

Science and Technology on MgO Protecting Materials for ac Plasma Displays

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Abstract

In order to clarify the heat annealing process for Magnesium Oxide (MgO), cathodoluminescent (CL) analysis was performed. Our results in the present work prove that the heat annealing has effects on not only removing water from the surface of MgO, but also increasing density of O and Mg defect pairs. It is the first work that the influence of annealing process on physical properties of the vacuum evaporated MgO thin films by using CL spectra.

1. Introduction

Since ac plasma displays (PDPs) were monochrome displays, material of the protecting layer has been MgO. Why has MgO been used as protecting materials for long time? It is the reason because MgO as protecting layer has the advantages of low firing voltage, very long lifetime, very wide memory margin, and transparency. The evaporation condition of MgO and preparation of evaporated MgO layer, however, have too sensitive to find the optimum controlling condition for the production.

The recent performance of the surface-discharge color ac-PDPs has been improved as luminance of 1,000 cd/m² and luminous efficiency of 1.8 lm/W. These values contribute to achieve power consumption of 306 W for 43 inch diagonal size. In order to achieve 200 W for the same size, we must improve luminous efficiency to be 2.5 lm/W at least.

There are a lot of ways to improve luminance and luminous efficiency. One of these is to improve the performance of the protecting materials. At the latter half of 70's, a new protecting material in place of MgO was researched, because high cost of the driver ICs must be decreased by lowering the sustaining voltage. On the analogy of cathode materials in CRT, BaO was expected to have superior performance compared with the optimized protecting material of CaO and SrO. The measured results indicated that the sustaining voltage of ac-PDP with BaO as a protecting material was not lower than that of the optimized CaO and SrO.

Since MgO was established as protecting material, protecting materials for ac PDPs have been evaluated by measuring the ion-induced secondary electron emission characteristics (i). The secondary electron measurement has the limit to evaluate the performance of the protecting materials, that is, the speculation of the firing voltage (Vf). Recently the physical properties except from the secondary electron emission characteristics have been required in order to improve and develop the advance protecting materials for ac PDPs including MgO.

As the first trial to this subject, the simulation about the behavior of MgO during evaporation has been studied by quantum mechanical approach. In order to clarify the problem, we have paid our attentions to clarify evaporation process of MgO. According to the results of Quadrupole Mass Spectroscopy (QMS) presented by the present authors, it is proved that MgO is decomposed into Mg and O [1]. Therefore, MgO are decomposed into Mg and O atoms at the first stage of the vacuum evaporation, and the

decomposed Mg and O atoms arrive on the substrate as building up one by one, and finally are recrystallized as MgO. From these results, it is easy to suppose that O₂ feeding during MgO evaporation is very effective for improving quality of the stoichiometrical quality of MgO thin films.

We fabricated vacuum evaporated MgO thin films by feeding O₂ under the several pressure of O₂. We reported that feeding O₂ to MgO has significant influence on the density of O and Mg defect pairs by the evaluation of CL analysis.

It is proved that blue peak in CL spectra is caused by the transition from O defects to Mg defects; red peak is caused by the transition of Mg defects to valence band. Intensity of blue peak is strongly dependent on the differences in pressure by feeding O₂ during evaporation. [2]

From our study it is confirmed that CL analysis for MgO is very useful evaluation tool for the vacuum evaporated MgO thin films. In the present work we tried to clarify the influence of annealing on the physical properties of the vacuum evaporated MgO thin films by CL analysis.

Annealing process for the vacuum evaporated MgO thin films, which is called, as activation of MgO, is very familiar and important to PDP processes engineers. Our results obtained in the present work are first the physical consideration to annealing treatment for the vacuum evaporated MgO thin films. Until today it has been believed that annealing of MgO thin films is understood as just removing water, carbon, etc from the surface of MgO thin films.

The influence of O₂ feeding on the CL spectra sure to be the first attempt, in addition to the ion-induced secondary electron emission characteristics of MgO thin film and this evaluation method for MgO thin films can be applied to the improvement of evaporation system. Only Aboelfotoh did the study of evaporated MgO by CL analysis. [3] His research about CL, however, was the only observation of CL and he did not characterize the evaporated MgO thin films.

2. Sample Preparation and Experiments for Cathodoluminescent Analysis

In the present work, samples of MgO for CL analysis are prepared by the electron beam evaporation under the condition of substrate temperature of 200 °C. Thickness of samples is 3,000 Å in order to clarify what kind of influence MgO has from the evaporation condition and the heat-treatment after evaporation deposition conditions. From our previous works, it is proved that MgO is decomposed into Mg and O atoms in the electron beam evaporation from the results by QMS, and seceding from the surface. It is supposed that they are piled up again arriving on the surface of the substrate and form an evaporated film.

Originally MgO is transparent and colorless and however, it is brownish when MgO is fabricated on the conditions which Oxygen does not supply during the evaporation. This is because composition of Mg and O of an evaporated film becomes Mg excess since a part of oxygen which evaporated from MgO is evacuated outside through a vacuum pump. Therefore, it

is necessary to supply Oxygen from outside during the evaporation in order to compensate oxygen of an insufficiency.

2.1 CL Analysis Apparatus

The outline of CL analysis equipment is shown in Fig.1. CL is a technique, which irradiates electron beam to a sample, and the corresponded light is emitted due to the transition from the excited states due to the

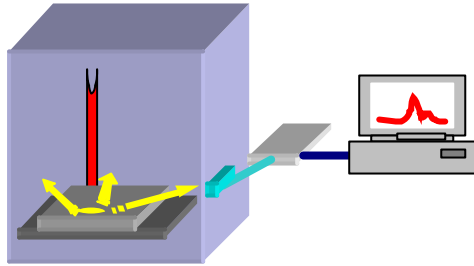


Fig.1 Schematic view of CL measurement equipment

electron bombardment to the lower states caused by some defects and the light is analyzed. The CL equipment of acceleration voltage, beam current, and pressure used in the present work are 7 kV, 200 nA, and 5.0×10^{-7} Pa, respectively. The cathode-luminescent light is carried through an optical fiber and changed into a spectrum signal by the spectroscope (made by OCEANOPTCSUSB-2000), and is inputted into a computer, and, analyzed results are obtained as for luminescence from a sample.

3. Experimental Results

3.1 Relationships between Sample Temperature under Analysis and Emission Spectrum

Figure 2 shows the relationships between the sample temperature under analysis and CL spectra. It is clarified that the luminescence intensity decreases around the spectra of a short wavelength region (the CL spectra between 300 and 600 nm) as it becomes high temperature; the spectra of a long wavelength region (the CL spectra between 650 and 800 nm) increases as high temperature. The spectra in short wavelength are considered that CL takes place due to the electron transition from Mg defects to O defects or from Mg defects to the valence band of MgO.

Generally, the energy of luminescence from a solid is not large part of the energy injected from the outside. Almost all injected energy turns into thermal energy. That is, it can divide roughly into the radiation changes accompanied by luminescence and the non-irradiative changes which are not accompanied by luminescence at process in which the excited electron

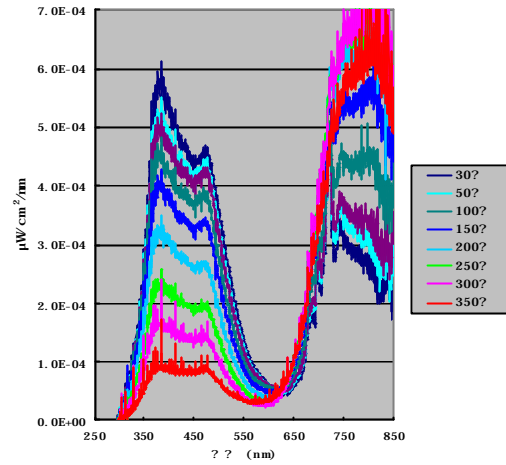


Fig.2 Relationships between the Change of sample temperature and CL Spectral Intensity

loses energy. It is considered that the transition processes with irradiative and non-irradiative changes described above are applicable to the luminescence from MgO by CL. The dependence of substrate temperature on the change of CL spectra is due to that the probability of these irradiative changes and non-irradiative changes are dependent on temperature.

The transition processes for which the electrons exist in the lattice defects are explained by the configuration coordinate model shown in Fig.3. The example which the sample temperature raises in the short wavelength region and CL luminescence becomes weaker is explained as follows. As shown the potential of an excited state and a ground state in the figure, there are two transition processes from the excited states to the ground state, which the electrons lose energy by irradiative or non-irradiative transition.

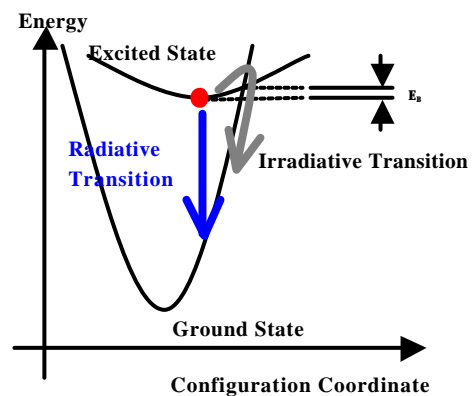


Fig. 3 The relationships between irradiative and non-irradiative transition in the Configuration Coordinate

In order to carry out non-irradiative transition, the electrons should get over the energy barrier E_B . It is considered that the temperature dependency of these non-irradiative transition is proportional to $\exp(-E_B/k_B T)$, where T is temperature and k_B is Boltzmann's constant. Luminescence in a short wavelength region becomes weaker by the rise of sample temperature because the probability of the electron transition by non-irradiative transition increases.

3.2 Influence of Oxygen Feeding under Vapor Deposition on CL Luminescence Intensity

CL analyses are performed for the MgO thin films which are formed under the conditions by feeding oxygen gas during MgO vapor deposition. The purpose of these experiments is to confirm what kind of influence is received by changing vapor deposition conditions and whether CL analyses are able to detect the difference of changes caused by the differences of formation conditions. Oxygen gas is made to flow in slightly in vacuum equipment. Vapor-deposition under the pressure in equipment is changed

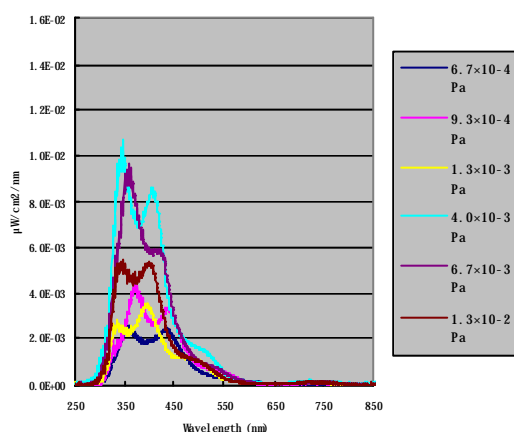


Fig. 4 Influence which exert on CL spectra Change of the degree of vacuum by the oxygen feeding under vapor deposition

Figure 4 shows that CL spectra from MgO formed under the condition of different degrees of the pressure by feeding oxygen gas. When we look the spectral forms of a short wavelength region, it is supposed that the spectral forms is seemed to be overlapped with several curves constituted with some peaks. When the amount of feeding oxygen gas is increased from 6.7×10^{-4} Pa gradually, spectral intensity also increases, and CL intensity becomes to be the maximum in 4.0×10^{-3} Pa. However, when the amount of oxygen feeding is increased further, it turns out that spectral intensity decreases. Luminescence is slightly accepted also from a long wavelength region.

3.3 Influence of Heat-treatment in Vacuum and Atmosphere on CL Spectra

CL analyses of the MgO thin films which are prepared by heat-treatment in vacuum and atmosphere before mounting the samples in CL analysis

equipment after the vacuum deposition.

The heat-treatment of MgO thin films after vacuum deposition is called activation process in the actual production processes of color plasma displays. The activation process is performed in order to remove the substances (mainly H_2O) adsorbed on the MgO surface and to obtain the pure MgO surface. The typical activation process in the experiments is performed at around 400 degrees C.

Figure 5 shows the CL spectra for MgO thin films which are heat-treated after they are fabricated under the different vacuum pressure due to oxygen feeding during the vacuum deposition. Comparing the results shown in Fig. 5 with those in Fig. 4, it is clear that the peak of long wavelength region increases by heating in vacuum. In the case of short wavelength region, it is clarified that the increase or decrease of spectral intensity before and after heating in vacuum is dependent on the difference in the pressure of the vapor deposition equipment by the oxygen feeding at the time to form vapor deposition film production.

The rate of change to the luminescence intensity before and after vacuum heating of the MgO thin film by which the pressure in vacuum equipment is formed in 6.7×10^{-4} Pa becomes by 181% of increase. In 9.3×10^{-4} Pa, it becomes 235% of increase and 514 % of increase in 1.3×10^{-3} Pa. CL intensity rate of increase is increasing with the amount increase of

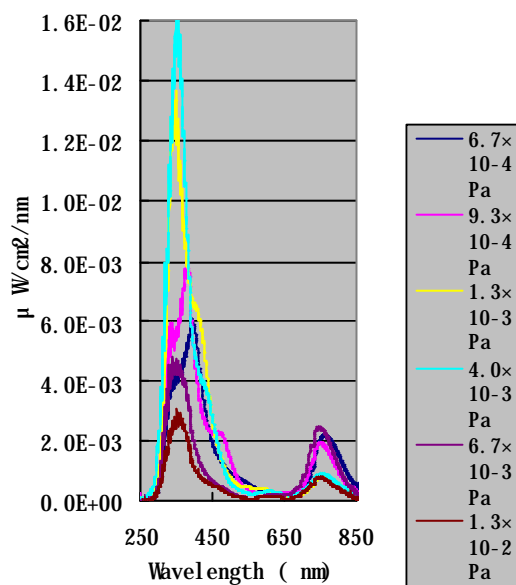


Fig 5 CL Spectra for MgO heat-treated in the vacuum

oxygen feeding. However, the case where increased oxygen feeding further and pressure in equipment is set to 4.0×10^{-3} Pa CL intensity becomes 165% of increase The increase width becomes to be reduced and further the increase width becomes reducing to be 54.6 % in 6.7×10^{-3} Pa and 53% of reduction in 1.3×10^{-2} Pa.

CL spectra from the MgO thin film heated in the atmosphere after vapor-depositing are shown in Fig. 6. It is clear that the observed luminescence of a short wavelength region shown in Fig.6 is indistinguishable as com-

pared with Figs. 4 and 5. The luminescence of a long wavelength region shown in Fig.6 is appeared strongly compared with those shown in Fig. 5. It is suggested that two or more luminescence peaks due to the transition of the specific energy levels caused by the defects overlap and the spectra of a long wavelength region also constitutes the spectra.

4. Consideration for CL Luminescence levels of MgO

CL spectra from MgO are divided roughly into luminescence from a short wavelength region (about 300 - 600 nm), and a long wavelength region (about 650 - 800 nm) as a wavelength range. Furthermore, since the tendencies of change which heat-treatment exerts on luminescence are different from each wavelength group, it is clear that the transition mechanisms for the luminescence are different for two so-called wavelength groups.

If the formation conditions of a MgO thin film, i.e., the fact that the oxygen feeding during vapor deposition and the heat-treatment after vapor deposition change CL spectra a lot, are taken into consideration, the emission spectra from MgO by CL may not be based on the impurities

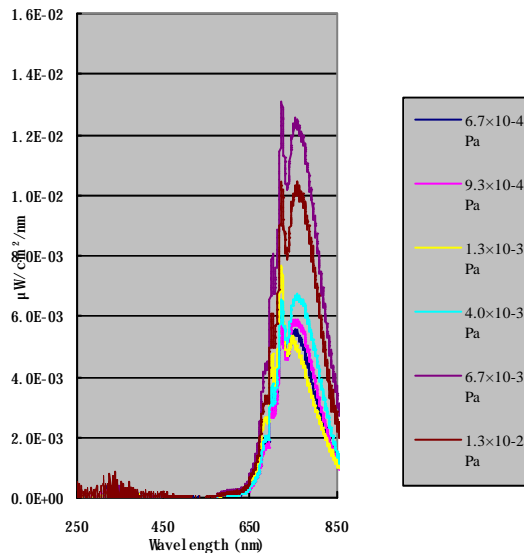


Fig.6 CL spectra from MgO thin film heated in the atmosphere

currently mixed in MgO, and should be oxygen defects and magnesium effects. Here, the emission spectra from MgO are considered.

1) As for the spectra of a short wavelength region, from the observed results shown in Fig. 4, it is clear that change has appeared in intensity by change of the degree of vacuum due to the oxygen feeding during vapor deposition. Since the source materials for vapor deposition are used the same one, it is difficult to consider that the impurities in a thin film increase according to vapor deposition conditions. Therefore, a possibility except from impurities can be considered, and it can be said that this is what is depended on an oxygen defect.

When the formation condition of MgO thin films is assumed to influence on the luminous efficiency of luminescence, such as structure of a thin

film, affects luminescence that is, even if an impurities atom does not fluctuate in a thin film, luminescence intensity may fluctuate by the upper and lower sides of luminous efficiency without the increase or decrease of impurities in MgO thin films.

2) Figure 5 shows the observed results of the samples heat-treated in the vacuum. Since the re-arrangement of the crystal takes place due to the movement of the lattice defects in an MgO crystal by heating, spectra corresponds to these defects change, the tendency of change in the spectra of a short wavelength region is unsteady by vacuum heating.

3) Assuming that the luminescence of a short wavelength region is based on oxygen defect, a spectra in short wavelength should be appeared due to the direct influences of the amount of oxygen feeding on the oxygen defects generation in MgO thin film. Based on the consideration described above, spectral intensity should be decreased uniformly, when the amount of oxygen feeding is increased from 6.7×10^{-4} Pa to 1.3×10^{-2} Pa, in thin film formation process. However, the observed CL spectra intensity is increased from the oxygen feeding from 6.7×10^{-4} to 4.0×10^{-3} Pa.

If an oxygen defect is a luminescence, luminescence from the sample produced by 6.7×10^{-4} Pa should become the strongest. The experimental result, however, is not observed as this supposition. Therefore, when it is considered that the spectra of a short wavelength region is depended on oxygen defects, luminous efficiency of luminescence in the short wavelength should be changed due to the formation condition of MgO thin films during the vacuum deposition.

4) If it is assumed that the spectra of a short wavelength region are based on oxygen defects, the experimental results that the dependence of change of the spectra after vacuum heating shown in Fig. 5 on the amount of oxygen feeding becomes the results are explained physically as follows. If the case where oxygen exists superfluously in MgO thin film temporarily is assumed, when vacuum heating of the thin film is carried out the excess oxygen move to oxygen defects, and should vanish oxygen defects.

Since the oxygen defects as the luminescence sources should decrease if such a reaction occurs mostly, the luminescence intensity becomes weaker. However, if luminous efficiency of luminescence should increase due to the improvement of the crystallinity, the intensity does not necessarily become weaker and the luminescence intensity is dependent on the balance of the oxygen defect density and crystalline.

Although the spectral intensity of the long wavelength region shown in Fig. 6 is large compared with those shown in Fig.5, the luminescence source of the spectra in this long wavelength region can be explained to be what is depended on Mg defects. That is, the fundamental physics about color centers indicates that oxygen in air entered superfluously into the MgO thin film by heating in the atmosphere is able to change the explanation as the defects of Mg atoms. That is, it is clarified that the increase of the spectral intensity of the long wavelength region of an MgO thin film by heat treatment in the atmosphere is caused by the increase in Mg defective density.

5. Conclusions

The luminescence of long wavelength region is considered to be related with O_2 which is confined in the inside due to the feeding oxygen gas during vapor deposition. From the experiments of the photoluminescence for KI and KBr [4] There are similarity between CL results and photolumines-

cence analyzed results. These similar relationships strongly indicate that the possibility of luminescence by O_2 in a film is considered because the luminescence intensity of a long wavelength region is increased by heating in the atmosphere.

It is clear that change of the properties given to the MgO thin film formation by the oxygen gas feeding during vapor deposition and after deposition by the heat-treatment is vividly regarded by CL analysis as change of CL spectra. From the results obtained from it is proved that these experiments, analysis of the MgO thin film by cathode luminescence gives useful information, when performing formation of an ac-PDP protection layer, and evaluation, and a possibility of being utilizable for protection layer evaluation.

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