On the Preparation and Characteristics of Hydration Free Magnesium Oxide Films for Plasma Display Panels

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Abstract: *The excellent emissive and protective properties of magnesium oxide are deteriorated by $Mg(OH)_2$ formation through chemisorption of water. To address this issue, MgO thin films (thickness ~550nm) have been prepared on glass substrate by spin coating using a 0.37M Mg ion solution of magnesium nitrate hexahydrate in ethanol and subsequent annealing at 500^0C for 2-4h in air and oxygen ambient. These films have been characterized by X-ray diffraction for phase and preferred orientation, atomic force microscopy (AFM) for surface morphology, UV-Visible spectrophotometer for optical transmittance and FTIR spectroscopy for detection of –OH bond. It is shown that MgO films possess an f.c.c. (NaCl-type) structure with lattice parameter a ~ 4.213Å and assume <100> and <110> preferred orientation on annealing in air or oxygen atmosphere. The {100} and {110} type planes contain both the oxygen and magnesium ions and are neutral, having no/ poor tendency of hydration. Moreover, these films exhibit (i) high optical transmittance (~ 86-98%) in the wavelength range of 370-800 nm, (ii) pyramidal columnar morphology and (iii) absence of –OH bond signature after annealing for 3h or more. While the columnar morphology is responsible for excellent discharge characteristics of PDPs, reduction of potential reaction and scattering centres, namely grain boundaries and surface defects/steps are believed to provide high optical transmittance and stability. Besides, specific texture (crystal orientation) developed in films by annealing itself has poor selectivity for hydration.*

Keywords: MgO thin films; plasma display panels; dielectric protective layer.

Introduction

The excellent emissive and protective behaviour of MgO makes it quite unique for plasma display panel (PDP) application. However, its useful characteristics are susceptible to water as it forms $Mg(OH)_2$ easily. This leads to deterioration of mechanical as well as secondary electron emission properties of MgO coatings. Since its {100} and {110} crystallographic planes contain both oxygen and magnesium ions and are neutral (i.e., charge compensated automatically), chemisorption of small molecules like H_2O, CO_2 etc., on them is energetically unfavourable [1,2]. As a result, water on these planes can only be adsorbed. Nevertheless, there exists several experimental evidences that claim chemisorption of water and formation of $Mg(OH)_2$ on the crystal planes mentioned above [3,4]. This reaction is possible if the surface has defects such as steps, edges, corners, kinks, etc., where coordination number differs (i.e., 4 or 3 instead of 5), leading to deviation from charge neutrality in local regions and making chemisorption of water possible [5]. The number of surface defects and hence the nature of reactivity of MgO with small species (like H_2O, CO_2, etc.) however depends largely on the method of thin film preparation [6]. An attempt has therefore been made here to prepare hydration free thin films of MgO exhibiting high optical transmittance.

Experimental

A 0.37M Mg ion solution is first prepared by dissolving magnesium nitrate hexahydrate $[Mg(NO_3)_2.6H_2O]$ thoroughly in ethanol $[C_2H_5OH]$ and then dropping its fixed volume over a clean glass substrate spinning at 4000 rpm for 30s to cast a film layer. The layer is subsequently pyrolysed in a furnace at 500^0C for ~360s to evaporate residual species. This procedure is repeated several times to achieve the desired film thickness. Eventually, thin film is annealed at 500^0C for 2-4h in air or 3-4h in oxygen ambient. The phase and preferred orientation of thin films have been determined by a X-ray diffractometer (Thermo Electron Corp. model ARL X'TRA) with the CuK_α radiation (λ=1.5418Å). The surface morphology and roughness have been observed in an atomic force microscope (Molecular Imaging model PicoSPM). In addition, a fourier transform infrared spectrometer (Bruker model Vertex-70) and a UV-vis spectrophotometer (Hitachi model U-3310) have been employed for the detection of -OH bond and optical transmittance measurements, respectively.

Results and discussion

The analysis of various X-ray diffraction (XRD) patterns reveals that stable MgO is formed after annealing the cast thin films at 500^0C for 3h or more both in air and oxygen ambient. Fig. 1 shows some typical XRD patterns of thin films (thickness ~550nm) prepared on glass substrate after annealing in air or oxygen ambient at 500^0C for 4h. These patterns correspond to periclase phase of MgO having an f.c.c. (NaCl-type) structure. As only 200, 220 diffraction peaks are observed in both the patterns, thin films formed appear to be textured, i.e., have preferred orientation. The values of lattice parameter of the films are 4.232±0.005Å, 4.228±0.005Å and 4.218±0.005Å for annealing condition of 3-4h in air, 3h in oxygen, and 4h in oxygen, respectively (known bulk lattice parameter for MgO being 4.213Å [7]). The relative

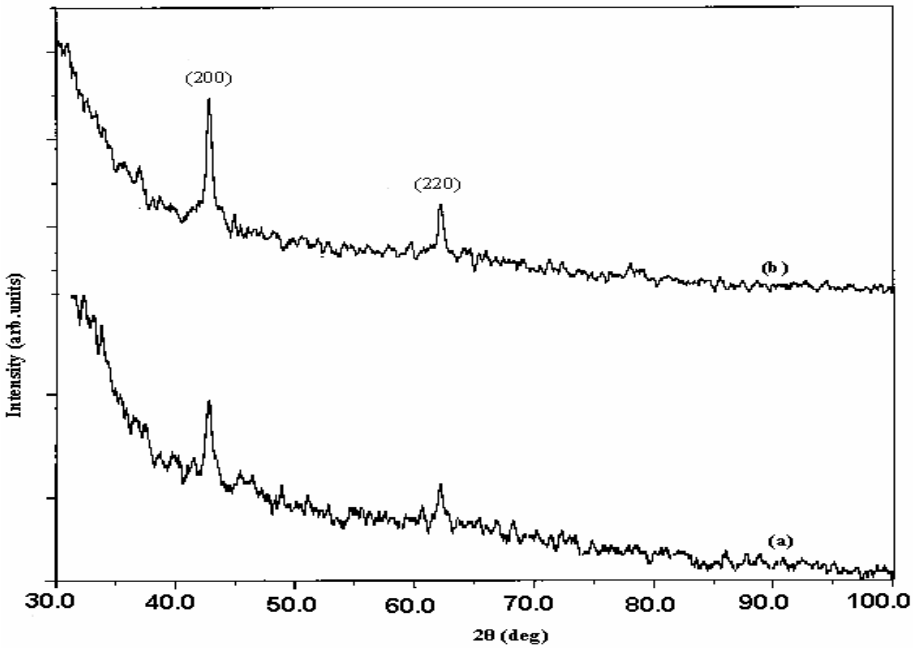

Figure1. X-ray-diffraction pattern of MgO thin films after annealing at 500^{0}C for (a) 4h in air and (b) 4h in oxygen ambient depicting preferred orientation

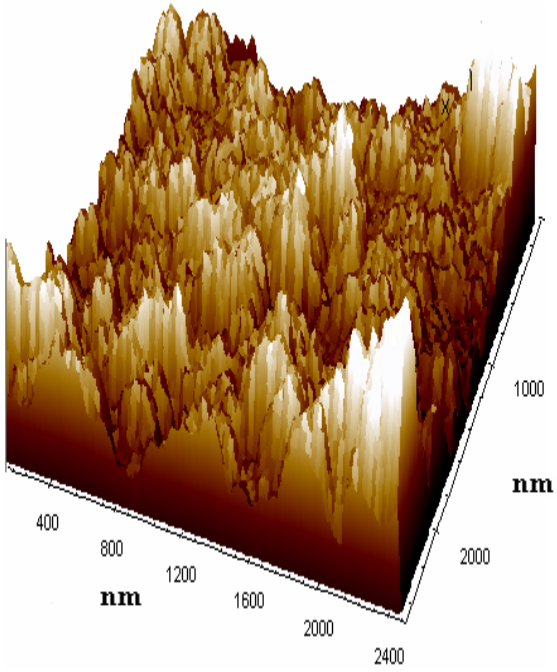

Figure 2. Morphology of MgO thin films after annealing at 500^{0}C for 4h in air as observed in AFM; notice pyramidal columnar growth structure

intensity ratio of 200 and 220 peaks, however, varies with the annealing environment and time duration, e.g., annealing in air and oxygen for longer duration (i.e., more than 3h) leads to improvement in tendency for assuming <100> and <110> orientation, respectively. Though the studies of MgO thin films prepared by spin coating are lacking, many reports are available based on physical vapour deposition techniques [3, 8-14]. MgO films prepared by electron beam evaporation on soda lime glass substrates have shown <100> preferred orientation when annealed at 400^{0}C for 2h in air [13]. Orientation variation with the deposition method and oxygen flow rate has also been reported earlier [10,14]. The possible cause for the observed preferred orientation of MgO thin films with annealing environment and time may be attributed to the mobility of ions. As, for example, annealing in oxygen rather than air can possibly annihilate some stoichiometry-related point defects (viz., oxygen vacancies) more, causing reduction in ion mobility[8,9].

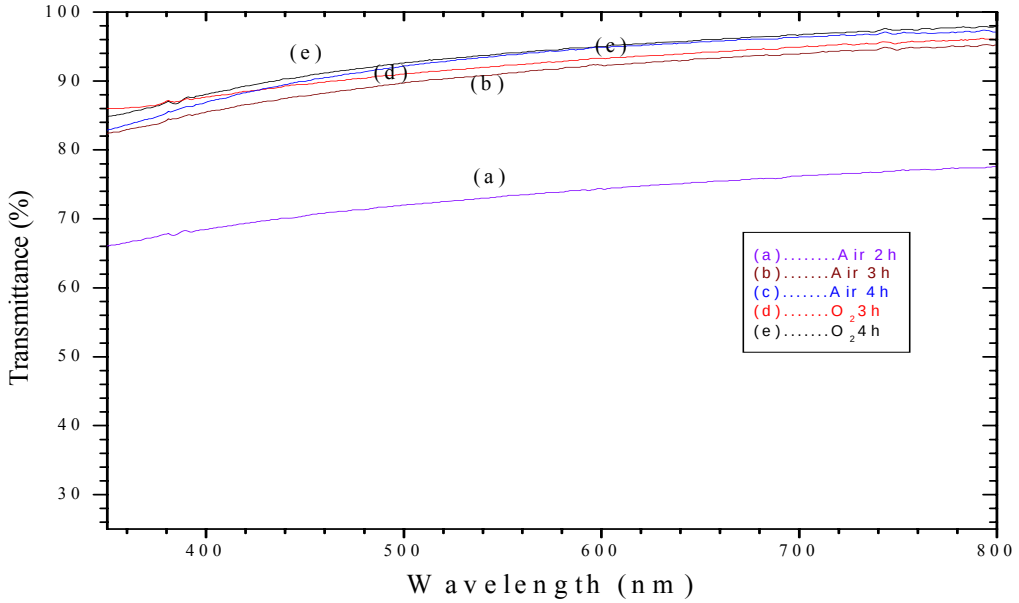

Figure 3. Optical transmittance spectra of MgO thin films deposited on glass substrate after annealing at 500^0C in air for 2-4h and in oxygen ambient for 3-4h.

The morphology of thin films as observed in AFM (non-contact mode) invariably shows pyramidal shape columnar growth after annealing in air or oxygen. However, the process is relatively slow in oxygen ambient, takes longer time span to develop the pyramidal morphology, and exhibits low surface roughness. Figure 2 depicts a typical pyramidal morphology of MgO film after annealing in air at 500^0C for 4h. Since the sloping sides of pyramids appear to be quite smooth (fig.2), they are expected to have a few steps/defects sites, providing high stability due to inherent poor affinity with water. Annealing process for longer duration causes coalescence of grains and reduction in the overall surface roughness. Park et. al. [12] have recently observed excellent discharge characteristics in MgO thin films that comprise of columnar grains of triangular shape.

Figure 3 shows optical transmittance of MgO films after annealing in air and oxygen at 500^0C for different lengths of time in the wavelength range of 370-800nm. These reveal the transmittance as ~86-98% for films annealed for 3h or more. These figures are appreciably higher than those reported by Kim et al. [10] and Kang et al. [15] for MgO films prepared by RF sputtering (in humid conditions RH~95%) and plasma-enhanced metal-organic chemical-vapor deposition (PE-MOCVD) method, respectively (their transmittance values are ~79-91% and ~70-85%, respectively). The cause of higher transmittance in the present case can be attributed to the absence of –OH bonds, as revealed by FTIR spectroscopy and discussed below. Needless to say that MgO thin films prepared by physical vapour deposition methods exhibit higher optical transmittance (values being $\geq$ 90%) and no evidence of hydration as revealed by XPS [10]. A notable feature of present work is utilisation of a simple method for the preparation of hydration free MgO films. The films after annealing for longer duration (say, 4h) show improvement in the transmittance level (fig.3) due to progressive annihilation or decrease of scattering centres like defects, grain boundaries, etc.

FTIR transmittance spectrum of MgO films after annealing at 500^0C for 2h in air contains a broad absorption at 3627 cm^{-1}, providing evidence for the presence of hydroxyl (OH) group. However, annealing for longer duration (i.e., 3h or more) leads to disappearance of the above band, rendering the films to be hydration free. Moreover, the films are expected to be less susceptible to moisture as they exhibit <100> and <110> preferred orientation only (both {100} and {110} surfaces being neutral if contain no defects and hence display no affinity with water). In contrast, MgO contains alternating layers of Mg^{2+} and O^{2-} ions in <111> orientation and may terminate on either with polar character. In such a case, if Mg^{2+} ions form the terminating layer, exposure to moisture may result into hydroxide formation using dissociative hydroxyl group. However, if O^{2-} ions represent the outer surface, H^+ ions can link via dissociative adsorption of water or moisture diffusion can occur to the underline Mg^{2+} layer for reaction. Indeed, hydration found to occur readily in <111> oriented MgO films [16].

Conclusions

It is possible to prepare hydration free MgO thin films of pyramidal columnar morphology, <100> and <110> preferred orientation, and high optical transmittance (~86-98%) in the wavelength range 370-800nm by a simple method involving spin coating of magnesium nitrate hexahydrate solution in ethanol and annealing at 500^0C in air or oxygen ambient for 3h or more. The emergence of defect less {100} and {110} surfaces is key to suppress the presence of hydroxyl ions and to produce hydration free MgO films.

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