Band Gap Energy Engineering of Electron Emission Layer of ac-PDPs

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Abstract

Ternary oxides with controlled band gap energy and reduced reactivity against moisture and carbon dioxide gas were designed and studied as a potential material for protective layer of ac-PDPs. The results showed a significant reduction in firing voltage and improved environmental stability.

1. Introduction

Recently, Xe content in discharge gas of ac-PDP is being increased to improve the luminous efficiency of the device [1]. If the content were to increased up to 50%, the efficiency was projected to be enhanced by a factor of three compared with that of Ne-4%Xe discharge gas. The increase in Xe content, however, leads to rise in firing voltages by a factor of two, give back the merits of enhanced efficiency. The cause of increase in firing voltages has been well-documented in a previous study [2].

The Auger neutralization process has been recognized as a predominant mechanism of secondary electron emission from MgO layer of ac-PDPs. In this process, the secondary electron is emitted only when the neutralization energy of an ion is larger than the twice the sum of band gap energy and electron affinity of MgO as in eqn. 1) [3].

$$E_i - 2(E_g + \chi) > 0 \quad \text{eqn. 1)}$$

where E_i is the ionization energy of the gas, E_g the band gap energy and χ the electron affinity of MgO layer, respectively. For gases of low ionization energy like Xe, it is difficult to emit the secondary electrons via the Auger neutralization process on wide band gap materials such as MgO layer. In order to emit secondary electrons via the Auger neutralization reaction with Xe ions, the protective layer material needs to have a band gap energy less than 5.2eV.

There have been several attempts to reduce the band gap energy of electron emission materials [4]. In his work, Yan et al alloyed MgO matrix with materials of low band gap energy such as BaO. With the binary oxide protective layer, the firing voltage became reduced dramatically and luminous efficiency was enhanced significantly.

Actual applications of binary oxides as a protective layer of ac-PDPs, however, have been hampered by their strong reactivity with moisture and carbon dioxide gas in the atmosphere. As the reaction products such as hydroxides and carbonates degrade the yield of secondary electrons, the firing voltage could be increased significantly if the reactions are not controlled properly. In addition, the binary oxides, which are mainly the oxides of alkaline earth elements, have poor solubility to each other because of large difference in their ionic radii. Thus, it is rather difficult to develop binary compounds of controlled band gap energy since the range of the band gap energy depends on the solubility.

In this study, we investigated a possibility of using ternary oxide systems as a protective layer that can generate secondary electrons through Auger neutralization reaction with Xe ions. In ternary oxide systems, solubility of alloying oxides could be improved dramatically by compensating defects created by aliovalent cations of the alloying oxides [5]. In a ternary Li_2O-MgO-In_2O_3 system, for example, the cations of alloying oxides (Li_2O and In_2O_3), which have similar ionic radii with that of matrix cation (Mg^{2+}), would replace the matrix cation substitutionally when alloyed as in eqn. 2).

$$Li_2O + In_2O_3 \xrightarrow{3MgO} Li_{Mg}^{-} + In_{Mg}^{+} + 3O_O \quad \text{eqn. 2)}$$

If the concentration of Li ions on Mg sites is same as that of In ions on Mg sites, the effective negative

charge associated with the Li ions would be compensated exactly by the effective positive charge of the In ions. Under this condition, the ternary oxide would become electrically neutral and therefore, the solubility for the aliovalent cations in the matrix would be enhanced significantly if their radii are similar to each other.

Thus, in this study, we attempted several ternary oxide systems suitable for MgO and CaO oxide matrices. The oxides were selected since they have modest reactivity with moisture and carbon dioxide gas and symmetric face centered cubic crystal structure. Using the ternary oxides, test panels were prepared and their firing voltages were compared with that of the conventional MgO protective layer.

2. Experimental

Two ternary oxide systems, Li_2O-MgO-In_2O_3 and Na_2O-CaO-Ce_2O_3, were selected for this study. The alloying oxide components were selected since they have similar ionic radii with cations of the matrix oxide. Oxides of each component were mixed and compacted into pellets. The pellets were calcinated and sintered by heating up to 1200°C. The pellets sintered at the temperature for 30 minutes were cooled rapidly to ambient temperature in order to prevent any potential reactions occur during slow cooling process.

The yield of secondary electrons of such ternary oxide protective layers was examined by measuring firing voltages of test panels with their coatings. Front plate of the test panels consisted of glass substrate, ITO/Ag BUS electrode, glass dielectric layer and the protective film of ac-PDPs. The protective was formed by evaporating the ternary oxide pellets using an electron-beam evaporator. On the rear glass substrate, Ag address electrode, barrier ribs, and green phosphor layer were formed in succession following the conventional processing routes. The front and rear plates were sealed and filled with Ne-20%Xe discharge gas of 500 torr. Resolution of the mini-sized panels was equivalent to VGA grade of 42-inch diagonal.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of ternary Na_2O-CaO-Ce_2O_3 oxides with several different concentrations of Na_2O relative to Ce_2O_3. In this ternary system, the aliovalent defects are compensated when the concentration of Na^+ ion on Ca^{2+} lattice site is the same as that of Ce^{3+} ion on Ca^{2+} lattice site.

As expected, a single phase solid solution of CaO was formed with the composition of $[(Na_{2/4}\ Ce_{2/4})_{0.4}\ Ca_{0.6}]O$. There were small peaks from other phases, but the material consists of mostly the single solid solution phase of CaO. The formation of single phase with 40 mol% of oxide addition is extraordinary by itself since the solubility of aliovalent oxide components is much less than 1% in general. Therefore, this result demonstrates that the ternary oxide system could increase the candidate oxides for alloying and thereby expand the range of band gap energy modification for protective materials for ac-PDPs.

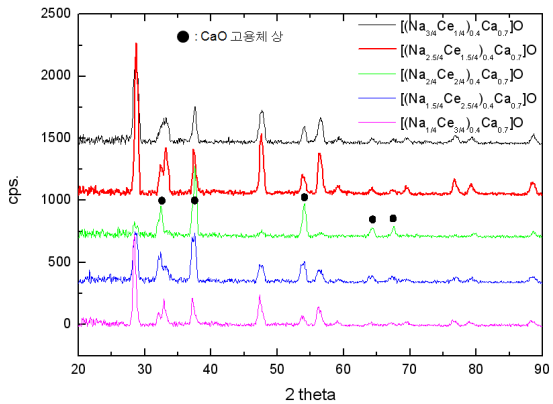

Fig. 1. X-ray diffraction pattern of ternary Na_2O-CaO-Ce_2O_3 oxides with varying relative concentrations of Na_2O and Ce_2O_3 oxides.

Fig. 2 shows a SEM micrograph of $[(Na_{2/4}\ Ce_{2/4})_{0.4}\ Ca_{0.6}]O$ thin film after exposing to ambient environment for 48 hours. The film was formed on a glass substrate heated to 370°C via an e-beam evaporation process. After the exposure, a fraction of the surface area were hydrated (central part of the figure), but the degree of the reaction was not as significant as monolithic CaO thin film. When a CaO thin film was exposed to the ambient atmosphere, the film disintegrated readily into fragments within a few minutes because of its rapid reaction with moisture and carbon dioxide gas. The ternary oxide film, however, reacted very slowly with environmental gases. This results indicate that the alloying with Na^+ and Ce^{3+} ions must have reduced the reactivity of the film with environmental gases.

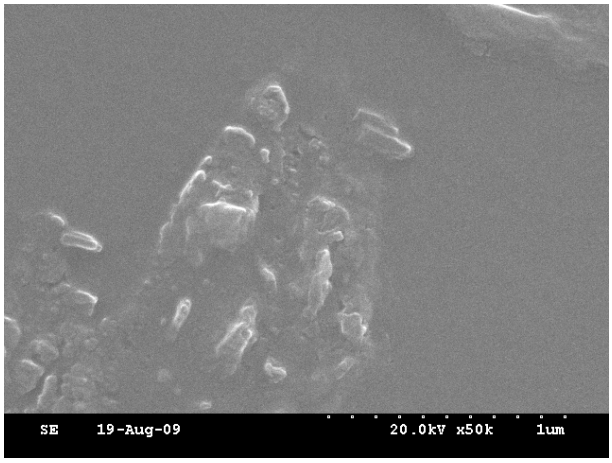

Fig. 2. SEM micrographs of $[(Na_{2/4}\ Ce_{2/4})_{0.4}\ Ca_{0.6}]O$ thin film after exposing to ambient environment for two days.

Fig. 3 shows firing voltage of test panel with $[(Na_{2/4}\ Ce_{2/4})_{0.4}\ Ca_{0.6}]O$ thin film as protective layer. The voltage was measured as a function of aging time. For comparison, the firing voltage with conventional MgO thin film was also measured and plotted in the same figure. The reference firing voltage is rather high because high Xe content in the discharge gas as well as thick glass dielectric layer (~50μm) used in the test panel. As shown in the figure, the firing voltage of the test panels with the ternary $[(Na_{2/4}\ Ce_{2/4})_{0.4}\ Ca_{0.6}]O$ oxide thin film was almost 60 volts lower than that of MgO thin film.

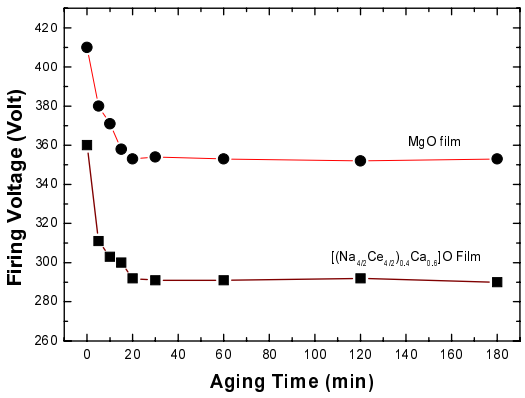

Fig. 3. Firing voltages of test panels with $[(Na_{2/4}\ Ce_{2/4})_{0.4}\ Ca_{0.6}]O$ thin film as the protective layer of the panel.

The firing voltage of test panel with ternary $[(Li_{3/4}\ In_{1/4})_{0.4}\ Mg_{0.6}]O$ oxide thin film is shown in Fig. 4. In this case also, the firing voltage was decreased almost by 50volt. These results clearly show that the ternary solid solution oxide is very effective in reducing the band gap energy of the oxide matrix and thereby reduces the firing voltage.

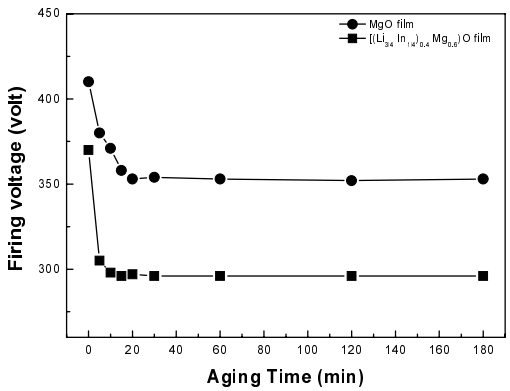

Fig. 4. Firing voltages of test panels with $[(Li_{3/4}\ In_{1/4})_{0.4}\ Mg_{0.6}]O$ thin film as the protective layer of the panel.

4. Summary

In this study, a possibility of using ternary solid solution oxide systems as protective layer of ac-PDPs was studied. Based on their ionic radii and environmental stabilities, two ternary oxide systems, Li_2O-MgO-In_2O_3 and Na_2O-CaO-Ce_2O_3, were selected for this study. The results demonstrated that a single phase solid solution of ternary oxide system could be obtained even at 40 mol% of alloying if the aliovalent defects are compensated. In addition, the ternary system reduced the firing voltages of test panels, indicating the band gap energy of the oxide system has reduced significantly.

5. Acknowledgement

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