

Electrical properties of evaporated MgO-TiO₂ protective layer for AC PDP

RAKHWAN KIM, YOUNGHYUN KIM, JONG-WAN PARK*

Department of Metallurgical Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-ku, Seoul 133-791, South Korea

E-mail: jwpark@email.hanyang.ac.kr

Secondary electron emission from a protective layer in AC PDP is known to be dominated by potential emission mechanism, which is sensitive to its energy band structure. Therefore, the secondary electron emission property can be modified by a change in the energy band structure of the protective layer. The addition of controlled amount of titanium oxide into the conventional magnesium oxide protective material might affect the overall voltage characteristics of panels due to the fact that TiO₂ has higher dielectric constant than MgO and that the ion radius of Ti is similar to that of Mg. The electrical properties of panels with protective layers evaporated from the starting materials with different [TiO₂/(MgO + TiO₂)] ratios were investigated. When the [TiO₂/(MgO + TiO₂)] ratios of 0.1 and 0.15 were used, the panel exhibited a sustaining voltage of 122 V, which was 16 V smaller than that of the pure MgO, without lowering its memory margin. The relative dielectric constant of Mg_{2-2x}Ti_xO₂ films increased with addition of TiO₂ to the pure MgO, however, it then suddenly decreased above the [TiO₂/(MgO + TiO₂)] ratio of 0.1. The surface roughness of Mg_{2-2x}Ti_xO₂ had a minimum when the [TiO₂/(MgO + TiO₂)] ratio in the starting materials was 0.1. The variation trends of the relative dielectric constant and the surface roughness of Mg_{2-2x}Ti_xO₂ films with increasing [TiO₂/(MgO + TiO₂)] ratio in the starting materials were found to be consistent with that of the voltage characteristics.

© 2001 Kluwer Academic Publishers

1. Introduction

Large plasma display panels (PDP) are already competing effectively against cathode-ray-tube (CRT) and liquid-crystal (LC) projectors. However, PDP technology still needs improvement to compete more widely in terms of display quality and production cost, etc. Especially, the complex circuit, which results in need of high cost ICs is a very serious problem. One solution to this problem is to exploit new driving circuits, which require simple electronics. A second solution is to choose proper component materials which can reduce the required voltage for discharging, and which will then be compatible with integrated circuits [1]. These material researches include discharging gas, electrode, dielectric layer and protective layer. In particular, the protective layer that is overcoated on low-melting-point glass i.e., dielectric layer, is very important since it is directly adjacent to plasma environment [2]. Generally, MgO 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) [3]. However, the operating voltage is still too high to be compatible with ICs and therefore, further voltage reduction of panel is desirable. The voltage

for discharging has been known to depend mainly on secondary electron emission coefficient and then work function of a protective layer, if other variables such as gas composition, electrode gap, electrode width and barrier height are constant [4]. It was reported that the secondary electron emission might be caused by either kinetic emission mechanism or potential emission mechanism. However, it is reasonable that the potential emission mechanism prevails since colliding ions have smaller energy than 50 eV in PDP, which is not enough for kinetic emission [5]. Therefore, the energy band structure of the protective layer plays an important role on secondary electron emission. Besides this, it was reported that ionization potential of a gas ion could be varied according to the insulator surface by the potential emission mechanism [6]. From the above consideration, we now introduce panels with Mg_{2-2x}Ti_xO₂ protective layers so as to replace the conventional MgO protective layer. In fact, it is known that the ion radius of titanium is similar to that of Mg and TiO₂ itself has high relative dielectric constant of 40–80. Thus, the purpose of this work is to modify the insulator surface by addition of TiO₂ into MgO and to improve the electrical performance of the protective layer.

* Author to whom all correspondence should be addressed.

2. Experimental details

To fabricate evaporation sources, MgO and TiO₂ powders of 99.95% purity purchased from Cerac were used to prepare powder mixtures of desired compositions as a function of TiO₂ content in MgO. The powder mixtures were ground and then cold-pressed unidirectionally into disks at the pressure of 2,000 Pa. Heat treatment at 1000 °C were performed for 3 h in a vacuum furnace for densification of the cold-pressed mixture pellets. E-beam evaporation chamber was pumped by an oil-diffusion pump to a base pressure of 5×10^{-4} Pa. Input power of electron gun was 1.2 kW and high-voltage was fixed constant at 4 kV. Substrates were not heated and no oxygen gas was introduced into the chamber. The film thickness was controlled by evaporation time and was later measured by using a surface profilometer. The relative dielectric constant was determined from capacitance-voltage (C-V) measurements at 1 MHz using a metal-insulator-semiconductor (Ag/Mg_{2-2x}Ti_xO₂ film/p-Si) structure [7]. Surface morphology of films was analyzed by an atomic force microscopy. The fabricated test panel has the structure of surface-discharge type of ac plasma display, which is shown in Fig. 1 [8]. The sustain electrodes with electrode width and gap of 200 μm and 100 μm, respectively, are parallel to each other and are covered by dielectric layers of 30 μm in thickness in the front glass. The protective layers of 0.3 μm thickness with various Ti contents were deposited on dielectric layers by electron beam evaporation method. The voltage characteristics of the panels such as firing voltage and minimum sustaining voltage were then evaluated in He gas of 300 Torr at a driving frequency of 20 kHz.

3. Results

Film composition obtained by energy dispersive spectrometry (EDS) is shown in Table I. As the [TiO₂/(MgO + TiO₂)] ratio in the starting materials increased from 0 to 0.3, cation ratio i.e., [Ti/(Mg + Ti)] in the films also increased from 0 to 0.117. The deposited films were thus depleted to some degree in Ti content in comparison with the initial Ti content in the starting materials. It was well anticipated from the fact that TiO₂ has much lower vapor pressure than that of MgO [9].

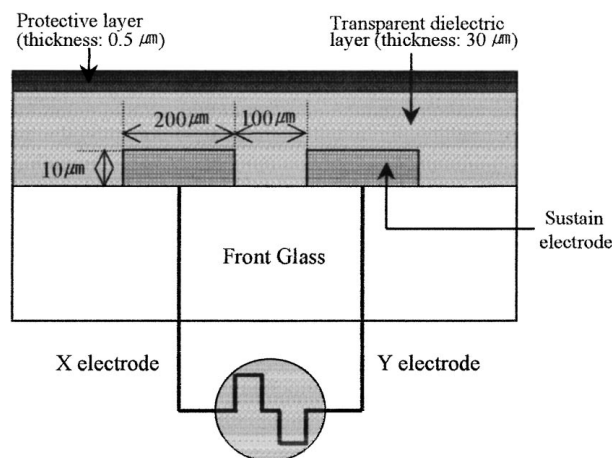


Figure 1 Schematic diagram of the fabricated panel structure.

TABLE I Composition of Mg_{2-x}Ti_xO_{2x} films

[TiO ₂ /(MgO + TiO ₂)] in Starting Materials	Concentration of Elements in Film (at %)			Cation Ratio [Ti/(Mg + Ti)]
	Mg	Ti	O	
0	49.4	0	50.6	0
0.05	45.1	1.2	53.7	0.026
0.1	43.14	2.45	54.41	0.054
0.15	42.41	3.16	54.43	0.069
0.2	41.24	4.2	54.56	0.092
0.3	39.6	5.23	55.17	0.117

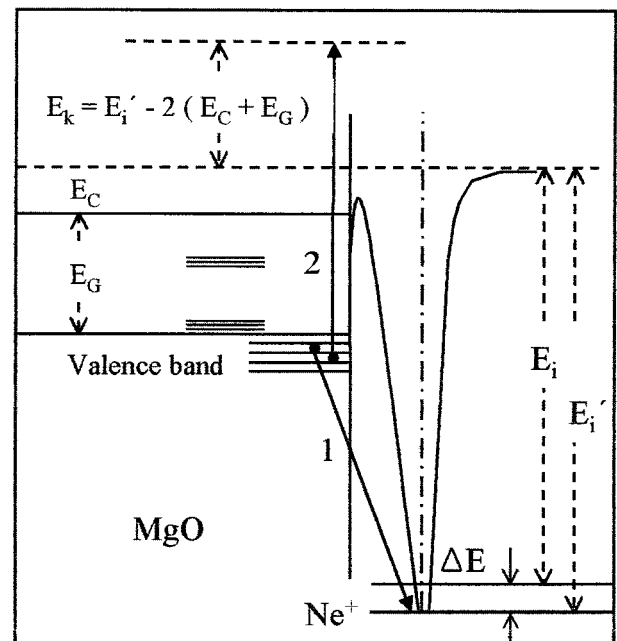


Figure 2 Schematic diagram of Auger process of Ne⁺ ion at MgO surface, reference: [10].

Fig. 2 shows schematic diagram of the Auger neutralization mechanism [10]. The ionization potential shift, denoted as ΔE ($E_i' - E_i$), is affected by the dielectric constant of protective layer according to

$$\Delta E = 3.6Q^2(\varepsilon - 1)/D(\varepsilon + 1) \quad (1)$$

where Q is ion charge, ε dielectric constant and D ion's distance from the surface, respectively [6]. The equation reveals that as dielectric constant ε increases, both the ionization potential shift and the probability of secondary electron emission from insulator surface increase. From this consideration, we attempt to increase the dielectric constant of the MgO-base protective layer by addition of TiO₂ that has higher dielectric constant than that of MgO.

Fig. 3 shows the relative dielectric constant of Mg_{2-2x}Ti_xO₂ films as a function of [TiO₂/(MgO + TiO₂)] ratio in the starting materials. Theoretically, the bulk MgO has the relative dielectric constant of 9.8, but the evaporated MgO film has the value of 8.5 probably due to some defects such as micropore. With addition of TiO₂ to the pure MgO, the relative dielectric constant of Mg_{2-2x}Ti_xO₂ films increased because the pure TiO₂ has relative dielectric constant of 40–80, much

higher than that of MgO. This phenomenon is thought to be suitable for Maxwell Garnett expression, which assumes that the concentration of one component is much larger than that of the others in heterogeneously

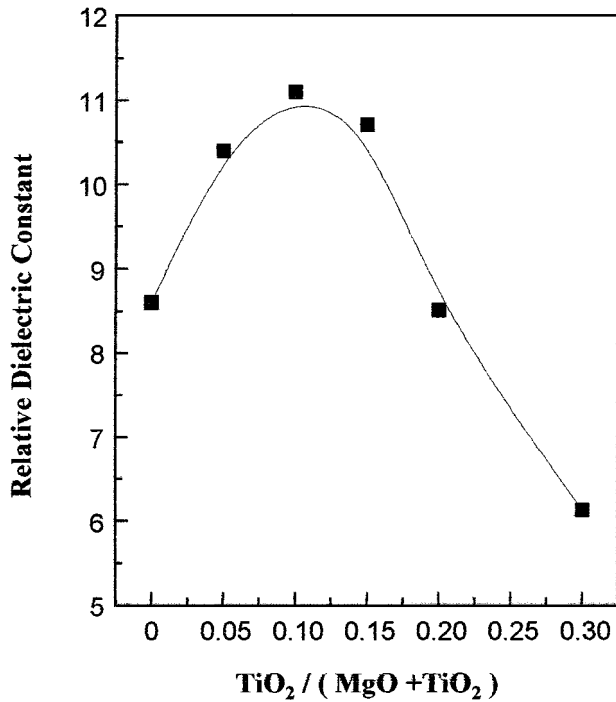


Figure 3 Relative dielectric constant of $Mg_{2-2x}Ti_xO_2$ films as a function of $[TiO_2/(MgO + TiO_2)]$ in starting materials.

mixed films. However, when the $[TiO_2/(MgO + TiO_2)]$ ratio in the starting materials is larger than 0.1, the relative dielectric constant of films decreases after reaching a maximum. Thus, these results show that addition of a controlled amount of TiO_2 into MgO can effectively contribute to improvement of the electrical characteristics of the protective layer such as relative dielectric constant.

The surface morphology of $Mg_{2-2x}Ti_xO_2$ films was observed by atomic force microscopy (AFM). Fig. 4a shows the topography of the pure MgO film, $x = 0$, which has rounded particles of about $0.1 \mu m$ in mean diameter. The particles look very small when x is 0.1 or 0.15, compared to those of the pure MgO. However, the overall morphologies of films are not greatly affected by addition of TiO_2 . Fig. 5 shows the surface roughness of $Mg_{2-2x}Ti_xO_2$ films as a function of $TiO_2/(MgO + TiO_2)$ ratio in the starting materials obtained by AFM. $Mg_{1.8}Ti_{0.1}O_2$ film has the lowest surface roughness probably due to smaller particle size, which is expected to result in stable voltage characteristics in long time operation of panels.

The firing voltage (V_f) is the voltage amplitude for plasma ignition without wall charge and the minimum sustaining voltage (V_{sm}) is the minimum voltage amplitude which will sustain discharge sequence. Both firing and minimum sustaining voltages limit the bistable range of the sustain waveform [1]. Bistability, that is to sustain a discharge at a voltage lower than that required

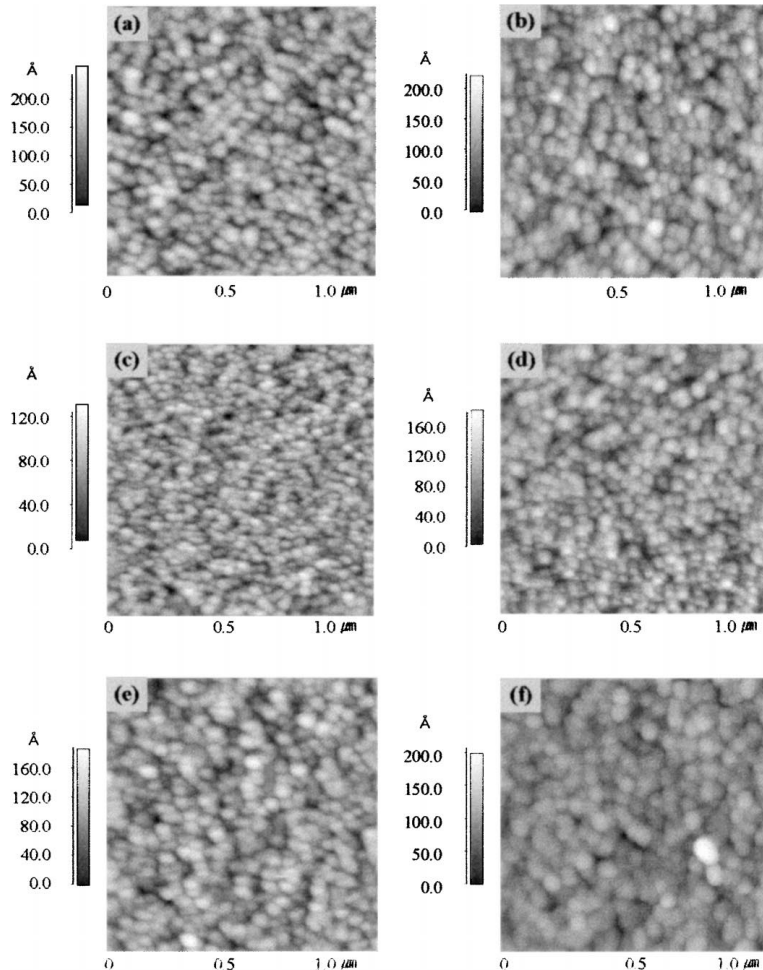


Figure 4 AFM Images of $Mg_{2-2x}Ti_xO_2$ films as a function of $[TiO_2/(MgO + TiO_2)]$ ratio in the starting materials; (a) 0, (b) 0.05, (c) 0.1, (d) 0.15, (e) 0.2 and (f) 0.3.

TABLE II The sustaining voltage and memory margin of panels with $Mg_{2-x}Ti_xO_{2x}$ protective layers as a function of $[TiO_2/(MgO + TiO_2)]$ ratio in the starting materials

$[TiO_2/(MgO + TiO_2)]$ in Starting Materials	Voltage Characteristics	
	Sustaining Voltage	Memory Margin
0	138 V	0.456
0.05	128 V	0.550
0.1	122 V	0.567
0.15	122 V	0.593
0.2	128 V	0.495
0.3	130 V	0.543

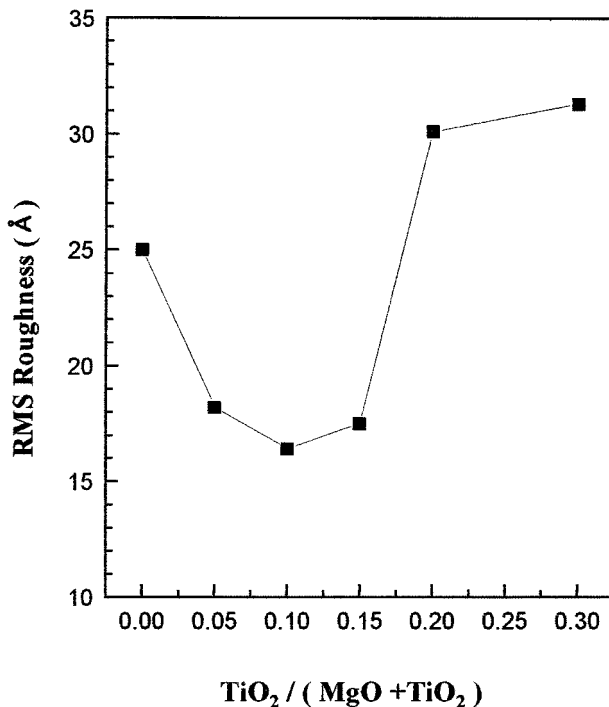


Figure 5 Surface roughness of $Mg_{2-2x}Ti_xO_2$ films as a function of $TiO_2/(MgO + TiO_2)$ ratio in the starting materials.

to initiate it, is a characteristic feature of AC PDP. Therefore, the larger the difference between the firing voltage and minimum sustaining voltage, defined as memory margin, the more stable the operation can be. The results of electrical measurement as a function of the $[TiO_2/(MgO + TiO_2)]$ ratio in the starting materials is shown in Fig. 6 and Table II. Because other variables that can affect voltage characteristics of panels were kept constant, changes in voltage of panels are entirely due to the change in composition of protective layers in this work. The firing voltage and minimum sustaining voltage of panels with the conventional MgO protective layer is 155 V and 120 V, respectively. With addition of TiO_2 to the pure MgO, both voltages are drastically decreased. The lowest firing voltage, which is smaller than that of MgO by 13 V, is obtained when the $[TiO_2/(MgO + TiO_2)]$ ratio is 0.1. The minimum sustaining voltage is 101 V when the $[TiO_2/(MgO + TiO_2)]$ ratio in the starting materials is 0.15.

The values of sustaining voltage, V_s , defined as $(V_f + V_{sm})/2$ and memory margins, defined as

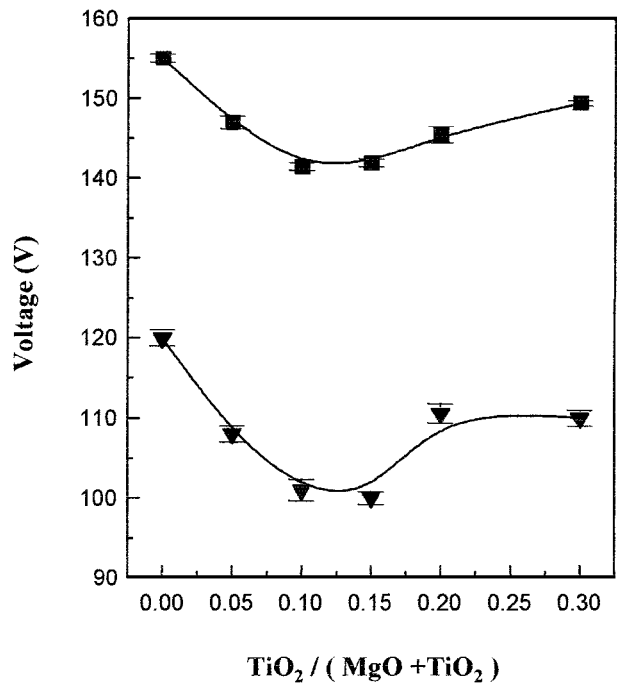


Figure 6 Firing voltage and minimum sustaining voltage of panels with $Mg_{2-2x}Ti_xO_2$ protective layers as a function of $[TiO_2/(MgO + TiO_2)]$ ratio in the starting materials.

$2 \times (V_f - V_{sm}) / V_f$ are presented in Table II. The sustaining voltage of the conventional MgO protective layer is 138 V. The panels of all the protective layers that contain titanium oxide show lower sustaining voltage than that of the conventional MgO protective layer. The lowest sustaining voltage, 16 V lower than that of MgO, is obtained when the $[TiO_2/(MgO + TiO_2)]$ ratio in the starting materials is 0.1 or 0.15. The MC values also increases with the $[TiO_2/(MgO + TiO_2)]$ ratio in the starting materials until 0.15 since the minimum sustaining voltage decreases more rapidly than the firing voltage as shown in Fig. 6. Therefore, the sustaining voltage can be effectively decreased without lowering the MC value when the $[TiO_2/(MgO + TiO_2)]$ ratio in the starting materials is 0.1 or 0.15. With addition of excess TiO_2 content $\{[TiO_2/(MgO + TiO_2)] \text{ ratio} > 0.15\}$, the sustaining voltage increases gradually again in proportion to the TiO_2 content, which is consistent with the variation trend of relative dielectric constant shown in Fig. 3. It is thought that the addition of TiO_2 to MgO lowers the panel operating voltage probably due to changes in the energy band structure of the films, which is open to further study. Besides this, the increase in the relative dielectric constant of protective layer in accordance with addition of TiO_2 to MgO might have influence on the voltage characteristics, which is still under study. Furthermore, the relationship between the electrical characteristics of the panel and the dielectric constant of the protective layers seems to coincide somehow with the trend that the surface roughness varies with TiO_2 concentration (Fig. 5).

4. Conclusion

We attempted to modify the relative dielectric constant of the protective layer by addition of a controlled

amount of TiO₂ into MgO. The Mg_{2-x}Ti_xO_{2x} system as a protective layer for dielectric materials was prepared by e-beam evaporation method. The firing and minimum sustaining voltages could be drastically decreased without lowering MC value when the [TiO₂/(MgO + TiO₂)] ratio in the starting materials was 0.1 or 0.15. However, the relative dielectric constant of the mixed films was not greatly increased in spite of addition of TiO₂ of high dielectric constant. Addition of a small amount of TiO₂ into MgO was found to effectively improve the electrical characteristics, such as dielectric constant and voltage characteristics. By increasing the [TiO₂/(MgO + TiO₂)] ratio in the starting materials the variation trends of the relative dielectric constant and the surface roughness of Mg_{2-x}Ti_xO_{2x} films were found to be consistent with that of the voltage characteristics.

Acknowledgment

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

References

1. T. SHINODA, H. UCHIIKE and S. ANDOH, *IEEE Trans. Electron Devices* **ED-26**(8) (1979) 1163.
2. K. YOSHIDA, H. UCHIIKE and M. SAWA, in Proceedings of 5th IDW in Japan (1998) p. 515
3. T. URADE, T. IMEMORI, M. OSAWA, N. NAKAYAMA and I. MORITA, *IEEE Trans. Electron Devices* **23** (1976) 313.
4. H. UCHIIKE, K. MIURA, N. NAKAYAMA, T. SHINODA and Y. FUKUSHIMA, *ibid.* **23** (1976) 1211.
5. N. J. CHOU, *J. Vac. Soc. Technol.* **14** (1) (1977) 307.
6. DANIEL V. MCCAUGHAN, R. A. KUSHNER and V. T. MURPHY, *Phys. Rev. Lett.* **30** (13) (1973) 614.
7. SEOGHYEONG LEE and JONG-WAN PARK, *J. Appl. Phys.* **80** (1996) 5260.
8. J. CHO, R. KIM, K.-W. LEE, G.-Y. YEOM, J.-Y. KIM and J.-W. PARK, *Thin Solid Films* **350** (1999) 173.
9. G. V. SAMSONOV, "The Oxide Handbook 2nd ed." (IFI/Plenum Data Corporation, New York, 1982) p. 206.
10. M. O. ABOELFOTOH and OMESH SAHNI, *IEEE Trans. Electron Devices* **ED-28**(6) (1981) 645.

Received 22 September 1999
and accepted 10 August 2000