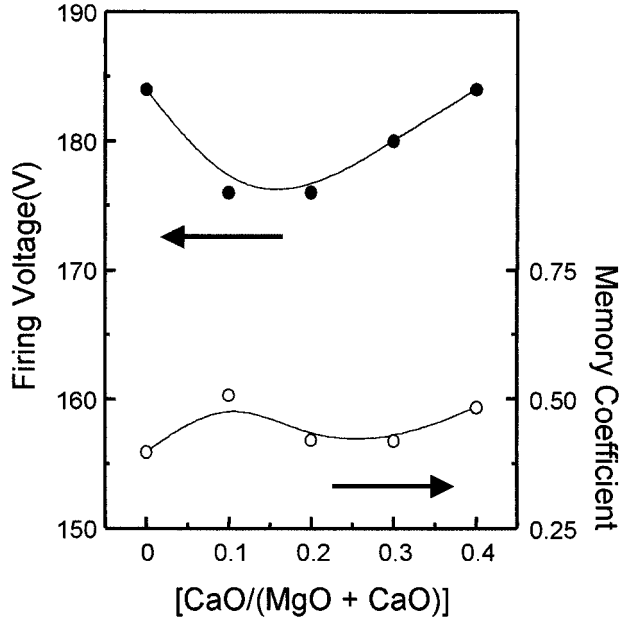

Figure 1 Firing voltage and memory margin of $Mg_{1-x}Ca_xO$ films as a function of [MgO/(MgO + CaO)] ratio in starting materials.

The firing voltage decreased rapidly with the addition of a small amount of the CaO to the pure MgO. When an excessive CaO content {[CaO/(MgO + CaO)] ratio > 0.2} was used, the firing voltage however, increased gradually in proportion to the CaO concentration. This reveals that the panel with the [CaO/(MgO + CaO)] ratio in the starting powder mixture in the range between 0.1 or 0.2 can be operated at the smallest V_f value. In the case of the MC value, the panel with the CaO content of 0.1 showed a maximum in Fig. 1. The large MC value means that there is a high probability of stable operation of the panel. The more desirable concentration of the CaO in the mixture, however, is considered to be 0.1 because the MC value is slightly larger than that of 0.2. Detailed descriptions of the reasons why the voltage characteristics of the MgO-CaO protective layers were lower than that of the conventional MgO protective layer and the effect of CaO addition on the physical properties were reported elsewhere [3].

The aging characteristics of the panels with the protective layer of the MgO and $Mg_{0.9}Ca_{0.1}O$ protective layers were examined in terms of the sustaining voltage as a function of the aging time as shown in Fig. 2 in order to compare the voltage stability of the $Mg_{0.9}Ca_{0.1}O$ protective layer which exhibited the best electrical performance among the films of the MgO-CaO system. The sustaining voltage of the pure MgO protective layer exhibits a gradual decrease in the initial stage and then approaches a stable voltage after aging for about 400 min. However, the $Mg_{0.9}Ca_{0.1}O$ protective layer shows a steeper slope in the sustaining voltage in the earlier stage of about 200 min and then exhibits a slower decrease until it resumes a stable voltage characteristic by the time of about 700 min. This time taken for the $Mg_{0.9}Ca_{0.1}O$ protective layer is much longer than that of the panel with the pure MgO protective layer. As mentioned above, the aging process has to be minimized in order to cut down the production cost and the

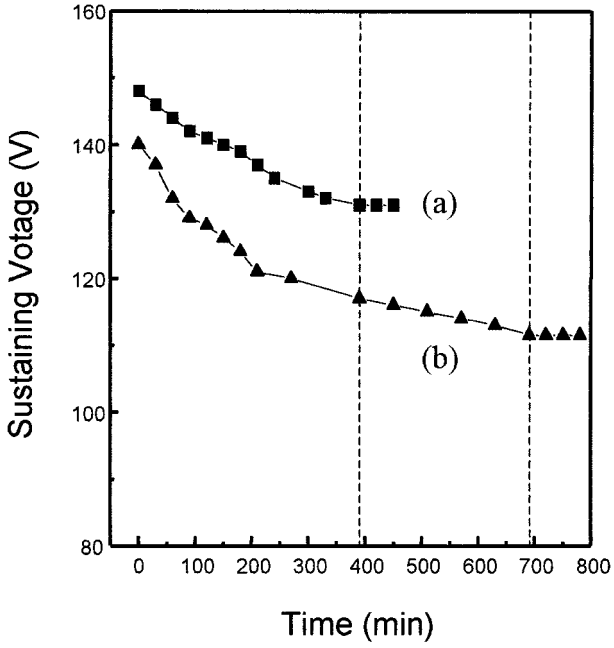

Figure 2 Aging characteristics of panels with (a) MgO and (b) $Mg_{0.9}Ca_{0.1}O$ protective layers.

processing time of the AC PDP. Therefore, it is believed that the improvement in the aging characteristics as well as a low firing voltage and a high MC value are essential factors for the successful substitution of $Mg_{0.9}Ca_{0.1}O$ for the conventional MgO protective layer. In this study, the annealing process was introduced for the purpose of improving the aging characteristics of the $Mg_{0.9}Ca_{0.1}O$ protective layer.

Fig. 3a and b show Auger depth profile of the $Mg_{0.9}Ca_{0.1}O$ films before and after annealing at 400 °C for 5 h. Even though the annealing process was done in nitrogen gas ambient, nitrogen gases were not absorbed on the film surface, but contents of oxygen increased at the film surface due to oxygen remained in chamber wall. This increase in the oxygen content in the film is believed to alter the energy band structure and then affect the secondary electron emission characteristics of protective layers [6], resulting in higher sustaining voltage of $Mg_{0.9}Ca_{0.1}O$ film annealed for 5 h at 400 °C in the final stage of aging characteristics than that of as-deposited MgO film.

The X-ray diffraction patterns obtained from the as-deposited MgO and $Mg_{0.9}Ca_{0.1}O$ films, respectively, are shown in Fig. 4a and b. Fig. 4c and d show the X-ray diffraction patterns of the $Mg_{0.9}Ca_{0.1}O$ film after the annealing at 400 °C for 3 h and 5 h, respectively. The XRD pattern of the pure MgO film (Fig. 4a) shows (111) orientation along with small peaks of (200), (220) and (222). When CaO is added to the MgO (Fig. 4b), increases in the intensities of both (111) and (200) peaks are observed with the corresponding peak shifting to lower diffraction peak positions. But, the crystalline structure of the $Mg_{0.9}Ca_{0.1}O$ film is still cubic and no further phase transformation is detected. After the subsequent heat treatment of the $Mg_{0.9}Ca_{0.1}O$ film for up to 5 h, no obvious change can be found, as shown in Fig. 4c and d.

Because the voltage characteristics of AC PDP are highly affected by the surface properties of the

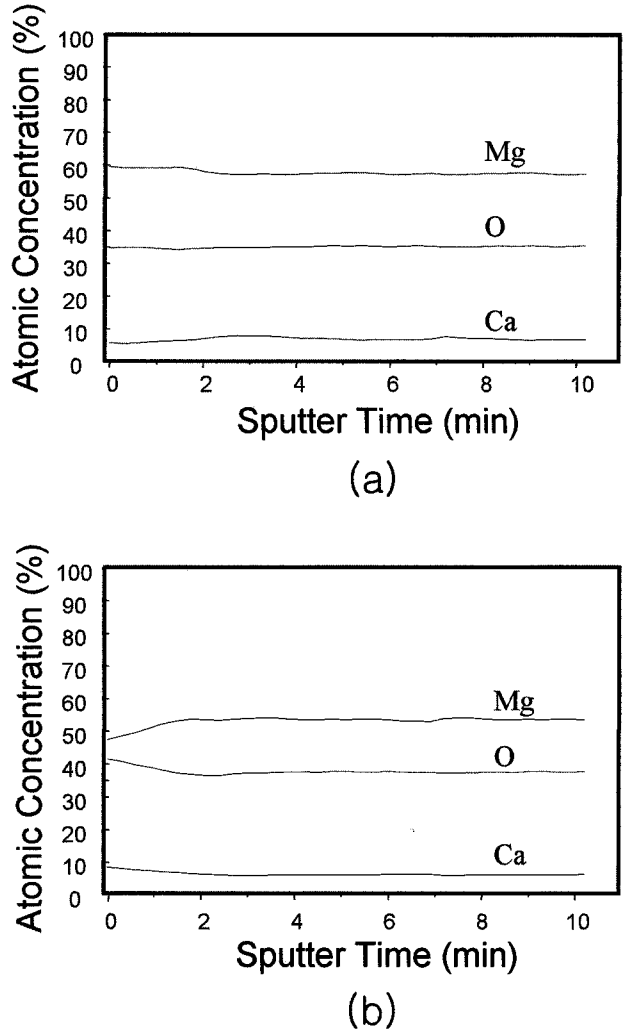

Figure 3 Auger depth profile of (a) as-deposited $Mg_{0.9}Ca_{0.1}O$ film and (b) $Mg_{0.9}Ca_{0.1}O$ film after annealing at 400 °C for 5 h.

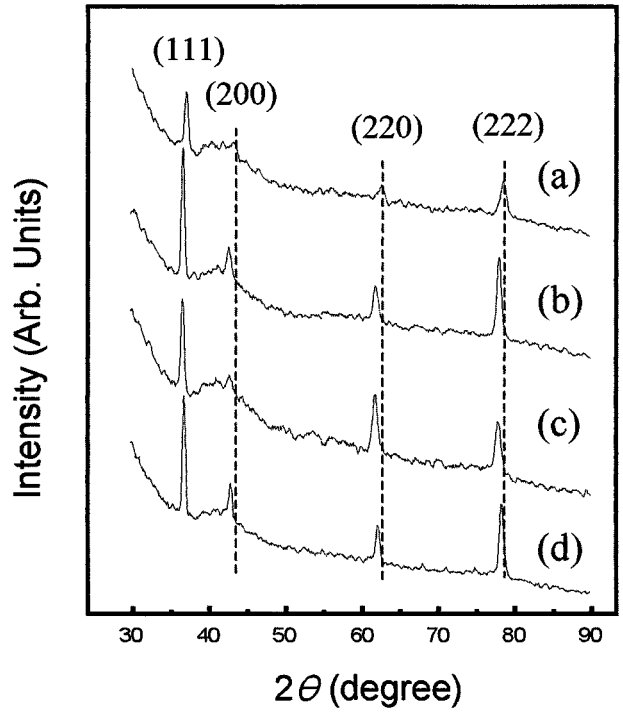

Figure 4 XRD patterns of (a) as-deposited MgO film, (b) as-deposited $Mg_{0.9}Ca_{0.1}O$ film, (c) $Mg_{0.9}Ca_{0.1}O$ film after annealing at 400 °C for 3 h, and (d) $Mg_{0.9}Ca_{0.1}O$ film after annealing at 400 °C for 5 h.

protective layer, the surface morphologies of the $Mg_{0.9}Ca_{0.1}O$ film before and after the annealing process were investigated by the field emission scanning electron microscopy (FE SEM). Fig. 5 shows the FE SEM images of the specimens: (a) the as-deposited $Mg_{0.9}Ca_{0.1}O$ film, (b) the $Mg_{0.9}Ca_{0.1}O$ film after the annealing process for 3 h, and (c) the $Mg_{0.9}Ca_{0.1}O$ film after the annealing process for 5 h, respectively. After annealing for 3 h, the grain size of the $Mg_{0.9}Ca_{0.1}O$ film was found to have increased and the micro cracks which were formed before the annealing increased in size and amount probably due to the agglomeration of particles. Such large cracks tend to induce voltage instability and furthermore, reduce the life span of the PDP because the dielectric layers cannot be effectively

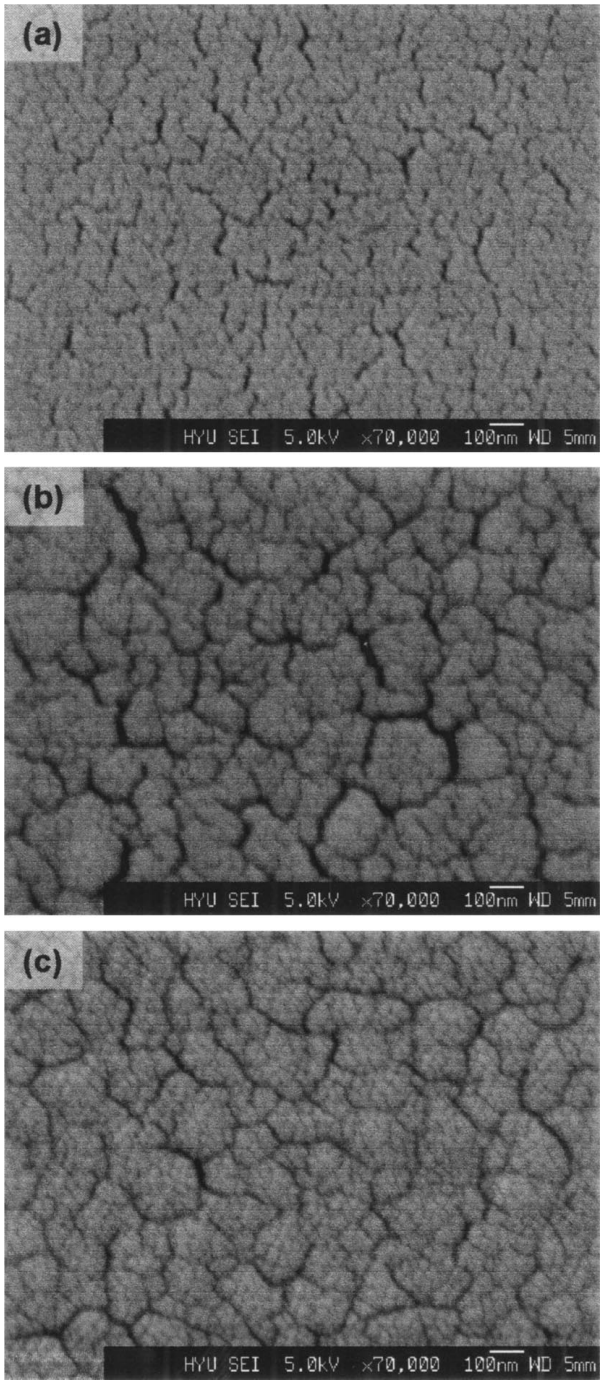

Figure 5 FESEM images of $Mg_{0.9}Ca_{0.1}O$ film (a) as-deposited, (b) after annealing at 400 °C for 3 h, and (c) after annealing at 400 °C for 5 h.

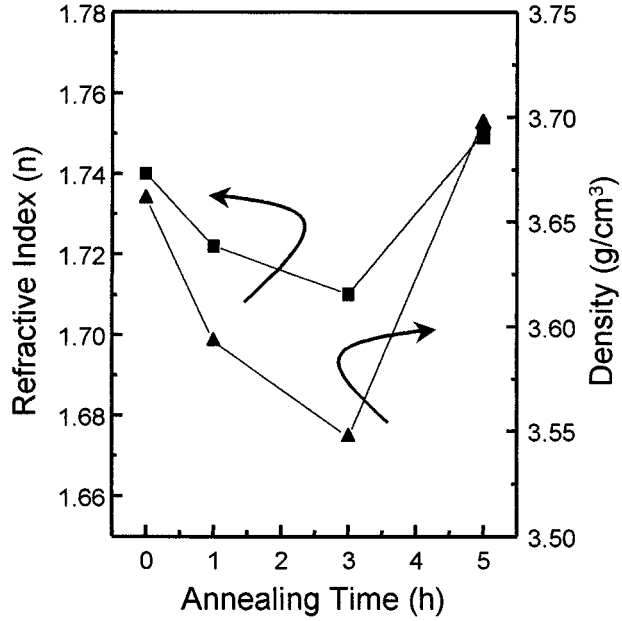

Figure 6 Refractive index and density of $Mg_{0.9}Ca_{0.1}O$ film as a function of heat treatment time.

protected during long periods of operation. However, the surface morphology of the $Mg_{0.9}Ca_{0.1}O$ film after annealing for 5 h is observed to be uniform and dense with a reduction in crack size. Therefore, a heat treatment of well over 3 h is needed in order to obtain good surface property without increasing the crack size.

The film density can be calculated from the refractive index by the Lorentz-Lorentz equation,

$$\rho = K(n^2 - 1)/(n^2 + 2)$$

where ρ, K, and n are the film density, a constant and the measured refractive index, respectively. The K value is 9.078, which was calculated from the refractive index (1.737) and the density (3.65 g/cm^3) of the bulk MgO [7]. Fig. 6 shows the refractive index and the calculated film density. The refractive index and the density of the as-deposited $Mg_{0.9}Ca_{0.1}O$ film are 1.74 and 3.632 g/cm^3, respectively. As the heat treatment time increased to 3 h, the refractive index of the film slightly decreased and the film density also decreased. However, both the refractive index and the density of $Mg_{0.9}Ca_{0.1}O$ film increased abruptly when annealed for up to 5 h. Such increases in the density and the refractive index are thought to be due to the increase in the packing ratio of the film by the heat treatment because the cubic structure of the film remained unchanged and no phase change had occurred, as shown in Fig. 4. Uchiike *et al*. also suggested that the increase in the film density might affect the electrical characteristics of the panels, which however, is open to further in-depth study [8]. The above experimental consideration reveals that the heat treatment at 400 °C for 5 h improved the physical properties of the $Mg_{0.9}Ca_{0.1}O$ film such as the crystallinity, the surface morphology and the film density.

The aging characteristics of the $Mg_{0.9}Ca_{0.1}O$ film annealed for 5 h that exhibited the best properties in terms of the surface morphology and the film density, were examined using He gas of 300 Torr as the discharging gas

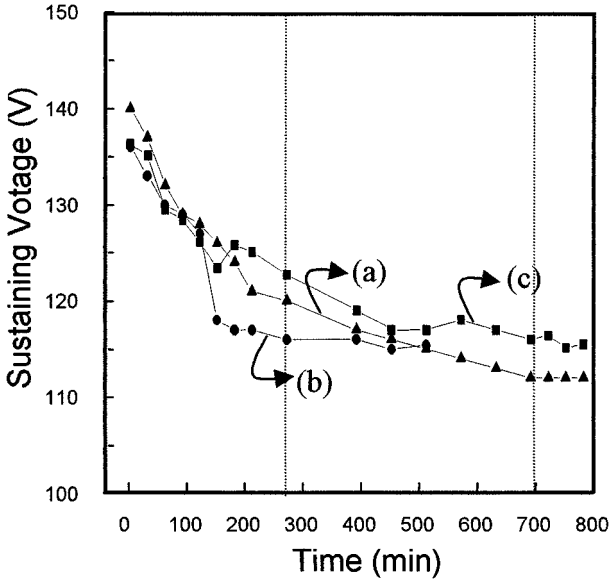

Figure 7 Aging characteristics of panels with $Mg_{0.9}Ca_{0.1}O$ film (a) as-deposited, (b) after annealing at 400 °C for 3 h, and (c) after annealing at 400 °C for 5 h.

as shown in Fig. 7. The aging curves of the as-deposited and annealed at 400 °C for 3 h $Mg_{0.9}Ca_{0.1}O$ films were replotted in Fig. 7 for comparison. The $Mg_{0.9}Ca_{0.1}O$ film after the annealing for 5 h exhibited the initial sustaining voltage of 136 V (curve (b)), which is 4 V smaller than that of the as-deposited $Mg_{0.9}Ca_{0.1}O$ film (curve (a)) and became stable at 116 V by the time of 270 min, which is much shorter than that of the as-deposited film in spite of slightly higher voltage by 4 V. One feature is that the sustaining voltage of the $Mg_{0.9}Ca_{0.1}O$ film annealed for 5 h is lower in the initial aging period but higher than that of the as-deposited $Mg_{0.9}Ca_{0.1}O$ film after obtaining a stable voltage. This initial decrease in the sustaining voltage after the annealing is a general effect of heat treatments due to significant reduction in the amount of impurities such as OH groups which was contained in the as-deposited film before the annealing [9, 10]. Meanwhile, the higher sustaining voltage of the annealed film in the final stage after the stabilization of the voltage, seems to be related to increased contents of oxygen in surface of film. However, in the case of the $Mg_{0.9}Ca_{0.1}O$ film annealed for 3 h which showed low density and much crack, the initial decrease in the sustaining voltage showed a similar curve to the film annealed for 5 h due to same reason, however, in later stage, it was unstable, showing the highest sustaining voltage of all sample.

From this fact, It is confirmed that the aging characteristics of the panels with the $Mg_{0.9}Ca_{0.1}O$ protective layer could be greatly improved by proper heat treatment despite small increases in the sustaining voltage.

4. Conclusions

To replace the conventional MgO protective layer, the $Mg_{0.9}Ca_{0.1}O$ protective layer was deposited by the e-beam evaporation method. The $Mg_{0.9}Ca_{0.1}O$ protective layer had lower firing and sustaining voltages but exhibited poor aging characteristics compared to the MgO protective layer. The annealing process in the nitrogen gas at 400 °C was introduced in order to improve the aging characteristics of the $Mg_{0.9}Ca_{0.1}O$ protective layer in this work. The film structure remained unchanged and no further phase transformation was detected in the subsequent heat treatment. However, the surface morphology of the $Mg_{0.9}Ca_{0.1}O$ protective layer was greatly affected by the annealing condition. After annealing for 3 h, the grain size of the $Mg_{0.9}Ca_{0.1}O$ film was found to have increased and the micro cracks, which were formed before the annealing, increased in size and amount probably due to the agglomeration of particles. But, the uniform film without micro cracks was obtained through the annealing in nitrogen gas for 5 h. The refractive index value of the film was also increased by the annealing in the nitrogen gas for 5 h due to an increase in film density. During the aging process, the initial sustaining voltage of the annealed $Mg_{0.9}Ca_{0.1}O$ protective layer decreased slightly compared to that of the as-deposited film but exhibited a little increase after the stabilization of the sustaining voltage probably due to the increased contents of oxygen in surface of film. However, this aging process to get a stable voltage was much shorter than that of the panel with the as-deposited $Mg_{0.9}Ca_{0.1}O$ protective layer. Therefore, it was confirmed that the aging characteristics of the panel were affected by the surface properties such as the surface morphology, the film density on protective layers and that the annealing process in the nitrogen gas at 400 °C for 5 h could improve the aging characteristics of the $Mg_{0.9}Ca_{0.1}O$ film.

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