Low-voltage characteristics of MgO-CaO films as a protective layer for AC plasma display panels by e-beam evaporation

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The MgO-CaO composites films were prepared by e-beam evaporation to improve both operating voltages and memory coefficient of a protective layers for AC plasma display panels (PDPs). The effects of CaO addition to the conventional MgO films on both the electrical properties and the structural changes of the $Mg_{1-x}Ca_xO$ thin films deposited on the slide glass substrates were investigated. Atomic force microscopy (AFM) results revealed that the $Mg_{0.8}Ca_{0.2}O$ film had a very rough surface due to the formation of a second phase on the surface. By adding controlled amount of CaO, the Mg-Ca-O films showed a firing voltage of 176 V that is lower than that of the conventional 100% MgO film. The deposition rates of 40–100 nm/min were obtained as a function of [CaO/(MgO + CaO)] ratio of the evaporation source materials. © *1999 Kluwer Academic Publishers*

1. Introduction

Plasma display panels (PDPs) are already available for commercial sales and expected to be one of the leading flat panel display systems with large panel areas in the near future. PDPs, however, have serious problems to solve, such as short lifetime performance and high firing voltage (V_f) which resulted in need of high cost ICs. In the AC-type PDP, MgO thin film has been widely used as a surface protective layer for dielectric materials owing to its very low sputtering yield (0.36 for bombarding argon ion of 600 eV), work function (3.1–4.4 eV), very large band gap (7.3 eV) and large secondary electron emission coefficient (Y) [1]. Nevertheless, the current MgO protective layer is thought to be still not one of the best materials to meet the demand of advanced high vision PDPs with good light emission efficiency, low power consumption and high image fidelity. Thus, in order to cut down the production cost to the level of the CRTs, and to improve the overall performance of PDPs, new materials for protective layers with better characteristics are needed. Therefore, intensive researches have been carried out to find the materials which will reduce the demanding voltage for discharging and which will then be compatible with integrated circuits. Shinoda *et al.* studied the mixture of CaO-SrO system, which had the lowest firing voltage among the mixtures of various alkaline earth metal oxides [2]. The mixtures had, however, poor memory margins as compared to those of MgO films. Ahearn *et al.* studied the influence of controlled levels of important reactive impurities on the aging characteristics of the operating voltages, but their results did not obtain lower operating voltages [3].

In this work, new panels by adapting Mg-Ca-O films for a protective layer to replace the conventional pure MgO protective layer were fabricated. The relationships among firing voltage, the minimum sustain voltage, and memory coefficient of Mg-Ca-O thin films were evaluated as a function of Ca contents in films.

2. Experimental details

The MgO and CaO powders of 99.95% purity (Cerac Co.) were used for powder mixtures of various desired compositions. Powder mixtures were ground and then cold-pressed into disks to use as evaporation sources at the pressure of 2000 Pa. Heat treatment at 1200 °C in

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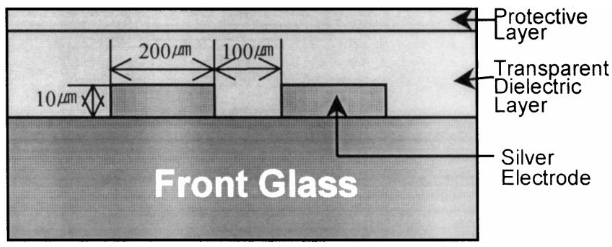

Figure 1 Schematic diagram of fabricated panel structure.

TABLE I Composition of $Mg_{1-x}Ca_xO$ thin films obtained by EDS

[CaO/(MgO + CaO)] of starting materials	Concentration of elements (at %)		
	Mg	Ca	O
0	49.4	0	50.6
0.1	47.1	1.3	51.6
0.2	42.44	6.55	51.01
0.3	42.24	7.6	50.16

vacuum were performed for 3 h. E-beam evaporation chamber was pumped by an oil-diffusion pump to a base pressure of 5×10^{-4} Pa. The film thickness was controlled by evaporation time and measured by using a surface profilometer. The surface morphology of the films was obtained by a scanning electron microscopy (SEM). Surface roughness of the film was characterized by employing a atomic force microscopy (AFM).

To test voltage characteristics of panels, dielectric layers were printed on soda-lime glass substrates, followed by deposition of electrodes which has the line width and gap of 200 and 100-μm, respectively. Fig. 1 shows the schematic diagram of fabricated panel, which is surface-discharge ac plasma display type. Voltage characteristic of panels was examined in a specially designed chamber filled with He gas at 300 Torr.

To reduce the operating voltage of panels, a layer of MgO and CaO mixture of 2000 Å in thickness was evaporated as a protective layer in place of the conventional MgO [4, 5]. It was reported that alkaline earth metal oxides had low work functions which were closely related to high secondary electron emission coefficients [2]. A high-voltage 180° bent-beam electron gun with input power of 1.4 kW was used and accelerating high-voltage was fixed constant at 7.0 kV. No oxygen gas was introduced in the chamber.

Andreadakis [6] reported the result of comparison between non-barrier and barrier structures for devices filled with three different gases. Thus, it would have better operating characteristics of MgO-CaO films than our results, if barrier ribs were introduced to the panels.

3. Results

Fig. 2 shows the relationship between evaporation rate and composition of $Mg_{1-x}Ca_xO$ films. Deposition rate

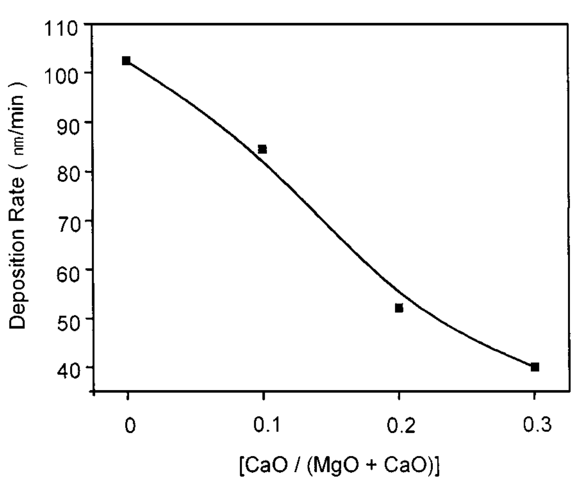

Figure 2 Deposition rate of $Mg_{1-x}Ca_xO$ thin films.

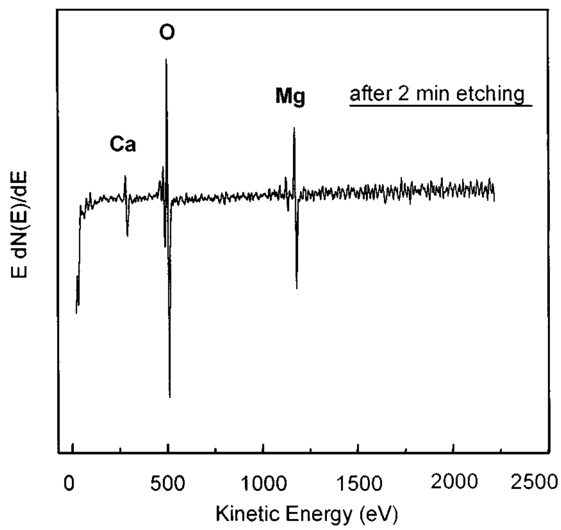

Figure 3 AES spectrum of MgO-10% CaO film.

of the films is in the range of 40–100 nm/min. Decrease in the deposition rate was observed with increasing the [CaO/(MgO + CaO)] ratio. It is difficult to find out the exact mechanism for the decrease of deposition rate with the increase in CaO amount. This lower deposition rate was, probably, attributed to the lower vapor pressure of CaO than that of MgO. Such trend is confirmed by the variation of the composition of the deposited films.

The chemical compositions of the film, by energy dispersive spectrometry (EDS), were shown in Table I. As the ratio of evaporation source materials [CaO/(MgO + CaO)] increased, a deviation from the linear relationship in Ca concentration between the starting materials and the deposited films was observed resulting from the lower vapor pressure of CaO compared to that of MgO [5]. The deposited films were thus depleted to some degree of Ca concentration [7].

The spectrum of the Auger electron spectroscopy (AES) for the $(Mg_{0.9}Ca_{0.1})O$ film after 2 min Ar ion etching is shown in Fig. 3. Both Ca and Mg peaks with kinetic energies of 292 and 1183 eV, respectively, were observed. No other peak, except Ca, Mg and O peak, is observed. These results confirm that the deposited Mg-Ca-O films are well produced by e-beam evaporation from mixed sources of MgO-CaO powders in our experiment.

Field-emission scanning electron microscopy (FE-SEM) of the deposited $Mg_{1-x}Ca_xO$ films as a function of [CaO/(MgO + CaO)] ration were investigated and the results were shown in Fig. 4. When $x = 0.1$, surface morphology of the film is fine and uniform in

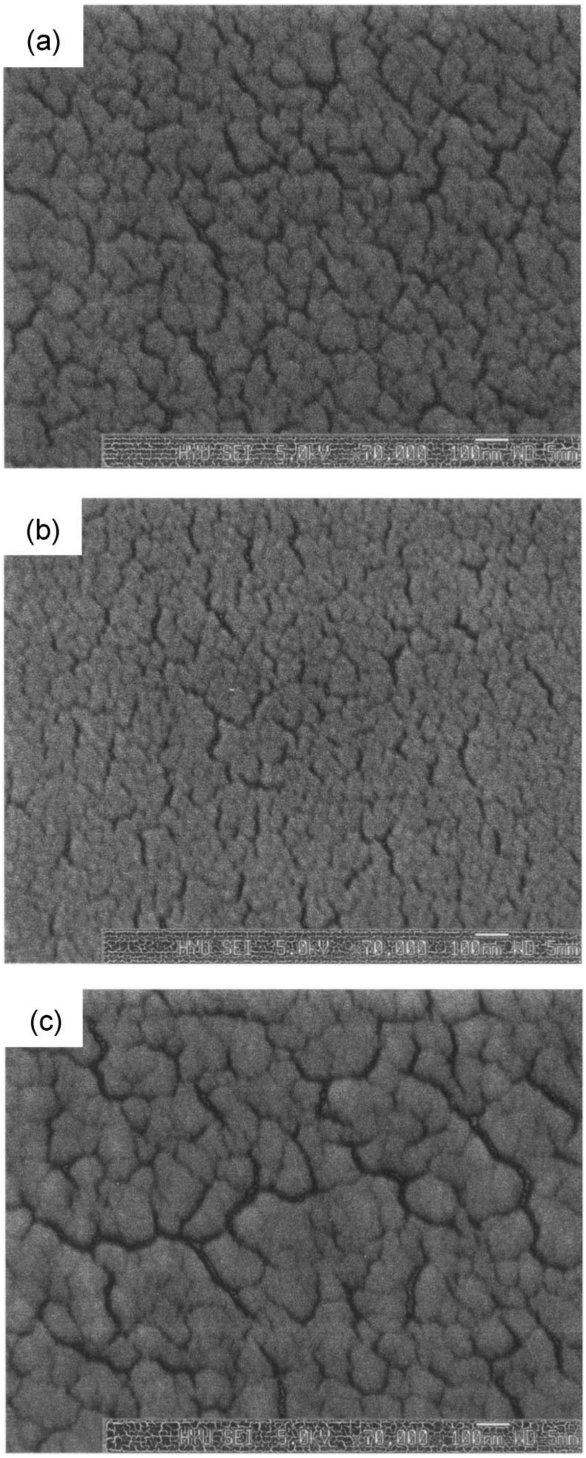

Figure 4 FESEM images of $Mg_{1-x}Ca_xO$ thin films with different x values; (a) $X = 0$ (b) $X = 0.1$ and (c) $X = 0.2$.

contrast to that of the pure MgO. It is shown that films of a proper composition can be very uniformly deposited by e-beam evaporation and it might be expected that the operating voltage stability of panels have the improvement in long time operations. However, excess addition of CaO to MgO, when x is 0.2, makes the film surface appear to undergo some type of agglomeration and have macro-cracks as shown in Fig. 4c, which results in loss of voltage stability characteristics. It is thought that this observation is confirmed by images of atomic force microscopy (AFM) in Fig. 5. Fig. 5a shows the topography of the pure MgO film, $x = 0$, which has rounded particle of 0.3 μm in mean diameter. When x is 0.05 and 0.1, the particles on the surfaces become smaller in size as shown in Fig. 5b and c. Not a definite explanation can be made at this moment for the reason why the addition of CaO to MgO results in decrease in particle size. When x is 0.2, a mixture of larger particles and smaller light particles can be observed on the surface of the film. The latter appears to be a secondary phase formed from an over-saturated solid solution. Fig. 6 shows the surface roughness of $Mg_{1-x}Ca_xO$ films as a function of x in the starting materials obtained by AFM. Surface roughness of $Mg_{1-x}Ca_xO$ films is found to relation to the concentration of CaO. When x is 0.1, the film has the lowest surface roughness, which results in stable voltage characteristics. It is, however, noticed that the film, when x is 0.2, shows a great increase in the surface roughness. The precipitation of the secondary phase as shown in Fig. 5d when x is 0.2 is found to be well associated the increase in the surface roughness in the film.

In order to investigate the discharge voltage properties of the MgO-CaO films, firing voltage (V_f) and sustaining voltage (V_s) were measured with different concentrations of CaO in the starting materials as shown in Fig. 7. The V_f of the panel with $(Mg_{0.9}Ca_{0.1})O$ film for protective layer is 176 V and is lower than that of the panel with conventional 100% MgO film. It is thought that the addition of CaO to MgO lowers the panel operating voltage because of the work function [7] of CaO (1.76 eV) less than that of MgO (3.1–4.4 eV) and the surface smoothening effect of CaO. Memory coefficient (MC) for MgO-CaO system used in figure is defined by the equation [2].

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

If MC is very large, it means that there is very high probability of stable operation of the panel. When the CaO concentration in the starting powder mixture is 0.1 or 0.2, panels can be operated at small V_f values. However, 0.1 is more desirable concentration of CaO because the MC value is slightly larger than that of 0.2. Furthermore, the MC value of $Mg_{0.9}Ca_{0.1}O$ is larger than that of MgO, indicating an improvement in the panel operation by adopting a proper protective layer.

Although CaO-SrO system had the lowest V_f among mixtures of various alkaline earth metal oxides, which reported by Shinoda [2], however, the mixtures had relatively poor memory margins as compared to MgO. In contrast to his result, our $Mg_{0.9}Ca_{0.1}O$ sample had a larger MC value as well as better operating voltage performance than those of the pure MgO. The fact that all our $Mg_{1-x}Ca_xO$ samples are still MgO-base might be one of the reasons for the better properties.

4. Conclusion

Films of the $Mg_{1-x}Ca_xO$ system as protective layer for dielectric materials is prepared by e-beam evaporation method in an effort to lower the V_f and V_s of AC PDP. Voltage test is examined in a specially designed chamber. Deposition rate of the films is in the range of

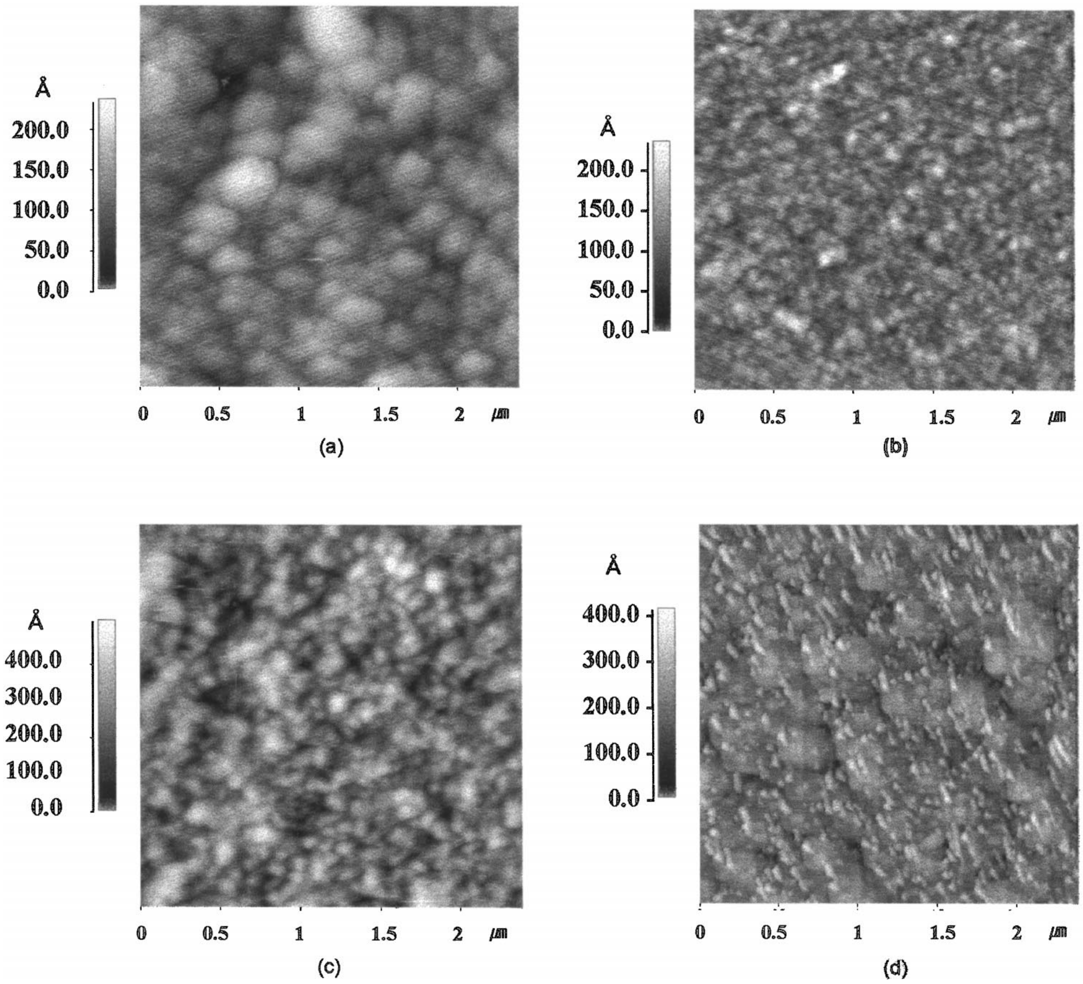

Figure 5 AFM images of $Mg_{1-x}Ca_xO$ thin films with different x values; (a) $X = 0$ (b) $X = 0.05$ (c) $X = 0.1$ and (d) $X = 0.2$.

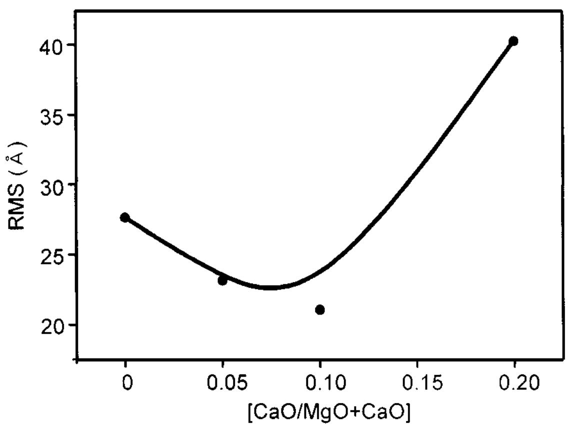

Figure 6 Surface roughness of $Mg_{1-x}Ca_xO$ thin films by AFM.

40–100 nm/min. Decrease in the deposition rate was observed with increasing the [CaO/(MgO + CaO)] ratio. When the CaO ratio is 0.2, a secondary phase was formed from the matrix of MgO-CaO solid solution which was apparently related to the abrupt image changes by SEM and AFM observations. Voltage characteristics of both V_f and V_s for the deposited Mg-Ca-O films were improved with the [CaO/(MgO + CaO)] ratio of 0.1. By adding a controlled amount of CaO, the deposited Mg-Ca-O films exhibited a firing voltage of 176 V that is lower than that of the conventional 100% MgO film.

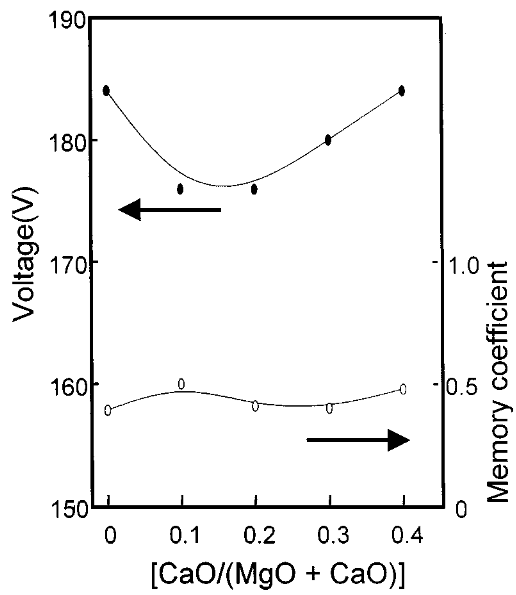

Figure 7 V_f and Memory coefficient of MgO thin films as a function of [CaO/(MgO + CaO)].

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