Effect of Impurity in Discharge Gas on High $\gamma$ Properties of Newly Developed CeSrO Film for Novel Plasma Display Panel

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SUMMARY

The discharge properties and chemical surface stability of CeO$_2$ containing Sr (CeSrO) as the candidate for high-\(\gamma\) protective layer of noble plasma display panels (PDPs) are characterized. CeSrO films have superior chemical stability, because of the decrease in reactivity on surface due to their fluorite structure. The discharge voltage is 50 V lower than that of MgO films for a pure discharge gas of Ne/Xe = 85/15 at 60 kPa. However the topmost surface, monolayer, of the CeSrO film relevant to the discharge property is hardly recovered from the damage by CO$_2$ impurity in discharge gas. We can expect that by pumping down to a sufficiently low CO$_2$ partial pressure (lower than 1 \(\times\) 10$^{-3}$ Pa), PDP panels with very high efficiency are realized with CeSrO protective layer.

key words: PDP, $\gamma$, protective layer, discharge, MgO

1. Introduction

MgO films are widely used as protective layers for plasma display panels (PDPs) due to their high sputtering resistance, superior wall-electron-keeping properties, exoelectron properties and high process resistance. Moreover, the secondary-electron-emission coefficient of MgO is high enough for Ne ions, which is necessary for the low voltage plasma discharge [1]. However, the $\gamma$ of MgO is quite low for Xe ions because the ionization energy of Ne is 22 eV whereas that of Xe is 12 eV [2]. In the Auger-neutralization scheme, only the electrons within the energy range from the vacuum level to the half of the ionization energy of the discharge gas contribute to the secondary-electron-emission, but the valence band top of MgO appears at 8.5 eV from the vacuum level [1]. On the contrary, in order to increase the luminous efficiency, Xe content of the discharge gas of PDPs needs to be raised because UV radiation is emitted by the excited Xe species. Therefore, the development of a high-$\gamma$ protective layer for Xe ions to replace MgO is strongly required.

Recently, the protective layers with high $\gamma$ for PDPs have been developed by many research groups. Shinoda et al. [3] and Motoyama et al. [4], [5] have proposed a Sr-CaO protective layer. Kim et al. [6] has researched a MgSr-CaO protective layer and Uchida et al. [7] has reported the characteristics of AC-PDP, where SrO is used as protective layer. We also report on the discharge properties and chemical stability of SrO containing covalent element Zr (SrZrO) [8]. However, the high $\gamma$ materials based on alkaline-earth oxides, such as CaO, SrO, BaO, SrCaO and SrZrO, have low resistances to the sealing process due to their chemically active characteristics. Impurity, such as carbonate and H$_2$O, will adsorb to the surface, and will decrease the $\gamma$ [9]. Therefore, it is quite important to develop the high $\gamma$ protective layer with high chemical surface stability.

We have developed a CeSrO (CeO$_2$ containing Sr) protective layer. As the concept, we attempt to prevent carbonation by adding covalent elements. The fourth group elements, such as Ti, Zr, Hf and Ce do not have d electrons because they are tetravalent. In the result, we found that the discharge properties and chemical stability of SrO containing Ce are the best in these four elements. However, the CeSrO does not show high $\gamma$ property adopted for a large panel such as 42 inch with high uniformity. Thus, we examined the effect of impurity in sealing process and pumping process on high $\gamma$ properties of CeSrO film with a demountable chamber system. In this paper, we report the discharge characteristics and the chemical stability to the sealing process and the pumping process of CeSrO.

2. Experimental

We prepared test element groups (TEGs) with the CeSrO films which were deposited by an electron beam evaporation method as shown in Table 1. The substrate temperature was 300°C, O$_2$ gas flow rate was 0.1 sccm, and deposition rate was 0.5 nm/sec. The compact made by sintering a mixture of SrCO$_3$ and CeO$_2$ powder at 1400°C for two hours in the air was used as the target. We prepared some targets with a different ratio of CeO$_2$ and SrCO$_3$, and made CeSrO films with different Ce contents. The TEGs had a dielectric layer ($\varepsilon_r$ ~11) and electrodes to examine discharge parameters. The electrodes were etched into two parts with the gap

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Typical deposition parameter.</th>
</tr>
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<tbody>
<tr>
<td>BG pressure</td>
<td>1.2 $\times$ 10$^4$ Pa</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>300°C</td>
</tr>
<tr>
<td>O$_2$ flow</td>
<td>0.1 sccm</td>
</tr>
<tr>
<td>High Voltage</td>
<td>7.5 kV</td>
</tr>
<tr>
<td>Beam current</td>
<td>185 mA</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>0.5 nm/sec</td>
</tr>
<tr>
<td>Thickness</td>
<td>400 nm</td>
</tr>
</tbody>
</table>

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by 80 μm (often called main gap). For comparison, we also prepared TEGs with the MgO and SrCaO films in a similar way.

X-ray diffraction (XRD) analysis with CuKα was made in order to identify the constituent phase and crystallinity. The chemical composition and state of the deposited protective layer was identified by using X-ray photoelectron spectroscopy (XPS) obtained by monochromatic AlKα emission. The topmost surface of the protective layer was identified by using meta-stable de-excitation spectroscopy (MDS)[10]–[12] with meta-stable helium (He*). MDS is an extremely surface-sensitive technique because only electrons at the topmost surface contribute to the MDS spectra, which is exactly the same to the plasma discharge of PDPs[13]. Therefore, the MDS has a big advantage in the characterization of the discharge phenomenon, compared with the other techniques.

In order to examine the tolerance to the sealing process, the TEGs were annealed at 500°C for two hours in the air. The discharge characteristic of each TEG was evaluated by the demountable chamber system: 1) set the TEG in the chamber, 2) evacuate the chamber, 3) anneal the TEG at 480°C for 8 hours in vacuum (under 5 × 10⁻⁶ Pa), 4) stop the evacuation after the TEG is cooled down to room temperature, 5) fill the chamber with the discharge gas of Ne/Xe = 85/15, 60 kPa, 6) give aging for two hours, 7) measure the discharge characteristics (Fig. 1). For comparison, we evaluated the discharge characteristics of each TEG without the annealing in the air. Chemical stability to the sealing process was evaluated by XPS in C1s and the valance band.

Next, we prepared 5, 13 and 42 inch test panels with MgO and Ce₀.₆Sr₀.₄O protective layers which were deposited by the electron beam evaporation method. Each panel had a dielectric layer (εᵣ ∼ 7) and two electrodes with the main gap 40 μm. We gave aging for seven hours and measured the discharge characteristics of each panel.

![Fig.1 Process flow of chamber experiment with sealing process.](image)

### 3. Results and Discussion

#### 3.1 Composition and Crystal Structure

XRD profiles of CeₓSr₁₋ₓO layers are shown in Fig. 2. At the Ce content of x > 0.5, several peaks confirming fluorite structure of CeO₂ are observed, and their peaks disappear with decreasing Ce content to be x = 0.26. It shows that Ce₀.₂₆Sr₀.₇₄O consists of amorphous structure. Then, at the Ce content of x < 0.1, some peaks confirming rock-salt structure of SrO are observed.

However, their peaks also disappear with decreasing Ce content to be x = 0.003, and another peaks confirming Sr(OH)₂ are observed. It is assumed to be caused by low chemical stability of Ce₀.₀₀₃Sr₀.₉₉₇O. From these results, it was found that the crystal structure of CeSrO changes with increasing Ce content from rock-salt to fluorite with the transition range of amorphous structure.

Moreover, diffraction peaks are shifted by change of a Ce content in CeSrO. Figure 3 shows the lattice constants estimated by the diffraction peaks of (111) plane of CeO₂.

![Fig.2 XRD profiles of CeₓSr₁₋ₓO layers.](image)
or (111) plane of SrO with Ce content of CeSrO layers. At the Ce content of $x \geq 0.5$, the lattice constant of fluorite structure decreases from 5.53 Å to 5.39 Å with increasing Ce content to be $x = 1.0$. On the other hand, at the Ce content of $x \leq 0.1$, lattice constant of rock-salt structure decreases from 5.16 Å to 5.12 Å with increasing Ce content to be $x = 0.1$. The ionic radius of Ce$^{4+}$ and Sr$^{2+}$ is 0.97 and 1.18 Å, respectively. Thus, these results suggest that substitution of Ce sites by Sr ions occurs in the fluorite structure, and substitution of Sr sites by Ce ions occurs in the rock-salt structure.

3.2 Discharge Characteristics

The sustain voltage of CeSrO as a function of the ratio of Ce/(Ce+Sr) is shown in Fig. 4. TEGs with deposited CeSrO layer were introduced into the discharge chamber after the annealing process at 500°C in the air as the sealing process. In our experiments, the sustain voltage of MgO as a reference was 185 V. At the Ce content of $x = 1$, i.e. CeO$_2$, the voltage is 15 V lower than that of MgO, and then, the voltage decreases to be 135 V with decreasing Ce content to be $0.6 \leq x \leq 0.7$. In the Auger neutralization theory, the high density of states at the lower energy band from the vacuum level is needed in order to emit the secondary electron in high-Xe-content discharge gas because the ionization energy of Xe is lower than that of Ne [14]. We consider the $\gamma$ was increased because the valence band of CeSrO with substitution of Ce sites by Sr ions in the fluorite structure was shifted to lower than that of CeO$_2$, the high $\gamma$ was kept even after the annealing process because of the high surface stability. However, the sustain voltage of the TEGs with the sealing process increases to be about 220 V with further decreasing Ce content. This result suggest that the extrinsic gas species are easily adsorbed to the surface of CeSrO consisting of the rock-salt or the amorphous structure, and the $\gamma$ decreased.

3.3 Chemical State

Figure 5 shows the XPS spectra in Cls of Ce$_x$Sr$_{1-x}$O ($0 \leq x \leq 1$) layers after the annealing at 500°C for two hours in the air. These spectra, the peak height around 285 eV which is caused by physical adsorption of hydrocarbon was not deviated so much except Ce$^0$. On the other hand, the peak around 290 eV caused by carbonation for Ce$_x$Sr$_{1-x}$O ($0 \leq x \leq 0.4$) is three times higher than that of Ce$_x$Sr$_{1-x}$O ($0.5 \leq x \leq 1$). This result shows that Ce$_x$Sr$_{1-x}$O ($0 \leq x \leq 0.4$) with the rock-salt or the amorphous structure is weak in carbonation, but Ce$_x$Sr$_{1-x}$O ($0.5 \leq x \leq 1$) has superior chemical stability due to their fluorite structure even after the annealing. Consequently, it was found that adding adequate amount of Sr in CeO$_2$ improves discharge characteristics and maintains the chemical surface stability.

Figure 6 shows the XPS spectra in the valence band of Ce$_x$Sr$_{1-x}$O ($0 \leq x \leq 1$) after the annealing at 500°C for two hours in the air. In these spectra, the peak height around 285 eV which is caused by physical adsorption of hydrocarbon was not deviated so much except Ce$_x$Sr$_{1-x}$O. On the other hand, the peak around 290 eV caused by carbonation for Ce$_x$Sr$_{1-x}$O ($0 \leq x \leq 0.4$) is three times higher than that of Ce$_x$Sr$_{1-x}$O ($0.5 \leq x \leq 1$). This result shows that Ce$_x$Sr$_{1-x}$O ($0 \leq x \leq 0.4$) with the rock-salt or the amorphous structure is weak in carbonation, but Ce$_x$Sr$_{1-x}$O ($0.5 \leq x \leq 1$) has superior chemical stability due to their fluorite structure even after the annealing.

Consequently, it was found that adding adequate amount of Sr in CeO$_2$ improves discharge characteristics and maintains the chemical surface stability.
low binding energy because of high resistance to carbonation. Moreover, the density of states of valence band top for Ce$_{x}$Sr$_{1-x}$O (0.6 $\leq$ $x$ $\leq$ 0.8) was higher than that of CeO$_2$ which is probably related to the substitution of Ce sites by Sr ions.

3.4 Panel Property

Figure 7 shows the sustain voltage of the panels with MgO and Ce$_{0.6}$Sr$_{0.4}$O protective layers. In the 5 inch panel, the sustain voltage of Ce$_{0.6}$Sr$_{0.4}$O was 47 V lower than that of MgO and the value is similar to that of the chamber experiment. However, when the panel size was larger, the voltage with Ce$_{0.6}$Sr$_{0.4}$O protective layer rose and that of Ce$_{0.6}$Sr$_{0.4}$O was 23 V higher than that of MgO in the 42 inch panel.

3.5 Further Analysis on Carbonation

The Ce$_{x}$Sr$_{1-x}$O (0.6 $\leq$ $x$ $\leq$ 0.7) protective layer has superior chemical stability against annealing at 500°C in the air, and the sustain voltage is 50 V lower than that of MgO in the chamber experiment. However, the CeSrO does not show high $\gamma$ property adopted for the larger panel such as 42 inch with high uniformity. Thus, we examined the effect of impurity in the sealing process and the pumping process on the high $\gamma$ properties of CeSrO film, whose Ce content is 0.6, with a different demountable chamber system.

3.5.1 Sealing Process Analysis

First, we supposed the CeSrO protective layer was deteriorated in the sealing process, and experimented as follows. We prepared TEGs with the CeSrO, whose Ce content is 0.6, MgO and SrCaO protective layers which were deposited by the electron beam evaporation method. The TEGs had a dielectric layer ($\varepsilon_r \sim 11$) and electrodes (main gap 80 $\mu$m). As the sealing process, the each TEG was annealed at 480°C for 30 minutes in (a) dry-air, (b) air including 10% CO$_2$, (c) air bubbled in 55°C water or (d) air including 10% CO$_2$ bubbled in 55°C water. The voltages of CeSrO and MgO do not change by annealing in air including CO$_2$ and H$_2$O. The voltage of SrCaO rises by over 64 V by annealing in dry-air or air including CO$_2$ and H$_2$O. The voltage of SrCaO could not be measured when annealed in the air including CO$_2$ and H$_2$O.
by the annealing in dry-air (a). The voltage rose by 95 V by the annealing in air bubbled in 55°C water (c). In addition, when the SrCaO TEG was annealed in the air including CO₂ bubbled in 55°C water (d), the voltage could not be measured (over 300 V).

3.5.2 Pumping Process Analysis

Secondly, we supposed the CeSrO protective layer is deteriorated by impurity remaining in pumping process [15], [16], and experimented as follows: 1) set CeSrO, whose Ce content is 0.6, MgO and SrCaO TEGs without sealing process, 2) evacuate the chamber, 3) flow CO₂ gas and control the pressure 1×10⁻⁵~1×10⁻¹ Pa, 4) anneal the TEGs at 480°C for 8 hours, 5) stop the evacuate and CO₂ flow after the TEGs are cooled down to room temperature, 6) fill the chamber with the discharge gas of Ne/Xe = 85/15, 60 kPa, 7) give aging for two hours, 8) measure the discharge characteristics (Fig. 10). MgO and SrCaO protective layers were also examined.

The sustain voltages of CeSrO, MgO and SrCaO are shown as a function of the pressure of CO₂ gas remaining in the pumping process in Fig. 11. With increasing the CO₂ gas pressure over 1×10⁻³ Pa, the sustain voltage of the each protective layer was increased. In CeSrO, when the pressure of CO₂ gas was over 1×10⁻³ Pa, the sustain voltage rose; the voltage at 1×10⁻⁵ Pa was 35 V higher than that at 1×10⁻³ Pa. In MgO, the voltage at 1×10⁻² Pa was 20 V higher than that at 1×10⁻³ Pa. In SrCaO, the voltage at 1×10⁻² Pa was 29 V higher than that at 1×10⁻⁵ Pa.

3.5.3 Recovering Effect of Anneal in Vacuum

From these results, it was found that the CeSrO is not influenced by CO₂ and H₂O in the sealing process, but the pumping process should be performed in the lower CO₂ residue than 1×10⁻³ Pa to keep the high γ property.

This seems to show that CeSrO films are deteriorated by CO₂ remaining in the pumping process, but that the deteriorated films are hardly recovered by the annealing in the pumping process and the aging when CO₂ is remained.

To examine the possibility of the recovery, we carried out the surface characterization of the CeSrO film, whose Ce content is 0.6, through the pumping process (Fig. 10) with XPS and MDS. The pressure of CO₂ gas remaining in the pumping process was from 1×10⁻⁵ to 1×10⁻² Pa.

Figure 12 shows valence band spectra by XPS and MDS. The sustain voltage at the pressure of CO₂ 1×10⁻² Pa
was 35 V higher than that at $1 \times 10^{-5}$ Pa, but the XPS spectra showed almost no difference. On the other hand, MDS spectra showed that when the remaining CO$_2$ gas pressure was high, the density of states near the valence band top was low. The characterization region of MDS corresponds to the topmost surface while the region of XPS corresponds to several nm inside from the topmost surface of the material.

Thus, the topmost surface, or monolayer, of the film governs the discharge property and is hardly recovered from the damage due to the residual CO$_2$ impurity of the atmosphere in the pumping process.

3.5.4 Effect of CO$_2$ in Pumping and in Aging

To examine the effect of CO$_2$ in the discharge gas, we examined the discharge characteristics of CeSrO, whose Ce content is 0.6, MgO and SrCaO TEGs after the sealing process (a) without CO$_2$, or with CO$_2$. Where CO$_2$ were included (b) only in the anneal process, (c) only in the discharge gas or (d) both in the anneal process and in the discharge gas. The CO$_2$ gas pressure was set to be $1 \times 10^{-2}$ Pa for the each case and the each TEG was aged for two hours (Fig. 13).

The sustain voltages of CeSrO, MgO, and SrCaO through the each process and after aging for two hours are shown in Fig. 14. The sustain voltages of CeSrO after the each process as a function of the aging time are shown in Fig. 15.

In CeSrO, the voltage did not rise when CO$_2$ remained only in anneal process (b), but the voltage rose by 33 V when CO$_2$ remained in discharge gas (c and d). Similarly, in MgO, the voltage rose by 7~20 V when CO$_2$ remained in the discharge gas (c and d). On the other hand, the different result was obtained in SrCaO. In SrCaO, the voltage did not change when CO$_2$ remained only in the discharge gas (c), but the voltage rose by 28 V when CO$_2$ remained in the anneal process (b and d). Considering this result and the data shown in Fig. 9, The topmost surface of the CeSrO film may be deteriorated in the sealing process, but it is recovered in the pumping process when performed under the low CO$_2$ residue. However, as indicated in Fig. 14, The topmost surface of the SrCaO film is deteriorated by CO$_2$ in the sealing process, and the deteriorated film is never recovered by the pumping process and the aging.

Consequently, we consider that the remaining CO$_2$ in the pumping process for a larger panel such as 42 inch is not low enough to show high $\gamma$ property uniformly even for the CeSrO film.

4. Conclusions

We have characterized the discharge characteristics and chemical surface stability of CeO$_2$ containing Sr (CeSrO), and came to the conclusions stated below.

(1) Adding adequate amount of Sr in CeO$_2$ improves the discharge characteristics such as sustain voltage, which is 50 V lower than that of MgO under a pure discharge gas of Ne/Xe.
Especially, CeSrO films consisting of fluorite structure have superior chemical stability. (3) Especially, Ce0.6Sr0.4O film has superior discharge properties and high γ properties, and we have confirmed that the film has high density of states near valence band top by MDS, which shows that the topmost surface, monolayer, of the protective layer governs the discharge property. When the remaining CO2 gas pressure is lower than 1 × 10−3 Pa, the Ce0.6Sr0.4O film is recovered from the carbonation by pumping process and aging, and shows high γ property. (4) SrCaO film is easily deteriorated by CO2 in anneal process, and the deteriorated film is never recovered in pumping process and in aging.

From these results, we can expect that when pumping process is performed in a low CO2 residue atmosphere (lower than 1 × 10−3 Pa), PDP panels with very high efficiency are realized with CeSrO protective layer.

References


Masahiro Sakai received his B.E. and M.E. degrees in industrial chemistry from the University of Tokyo, Japan, in 1990 and 1992, respectively. He is now working at the Image Device Development Center of Panasonic Corp. Since 2008, he has been an associate editor of the IEEE Journal of Display Technology.

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Yasushi Yamauchi studied experimental physics at the Department of Applied Physics, Osaka University, and then in 1985 he received his doctoral degree in surface science. In the same year, he joined the National Institute for Material Science and has worked there ever since. Presently, his specific interests are centered in exploring spin-sensitive surface phenomena and beam technologies associated with future device development.