# Synthesis of nano-sized MgO particle and thin film from diethanolamine-stabilized magnesium-methoxide

Hyun Suk Jung, Jung-Kun Lee,[1] Jin Young Kim, and Kug Sun Hong[*]

*School of Materials Science & Engineering, Seoul National University, Seoul, South Korea*

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## Abstract

The effects of diethanolamine (DEA) addition on the crystallization behavior of magnesium methoxide and the stabilization behavior of the Mg-alkoxide were investigated using differential scanning calorimetry, thermogravimetry, X-ray powder diffraction, transmission electron microscopy, and X-ray photoemission spectroscopy. 20 mol% DEA additions to magnesium methoxide showed enhanced stability such that a time-dependent change in the sol was not observed in air. Moreover, the DEA addition enhanced the crystallization process. Crystalline MgO in the 20 mol% of DEA-added magnesium methoxide powder was observed at 300°C for samples processed in $O_2$ and a high degree of crystallinity was observed at 400°C when processed in $O_2$. The enhanced crystallization of Mg-methoxide with added DEA in $O_2$ is discussed in terms of structural relaxation and heat generation during the ignition of an organic species of DEA. Using a DEA added sol, a MgO thin film with a high degree of crystallinity was prepared at 400°C in $O_2$.

## 1. Introduction

Nano-crystalline MgO is a very important scientific and commercial material. Nano-sized MgO powder is widely used as a catalyst in chemical industries [1–8] and MgO thin films are used as buffer layers for superconducting and ferroelectric thin films [9–15]. Recently, MgO thin films have attracted attention for use as protective layer in alternating current-plasma display panels (AC-PDP) [16–20]. MgO thin films used as protective layer for AC-PDP have been fabricated by physical vapor deposition (PVD) techniques such as sputtering, and electron beam deposition. However, these processes are incompatible to the manufacture of AC-PDP cells, which are based on thick film processes [21]. Sol–gel process is one of the methods which can solve this problem. The sol–gel process also has the advantage of low cost. Previous research confirmed that a MgO thin film prepared using the sol–gel process could be used as the protective layer in an AC-PDP cell [22].

In order to prepare reproducible MgO films via the sol–gel process, maintaining the stability of sol is critical. Generally, alkoxides are hygroscopic in nature and the condition of an alkoxide can be easily changed. If the viscosity of sol is changed or precipitation is formed in sol, it is difficult to obtain reproducible properties of the resultant films. Chemical modification of alkoxide is commonly employed to control the hydrolysis and condensation reaction rates. Several stabilizers have been introduced to increase the stability of sols [23,24]. Diethanolamine (DEA) is frequently used as a stabilizer in various sol–gel systems [24–27]. It is known that an alcoholic exchange reaction between alkoxide and alkanoamines such as DEA can yield stable compounds with chelates through O–$M$–O or O–$M$–N bonds [28]. Sharma et al. [29] proposed Mg-diethanolaminate to have a core structure with a chelated diethanolaminate ligand.

So far, most research has focused on the effects of stabilizers on the alkoxides [24–27]. However, one of the major requirements of the MgO thin film is a low crystallization temperature. A soda-lime silicate with a

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[*]Corresponding author. Fax: +82-2-886-4156.

*E-mail address:* kshongss@plaza.snu.ac.kr (K.S. Hong).

[1]Current address: Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

low melting temperature is used as a substrate for plasma display panels. Moreover, a high degree of crystallinity in the MgO thin films is required to exhibit good secondary electron emission characteristics [22]. This means that complex effects of the additives (stabilization and crystallization) would be advantageous for the application of MgO sols. Nonetheless, research regarding the change in the crystallization behavior in stabilizer-added sols is not available for the MgO system.

In this study, DEA was added to Mg-alkoxide and a stable MgO sol was prepared. The effect of DEA on the crystallization of nano-sized MgO powder was investigated and the crystallization behavior of MgO was explained in terms of the structural relaxation with the formation of Mg–O bonds and the heat generation during the ignition of an organic species of DEA. The low temperature crystallization of MgO thin films prepared from a DEA-stabilized sol was also discussed.

## 2. Experimental

### 2.1. Preparation of powders

In an $N_2$-filled glove box, DEA (99%, Aldrich) was added to magnesium methoxide (7.6 wt% in methanol, Aldrich) in amounts of 0% and 20 mol%. Water was not added into the Mg-alkoxide. The powders were dried in a vacuum chamber and were designated as D0 and D20 with respect to the DEA mol%. The powders were heated at a rate of 5°C/min in $N_2$ or $O_2$. When the samples reached a specific experimentally pre-determined temperature they were immediately quenched.

### 2.2. Preparation of thin films

The MgO films were deposited on Si (100) substrates by dip coating in a glove box. The films were deposited from D0 and D20 sols whose concentration was same as described above. The thickness of the films were measured using an ellipsometer (Rudolph Research) and were approximately 180 nm. The dried D0 and D20 films were annealed at 400°C in $O_2$ for 1 h.

### 2.3. Characterization

Thermogravimetric analysis (TG, Model: Perkin-Elmer TGA 7) and differential scanning calorimetric analysis (DSC, Model: Perkin-Elmer DSC 7) in the temperature range of 50–600°C (with heating rate of 5°C/min) was performed on the D0 and D20 powders under $N_2$ and $O_2$ atmosphere, respectively.

The crystal structure of powders was investigated using X-ray diffraction (XRD, Model: MAC science M18XHF-SRA). Transmission electron microscopy

(TEM, Model: JEOL JEM 200-CX for powders) was used to investigate the morphology and the crystal structure of powders and thin films. X-ray photoelectron spectra (XPS, Model: ARIESARSC 10MCD) were acquired for determination of the binding state of $Mg^{2+}$ ion. The surface of each sample was sputtered with Ar ion at the rate of 0.2 nm/min for 10 min before the measurement.

## 3. Results

The stability for D0 and D20 sols were summarized in Table 1. When exposed to air during 30 min, D0 sol showed white precipitates. The addition of 20 mol% DEA allowed the Mg-methoxide to be stable. No precipitate was observed in the D20 sol. DEA was considered to modify and stabilize the Mg-methoxide. In many other systems, the role of DEA as stabilizer has been reported [24–27].

Figs. 1(a–d) show TG and DSC curves for as-dried D0 and D20 samples processed in $N_2$ and $O_2$, respectively. In all cases the primary weight loss of between 8 to 18 wt% occurred roughly at 150°C. The primary weight loss originates from the desorption of residual methanol or physically adsorbed water [13]. The onset temperature of secondary weight loss in $N_2$ and $O_2$ were similar, near 300°C for both D0 and D20 powders. This weight loss is assigned to the thermal decomposition of an alkoxy group [30]. As shown in Figs. 1(a) and (b), endothermic peaks are observed at approximately 400°C for D0 and D20 powders processed in $N_2$. These results indicated that oxidation reaction did not occur during the thermal decomposition of both D0 and D20 in $N_2$. In Figs. 1(c), a DSC curve for D0 powder in $O_2$, a weak exothermic peak without any weight loss was found between 150°C and 300°C. An exothermic peak with secondary weight loss were observed at approximately over the 300°C. This peak originates from the oxidation of an alkoxy group. In the case of D20 a very broad exothermic peak without associated weight loss was also observed in the range of 120–300°C and its intensity was much larger than that of D0 powder, as shown in Fig. 1(d). An exothermic peak accompanied by significant weight loss was observed at approximately 300–400°C. This peak was also stronger than the high temperature exothermic peak seen in the D0 processed

Table 1
Stability of both D0 and D20 sols

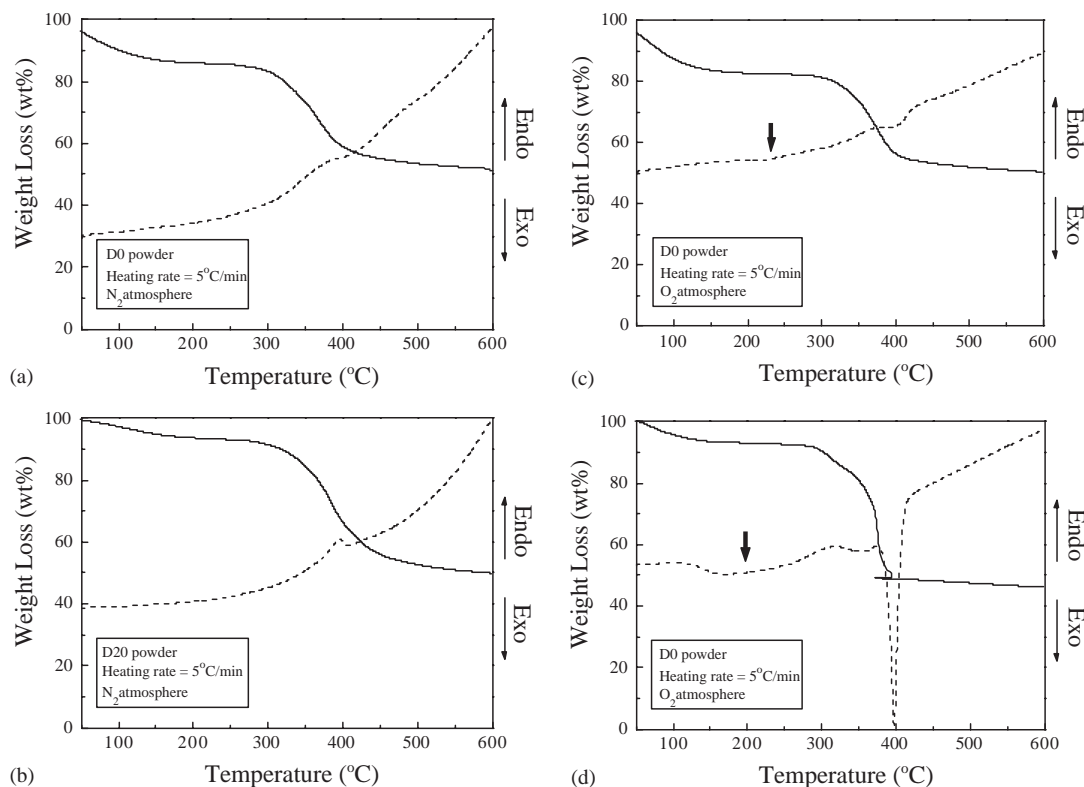| Sample | Amount of DEA (mol%) | Time to precipitate (min) | Color of gel |
|---|---|---|---|
| D0 | 0 | 30 | White |
| D20 | 20 | No precipitation | Transparent |

Fig. 1. TG (solid line) and DSC (dashed line) curves for (a) D0 in $N_2$, (b) D20 in $N_2$, (c) D0 in $O_2$, and (d) D20 in $O_2$.
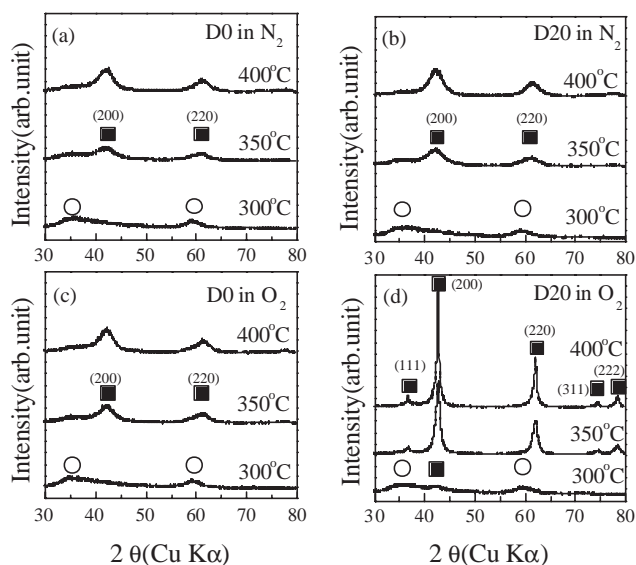


Fig. 2. XRD reflections of quenched powders for (a) D0 in $N_2$, (b) D20 in $N_2$, (c) D0 in $O_2$, and (d) D20 in $O_2$. (○: Mg-alkoxide, ■: MgO).

in $O_2$. This phenomenon is considered to be related to the ignition of organics containing DEA.

XRD patterns of the quenched D0 and D20 powders in $N_2$ and $O_2$ are shown in Fig. 2. In $N_2$ both D0 and D20 showed similar crystallization behavior. The MgO reflections were observed in both D0 and D20 powders quenched at 350°C. The intensities of MgO reflections in both powders quenched at 350°C and 400°C were very similar. However, in $O_2$ atmosphere, the crystallization behavior of D20 powder was significantly different. In $O_2$, the crystallization of D20 to MgO started at 300°C, lower temperature than when processed in $N_2$. The intensity of MgO reflections in the D20 powders quenched at 350°C and 400°C were much stronger than that of the D0 powders heat-treated under the same conditions. This indicates that the addition of DEA lowered the crystallization temperature and facilitated the crystallization process only when processed in an $O_2$ atmosphere.

TEM analysis revealed the morphology and crystal structure of D0 and D20 powders quenched at 400°C in $O_2$ atmosphere, as shown in Fig. 3. Approximately 10–15 nm-sized MgO particles were observed in D20 powder whereas D0 powder showed smaller sized (5–10 nm) MgO particles. In the inset of Figs. 3(a) and (b), spot-like ring patterns were observed in the selected area diffraction (SAD) image of D20 while the broad ring patterns were observed in D0 at the same aperture size. The face directions of MgO crystal in SAD pattern were in good agreement with the MgO reflections of XRD analysis. XRD and TEM results indicate that the crystallization of MgO powder was enhanced significantly when DEA-added Mg-alkoxide was heat-treated in an oxygen atmosphere.
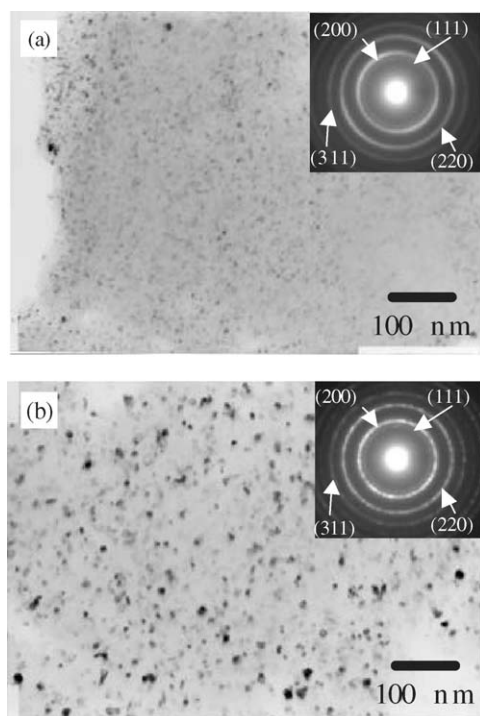
Fig. 3. TEM images of powders quenched at 400°C in $O_2$: (a) D0 and (b) D20.



Fig. 4. TEM images of thin films annealed at 400°C in $O_2$: (a) D0 and (b) D20.

Figs. 4(a) and (b) show the TEM micrographs of D0 and D20 thin films annealed at 400°C in $O_2$, respectively. In comparison to the crystallites much smaller than 10 nm found in D0 thin films, approximately 10 nm-sized crystallites were observed in the D20 thin film. Selective area diffraction (SAD) patterns of both D0 and D20 thin films are shown in the insets of Figs. 4(a) and (b), respectively. The weak and broad ring pattern of D0 thin film is suggestive of smaller-sized MgO crystals, whereas the spot-like pattern of D20 thin film represents a well-crystallized structure of MgO. The higher crystallinity of D20 film than that of D0 is consistent with the previously discussed results of powders.

## 4. Discussion

The addition of DEA to Mg-methoxide lowered the crystallization temperature and enhanced the crystallization process of MgO of samples only when processed in $O_2$. This enhanced crystallization was not observed when samples were processed in $N_2$.

The XPS spectra of the D0 and D20 powders as dried are shown in Fig. 5. C 1s level was used as an internal reference at 284.6 eV. As shown in Fig. 5(a), the binding energies (BE) of Mg 2p were 48.9 and 49.2 eV for D20 and D0 powders, respectively. The BE for the dried D20 was shifted to lower energy values. This lower BE for D20 reveals that there was a charge transfer to $Mg^{2+}$
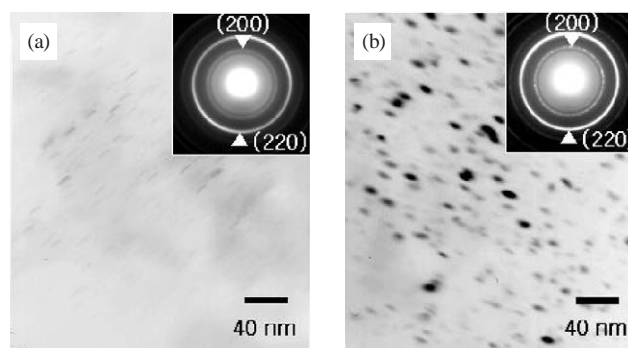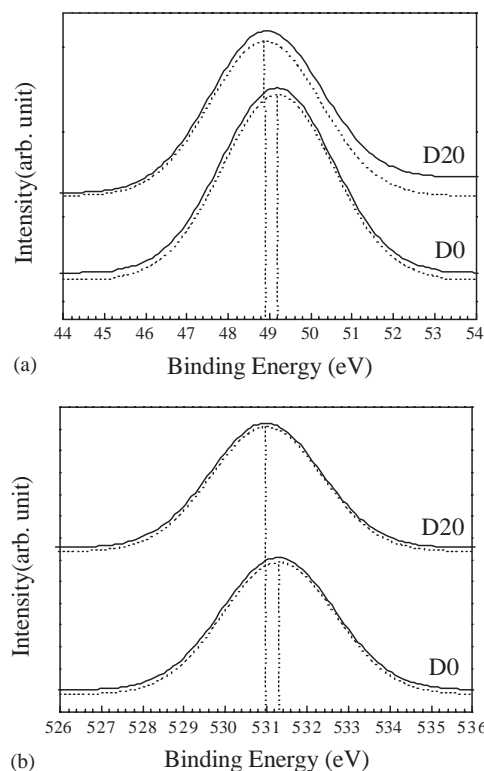


Fig. 5. XPS spectra of (a) Mg 2p and (b) O 1s for D0 and D20 powders.

ion during the addition of DEA to Mg-alkoxide. The electron acceptance of $Mg^{2+}$ makes it "less positive" and decreases its BE [31]. The nitrogen in the amino group of DEA was reported to act as an electron donor for the interaction between Al and DEA [32]. The alcohol present in the DEA molecule interacts to form an alkoxy bond whereas the amine is interacting with an aluminum atom via a Lewis acid-base interaction. The BE of O 1s were 531.3 and 531.0 eV for D0 and D20 powders, as illustrated in Fig. 5(b). It revealed that both D0 and D20 samples had no impurity such as $Mg(OH)_2$ and $MgO_2$ since the BE of O 1s peak in $Mg(OH)_2$ is 534.5 eV and that in $MgO_2$ is 533.5 eV. The difference

in BE of both D0 and D0 was considered to be correspondent with the interaction of $Mg^{2+}$ ion and DEA. Sharma et al. [29] proposed the structure of Mg-diethanolaminate as a core structure with a chelated diethanolaminate ligand as illustrated in Fig. 6. The interaction of nitrogen in the amino group with the metal was also reported using the infrared (IR) spectroscopy [29]. Compared with that of free DEA, the NH stretching mode associated with metallic diethanolaminates shown in IR spectral data was lowered by about $100\,cm^{-1}$. This confirmed the coordination of an amino group in DEA with central metal ions as shown in Fig. 6. The literature suggests that the shift in BE of Mg 2p during DEA addition results from the interaction of nitrogen in the amino group with $Mg^{2+}$ ions.

Fig. 7 shows the XPS spectra of Mg 2p for D20 powders as-dried, quenched at 250°C in $N_2$, and quenched at 250°C in $O_2$. It is noteworthy that the BE of the D20 powder quenched at 250°C in $O_2$ was shifted to a higher value, whereas the BE of the D20 powder quenched in $N_2$ was almost same as that of the dried powder. Considering the TGA results in Figs. 1(b) and (d) showing no weight loss at 250°C, it can be summarized that the decomposition of D20 powder did not start at $T \leqslant 250°C$. In this regard, the shift in BE of D20 to higher value without the weight loss in $O_2$ suggests that oxygen incorporates into Mg-diethanolaminate derivative and form Mg–O bond with the rupture of only Mg–N bond. Only the interaction between Mg and the amino group (donor group) is
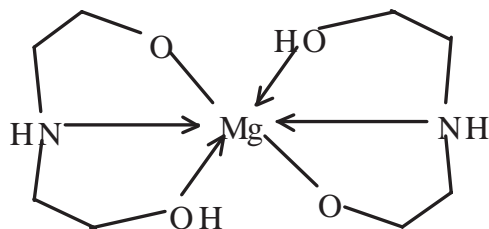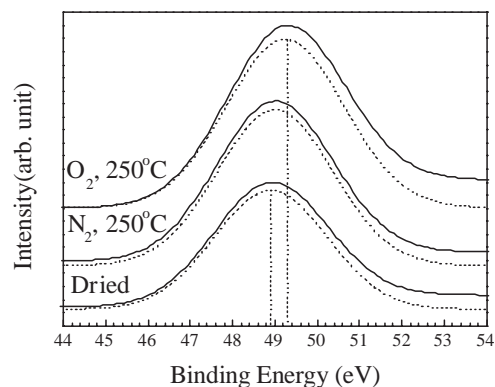


Fig. 6. Schematic structure of Mg-diethanolaminate.



Fig. 7. XPS spectra of Mg 2p for D20 powders as dried and quenched at 250°C in $N_2$ and quenched at 250°C in $O_2$.

broken and the other bonds between Mg and DEA are maintained.

It is notable that the broad exothermic peaks of DSC curves approximately from 200°C to 300°C were observed only in $O_2$, as shown in Figs. 1(c) and (d). There was no weight loss in this temperature range. In the sol–gel process, the broad exothermic peak without mass change is indicative of recrystallization or formation of a new phase [30]. In coprecipitated $PbTiO_3$, Lee et al. [33] also assumed that the broad exothermic peak originated from the structural relaxation of the amorphous coprecipitate, which was considered to be more disordered structure. In the present results, the broad exothermic peak without associated weight loss is considered to originate from structural relaxation. It should be noted that the broad exothermic peak for D0 was very subtle, whereas that for D20 was apparent. It suggests that the degree of structural relaxation in D20 is much larger than that of D0. The D20 having the core structure with the chelated bulky DEA ligand is thought to have more open and more disordered structure than that of D0. The structural relaxation of D20 occurred in only $O_2$ atmosphere. This structural relaxation is considered to correlate with the incorporation of oxygen into Mg-diethanolaminate derivative and the formation of Mg–O bonds with the rupture of Mg–N bonds.

In view of the results of this study, the low temperature crystallization of D20 processed in an $O_2$ atmosphere is attributed to structural relaxation accompanying the formation of Mg–O bonds with the associated rupture of Mg–N bonds. Since the structural relaxation was not observed or negligible in D0 and D20 processed in $N_2$ and D0 processed in $O_2$, the associated low temperature crystallization to MgO did not occur.

Comparing Figs. 1(c) and (d), the strong exothermic peak at approximately 400°C was observed in D20 whereas the same peak in D0 was very weak. This strong exothermic peak is related to the ignition of organics including DEA, which decomposed from a Mg-diethanolaminate derivative. The heat generation from this ignition of organics might provide the driving force for consecutive crystallization process and enhance the crystallinity of MgO in the D20 powder. Narrenda et al. [34] prepared lead magnesium niobate (PMN) powder using excessive heat from the ignition of a metal carboxylate gel. They reported that temperature abruptly rose to 1300°C at a rate exceeding $\sim 8000°C/$min because of the oxidation of the gel. The caloric value was calculated from the integration of the exothermic peak area in DSC curve for both D0 and D20 processed in $O_2$. The results are summarized in Table 2. The caloric value for D20 is about 11 times of that of D0.

These results revealed that enhancement of crystallization process to MgO in D20 powder in $O_2$ was due to the low temperature structural relaxation and the

Table 2
Caloric values of heat during exothermic ignition of D0 and D20 powders

| Sample | $\Delta H$ (J/g) |
|--------|------------------|
| D0 | −435 |
| D20 | −4783 |

ignition of organics providing the driving force for further and continued crystallization. In addition, the result of MgO films shows that this method is applicable to prepare low temperature preparation of thin films.

## 5. Conclusions

The effect of diethanolamine (DEA) on the stabilization of Mg-methoxide and on the crystallization behavior was investigated. DEA played an important role in stabilizing the Mg-methoxide. When 20 mol% DEA was added to Mg-methoxide, no precipitation by hydrolysis was observed in air. DEA was also found to facilitate the crystallization process of MgO powder in $O_2$. The addition of DEA lowered the crystallization temperature and enhanced the crystallinity of MgO powder in $O_2$. The enhanced crystallization of MgO by the addition of DEA in $O_2$ can be explained in terms of structural relaxation with the associated formation of Mg–O bonds and the heat generation effect during the ignition. Using this method, a well-crystallized MgO thin film heat-treated at $400^\circ$C in $O_2$ was successfully obtained.

## References

[1] S. Utamapanya, K.J. Klabunde, J.R. Schlup, Chem. Mater. 3 (1991) 175.
[2] J.V. Stark, K.J. Klabunde, Chem. Mater. 8 (1996) 1913.
[3] H. Itoh, S. Utamapanya, J.V. Stark, K.J. Klabunde, J.R. Schlup, Chem. Mater. 5 (1993) 77.
[4] A.V. Chadwick, I.J.F. Poplett, D.T.S. Maitland, M.E. Smith, Chem. Mater. 10 (1998) 864.
[5] S.Y. Kuz'mitskaya, V.I. Zaikovskii, Kinet. Catal. 38 (1997) 848.
[6] R. Portillo, T. Lopez, R. Gomez, A. Bokhimi, O. Morales, Novaro, Langmuir 12 (1996) 40.
[7] A. Bokhimi, T. Morales, R. Lopez, J. Gomez, J. Solid State Chem. 115 (1995) 411.
[8] J.V. Stark, D.G. Park, I. Lagadic, K.J. Klabunde, Chem. Mater. 8 (1996) 1904.
[9] D.K. Fork, F.A. Ponce, J.C. Tramontana, T.H. Geballe, Appl. Phys. Lett. 58 (1991) 2994.
[10] A. Matsuda, Y. Yamanaka, M. Tazoe, T. Nakamura, A. Morimoto, T. Shimizu, J. Cryst. Growth 158 (1996) 84.
[11] T. Venkatesan, E.W. Chase, X.D. Wu, A. Inam, C.C. Chang, Appl. Phys. Lett. 53 (1998) 243.
[12] H. Choi, S. Hwang, J. Mater. Res. 15 (2000) 842.
[13] A.A. Rywak, J.M. Burlitch, T.M. Loehr, Chem. Mater. 7 (1995) 2028.
[14] J.G. Yoon, K. Kim, Appl. Phys. Lett. 66 (1995) 2661.
[15] X. Fu, Z. Song, G. Wu, J. Huang, X. Duo, C. Lin, J. Sol–Gel Sci. Technol. 16 (1999) 277.
[16] T. Urade, T. Iemori, M. Osawa, N. Nakayama, I. Morita, IEEE. Trans. Electron. Devices 23 (1976) 313.
[17] S. Hidaka, M. Ishimoto, N. Iwase, K. Betsui, H. Inoue, IEICE Trans. Electron. E82-C (1999) 1984.
[18] K. Yoshida, H. Uchiike, M. Sawa, IEICE Trans. Electron. E82-C (1999) 1798.
[19] M.O. Aboelfotoln, J.A. Lorenzen, J. Appl. Phys. 48 (1977) 4754.
[20] C.H. Park, Y.K. Kim, B.E. Park, W.G. Lee, J.S. Cho, Mater. Sci. Eng. B60 (1999) 149.
[21] I. Koiwa, T. Kanehara, J. Mita, J. Electrochem. Soc. 142 (1995) 1396.
[22] H.S. Jung, J.K. Lee, H.J. Youn, K.S. Hong, J. Appl. Phys. 92 (2002) 2855.
[23] C. Sanchez, J. Livage, M. Henry, F. Babonneau, J. Non-Cryst. Sol. 100 (1988) 65.
[24] Y. Takahashi, A. Ohsugi, T. Arafuka, T. Ohya, T. Ban, Y.J. Matsuoka, Sol–Gel Sci. Technol. 17 (2000) 224.
[25] Y. Takahashi, Y.J. Matsuoka, J. Mater. Sci. 23 (1988) 2259.
[26] Y. Takahashi, K. Yamacuchi, J. Mater. Sci. 25 (1990) 3950.
[27] Y. Ohya, H. Saiki, Y. Takahashi, J. Mater. Sci. 29 (1994) 4099.
[28] D.C. Bradley, R.C. Mehrotra, Alkoxides, Academic Press, London, 1978, p 227.
[29] M. Sharma, A. Singh, R.C. Mehrotra, Polyhedron 19 (2000) 77.
[30] H. Thoms, M. Epple, H. Viebrock, A. Reller, J. Mater. Chem. 5 (1995) 589.
[31] S. Ardizzone, C.L. Bianchi, M. Fadoni, B. Vercelli, Appl. Surf. Sci. 119 (1997) 253.
[32] M. Abel, A. Rattana, J.F. Watts, Langmuir 16 (2000) 6510.
[33] M. Lee, B. Choi, J. Am. Ceram. Soc. 74 (1991) 2309.
[34] Y. Narendar, G.L. Messing, J. Am. Ceram. Soc. 80 (1997) 915.