

The effects of oxygen and hydrogen on the surface morphology of MgO films deposited by ion-plating

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The effects of oxygen and hydrogen on the surface morphology of MgO films, deposited by ion-plating, which is the protective layer of plasma display panels (PDP), were investigated. The surface morphology and crystalline planes were influenced not by the amount of oxygen but by the amount of hydrogen; the shapes and sizes of grains were changed from small triangles (50 nm), to large triangles (100-200 nm), to lozenge-shapes (100 nm), and then to very small (under 20 nm) round shapes with increasing amounts of hydrogen. The preferred orientations of the MgO films were (111) and (222) without hydrogen. However, (111) and (222) peaks decreased, and (200) planes appeared, with larger amounts of hydrogen. The crystallinity of the MgO film was hardly detected in the case when excess hydrogen (over 90 sccm) was introduced.

Key words: MgO, Hydrogen, Oxygen, Surface morphology, PDP.

Introduction

Since 2000, mass production of plasma display panels (PDPs) caused the TV market to rapidly shift from CRTs to flat panel displays. PDPs have grown in flat TV market share because of their excellent image quality and because the materials used in PDPs have been developed over several years. Researchers in ceramic engineering have been interested in the panels of PDPs because they are composed of over 90% ceramics, such as a glass substrate, frit, and MgO.

MgO is one of the most important materials among the ceramic parts in panels. It has been known since the 1900s that MgO has a very high secondary electron emission coefficient, which is an important component of electron multipliers. Because of this, MgO affects the discharge phenomena in the cell of PDPs and is commonly used as a protective dielectric material.

Thus, many researchers have studied the relation between MgO and discharge in a cell and have found that there is a close connection between the secondary electron emission and the characteristics of MgO films [1]. Several efforts have been made to control the surface characteristics of MgO, including modification of the oxygen partial pressure during deposition or a plasma treatment after film deposition. In particular, the deposition process itself has been changed into RF sputtering [2] and ion-plating [3] in order to enhance the density of MgO films.

Recently, researchers have focused on enhancing the

secondary electron emission from MgO. A new MgO film, called CEL (crystal emissive layer), has been introduced, which is deposited by spraying evaporated MgO on top of a normal E-beam layer [4]. Several dopants have also been examined to modify the energy levels of MgO [5, 6]. NEC reported that the discharge delay time was decreased by doping with hydrogen because this dopant increased the volume resistance of MgO [7].

In this study, the changes in the microstructure and the crystalline phase of MgO films by changes in the amounts of oxygen and hydrogen during ion-plating were investigated by an ellipsometer, XRD, and SEM. The causes of these changes are also discussed.

Experimental

The equipment for MgO deposition was based on a commercial model from Anelva and was made by SDI and is shown in Fig. 1. The process was classified as plasma-assisted physical vapor deposition (PAPVD) and designed for deposition on 42 inch (1067 mm) glass sheets [3]. The vacuum level of the ion-plating chamber had a base pressure of 1×10^{-4} Pa, and the working pressure was 0.035 Pa with oxygen and hydrogen. Sensors for

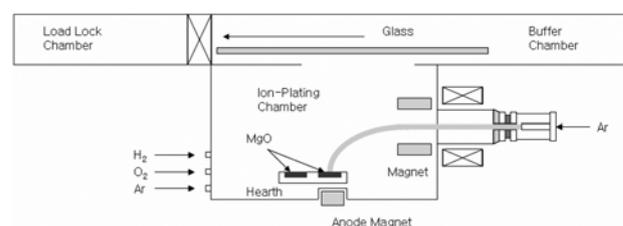


Fig. 1. Schematic diagram of the ion-plating deposition system.

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Table 1. The oxygen and hydrogen conditions (unit: sccm)

Oxygen	Hydrogen
200	0, 20, 40, 60
220	0, 20, 40, 60, 70, 90
240	0, 20, 40, 60
260	0, 20, 40, 60
280	80

O₂ and H₂ were installed in the chamber to measure the partial pressure of each gas. Ar was used as a carrier gas (15sccm). The plasma beam generated by the plasma gun was focused on an MgO source, and the MgO vapor from the source was deposited on the glass. Because the glass sheet was wide and long, MgO was deposited with the glass moving. The glass sheet was rolled in the chamber, and the shutter at the ceiling was opened. In order to maintain a constant depositional thickness, the glass sheet moved at a constant speed after the ceiling was opened. The thickness of the MgO film was 7000, and the thickness deviation was under 1000. The oxygen and hydrogen conditions used in this study are shown in Table 1.

The MgO source was manufactured by C&Chem Co., which synthesized MgO powder and made a tablet using a traditional ceramic process. The tablet was 5 mm in diameter and 1 mm thick. A dielectric layer was printed on the glass substrate, and MgO was deposited onto it to match the product condition. The crystalline phase of the MgO film was analyzed by an X-ray diffractometer (XRD) [Philips PW-1710]. The thickness and refractive index were measured by an ellipsometer [J.A. Woollam Co. Inc., Model: VASE]. In the ellipsometric analysis, the Cauchy model was used, in which the outer layer of the MgO has a relative density of 1/2. The packing density (ρ) was evaluated indirectly from the refractive index of the films. The relationship between the packing density and the refractive index of the films was suggested by Bragg-Pippard [2] as eq. (1):

$$\rho = \frac{(n_0^2 + n^2)(n_0^2 - n_f^2)}{(n_0^2 - n^2)(n_0^2 + n_f^2)}, \quad (1)$$

where n_0 is the refractive index of the void, n is the equivalent refractive index ($n = 1.737$ at 633 nm), and n_f is the measured index of film, respectively.

The microstructures on the surface of the MgO films with the conditions shown in Table 1 were observed with FE-SEM (JEOL JSM-6340F).

Results and Discussion

Fig. 2 shows a contour plot of packing density calculated with eq (1) and the surface layer thickness of the MgO film, which was influenced by the amount of H₂ and O₂ amounts. The former seems not to change according to the oxygen supply. This is consistent with the results of Kim et al.'s study [2], which was related to an arc method.

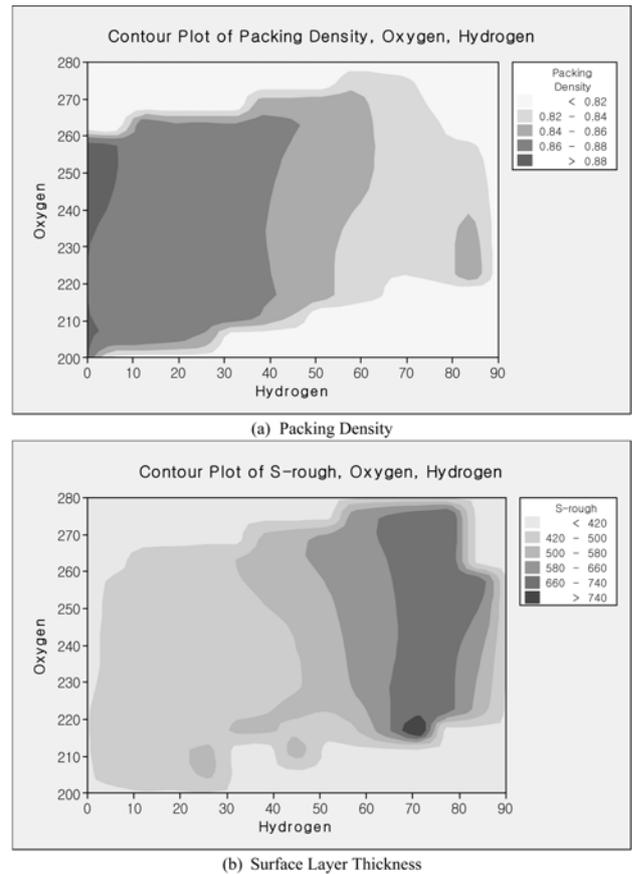


Fig. 2. Packing density and surface layer thickness of MgO deposited by ion-plating with oxygen and Hydrogen.

From the ellipsometric results, the thickness of the surface layer, which was defined as the Cauchy layer, did not change with the amount of oxygen, but it did change with the amount of hydrogen. More hydrogen resulted in a greater thicknesses of the Cauchy layer, until a specific amount of hydrogen of 70-80 sccm. While it was about 400 Å without hydrogen, it was increased to 700 Å with hydrogen, which made up 10% of the total thickness of the MgO films with 80 sccm of H₂. Above 90 sccm of hydrogen, the surface layer was reduced, and the packing density rose dramatically. This implies that the introduction of hydrogen had an effect on the MgO film growth and morphology during the ion-plating deposition.

The surface morphologies of the MgO films, with varying amounts of oxygen and hydrogen, are shown in Fig. 3. When only oxygen was introduced, the grain size was about 50 nm, and the surface morphology was not influenced by the amount of oxygen; the grains maintained their triangular shape. In the case of hydrogen, a different surface morphology appeared, and its unevenness increased, as was expected from the ellipsometric results. This was caused by the growth of a portion of the triangular grains together with an increase in hydrogen to 40 sccm (Fig. 3). When hydrogen was increased above 40 sccm, the grains between 100 and 200 nm in size filled the surface. In particular, most triangular grains were randomly oriented,

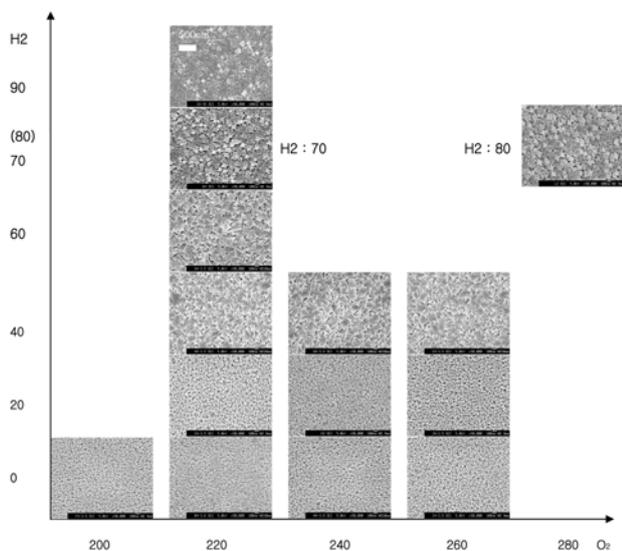


Fig. 3. The surface morphology of MgO deposited by ion-plating with oxygen and hydrogen

but some symmetrically-formed grains shared an edge. This implies that hydrogen affected the nucleation density and the crystal growth direction. When 70 sccm of hydrogen was added, new lozenge-shaped grains appeared about 100 nm in size, which was a result of the maximization of the Cauchy layer as shown in the ellipsometric results (Fig. 2). In the case of 90 sccm hydrogen, new round grain clusters about 10-20 nm in size appeared on the surface, and the surface roughness was reduced by about 400 Å.

Fig 4(a) shows the changes in XRD patterns with a change in the amount of oxygen. The main crystalline direction did not change, and the main planes were (111) and (222) in the range of the amounts of oxygen used in these experiments. The more hydrogen which was supplied and the bigger the triangular grains were, the clearer the (200) peak was, and the weaker were the (111) and (222) peaks. When hydrogen was more than 70 sccm, lozenge-shape grains developed, and the preferred orientation disappeared. Hydrogen affected the crystalline direction as well as the surface morphology, as shown in Fig. 3.

We conclude that the disappearance of the diffracting phase was not caused by the development of $\text{Mg}(\text{OH})_2$, because the amount of hydrogen was 1/10 the amount of the oxygen supplied from outside and the MgO source itself. It is necessary to consider the role of hydrogen on MgO deposition multilaterally. The MgO films in these experiments followed a structural zone model and had a typical surface morphology of columnar structures when only oxygen was present. However, the fact that larger grains and a change of crystalline direction occurred with more hydrogen indicates that the vapor pressures of Mg and oxygen were not sufficient to develop the nucleation sites in the nucleation model of capillarity theory and that hydrogen atoms disturbed the close-packing of the oxygen atoms [8]. It is thought that hydrogen disturbed the movement of oxygen atoms on the substrate, which

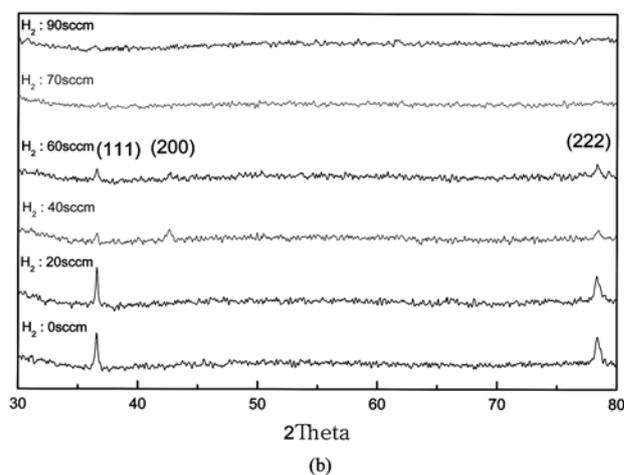
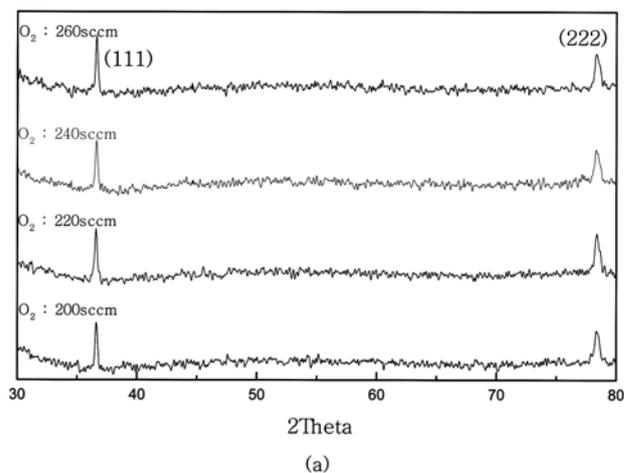


Fig. 4. XRD spectra of MgO films (7000) deposited by ion-plating (a) with oxygen only and (b) with hydrogen and 220 sccm O_2

decreased the nucleation density and increased the space between the nuclei, the grains coarsened, and this resulted in the (200) packing plane instead of the (111) or (222) as packing planes. Yu et al. [9] showed similar results, in which the preferred orientation of the MgO films and peak height was affected by the amount of oxygen. Without oxygen, the (200) peak was the main orientation, and an increase in the amount of oxygen increased the (111) peak height [9]. The crystallinity diminished with excess hydrogen (90 sccm in this study). Further study is necessary to elucidate the effect of excess hydrogen.

Conclusions

This study investigated changes of the morphology and the crystalline phase when oxygen and hydrogen were introduced in a MgO deposition process using ion-plating. Both were influenced by the amount of hydrogen, but oxygen hardly affected them; the shape and size of grains changed from small triangles (50 nm) to bigger triangles (100-200 nm), to lozenge-shapes (100 nm), and then to very small (under 20 nm) round shapes with increased amounts of hydrogen. The main crystalline planes of the

MgO film were (111) and (222) without hydrogen. However, when the amount of hydrogen increased, the (111) and (222) peaks decreased, and the (200) plane appeared. The crystallinity of the MgO film was not detectable in the case of excess hydrogen above 70 sccm. This implies that hydrogen decreased the saturated vapor pressure of oxygen from the MgO source and affected the nucleation and grain growth of MgO films in the ion-plating process.

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