Optimization of MgO secondary electron emission in plasma displays, by the adoption of a suitable getter configuration

- Part I: MgO degradation studies -

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Keywords : MgO Layer, Plasma Displays, Secondary Electron Emission, Getters

Abstract

The key role of MgO is well recognized in PDP's technology. During manufacturing, significant contamination of the oxide occurs. Getters can compete against the impurities sorption speed of the oxide layer. The analysis of the impact of a suitable getter configuration on the operational parameters of PDP's is the final goal of this study.

1. Introduction

The role of the MgO protective layer in PDP's is well recognized [1, 2]: it supplies feeding electrons for plasma ignition [3] and protects the underlying dielectrics, in virtue of its low sputtering yield. Moreover, its own dielectric characteristics assure wall charge storing during PDP operation. However, plasma display panels manufacturing processes include severe thermal cycles in strong environmental conditions, causing significant contamination (mainly due to H_2O and CO_2) of the MgO layer [4, 5]. The surface diminished cleanliness has detrimental effects on secondary electron emission (lowering γ), causing worse luminous efficiency (η) and increased breakdown voltages (V_b) in PDP's, being

$$\eta \propto a\gamma \exp\left(-b/\gamma\right)\left[\left(1+\gamma\right)\ln\left(1+1/\gamma\right)\right] \quad (1)$$

$$V_b \propto Apd / \ln\left[Bpd/\left(1+1/\gamma\right)\right] \quad (2)$$

with *pd* the Paschen parameter, *a* and *b* fitting constants depending on the material [6], and A and B parameters depending on the gas mixture.

SAES Getters has started a collaboration project with *Kwangwoon University*, in order to (i) identify the most detrimental sources of impurities and to (ii) check the effect of getter for preventing the MgO surface contamination [7].

In this paper the first stage of the joint project is presented, consisting in the γ-FIB (Focused Ion Beam) analysis of differently contaminated MgO films, with the aim of identifying the different influences of H_2O and CO_2 on the secondary electron emission capability of the PDP protective layer.

2. Experimental

6000 thick MgO films have been deposited by e-beam evaporation on 20x20 mm^2 glass substrates, at the rate of 5 s^{-1}. The evaporation chamber and deposition process are the very same used for the PDP protective layer deposition, at Plasma Display Research Center.

In order to investigate the effects of moisture and carbon dioxide contamination on γ, different sets of samples have been firstly prepared and analyzed at RT (20°C-25°C): (i) freshly deposited MgO films for reference, (ii), MgO films exposed to 20 Torr H_2O (100% RH) for 30 hours ($2.16 \cdot 10^{12}$ L) using N_2 buffer gas, (iii) MgO films exposed to 600 Torr CO_2 atmosphere for 1 hour ($2.16 \cdot 10^{12}$ L) (iv) MgO films submitted to processing *(ii)* and *(iii)* in series, (v) MgO films submitted to H_2O and CO_2 contamination at the same time: $P(H_2O)$ = 20 Torr and $P(CO_2)$ = 740 Torr atmosphere (30 hours).

All the processes involving moisture exposure have been carried out using an *ad-hoc* designed chamber, containing a vessel for liquid water, a rotary pump for system evacuation and a connection for N_2 or CO_2 gases inlet. Whenever CO_2 only exposure had been needed, we have made use of the gas inlet of the γ-FIB chamber itself.

The γ-FIB system (fig. 1) used for measuring the secondary electron emission from the MgO films has been deeply discussed elsewhere [8]. The Ne gas is ionized by the electrons coming from the heated filament. The accelerating potential (V_i) driving the Ne^+ ions onto the sample surface is given by the positively biased anode: in these experiments the range 100V-200V has been chosen. The ion beam is focussed by the single electrostatic Einzel lens and scanned by the quadrupole deflector, permitting to move the beam spot (50 μm) within a 300 μm radius area around the centre of the sample.

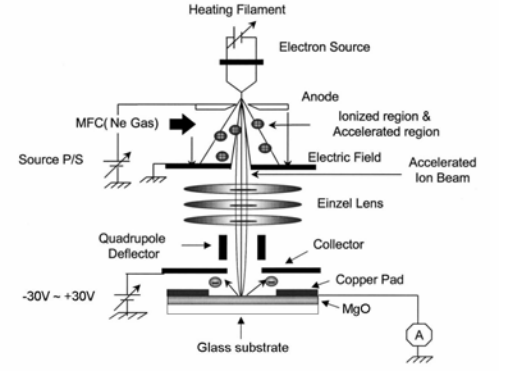

Fig. 1. γ-FIB system architecture.

Collector biasing allows to discriminate between the different contributions to the current, flowing from copper pad to ground: ionic plus electronic (I_i+I_e) at +30V or ionic only (I_i) at -30V. Thus, the secondary electron emission yield can be readily obtained for different accelerating potentials, being $\gamma = I_e/I_i$.

Low Ne^+ energy spread and good current stability ($\Delta I/I < 1\%$) are achieved under the abovementioned experimental configuration. Vacuum is maintained below $2 \cdot 10^{-6}$ Torr during the experiments. The MgO secondary electron emission study herein presented will be followed by a thorough experimental analysis involving real test-oriented PDP's: ten 4 monochrome (blue phosphors) AC plasma display panels are being manufactured, varying frit peak temperature, frit cycle time, exhausting/baking peak temperature, exhausting/baking time and aging. Then, fundamental operational parameters will be measured: breakdown voltage, sustaining voltage (and voltage margin), luminance (cd/m^2), luminous efficacy (lm/W) and jitter lag time. In this way, the most critical process steps for MgO contamination will be identified. PDP performances with getter will be tested as case studies: the main results will be discussed in a further paper.

3. Results and discussion

It is well established that secondary electron emission due to ion (Ne^+ in our case) impact on a sample is strongly affected by the surface cleanliness [9]. In particular, adsorbed gas atoms introduce localized electronic states at the surface, from which Auger electrons can be scattered: the effect can be the lowering of the emission yield. In addition to being simply physisorbed, CO_2 and moisture can also react with the MgO surface, giving rise to hydroxide and/or carbonate formation: in this case lower emission currents are expected, due to MgO shielding by the contaminated surface areas.

H_2O vs CO_2 exposure (RT)

Figure 2 shows the secondary electron emission coefficient γ for samples exposed to CO_2 and H_2O at room temperature, compared to a freshly deposited (Ref.) MgO film.

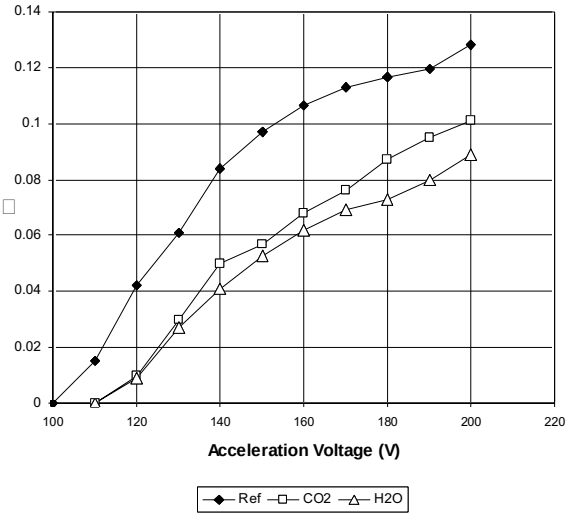

Fig. 2. γ values for reference, CO_2 exposed and H_2O exposed samples.

As expected, moisture detrimental effect on γ is more evident with respect to CO_2. In fact, it has been shown by synchrotron X-Ray photoemission spectroscopy that water easily dissociates to hydroxyl both on low defects MgO(100) surface areas and in correspondence of surface lattice defects, already at $1.8 \cdot 10^4$ L [10, 11]. On the contrary, carbonate formation from CO_2/MgO interaction is thermodynamically favoured only at MgO surface step edges (O_{4c}^{2-} sites) and for particular adsorbed CO_2 molecule rotation angles [12]. Since moisture dissociative adsorption is dominant at RT, with respect

to physisorption (mainly present at low temperatures) [13], our γ data most probably refer to a $Mg(OH)_2$ covered surface in the case of the H_2O contaminated sample and to a surface with predominantly physisorbed carbon dioxide molecules in the case of the CO_2 contaminated one.

The obtained empirical correlation between the secondary electron emission coefficients (fig. 3) is $\gamma_{CO2} = 1.14 \cdot \gamma_{H2O}$. In both cases, I_e is under the system detectable limit for $V_i < 120V$.

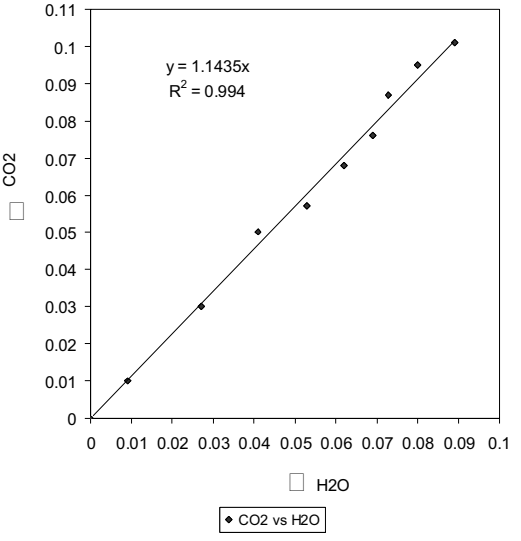

Fig. 3. Evaluation of the ratio between γ values, after CO_2 or H_2O exposure (2.16 10^{12} L).

H_2O plus CO_2 exposure (RT)

Just after γ-FIB analysis of the hydrated MgO, the samples have been exposed to 600 Torr CO_2 for 1 hour and then re-scanned. Fig. 4 shows the results, together with Ref. and MgO film exposed to combined H_2O/CO_2 at RT: $P(H_2O)/P(CO_2)$ = 1/74 (total pressure 1 atm) for 30 hours.

The γ lowering due to successive exposure is less marked than the combined exposure case: especially, the former curve is much similar to the one corresponding to moisture contamination only (shown in fig. 2), with a variation $\Delta\gamma/\gamma \sim 3\%$, at $V_i = 200$ V. Actually, it has been observed by P. Liu *et al.* [10], that additional water can be physisorbed on the hydroxyl layer, after the surface is fully hydroxylated: thus, CO_2 molecules could hardly hit the $Mg(OH)_2$, because of the presence of the passivating water layer.

The slightly different γ curve offset (ΔV_0=10V) in the two cases (H_2O only and successive H_2O/CO_2, fig. 2 and fig. 4 respectively) can be a secondary effect due to the sputtering (cleaning) action of Ne^+ atoms impinging on the contaminated surface (CO_2 exposure has been carried out after some hours of FIB on the very same samples).

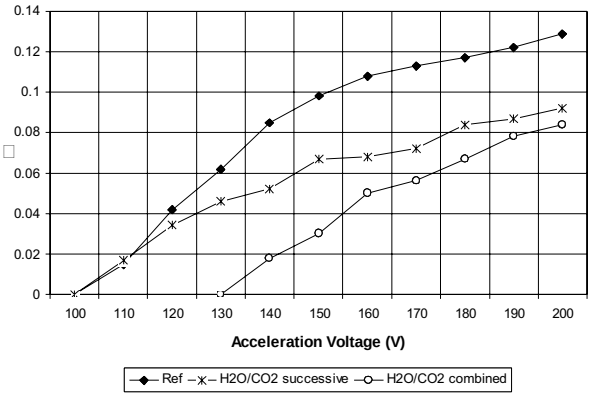

Fig. 4. Comparison amongst successive H_2O/CO_2, combined H_2O/CO_2 exposure and Ref γ values.

Under simultaneous H_2O/CO_2 contamination, it is expected that the two-step carbonate formation process

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad (3)$$

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O \qquad (4)$$

can be favoured. The big differences in secondary electron emission yield, with respect to Ref (ΔV_0=30V and $(\gamma_{Ref} - \gamma_{H2O/CO2})/\gamma_{Ref} > 34\%$, at $V_i = 200$ V), could be explained considering important surface changes, such as extended carbonate formation. The H_2O product in reaction (4) is a further issue.

High temperature H_2O plus CO_2 exposure

The regime cell temperature during PDP operation is estimated to be around 90°C-100°C. Thus, we have decided to perform γ measurements on pre-hydrated MgO films (100% RH at RT) exposed to CO_2 ($2.16 \cdot 10^{12}$ L) at 100°C, in order to "simulate MgO contamination during plasma discharge, under the worst atmosphere conditions (fig. 5).

Since at 100°C both H_2O and CO_2 physisorption is not expected, we attribute the further lowering of γ ($\gamma_{100°}/\gamma_{RT} \sim 0.78$) to a more effective carbonate formation, through the chain reactions (3) and (4). At sufficiently high (> 120V) acceleration voltages, the following linear empirical correlation among γ values holds:

$$\gamma_{H2O/CO2}(V,T) = C(T) \cdot \gamma_{Ref}(V - \Delta V_0), \qquad (5)$$

being the offset ΔV_0=30V and the experimental C(T)

parameter obtained by the linear fit in fig. 6: we have C(100°C) = 0.557 and C(RT) = 0.710.

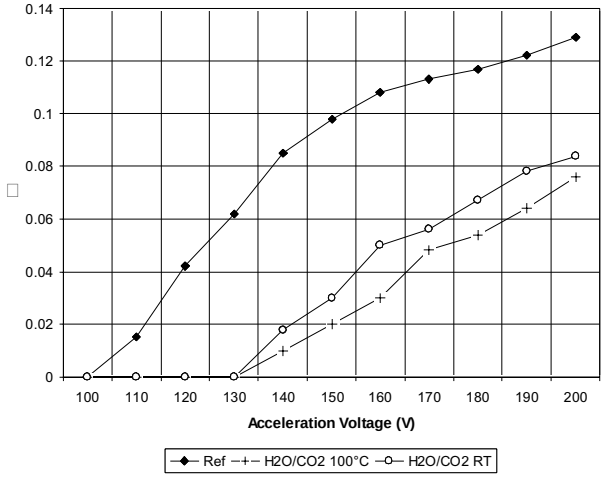

Fig. 5. Comparison amongst 100°C and RT H_2O/CO_2 exposure γ values.

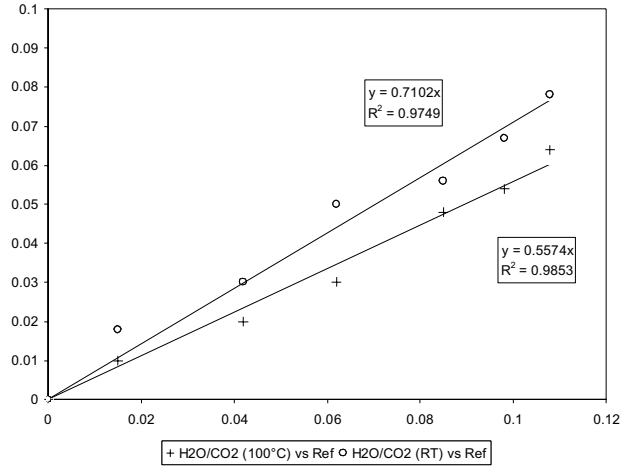

Fig. 6. Determination of the experimental parameter C(T), comparing $\gamma_{H2O/CO2}(T)$ with γ_{Ref} in the range 130V – 190V.

Table 1 summarizes the γ values obtained for the different samples at V_i=180V (typical value for PDP firing voltage [14]).

TABLE 1. Comparison of secondary emission coefficients γ at 180 V accelerating voltage.

	$\gamma \cdot 10^{-3}$
Ref. (clean MgO)	117
CO_2	87
H_2O	73
H_2O/CO_2 combined (RT)	67
H_2O/CO_2 combined (100°C)	54

4. Summary

We have demonstrated that intense exposure to moisture and carbon dioxide can greatly diminish the secondary electron emission capability of e-beam deposited MgO: lower values for γ reflect in worse PDP performances.

The detrimental effects of H_2O and CO_2 have been isolated, resulting water more harmful to MgO surface, due to its high sticking coefficient and probability of forming $Mg(OH)_2$. CO_2 contamination is believed to be ascribed essentially to physisorption.

At 100° C the contribution of physical adsorption is considered negligible: the simultaneous exposure to water and CO_2 molecules leads to less than 47% of the Ref γ value (V_i=180V), quite probably due to MgO surface carbonation. The same chemical reaction appears a bit less favoured at RT.

A suitable getter material able to contrast the MgO protective layer worsening should primarily act as water absorbent (dryer), in order to prevent both water physisorption and hydroxylation: blocking $Mg(OH)_2$ formation also impede the hydroxide promoted surface carbonation. CO_2 sorption is considered of minor importance, because of the low adsorption probability of CO_2 molecules, especially at high temperature (PDP operating temperature) and the very low effectiveness of direct MgO carbonation.

5. References

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