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Electrical and optical properties of MgO films deposited on soda lime glass by a sol-gel process using magnesium acetate

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Crystalline films of periclase and β-MgO with or without $Mg(OH)_2$ were deposited on soda lime glass substrates by a sol-gel process using magnesium acetate [$Mg(CH_3COO)_2 \cdot 4H_2O$]. MgO films were annealed by RTP under various atmospheres (Ar, H_2 and O_2) at 500 for 5 minutes and the crystallization of MgO was examined according to the RTP conditions and the cleaning methods of the glass substrates. The degrees of crystallization of MgO films were dependent on the RTP conditions and the cleaning methods of the glass substrates. An MgO film which was annealed by RTP under an O_2 atmosphere and a cleaning method of CM2, showed good crystallization of periclase-MgO and β-MgO, and $Mg(OH)_2$ phase was not observed. When the electric field was increased, the dielectric constant approached 8.2 with a dissipation factor of 2.3%. With an increase in the frequency, the dielectric constant decreased slowly until the dissipation factor increased at the dispersion frequency. All the MgO films were highly transparent (above 90%) and the refractive index of MgO film with thickness of 250 nm approached 1.71.

Key words: MgO film, Rapid thermal processing (RTP), Periclase-MgO, β-MgO, Optical property.

Introduction

MgO films are widely used as a protective layer for AC-plasma display panels because of their high durability, good protection characteristics against ion bombardment, high secondary electron emission coefficient and high transparency [1]. MgO has a low dielectric constant (k' = 9.65) for the high T_c superconductor, a low refractive index (n = 1.72 as compared to 3.86 for GaAs) which are useful for optical confinement in ferroelectric/MgO/semiconductor waveguide structures and especially a lattice constant of 4.213 [2, 3]. Several methods for the preparation and characterization of MgO films have been developed, such as ion-beam-assisted deposition, metalorganic chemical vapor deposition, electron beam evaporation, pulsed laser deposition and sputter deposition, etc. [4-7]. However, these methods are incompatible to the manufacture of ferroelectric films and AC-PDP cells, which are based on thick film methods [8]. The sol-gel method is one of the practical methods which can solve this problem, and this method has emerged as a variable deposition process capable of producing high quality oxide and non-oxide films. Compared with other deposition methods, the sol-gel method has the advantages of simplicity, low equipment cost, high deposition rate and easy preparation of large films using stable liquid precursors [8, 9]. Most of the recent activities in sol-gel processing of MgO films involve the use of magnesium alkoxide, although other starting materials have also been used. However, alkoxides are expensive and are not easy to handle due to their high sensitivity to moisture [8]. Another important point is that sol-gel derived crystalline MgO films have been deposited on Si wafers of different crystallographic characteristics. Apparently, fabrication of such films using glass substrates has not been successful. There have been many studies of the preparation of MgO films using a sol-gel process [8-10]. However, a few researches regarding the dielectric properties of MgO films with crystallization of the MgO have been reported.

In this study, crystalline MgO films were deposited on soda lime glass substrates by a sol-gel process using magnesium acetate [$Mg(CH_3COO)_2 \cdot 4H_2O$], and the crystal structure, electrical and optical properties of MgO films with rapid thermal processing(RTP) conditions under different atmospheres and with different cleaning methods of glass substrates were examined.

Experimental Procedure

MgO sol was synthesized by dissolution of Mg $(CH_3COO)_2 \cdot 4H_2O$ in C_2H_5OH pre-dried by contact with freshly-activated Zeolite 4A molecular sieve under agitation. Acetic acid (CH_3COOH) was added to this solution with stirring for 1 hr. The sol compositions were 1 : 1 : 25 (molar ratio of magnesium acetate: acetic acid: ethanol). The MgO sol thus produced had a life of 15 days. Soda lime glass substrates were cleaned with a soap solution and distilled water, and then the substrate was treated

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with ultrasonic waves in *i*-C_3H_7OH for 10 minutes and finally degreased with *i*-C_3H_7OH vapor. No other surface treatment was conducted on the substrates before the deposition operation (CM1). The glass substrates for RTP under an O_2 atmosphere used the same cleaning method as for CM1 and then they were immersed into dried C_2H_5OH for 24 h followed by air drying (CM2). Then MgO films were deposited on the glass substrates by a dip-coating technique with intermediate drying at 100°C for 30 minutes. Multi-dipping (3 layers) was taken to obtain films with a thickness range of 150-250 nm. MgO films thus produced were annealed by rapid thermal processing (RTP) conditions at 500 °C for 5 minutes. RTP was carried out under different conditions (Ar, H_2 and O_2 atmospheres). RTP conditions and degrees of crystallization of MgO films are summarized in Table 1.

The crystal structures and microstructures of MgO films were investigated by XRD and SEM. The thickness and optical refractive index (wavelength 632.8 nm) of MgO films were measured by an ellipsometer. The transmittances of MgO films at 550 nm were measured by a UV-vis spectrometer. Dielectric properties of MgO films were measured by an impedance analyzer.

Results and Discussion

Fig. 1 shows XRD patterns of MgO films deposited on glass substrates by RTP under different atmospheres at 500 °C for 5 minutes and different cleaning methods of the substrates. The degrees of crystallization of periclase and β-MgO are summarized in Table 1. The main peaks due to periclase-MgO with a (200) orientation, β-MgO with a (400) orientation and an additional peak of $Mg(OH)_2$ were observed after RTP under Ar, H_2 and O_2 atmospheres and when the glass substrates were cleaned by the CM1 method. The peak intensity of periclase-MgO in the film annealed at 500 in an O_2 atmosphere could be seen to be increase a significantly more than that in Ar and H_2 atmospheres. XRD patterns of MgO films showed good crystallization of the periclase and â-MgO, when the MgO films were annealed by RTP under an O_2 atmosphere and the glass substrate was cleaned by the CN2 method. The peak due to $Mg(OH)_2$ crystallization disappeared and the film was strongly textured with a preferential orientation along the (200) plane. The observed relationship between the degree of periclase-MgO with (200) orientation and RTP condition may be explained in terms of the migration

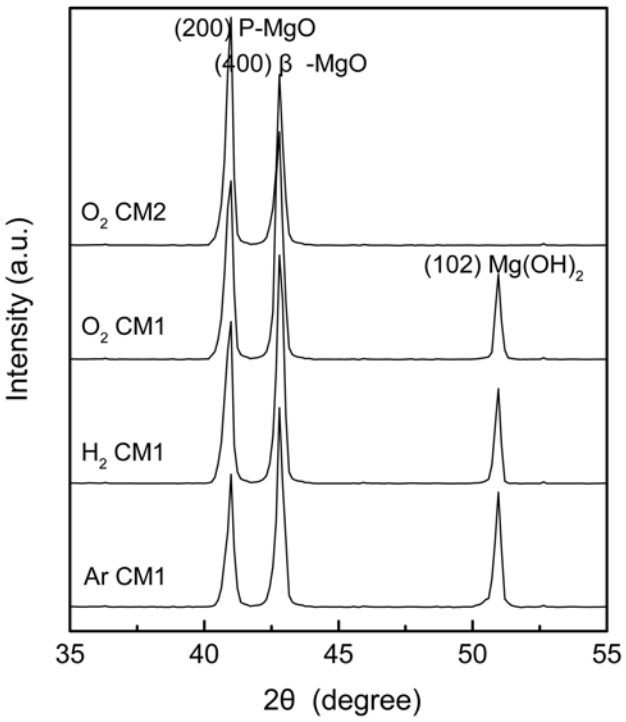

Fig. 1. XRD patterns of MgO films by RTP with different atmospheres and cleaning methods.

of molecules onto the growing surface [1]. MgO is expected to achieve a (200) preferred orientation that has a low energy configuration during nucleation. The absorbed Mg and O atoms with a higher mobility enhanced by RTP under an O_2 atmosphere could easily move to equilibrium atomic sites on the surface forming MgO with a (200) orientation which is various energetically stable [5]. The formation of β-MgO has been linked to its lattice matching with β-magnesium acetate and orientation constraints arising out of the substrate structure [3]. The formation of hydrates was apparently facilitated by the presence of four molecules of water of crystallization of magnesium acetate, the possible presence of water in the ethanol even after drying and the absorbed water on the surface of the glass substrates [1, 3]. In the case of the CM2 cleaning method, the surface water was removed, which helped the formation of crystalline MgO films without any hydroxide phase.

Fig. 2 shows SEM micrographs of MgO films deposited on glass substrates using RTP under different atmospheres

Table 1. RTP conditions and degrees of crystallization of MgO films

Mg acetate:acetic acid (molar ratio)	Clean method	RTP condition	Temperature (°C)	XRD peak height ratio [periclase(200):β,-MgO(400)]
1 : 1	CM1	5minutes, Ar	500	1 : 1.47
1 : 1	CM1	5minutes, H_2	500	1 : 1.35
1 : 1	CM1 CM2	5minutes, O_2	500	1 : 1.23 1 : 0.83

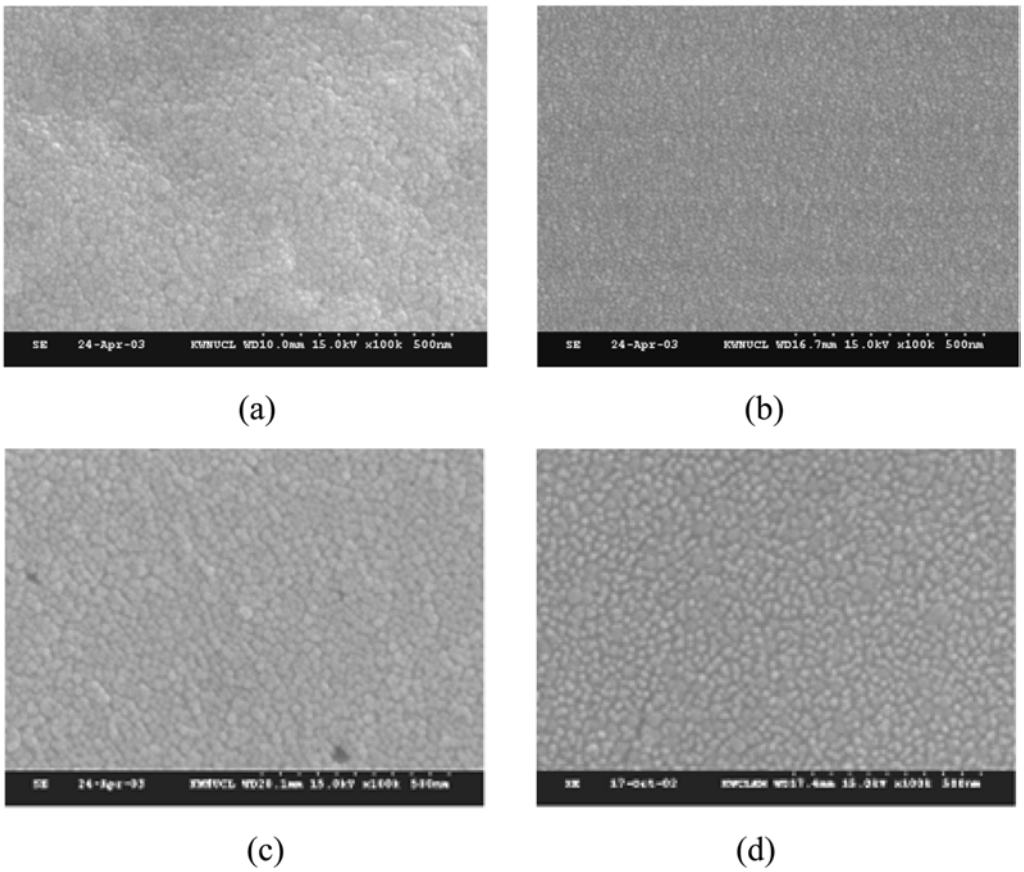

Fig. 2. SEM micrographs of MgO films with different RTP conditions and methods of cleaning the substrates. (a) Ar, CM1, (b) H_2, CM1, (c) O_2, CM1 and (d) O_2, CM2

at 500 for 5 minutes and different cleaning methods of the substrates. Well crystallized and less-dense films could be obtained when the gel film was annealed by RTP under an Ar atmosphere. The average grain size was about 30~40 nm. When annealed by RTP under a H_2 atmosphere, the products were found to contain smaller and dense crystallites (Fig. 2 (a) and (b)). When annealed in an O_2 atmosphere there was an increase in the grain size(Fig. 2 (d)) and a well-crystallized film could be obtained when the substrate was cleaned by the CM2 method, while in case of cleaning with the CM1 method, the microstructure of MgO films was less dense. This apparently indicates an inhibiting role of $Mg(OH)_2$ in the grain growth of the crystalline films [1].

Fig. 3 shows optical transmittance in the visible range of wavelength (at 550 nm) of MgO films with different RTP conditions and methods of cleaning the substrates. All the MgO crystalline films were highly transparent (above 90%). The transmittance of the MgO film annealed in an O_2 atmosphere and cleaned with CM2 method was increased by about 4% compared with the other RTP conditions.

Fig. 4 shows the variation of dielectric constant and dissipation factor of MgO films with RTP under an O_2 atmosphere at 500 for 5 minutes and using cleaning method CM2 as a function of electric field. The dielectric constant at 1 kHz without the electric field was 7.3, with a dissipation factor of

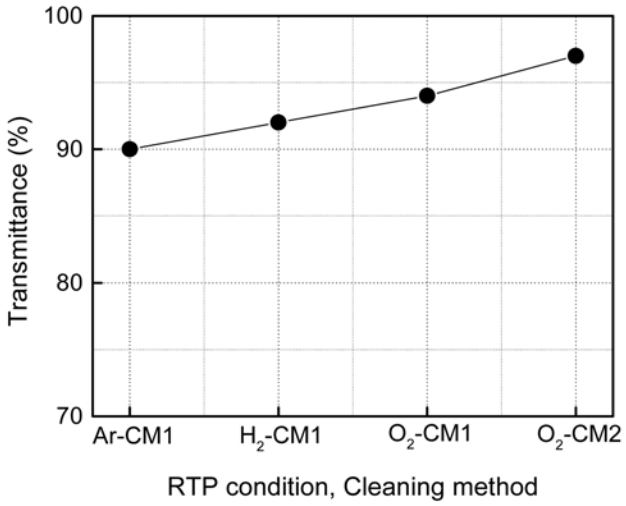

Fig. 3. Transmittance of MgO films with different RTP conditions and methods of cleaning the substrates.

4.5%. When electric field was increased, the dielectric constant approached 8.2 with a dissipation factor of 2.3%. Accordingly, the sol-gel derived MgO films apparently have a dielectric strength higher than 7.9×10^5 V/cm [9, 10].

Fig. 5 shows the variation of dielectric constant and dissipation factor of MgO films with RTP under an O_2 atmosphere at 500 for 5 minutes and with cleaning

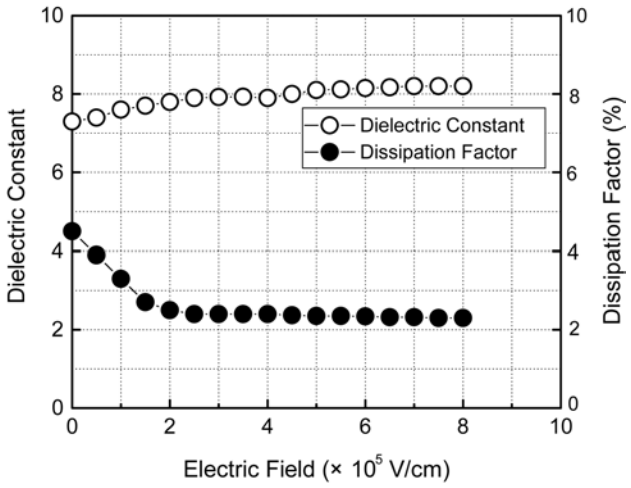

Fig. 4. Variation of dielectric constant and dissipation factor of MgO films with RTP under an O_2 atmosphere and with cleaning method CM2 as a function of the electric field.

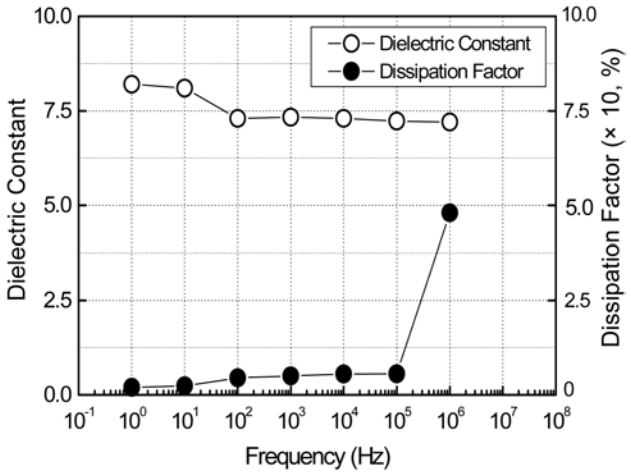

Fig. 5. Variation of the dielectric constant and dissipation factor of MgO films with RTP under an O_2 atmosphere and with cleaning method CM 2 as a function of frequency.

method CM2 as a function of frequency in the range of 100-10^6 Hz. The dielectric constant and dissipation factor of MgO films at a frequency of 1 KHz were 7.3 and 4.5%, respectively. With an increase in the frequency, the dielectric constant decreased slowly until the dissipation factor increased dramatically at the dispersion frequency. MgO films had a low dielectric constant and dissipation factor. On the other hand, the rapid increase of the dissipation factor at a frequency above 10^5 Hz may have been caused by a contact resistance between the probe and the electrode. The dielectric constant obtained in this study is higher than that of polycrystalline MgO, 3.20, but is smaller than that of a MgO single crystal 9.65 [5].

Fig. 6 shows the optical refractive index of MgO films with thickness in the range of 150-250 nm. The refractive index of MgO films was increased with an increase in the film thickness. A trend of increasing refractive index with film thickness was observed, which was similar

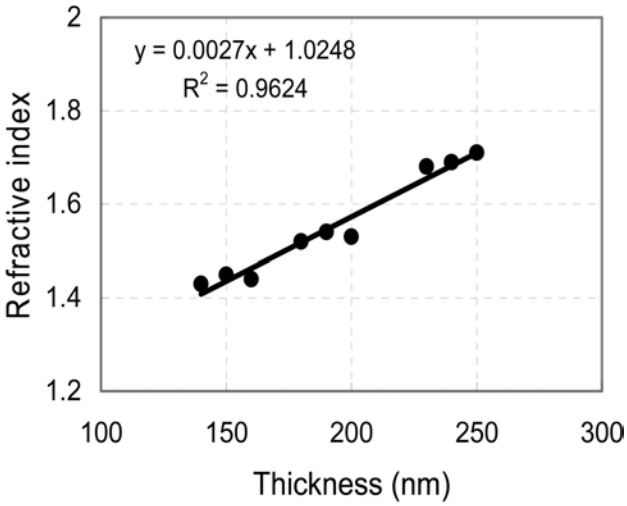

Fig. 6. Optical refractive index of MgO films with RTP under an O_2 atmosphere and with cleaning method CM2 as a function of thickness.

to a previous report on a ferroelectric film prepared by a sol-gel technique [10]. The rerefractive index of a MgO film with a thickness of 250 nm approached 1.71, which corresponded to the results obtained by the process of pulsed laser deposition [8] and a sputtering technique [7].

Conclusions

The main peaks due to periclase-MgO with a (200) orientation, β-MgO with a (400) orientation and an additional peak of $Mg(OH)_2$ were observed after RTP under Ar, H_2 and O_2 atmospheres and with cleaning method CM1. When the film was annealed by RTP under an O_2 atmosphere and with cleaning method CM2, the MgO film showed good crystallization of periclase and β-MgO, and the $Mg(OH)_2$ phase was not observed. Well- crystallized and dense films could be obtained when the MgO film was annealed by RTP under an O_2 atmosphere and with cleaning method CM2. A dielectric constant at 1 kHz without an electric field was 7.3, with a dissipation factor of 4.5%. When the electric field was increased, the dielectric constant approached 8.2 with a dissipation factor of 2.3%. The dielectric constant and dissipation factor of MgO films at a frequency of 1 kHz were 7.3 and 4.5%, respectively. With an increase in the frequency, the dielectric constant decreased slowly until the dissipation factor increased dramatically at the dispersion frequency. The transmittance of MgO films annealed in an O_2 atmosphere and with cleaning method CM2 was increased by about 4% compared to that of the other RTP conditions. The refractive index of an MgO film with a thickness of 250 nm approached 1.71.

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