

Effect of CaO addition on the firing voltage of MgO films in AC plasma display panels

Jinhui Cho^a, Rakhwan Kim^a, Kyoung-Woo Lee^a, Geun-Young Yeom^b, Jung-Yeul Kim^c, Jong-Wan Park^{a,*}

^aDepartment of Metallurgical Engineering, Hanyang University, Seoul 133-791, South Korea

^bDepartment of Materials Engineering, Sung Kyun Kwan University, Suwon, South Korea

^cDepartment of Semiconductor Engineering, Uiduk University, Kyongju, South Korea

Received 2 January 1999; received in revised form 22 March 1999; accepted 2 April 1999

Abstract

In order to improve both operating voltage and memory coefficient of a protective layer for AC plasma display panels, controlled amount of alkaline earth oxide (CaO) was added to the pure MgO to replace the conventional pure MgO protective layer. The effects of CaO addition on both the electrical properties (V_f and V_s) and the microstructure of the $Mg_{1-x}Ca_xO$ thin films deposited on slide glass substrates by e-beam evaporation were investigated. Distinct changes in both peak intensity and diffraction peak positions of Mg–Ca–O films were observed with increasing [CaO/(MgO + CaO)] ratio owing to the strong atomic interaction between Mg and Ca. When the [CaO/(MgO + CaO)] ratio was increased to 0.1, the intensities of both (111) and (200) peaks were observed to increase with corresponding peak shift to lower diffraction peak positions as a result of the strong interdiffusion from the Ca and Mg atomic interactions. When the [CaO/(MgO + CaO)] ratio of 0.1 was used, the deposited films exhibited an enhanced operating performance with an improved memory coefficient. By adding a controlled amount of CaO, the deposited Mg–Ca–O films showed a firing voltage of 176 V that is lower than that of the conventional 100% MgO film. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Plasma display panels; Protective layer; MgO–CaO film; Firing voltage

1. Introduction

Plasma display panels (PDPs) are already available for commercial sales and expected to be one of the leading flat panel display (FPD) systems with large panel areas in the near future. 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 and large secondary electron emission coefficient (γ) [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 research has been carried out to find materials which will reduce the demanding voltage for discharging and which will then be compa-

tible with integrated circuits. Aboelfotoh reported that the addition of Ni on MgO films improved the stability of the operating voltage [2]. However, he did not explain the effect of additives on the aging property of MgO films. Shinoda et al. studied the mixture of CaO–SrO system, which had the lowest V_f among mixtures of various alkaline earth metal oxides [3]. The mixtures had, however, poor memory margins as compared to those of MgO. Ahearn et al. studied the influence of controlled levels of important reactive impurities on the aging characteristics of the operating voltages, but they could not obtain low enough voltages [4].

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 content in films.

2. Experimental details

The MgO and CaO powders of 99.95% purity (Cerac Co.)

* Corresponding author. Fax: 82-2-2298-2850.

E-mail address: jwpark@email.hanyang.ac.kr (J.W. Park)

were used for powder mixtures of various desired compositions. The powder mixtures were ground and then cold-pressed into disks at the pressure of 2000 Pa. to use as evaporation sources. The sources were heat-treated in vacuum at 1200°C for 3 h for sintering. Films of Mg–Ca–O with $4000 \pm 1000 \mu\text{m}$ thickness were then deposited on the slide glasses by e-beam evaporation method at a deposition rates of 40–100 nm/min using a high-voltage 180° bent-beam electron-gun with an input power of 1.4 kW. No oxygen gas was introduced into the e-beam evaporation chamber.

The composition of the films was measured by energy dispersive spectroscopy (EDS). X-ray diffractometer (XRD) was used to determine the microstructure of the films. The surface images and roughness of the films were obtained by atomic force microscopy (AFM). To determine voltage characteristics of the panels, dielectric layers were printed on soda-lime glass substrates, followed by printing the silver electrodes which had the line width and gap of 200 and 100 μm , respectively. Panel for voltage characteristic measurement has the structure of surface-discharge type of ac plasma display. Voltage characteristics of the panels were then evaluated in a specially designed chamber filled with He gas at 300 Torr.

3. Results

Table 1 shows the chemical composition of the films determined by energy dispersive spectroscopy (EDS). The measured atomic ratios of both [Mg/O] and [(Mg+Ca)/O] for the films are close to one. However, 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 in Ca concentration.

XRD was used to determine the structural changes of the Mg–Ca–O films as a function of the [CaO/(MgO + CaO)] ratio. Fig. 1 shows the XRD results of 5000 μm thick $\text{Mg}_{1-x}\text{Ca}_x\text{O}$ films deposited on slide-glass substrates. The XRD pattern of pure MgO film shows (111) preferred orientation with diffraction peak position of $2\theta = 36.95^\circ$ and a

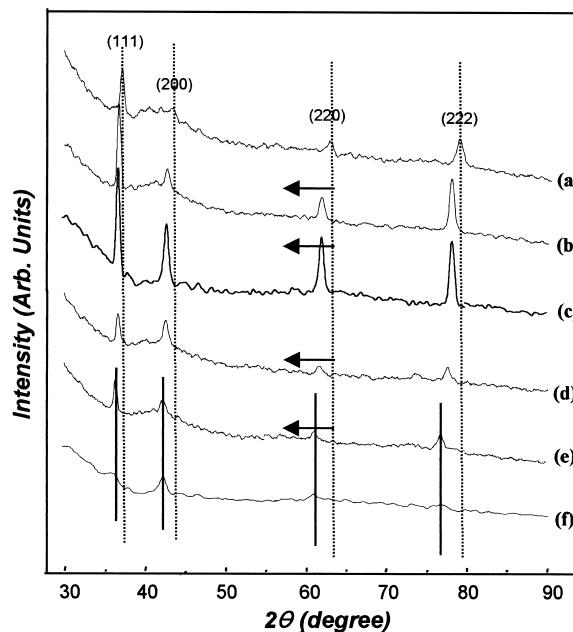


Fig. 1. XRD patterns of the $\text{Mg}_{1-x}\text{Ca}_x\text{O}$ thin films as a function of [CaO/(MgO + CaO)] ratios: (a) 0, (b) 0.05, (c) 0.1, (d) 0.15, (e) 0.2 and (f) 0.3.

lattice parameter of 0.421 nm (Fig. 1a). It was reported that the crystallinity of MgO films had important effects on the voltage characteristics. An increase in the peak intensity of (111) MgO protecting layer resulted in the decrease in firing voltage [6]. Distinct changes in both peak intensities and diffracted peak positions of Mg–Ca–O films were observed with the addition of CaO contents. When the [CaO/(MgO + CaO)] ratio was increased to 0.1, an increase in the intensity of both (111) and (200) peaks were observed with corresponding peak shift to lower diffraction peak positions. When the [CaO/(MgO + CaO)] ratio of 0.2 was employed, the diffracted peak position appeared around $2\theta = 37.68^\circ$ with a lattice parameter of 0.428 nm [7]. The difference in the 2θ diffraction positions of (111) peaks between Fig. 1a,e is 0.73° . The increase in the intensity of (200) diffraction peak is associated with the segregation of Ca ions on the (001) surface of the MgO. [8] The changes in both diffracted peak positions and the increase in the lattice parameter with increasing CaO content were found to be closely related to the Ca–Mg interactions which resulted in lowering the angular positions of both (111) and (200) diffracted peaks. The atomic size of Ca is larger than that of Mg. Therefore, when a large number of Ca atoms substitute for Mg atoms in the NaCl-type structure, lattice distortion occurs in accordance with the increase in the lattice parameter of the films [5]. The above result might be also attributed to the increase in intrinsic stress of the film by the addition of CaO to MgO, which is apparently anticipated from the fact that the ionic radius of Ca ions are 35% larger

Table 1
Composition of $\text{Mg}_{1-x}\text{Ca}_x\text{O}$ 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	41.1	1.3	51.6
0.2	42.44	6.55	51.01
0.3	42.24	7.6	50.16

than that of Mg ions [9]. From the results of both XRD and EDS analyses, the solution limit of CaO in MgO films can be estimated to 0.13 in our experimental conditions. Dependence of stress as a function of $[CaO/(MgO + CaO)]$ ratio was shown in the Fig. 2. When the ratio of 0.1 was used, the maximum compressive stress was obtained. Another change was also observed in the full width at half maximum (FWHM) of XRD peaks for the deposited films. The peaks in Fig. 1b,c are increased in intensity and narrower than that of Fig. 1a.

Atomic force microscopic (AFM) images of the deposited $Mg_{1-x}Ca_xO$ films as a function of $[CaO/(MgO + CaO)]$ ratio were also investigated and the results were shown in Fig. 3. The surface topography of the pure MgO film, $x = 0$, is composed of grains that are uniform in size (which has rounded particles of 0.3 μm in mean diameter). As the CaO content was increased, the particles on the surfaces became smaller in size and the results were shown in Fig. 3b,c. Fig. 4 shows the dependence of surface roughness of $Mg_{1-x}Ca_xO$ films as a function of x in the starting materials determined by AFM images. The surface roughness of $Mg_{1-x}Ca_xO$ films was found to dependent upon the ratio of $[CaO/(MgO + CaO)]$. When $[CaO/(MgO + CaO)]$ ratio of 0.1, the deposited film had the lowest surface roughness, which resulted in stable voltage characteristics. When $[CaO/(MgO + CaO)]$ ratio was further increased, the film, however, showed an increase in the surface roughness.

In order to understand the discharge voltage characteristics of the MgO–CaO films, the firing voltage (V_f), the sustaining voltage (V_s) and the memory coefficient (MC) as a function of $[CaO/(MgO + CaO)]$ ratio were measured. Memory coefficient (MC) for MgO–CaO system was deter-

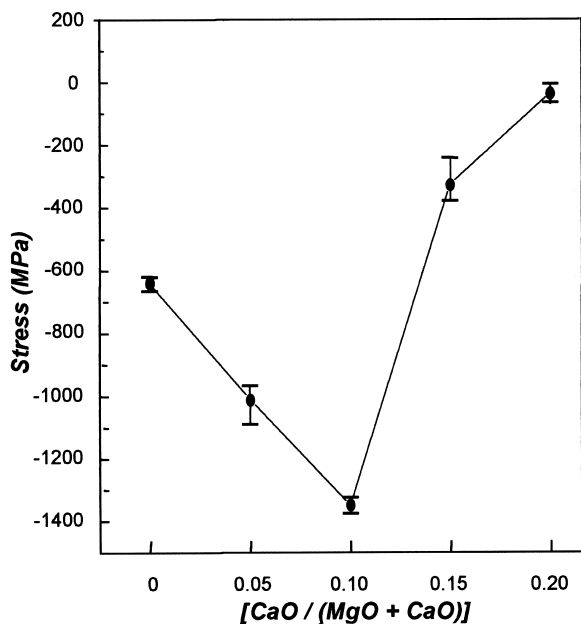


Fig. 2. Residual stresses of the $Mg_{1-x}Ca_xO$ thin films as a function of $[CaO/(MgO + CaO)]$ ratio.

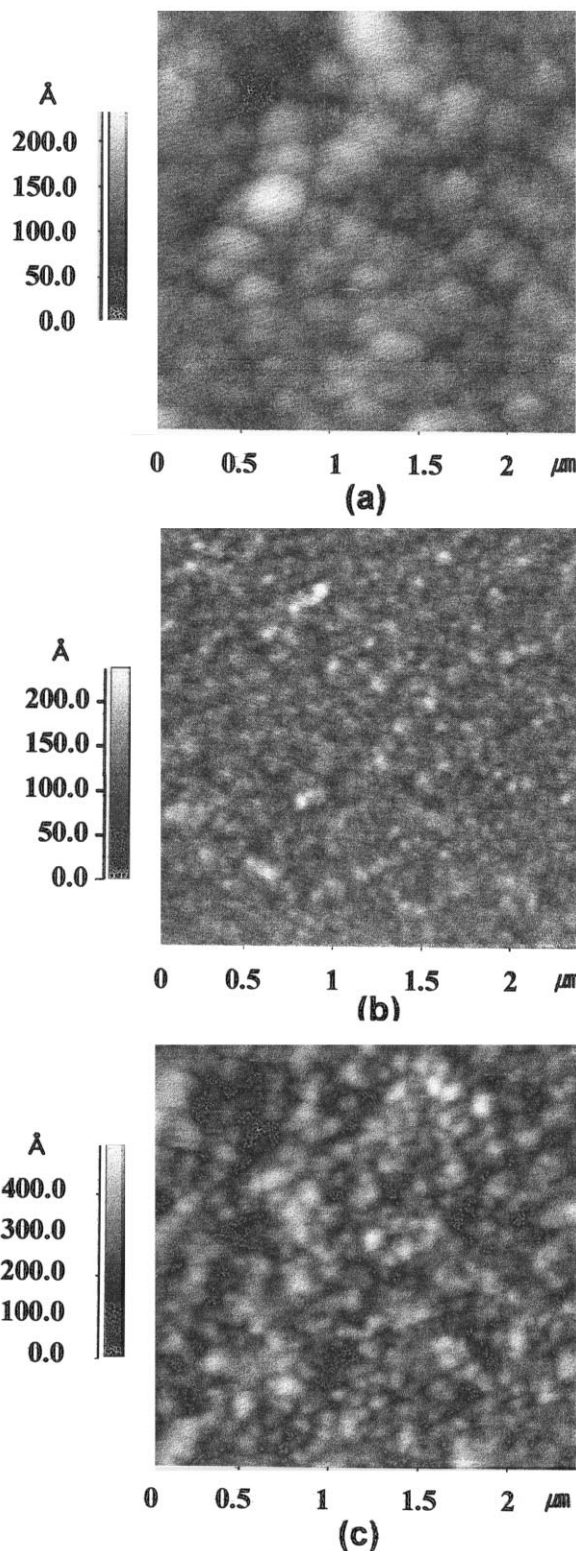


Fig. 3. AFM images of the $Mg_{1-x}Ca_xO$ thin films with different x values: (a) $X = 0$ (b) $X = 0.05$ and (c) $X = 0.1$.

mined by using the following equation [3]

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

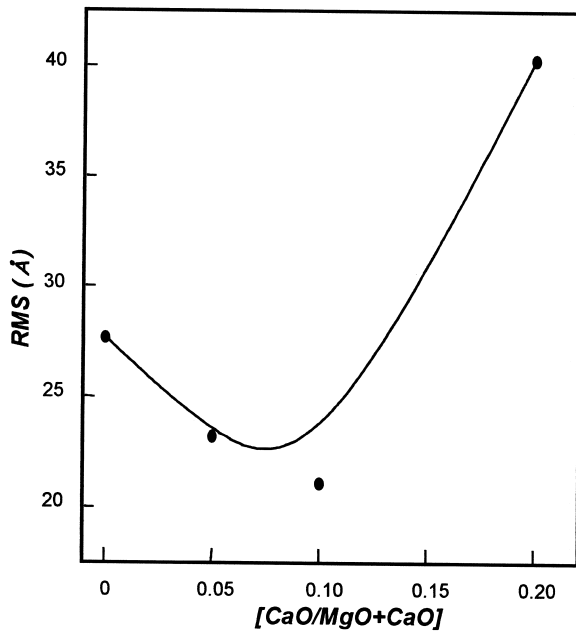


Fig. 4. Surface roughness of the $\text{Mg}_{1-x}\text{Ca}_x\text{O}$ thin films with different x values.

Both voltages were decreased rapidly with the addition of small amount of CaO to the pure MgO. When an excess CaO content $\{[\text{CaO}/(\text{MgO} + \text{CaO})]$ ratio(0.2) was used, both voltages were, however, increased gradually in proportion to the addition of CaO. The corresponding MC for MgO-CaO system depends on firing voltage (V_f) which, in turn, depends on $[\text{CaO}/(\text{MgO} + \text{CaO})]$ ratio and its surface conditions. With $[\text{CaO}/(\text{MgO} + \text{CaO})]$ ratio of 0.1 or 0.2, a stable panel operating voltage can be obtained. The results are shown in Fig. 5. If MC is very large, it means that there is very high probability of stable operation of the panel. It was revealed that the panel, whose $[\text{CaO}/(\text{MgO} + \text{CaO})]$ in the starting powder mixture was 0.1 or 0.2, can be operated at small V_f values. It is thought that the addition of CaO to MgO lowers the panel operating voltage probably due to the work function of CaO (1.76 eV) which is less than that of MgO (3.1–4.4 eV) and the surface smoothing effect of CaO [5]. More desirable concentration of CaO in the mixture, however, is 0.1 because the MC value is slightly larger than that of 0.2. One of the reasons for the low MC value in $x = 0.2$ may be related to the large surface roughness as shown in Fig. 3. Furthermore, the MC value of $\text{Mg}_{0.9}\text{Ca}_{0.1}\text{O}$ is larger than that of MgO, indicating an improvement in the panel operation by employing a proper protective layer. It has previously reported that the dielectric properties, surface density and chemical composition of the films had effects on the MC values have been reported [10]. Further studies are in progress in order to bring out the dominants factors for the enhanced MC values.

Although the CaO-SrO system had the lowest V_f among mixtures of various alkaline earth metal oxides, which

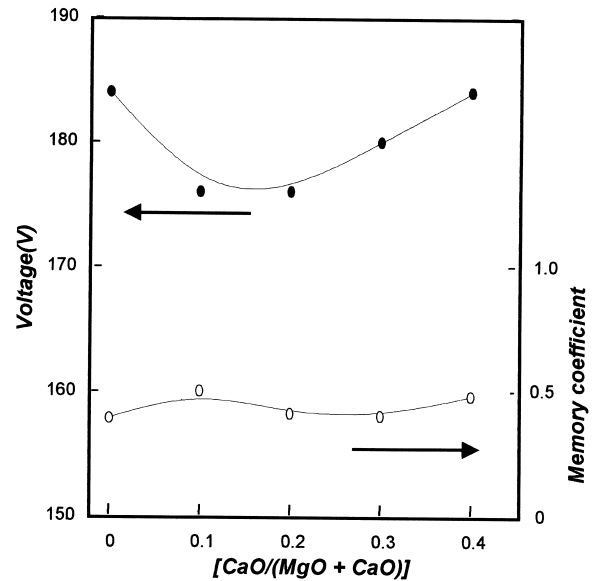


Fig. 5. V_f and memory margin of the $\text{Mg}_{1-x}\text{Ca}_x\text{O}$ thin films as a function of $[\text{CaO}/(\text{MgO} + \text{CaO})]$ ratio.

reported by Shinoda [3], however, the mixtures had relatively poor memory margins as compared to MgO. In contrast to his result, our $\text{Mg}_{0.9}\text{Ca}_{0.1}\text{O}$ sample had a larger MC value as well as better operating voltage performance than those of the pure MgO. The facts that all our $\text{Mg}_{1-x}\text{Ca}_x\text{O}$ samples were still MgO-base and our films were evaporated not from carbonated source but from oxides sources might be possible reasons for the better properties.

4. Conclusion

$\text{Mg}_{1-x}\text{Ca}_x\text{O}$ films have been prepared by e-beam evaporation method to be used as a possible substitute for the conventional pure MgO in a surface protective layer for dielectric materials. Distinct changes in both peak intensity and diffracted peak position of Mg-Ca-O films were observed with increasing $[\text{CaO}/(\text{MgO} + \text{CaO})]$ ratio due to the strong atomic interaction between Mg and Ca. The surface topography of the pure MgO film is composed of rounded grains of 0.3 μm in mean diameter. As the CaO content was increased, the particles on the surfaces became smaller in size. When the starting materials with $[\text{CaO}/(\text{MgO} + \text{CaO})]$ ratio of 0.1 was used, the deposited film has the lowest surface roughness, which results in stable voltage characteristics. Voltage characteristics of both V_f and V_s for the deposited Mg-Ca-O films were improved with increasing the $[\text{CaO}/(\text{MgO} + \text{CaO})]$ 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.

Acknowledgements

The authors wish to thank the PDP Research Division (G7 project) in KOREA financial support.

References

- [1] T. Urade, T. Imemori, M. Osawa, N. Nakayama, I. Morita, IEEE Trans Electron Devices 23 (1976) 313.
- [2] M.O. Aboelfotoh, IEEE Trans Electron Devices 29 (1982) 247.
- [3] T. Shinoda, H. Uchiike, S. Andoh, IEEE Trans Electron Devices 26 (1979) 1163.
- [4] S. Tominetti, A. Renzo, Proc. Asia Display 98 (1998) 639.
- [5] G.V. Samsonov, The Oxide Handbook, 2nd ed., IFI/Plenum Data Corporation, New York, 1982 p. 206.
- [6] Y.C. Kang, J.B. Baik, B.H. Lee, J.H. Choi, J.M. Kim, K.Y. Park, Mater. Res. Soc. Int. Symp. (1997) 471.
- [7] B.D. Cullity, Elements of X-ray diffraction, 2nd ed., Addison-Wesley, Reading, MA, 1978 p. 39.
- [8] E.A. Colbourn, W.C. Mackrodt, J. Mater. Sci. 17 (1982) 3021.
- [9] E.A. Brandes, Smithells Metals Reference Book, 6th ed., Butterworth and Co. Ltd., 1983 p. 4.
- [10] D.V. McCaughan, R.A. Kushner, V.T. Murphy, Phys. Rev. Lett. 30 (1979) 614.