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Effect of Reactive Gas Dopants on the MgO Surface in AC Plasma Display Panels

Abstract: Experimental results are presented for the influence of controlled levels of important reactive impurities (N_2, O_2, H_2O, CO_2) on the aging characteristics of the operating voltages of ac plasma display panels. Details are also given of a novel method of modifying the electronic properties of MgO surfaces by discharge processing in an oxygen-doped Ne-0.1% Ar Penning mixture.

Introduction

Magnesium oxide is generally recognized [1–3] as a stable overcoat material for ac plasma display panels. However, the electrical characteristics of the panel are a sensitive function of the surface properties of the thin MgO layer, which is in direct contact with the gas. This places rather stringent requirements on the level of reactive impurities which can be tolerated in the luminous gas mixture. One example of a common aging mechanism exhibited by an improper MgO layer is alternate-line-aging (ALA), which is the strong increase in the operating voltage of alternate lines of nonoperated cells between the lines of operated cells. An earlier study [2] has tentatively attributed the major alternate-line-aging effects, observed with overcoats of refractory oxides like MgO, to the transfer of hydroxides or hydroxyl groups (or simply the hydrogen) from operated to nonoperated discharge sites. The present paper goes further by introducing controlled levels (10–100 ppm) of reactive gas (N_2, O_2, H_2O, CO_2) impurities in the typical Ne-0.1% Ar Penning mixture gas fill and then monitoring their effects on the operating voltages of the ac panel. Finally, introduction of a 1% oxygen dopant in the conventional Penning mixture leads to a relatively low voltage (< 200 V) oxygen discharge process, which can be used to modify the electronic properties of the MgO layer.

Effects of contaminants on operating voltages

The experiments were performed in a demountable chamber, which is part of an ultrahigh-vacuum system with multiple ports for filling different gases. Facilities are provided for monitoring the experiments both optically and by mass spectroscopy. Further, the spacing between the experimental panel plates can be varied over a wide range extending from 5.08×10^{-5} m to about 2.54×10^{-2} m. The larger spacing is particularly useful for spreading the discharge at low pressures ($< 66.5 \times 10^2$ Pa) to get large-area cleaning of the panel plates. The investigations were conducted with specified impurities in pre-mixed research grade gas obtained commercially. The lower limit of controlled doping was set at 10 ppm due to the increasing uncertainty involved in specifying low contaminant levels in the presence of active adsorption at the chamber walls (despite the precautionary step taken of trying to saturate the adsorption of the reactive impurity at the walls by several preliminary flushes with the experimental gas mixture). The results presented in this paper are for an e-beam evaporated MgO layer deposited [4] at a rate of 1–10 nm per second on a substrate heated to 200°C. The aging trends in both the maximum ($V_{s\,max}$) and the minimum ($V_{s\,min}$) sustain voltages were measured for square-wave ($\approx$ 30-kHz) operation of an ac panel filled with 465.5×10^2 Pa of the typical Ne-0.1% Ar gas mixture containing prescribed levels of the chosen impurities. The effects of various contaminants on operating voltages were studied sequentially on a single panel. The chosen panel had an operating range defined by $V_{s\,max} = 93.6$ V and $V_{s\,min} = 83.4$ V for 465.5×10^2 Pa of the normal Ne-0.1% Ar mixture without any reactive impurities. Curves A and B of Fig. 1 show the initial operating voltage data for this panel, which is characterized by a quick "burn-in" and a

negligible amount of alternate-line-aging on running the lines of operated cells at an elevated voltage of 135 V for a few hours. The experiments with the reactive impurities were done in the following order of succession: N_2, H_2O, O_2, and finally CO_2. After experimenting with each mixture, we processed the panel in an attempt to regain the original operating voltages with the standard Ne-0.1% Ar mixture. The alternate-line-aging characteristics of the recovered panel were not tested. Depending on the nature of the impurity, the panel recovery was achieved in one of the stages of the following sequence of processes: 1) repeated gas flushes with burn-in of full panel at 135 V; 2) repeated gas flushes with wide area discharge processing at lower pressures ($\approx 13 \times 10^2$ Pa) and wider gap spacings; 3) vacuum bake cycle for a few hours (< 4 h) at 150°C. Extreme care must be taken to moderate the processing parameters so as not to change permanently the intrinsic MgO surface through intense processing conditions. Note that the panel could not be fully regained after experimenting with the mixture containing the CO_2 impurity.

Sample results are qualitatively summarized in Table 1, and they show the aging trends in both the maximum and the minimum sustain voltages for gas mixtures containing prescribed levels of the chosen impurities. As an example of the sequence of events followed in these measurements for oxygen and water vapor contaminants, we describe our procedure for the case of 50 ppm of oxygen as the reactive impurity. The operating voltages declined rapidly from an initial value of 170 V. Curves C and D of Fig. 1 follow the temporal behavior of $V_{s\,max}$ and $V_{s\,min}$ ten minutes after the initial firing. Note that after 15 min of operation of all cells, a panel margin of 22.2 V was measured with $V_{s\,max} = 133.3$ V and $V_{s\,min} = 111.1$ V. At this time, the burn-in voltage was fixed at 135 V for a period of 45 min, at the end of which the operating voltages stabilized at $V_{s\,max} = 106.7$ V and $V_{s\,min} = 96.8$ V. Now the ALA experiment was started by switching off alternate lines of cells and monitoring periodically the operating voltage margin of both operated and nonoperated cells for a few (< 6) hours. The stable voltages of the operated cells for oxygen and water vapor impurities, indicated in Table 1, refer to the ALA time sequence and were achieved after all cells had undergone the initial burn-in which accompanies the rapid (< 1 h) cleaning of the reactive impurity (as monitored by emission spectroscopy) at the discharge sites. For an impurity level greater than about 20 ppm in either H_2O or O_2, the adjacent nonoperated cells show an increase in operating voltages during this same ALA period of the experiment. The voltage characteristics for the operated and the nonoperated cells can be reversed by interchanging the states of the two adjacent lines of cells. The above result simulates the voltage trends observed with improperly produced MgO

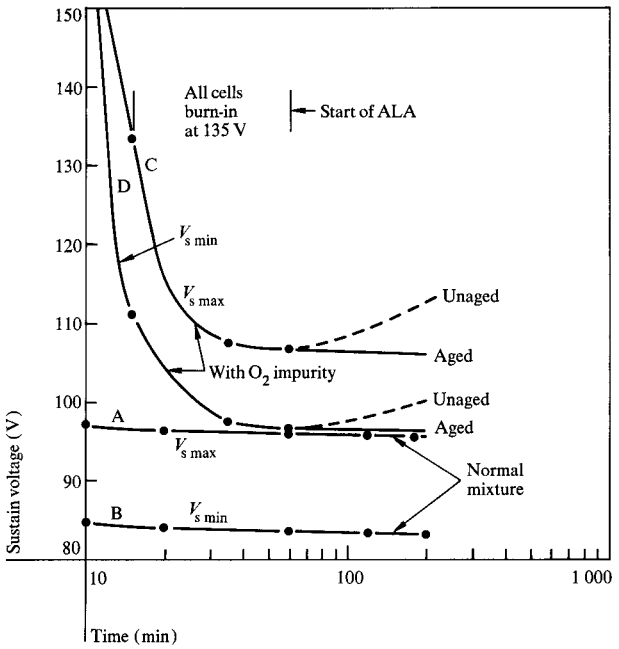

Figure 1 Burn-in and alternate-line-aging characteristics for ac panels with an Ne-0.1% Ar gas fill at 465×10^2 Pa (curves A and B) and with 50 ppm oxygen impurity (curves C and D).

Table 1 Effects of various contaminants on aging trends in operating voltages.

Contaminant (10-100 ppm)	*Change in operated cells*		*Change in adjacent unoperated cells*	
	$V_{s\,max}$	$V_{s\,min}$	$V_{s\,max}$	$V_{s\,min}$
$N_2 > 20$ ppm	increasing	increasing	stable	stable
< 20 ppm	stable	increasing	stable	stable
$H_2O > 25$ ppm	stable	stable	increasing	increasing
< 25 ppm	stable	stable	stable	increasing
$O_2 > 20$ ppm	stable	stable	increasing	increasing
$CO_2 < 20$ ppm	increasing	(no margin)	stable	(no margin)

devices and thus lends further credence to the hypothesis of a migrating radical [2] causing the aging in refractory oxide surfaces.

The remaining two impurities, N_2 and CO_2, in Table 1 show a voltage change only on the operated cells, with negligible effect on the adjacent nonoperated cells. For gas mixtures with these two impurities, the operating voltages of the panel start to increase after the initial firing. Thus, we used a minimal burn-in period and started the ALA experiment within a few minutes (< 5 min) of the initial firing of the full panel.

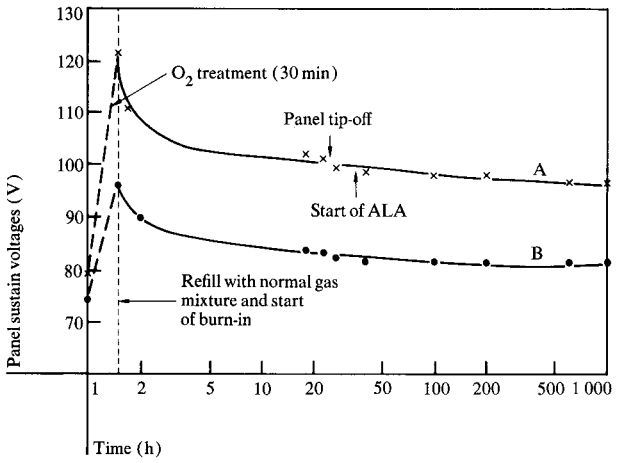

Figure 2 Burn-in and ALA characteristics for an oxygen-treated panel fabricated in a dry-air environment during sealing process. Sustain voltage vs time is shown for a 7-μm evaporated dielectric and 200-nm MgO topcoat with an Ne-0.1% Ar gas mixture at 465×10^2 Pa.

Table 2 Recovery from effects of reactive impurities.

Contaminant	*Comment on recovery process*
Nitrogen	Easily removed from surface by a vacuum bake cycle.
Water	Predominantly removed from surface during vacuum bake cycle with remainder removed from active discharge sites during burn-in. Wide area discharge processing does an effective job in cleaning the entire active area of panel.
Oxygen and hydrogen	Same as water vapor.
Carbon dioxide	Difficult to remove either by bake-out or burn-in. Carbon deposits found by Auger electron spectroscopy.

An impurity level of less than approximately 20 ppm of CO_2 is enough to cause an appreciable increase ($\approx$ 50 V in 2.5 hours) in the operating cell voltage with complete loss of panel margin. The effect of nitrogen impurity is less drastic in that even for impurity levels greater than 20 ppm, the change in the operating cell voltage is relatively small (< 10 V). These results indicate that the discharge cleanup of CO_2 and N_2 impurities forms adsorbed species on the MgO surface at the discharge sites, which, unlike the earlier case for H_2O and O_2, are not transferred from operated to nonoperated sites.

Table 2 summarizes the ability to reverse the effects of reactive impurities through additional processing and, thus, to recover the original operating voltages corresponding to an uncontaminated panel. Note that nitrogen contamination is the easiest to remove, while carbon dioxide does irreversible damage to the panel.

Oxygen discharge processing of MgO surfaces

Deliberate introduction of an increased ($\approx$ 1%) oxygen dopant in the Ne-0.1% Ar mixture produces an appreciable concentration of highly active oxygen at relatively low (< 200 V) voltages. The thin insulators of a typical ac panel can withstand these voltages without localized breakdowns, and this allows the possibility of modifying the MgO surface properties of a fully fabricated panel on the gas filling station. About 30 minutes of the discharge treatment is usually sufficient to correct for any possible oxygen deficiency introduced during the previous steps of panel fabrication. The panel is then thoroughly evacuated and refilled with the typical Ne-0.1% Ar mixture. For an illustration of this process, an oxygen deficiency was artificially created in a normal panel by repeated and prolonged baking in high vacuum. There were progressive drops in both $V_{s\,max}$ and $V_{s\,min}$, which were accompanied by a collapse in the bistable operating margin to about 3 V ($V_{s\,max}$ = 77.5, $V_{s\,min}$ = 74.5). Oxygen discharge processing gave a fivefold improvement in the bistable margin by increasing the maximum sustain voltage to a substantially higher degree than the minimum sustain voltage. This improvement is permanent for panels fabricated by firing in a dry air atmosphere to seal the two plates. Curves A and B of Fig. 2 show the aging curves for $V_{s\,max}$ and $V_{s\,min}$, respectively. There is a longer burn-in period than for the normal panel (curves A and B of Fig. 1) initially, but on attaining stable operating voltages, the oxygen processed panel gave a wide operating voltage margin with negligible alternate-line-aging effects. For panels sealed in an inert gas atmosphere, the initial widening of the margin is temporary, in that it slowly collapses to near its original value after about a hundred hours of operation (curves A and B of Fig. 3). Further, the panel showed pronounced ALA, which is in striking contrast to the previous panel. The tentative explanation for this different behavior is that the oxygen deficiency created during processing extends well into the bulk of the MgO film. The high temperature sealing in a dry air atmosphere corrects this deficiency throughout the bulk, and any extended vacuum bake only modifies the superficial surface layer, which can be fully restored by the oxygen discharge processing. However, for inert gas sealed panels, the oxygen deficiency extends into the bulk of the film, and the slow loss of the oxygen from the surface would gradually deplete the additional oxygen supplied to the surface layer by the oxygen discharge processing.

The dramatic increase in the operating voltage margin after oxygen processing can be simulated in a theoretical model [5] by increasing substantially the average kinetic

energy of the Auger-emitted secondary electrons from the MgO cathode [6], and, thereby, modifying favorably the dependence of γ, the effective secondary-electron emission coefficient, on the reduced electric field at the cathode. The detailed explanation for this increase in kinetic energy of the emitted electrons is not clearly understood at the present time. This increased average energy might tentatively be attributed to a preponderance of shallow acceptor levels (associated with chemically adsorbed oxygen on the surface) brought about by discharge processing in oxygen. This would result in a large increase in the density of filled states near the top of the valence band (i.e., shallow acceptor levels), thereby causing most of the Auger emission to come from these levels.

Conclusions

Results of experiments involving the influence of some important reactive impurities on the operating voltages of ac plasma panels show two distinct trends: 1) Impurities like H_2O and O_2 result in stable operating voltages for operated cells and an aging increase in the adjacent nonoperated cell voltages; 2) in contrast, reactive contaminants like N_2 and CO_2 result in an aging increase in the operating voltages of only the operated cells. The CO_2 contamination degrades the panel characteristics irreversibly.

The introduction of an increased oxygen dopant level (about 1%) in the typical Ne-0.1% Ar Penning mixture leads to an oxygen discharge process which can be used to modify the electronic properties of the MgO surfaces of a fully fabricated panel awaiting the final gas filling process. The earlier process steps of panel fabrication dictate whether this change in MgO surface properties is temporary or permanent.

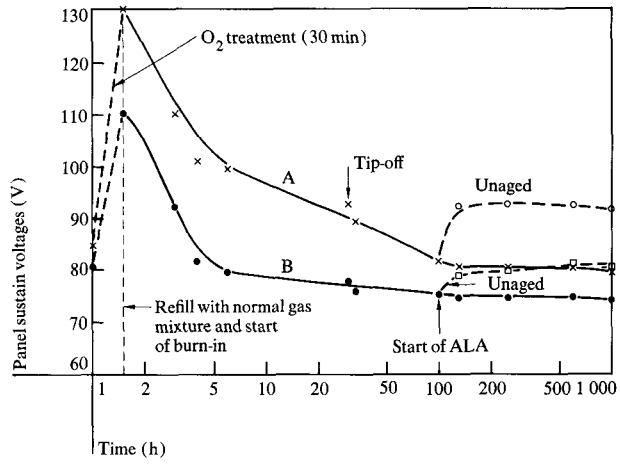

Figure 3 Burn-in and ALA characteristics for an oxygen-treated panel fabricated in an inert gas environment during the sealing process.

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