

Atomic Layer Deposition of MgF₂ Thin Films Using TaF₅ as a Novel Fluorine Source

Tero Pilvi,^{*,†} Esa Puukilainen,[†] Ulrich Kreissig,[‡] Markku Leskelä,[†] and Mikko Ritala[†]

Department of Chemistry, University of Helsinki, P.O. Box 55, FI-00014 University of Helsinki, Finland,
Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, P.O. Box 510119,
01314 Dresden, Germany

Received April 3, 2008. Revised Manuscript Received May 14, 2008

Magnesium fluoride is one of the most important optical thin film materials due to the good light transparency down to the vacuum ultraviolet (UV) range. A novel atomic layer deposition (ALD) process was developed for depositing MgF₂ thin films. Instead of the previously used fluorine sources, namely HF or TiF₄, we used TaF₅ as the fluorine precursor for the first time in ALD. The films were grown in a temperature range of 225–400 °C. The films were characterized by X-ray diffraction, X-ray reflection, atomic force microscopy, scanning electron microscopy, spectrophotometer, and elastic recoil detection analysis. Optical and electrical properties of the films were also studied. The films grew in columnar fashion onto silicon and all the films were polycrystalline. The film densities were close to bulk MgF₂. Films with a good stoichiometry and low impurity levels were achieved. The refractive indices were between 1.36 and 1.38 at $\lambda = 580$ nm. The permittivity of a film grown at 300 °C was 5.0. The transmittance of a film deposited at 350 °C was good even in the deep UV range. This type of novel ALD process using the new fluorine precursor TaF₅ is a convenient method also for depositing other metal fluoride thin films.

Introduction

As excimer lasers extend to deep and vacuum ultraviolet (UV) wavelengths, the requirements for low loss optical components increases drastically.¹ The usage of oxide materials is limited due to their intrinsic absorption. However, metal fluorides can be the material-of-choice because of their high transparency in deep UV ranges. MgF₂ is a dielectric material with a wide band gap and a low refractive index of 1.38.² As a result of the low refractive index, MgF₂ films have been used together with higher refractive index materials, e.g., LaF₃^{3–12} and Al₂O₃^{13,14} in optical multilayers, which

can be used, e.g., in high reflective mirrors for ArF excimer laser irradiation and narrow band-pass filters.⁴

The main deposition methods of MgF₂ films, as well as their limitations, are presented in more detail in our previous article,¹⁵ and the references therein. Briefly, physical vapor deposition methods are the most often used techniques for depositing MgF₂ films.

Chemical vapor deposition (CVD) methods have rarely been used for depositing MgF₂ thin films due to the problems in handling the hazardous fluorine sources, HF and F₂ gas.¹⁶ Atomic layer deposition (ALD) technique,^{17,18} in which the film grows via saturative surface reactions, belongs to the CVD methods. Benefits of the ALD method include the fact that uniform and conformal films are formed with good thickness accuracy and reproducibility.¹⁹ The problem in depositing metal fluoride thin films by ALD has been the lack of a good fluorine source. HF, obtained by thermally decomposing NH₄F, was used as the first fluorine source candidate in ALD for depositing CaF₂, ZnF₂, and SrF₂

* To whom correspondence should be addressed. E-mail: Tero.Pilvi@helsinki.fi

[†] University of Helsinki.

[‡] Forschungszentrum Rossendorf.

- (1) Wang, J.; Maier, R.; Dewa, P. G.; Schreiber, H.; Bellman, R. A.; Elli, D. D. *Appl. Opt.* **2007**, *46*, 3221.
- (2) Physical Constants of Inorganic Compounds. In *CRC Handbook of Chemistry and Physics, Internet Version 2007*, 87th ed.; Lide, D. R., Ed.; Taylor and Francis: Boca Raton, FL, 2007.
- (3) Targove, J. D.; Lehan, J. P.; Lingg, L. J.; Macleod, H. A.; Leavitt, J. A.; McIntyre, L. C. *Appl. Opt.* **1987**, *26*, 3733.
- (4) Zukic, M.; Torr, D. G.; Spann, J. F.; Torr, M. R. *Appl. Opt.* **1990**, *29*, 4284.
- (5) Duparre, A.; Ruppe, C.; Pischow, K. A.; Adamik, M.; Barna, P. B. *Thin Solid Films* **1995**, *261*, 70.
- (6) Welsch, E.; Eitrich, K.; Blaschke, H.; Kaiser, N. *Appl. Surf. Sci.* **1996**, *96–98*, 393.
- (7) Czigan, Z.; Adamik, M.; Kaiser, N. *Thin Solid Films* **1998**, *312*, 176.
- (8) Jakobs, S.; Duparre, A.; Truckenbrodt, H. *Int. J. Mach. Tools Manuf.* **1998**, *38*, 733.
- (9) Yang, M.; Gatto, A.; Kaiser, N. *Appl. Opt.* **2006**, *45*, 178.
- (10) Guenster, S.; Ristau, D.; Gatto, A.; Kaiser, N.; Trovo, M.; Sarto, F. *Proceedings of the 26th International Free Electron Conference FEL*; Bakker, R.; Giannessi, L.; Marsi, M.; Walker, R., Eds.; Comitato Conferenze Elettra, Trieste, Italy, 2004; Vol. 233.
- (11) Heber, J.; Muehlig, C.; Triebel, W.; Danz, N.; Thielsch, R.; Kaiser, N. *Appl. Phys. A* **2003**, *76*, 123.

- (12) Sarto, F.; Nichelatti, E.; Flori, D.; Vadrucchi, M.; Santoni, A.; Pietrantoni, S.; Guenster, S.; Ristau, D.; Gatto, A.; Trovò, M.; Danailov, M.; Diviacco, B. *Thin Solid Films* **2007**, *515*, 3858.
- (13) Shuzhen, S.; Jianda, S.; Chunyan, L.; Kui, Y.; Zhengxiu, F.; Lei, C. *Appl. Surf. Sci.* **2005**, *249*, 157.
- (14) Zhan, M.; Gao, W.; Tan, T.; He, H.; Shao, J.; Fan, Z. *Vacuum* **2005**, *79*, 90.
- (15) Pilvi, T.; Hatanpää, T.; Puukilainen, E.; Arstila, K.; Bischoff, M.; Kaiser, U.; Kaiser, N.; Leskelä, M.; Ritala, M. *J. Mater. Chem.* **2007**, *17*, 5077.
- (16) Fujihara, S.; Tada, M.; Kimura, T. *Thin Solid Films* **1997**, *304*, 252.
- (17) Leskelä, M.; Ritala, M. *Thin Solid Films* **2002**, *409*, 138.
- (18) Suntola, T. *Thin Solid Films* **1992**, *216*, 84.
- (19) Ritala, M.; Leskelä, M. In *Handbook of Thin Film Materials*; Nalwa, H. S., Ed.; Academic Press: San Diego, 2002; p 103.

films.²⁰ However, HF is not an ideal choice for ALD because of its unsafe chemical nature. Recently, we demonstrated that TiF_4 can be used as a fluorine precursor in ALD for depositing CaF_2 ,²¹ MgF_2 ,¹⁵ YF_3 (data not published yet), and LaF_3 .²² Good results were achieved by use of the TiF_4 precursor, but the main drawback was that some titanium impurities remained in the MgF_2 films, in levels from <0.1 to 2.8 at. %, which affected negatively the UV light transparency of the films. Therefore, there is a need for a better fluorine precursor.

The aim of this study was to demonstrate that TaF_5 could be used as a new fluorine precursor for depositing metal fluoride thin films by ALD. TaF_5 is a rather safe chemical. It has quite low vapor pressure because it is a solid at room temperature, and as a result it can be readily and safely handled and removed from the reactor exhaust gases. It also fulfills the main requirements for an ALD precursor, including high reactivity in a process, sufficient volatility, and good thermal stability.¹⁹ Furthermore, because of the larger size of Ta compared to Ti, tantalum may be less readily incorporated as an impurity into the MgF_2 films. This decrease in transition metal impurities would lead to the increase of UV light transmittance of the film. TaF_5 has earlier been used in CVD, e.g., to deposit metallic Ta films²³ as well as Ta_2O_5 films by plasma-enhanced CVD.^{24,25} TaF_5 has also been used in ALD for depositing Ta_2O_5 ,²⁶ and TaSi_x films,^{27,28} but in all these cases TaF_5 was used as a tantalum source, not as a fluorinating agent. In this work $\text{Mg}(\text{thd})_2$ ($\text{thd} = 2,2,6,6\text{-tetramethyl-3,5-heptadionato}$) was used as the cation precursor. $\text{Mg}(\text{thd})_2$ has been used in previous ALD processes, in addition to being used in our previous study on ALD of MgF_2 ,¹⁵ also for depositing MgO thin films.^{29,30}

Experimental Section

The films were grown in a hot-wall flow-type F120 ALD reactor (ASM Microchemistry Ltd., Helsinki, Finland). All films were deposited in the temperature range of 225–400 °C. The pressure inside the reactor was below 10 mbar. MgF_2 thin films were grown onto $5 \times 5 \text{ cm}^2$ Si(100) and Si(111) with native oxide. Other used substrates were $5 \times 5 \text{ cm}^2$ indium tin oxide (ITO) film on glass and $2.5 \times 5 \text{ cm}^2$ quartz. Magnesium β -diketonate, $\text{Mg}(\text{thd})_2$ (Volatec Oy, Porvoo, Finland), was evaporated from an open glass crucible at 125 °C and TaF_5 (Strem Chemicals Inc., Newburyport,

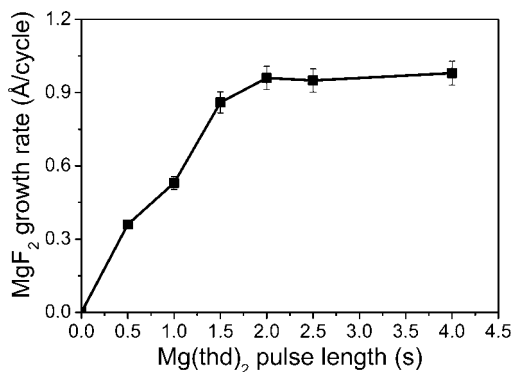


Figure 1. Growth rate of MgF_2 films on Si as a function of $\text{Mg}(\text{thd})_2$ pulse length at 300 °C. TaF_5 pulse and purge times were 1.0 s.

MA) at 45 °C inside the reactor. Nitrogen (NITROX UHPN 3000 nitrogen generator) was used as a carrier and a purge gas to separate flows of the precursors in the gas phase and to remove the excess reactants as well as the gaseous reaction byproduct.

The thicknesses and refractive indices of the MgF_2 thin films were determined from reflection or transmission spectra obtained with an Hitachi U2000 spectrophotometer in the wavelength range of 190–1100 nm. A fitting program was exploited in analyzing the spectra.³¹

Film thicknesses, densities, and crystalline structures were evaluated from X-ray reflection (XRR) and grazing incidence X-ray diffraction (GI-XRD) patterns measured with a PANalytical X'pert Pro MPD X-ray diffractometer.

Morphology of the films was studied by an Hitachi S4800 field emission scanning electron microscope (SEM) and a Veeco Instruments Nanoscope V atomic force microscopy (AFM). Before SEM analysis, the samples were sputter-coated with a thin layer of Au metal or Pd/Pt metal alloy (Cressington 208HR Sputter Coater). AFM studies were carried out in tapping mode in air using a phosphorus-doped silicon probe (RTESP) delivered by Veeco Instruments. The scanning frequency was 0.5 or 1.0 Hz. A few wide scans were performed from different parts of the samples to confirm the uniformity of the surface. Final images were measured from a scanning area of $2 \times 2 \mu\text{m}^2$ and no image processing except flattening was performed. Roughness values were calculated as root-mean-square values (R_q). Composition and impurity levels of the films were analyzed by elastic recoil detection analysis (ERDA) by use of a 35 MeV $^{34}\text{Cl}^{7+}$ projectile ion beam.³²

Permittivity and current density of the films were measured on Al/ MgF_2 /ITO/glass capacitor structures with Al dot electrodes on top of the MgF_2 film. The Al dots, with an electrode area of $2.04 \times 10^{-7} \text{ m}^2$, were fabricated by electron-beam evaporation through a shadow mask. The permittivity of the films was measured using a HP 4284A precision LCR-meter at 1 MHz. The leakage current densities were measured with a Keithley 2400 SourceMeter.

Results and Discussion

Film Growth. ALD growth characteristics of the MgF_2 films were studied on the silicon substrates. Poor quality films were obtained at temperatures below 225 °C and above 400 °C, including weak adhesion and increased variation in film thickness. Therefore, the growth behavior of the MgF_2 film was studied in the deposition temperature range of 225–400 °C. All the deposited MgF_2 thin films passed the Scotch tape adhesion test. The self-limited nature of the novel ALD process was verified at 300 °C by varying $\text{Mg}(\text{thd})_2$ pulse time (Figure 1). TaF_5 pulse length and purge times were both kept constant

- (20) Ylilammi, M.; Ranta-aho, T. *J. Electrochem. Soc.* **1994**, *141*, 1278.
- (21) Pilvi, T.; Arstila, K.; Leskelä, M.; Ritala, M. *Chem. Mater.* **2007**, *19*, 3387.
- (22) Pilvi, T.; Puukilainen, E.; Arstila, K.; Leskelä, M.; Ritala, M. *Chem. Vap. Deposition* **2008**, *14*, 85.
- (23) Ugolini, D.; Kowalczyk, S. P.; McFeely, F. R. *J. Appl. Phys.* **1991**, *70*, 3899.
- (24) Four, S.; Devine, R. A. B.; Luo, E. Z.; Wilson, I. H.; Cheng, H. S. *J. Non-Cryst. Solids* **1999**, *254*, 139.
- (25) Devine, R. A. B.; Vallier, L.; Autran, J. L.; Paillet, P.; Leray, J. L. *Appl. Phys. Lett.* **1996**, *68*, 1775.
- (26) Hill, C. W.; Derderian, G. J.; Sandhu, G. *J. Electrochem. Soc.* **2005**, *152*, G386.
- (27) Lemonds, A. M.; Bolom, T.; Ahearn, W. J.; Gay, D. C.; White, J. M.; Ekerdt, J. G. *Thin Solid Films* **2005**, *488*, 9.
- (28) Lemonds, A. M.; White, J. M.; Ekerdt, J. G. *Surf. Sci.* **2003**, *538*, 191.
- (29) Hatanpää, T.; Ihanus, J.; Kansikas, J.; Mutikainen, I.; Ritala, M.; Leskelä, M. *Chem. Mater.* **1999**, *11*, 1846.
- (30) Putkonen, M.; Johansson, L. S.; Rauhalä, E.; Niinistö, L. *J. Mater. Chem.* **1999**, *9*, 2449.

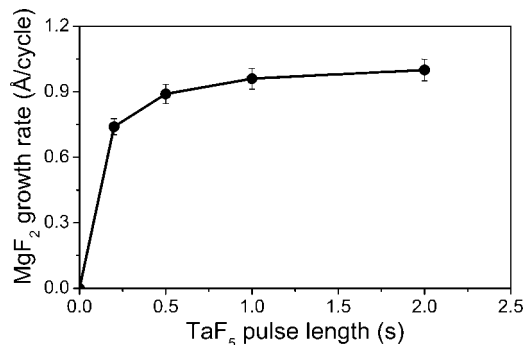
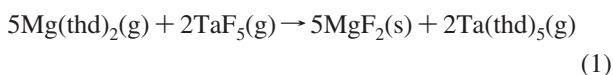


Figure 2. Growth rate of MgF₂ films on Si as a function of TaF₅ pulse length at 300 °C. Mg(thd)₂ pulse length was 2.0 s and purge times were 1.0 s.

at 1.0 s. Full saturation of the growth rate was obtained in a reasonably short time, within 2.0 s. In our previous ALD process of MgF₂ with Mg(thd)₂ and TiF₄ at 250 °C, the growth rate did not reach a constant level but slowly increased with the Mg(thd)₂ pulse time.¹⁵ The achieved growth rate of 1.0 Å/cycle (Figure 1) is less than 1.3 Å/cycle obtained by using Mg(thd)₂ and TiF₄ at 300 °C.

While the detailed reaction mechanism remains unidentified at the moment, the following net reaction (1) is suggested:



In the reaction of Mg(thd)₂ and TaF₅ (1), a solid MgF₂ is formed together with volatile Ta(thd)₅ and possibly some other volatile by-product. The key issue is how completely the impurities, especially H, O, C and Ta atoms, can be removed away from the final film.

The growth rate of MgF₂ film is shown in Figure 2 as a function of the TaF₅ pulse length at 300 °C. The Mg(thd)₂ pulse length was 2.0 s, and the purges were 1.0 s. Saturation of the growth rate was achieved after 1.0 s TaF₅ pulse. The nitrogen purges were also varied (data not shown) and 1.0 s purges were found sufficient for this ALD process.

The dependence of the film growth rate on the deposition temperature is illustrated in Figure 3. Pulse lengths were 2.0 s for Mg(thd)₂, and 1.0 s for TaF₅ as well as for the nitrogen purges. The maximum growth rate of 1.1 Å/cycle was achieved at 225–250 °C. At higher temperatures, the growth rate slowly decreased to 0.8 Å/cycle between 325 and 350 °C, until the growth rate rapidly decreased to 0.4 Å/cycle at 400 °C. Decreasing growth rate with an increase in deposition temperature was also observed earlier in ALD of MgF₂ from Mg(thd)₂ and TiF₄.¹⁵ A reason for the decrease of the growth rate can be that when the growth temperature is increased, the adsorption density of the fluorine source may decrease, which leads to the decrease of the growth rate as well.²¹ The monolayer thickness of MgF₂ is 1.53 Å, as calculated from the lattice parameters of the tetragonal crystal structure.¹⁵ The achieved maximum growth rate of 1.1 Å/cycle is therefore about 0.7 monolayer of MgF₂.

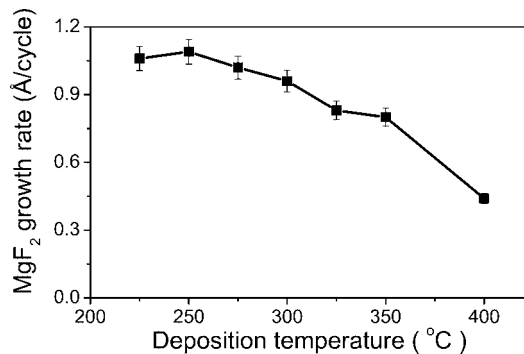


Figure 3. Growth rate of MgF₂ films on Si as a function of deposition temperature. Mg(thd)₂ pulse length was 2.0 s, whereas TaF₅ pulse and purges were 1.0 s.

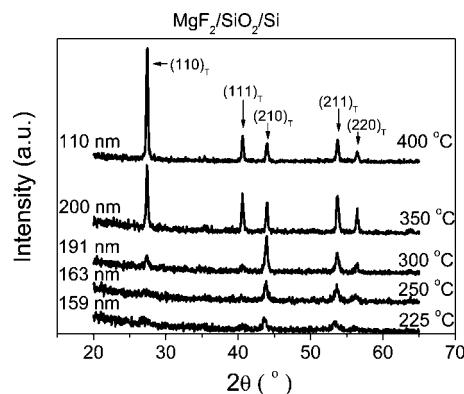


Figure 4. GI-XRD patterns of MgF₂ films grown on Si at 225–400 °C.

Film Properties. All the films were polycrystalline MgF₂ as determined by GI-XRD. Diffraction patterns of the films grown at 225–400 °C are depicted in Figure 4. Tetragonal (110), (111), (210), (211), and (220) reflections were obtained. The film grown at 225 °C showed only weak reflections; otherwise, the peaks were clearly seen, and the crystallinity of the films increased with the deposition temperature. For a deposition temperature of 300 °C, the (210) reflection is considerably stronger than the (110) and (111) reflections. For higher deposition temperatures (350 and 400 °C), the (110) reflections become the strongest ones, while the (111) and (210) reflections have about the same intensity. And at 400 °C the (110) reflection becomes about 4 times stronger than the (111) reflection.

The film morphology was analyzed by SEM and AFM (Figures 5–7). Inline with the XRD results, SEM images showed polycrystalline structure. While small grains were grown at 250–300 °C (Figure 5a,b), larger grains were formed at the higher deposition temperatures of 350 and 400 °C (Figure 5c,d). The morphology of the films was also determined from the cross-sectional SEM images (Figure 6). The growth mode of the film deposited at 250 °C (Figure 6a) is less columnar compared to that grown at 350 °C (Figure 6b) where a columnar structure of MgF₂ is clearly seen. Our previous ALD MgF₂ films,¹⁵ as well as evaporated MgF₂ films,⁵ were also grown in a columnar fashion on silicon. In contrast, our earlier ALD studies showed that CaF₂ grew in a more granular fashion than MgF₂ or LaF₃ on silicon at 350 °C when using TiF₄ as the fluorine source.³³ The

(31) Ylilammi, M.; Ranta-aho, T. *Thin Solid Films* **1993**, 232, 56.

(32) Putkonen, M.; Sajavaara, T.; Niinistö, L.; Keinonen, J. *Anal. Bioanal. Chem.* **2005**, 382, 1791.

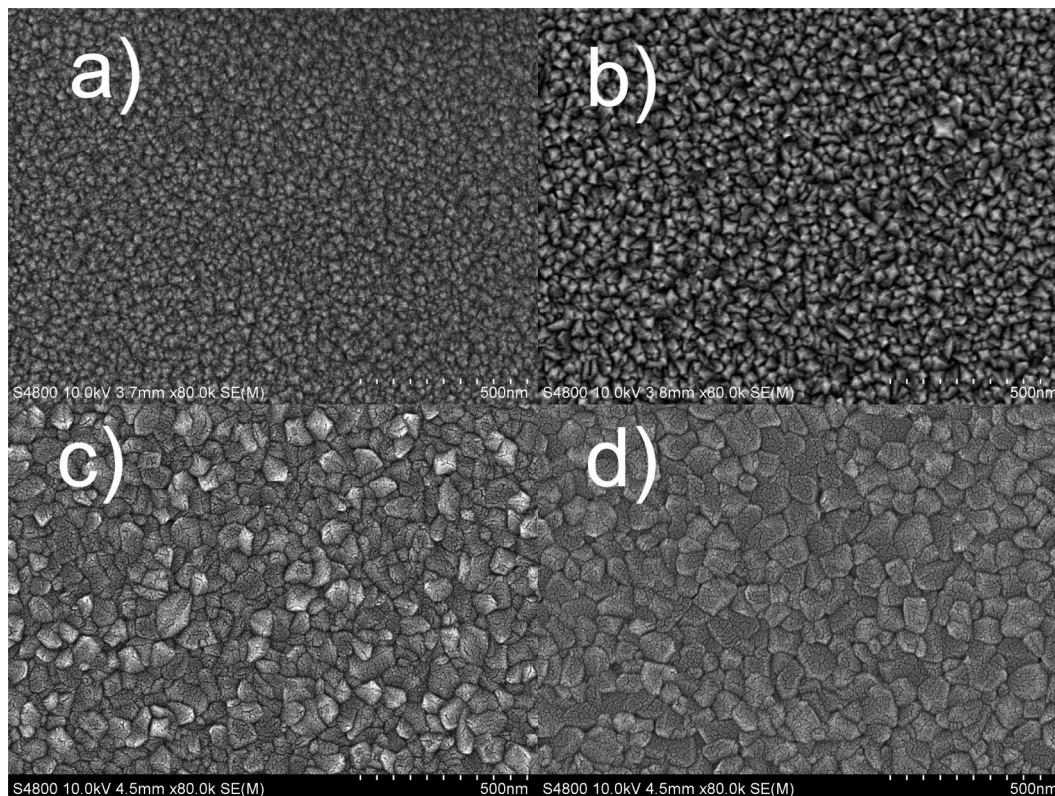


Figure 5. SEM images of MgF_2 films on Si. Deposition temperature and thickness of the films were (a) 250 °C, 163 nm, (b) 300 °C, 191 nm, (c) 350 °C, 200 nm, and (d) 400 °C, 110 nm.

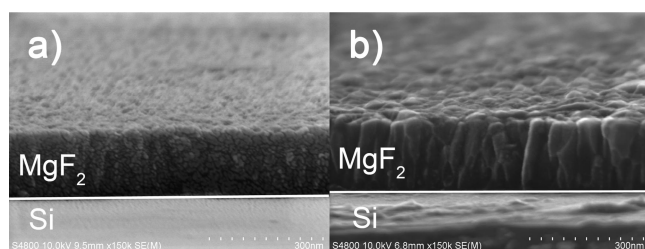


Figure 6. Cross-sectional SEM images of MgF_2 thin films deposited onto Si at (a) 250 °C and (b) 350 °C.

cross-sectional SEM images (Figure 6) show also that the surface roughness increased when the growth temperature was changed from 250 to 350 °C.

The surface roughness of MgF_2 films on the silicon substrate was measured by AFM (Figure 7). As expected, the roughness increased with increasing growth temperature. This increased surface roughness can be clearly seen in Figure 7. Even if the R_q roughnesses were above 7 nm with the films grown at 300–400 °C, still the roughness value of 8.7 nm of the 400 °C sample is considerably lower than that (23.0 nm) of the 147 nm thick MgF_2 film grown by ALD at 400 °C with TiF_4 as the fluorine source.¹⁵ This is an encouraging result because a rough film surface causes optical loss due to light scattering. Therefore, it seems possible to deposit uniform films with reasonable surface roughness by ALD even at high temperatures, which are often desired because purer ALD metal fluoride thin films are usually formed at high deposition temperatures.^{15,21,22}

The film compositions were determined by ERDA (Table 1). Generally the impurities in the films, namely, H, O, C, and Ta, decreased with increasing growth temperature, but at deposition temperature of 400 °C the impurity contents increased as compared to the film grown at 350 °C. The total impurity level (at. %) in the films was as follows: 19.3 at 225 °C, 8.4 at 250 °C, 2.8 at 300 °C, 0.6 at 350 °C, and 2.6 at 400 °C. The F/Mg ratio values were between 2.0 and 2.4, as seen in Table 1. Most of the films were fluorine-rich, especially the 225 °C sample with the ratio of 2.4, but on the other hand the 225 °C sample had also the total impurity level as high as 19.3 at. %.

Light transparency of the film depends heavily on the impurities, especially in the UV range.³⁴ MgF_2 films with highest quality were certainly achieved at growth temperatures of 300 and 350 °C, and therefore at these temperatures MgF_2 films were deposited also onto quartz for testing the UV light transparency. Figure 8 shows transmission spectra of MgF_2 films on quartz at 300 °C (dashed curve), at 350 °C (dash dot), and a reference spectrum of the bare quartz substrate (solid) in the wavelength range of 190–1100 nm. The transmission curve of the 350 °C sample drops below the pure quartz line only at 190–240 nm, and the transmission is clearly better than that in the 300 °C sample (Figure 8). The reason for the better light transmittance of the 350 °C sample is obviously the result of the lower impurity content (Table 1): 0.6 vs 2.8 at. %. The transparency of the 350 °C sample is even slightly better than that of the 350 °C sample

(33) Pilvi, T.; Ritala, M.; Leskelä, M.; Bischoff, M.; Kaiser, U.; Kaiser, N. *Appl. Opt.* **2008**, *47*, C271.

(34) CERAC Inc, *CERAC Coat. Mater. News* **2002**, *12*, 1; <http://www.cerac.com/pubs/CMNArchives.htm>.

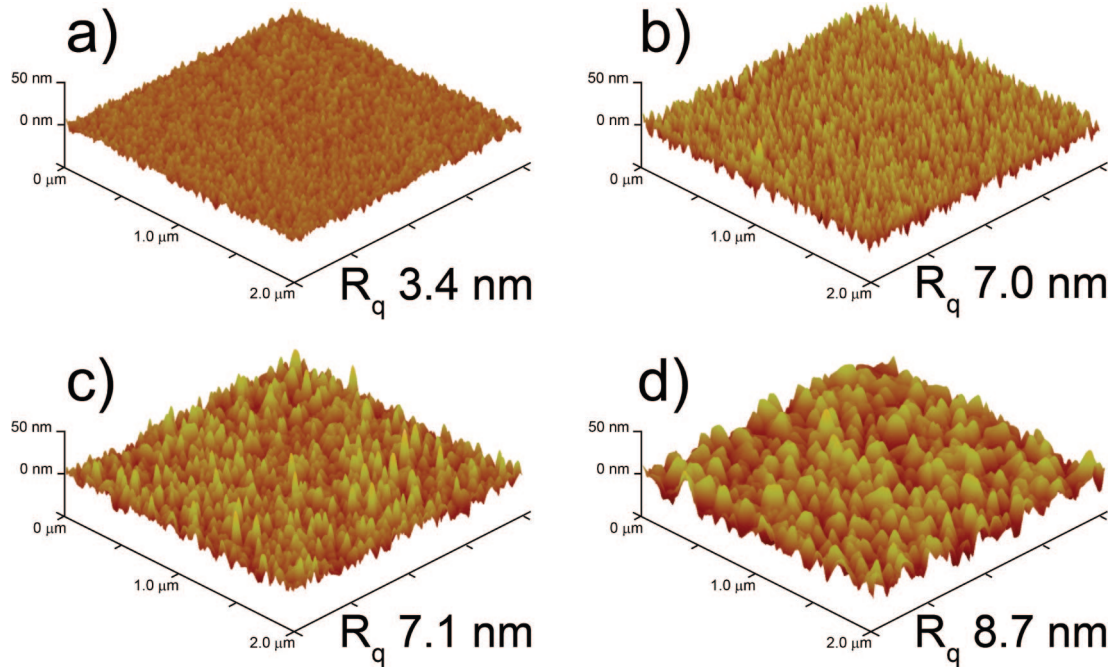


Figure 7. Tapping mode AFM images of MgF_2 thin films on Si. Deposition temperature and thickness of the film were (a) 250 °C, 163 nm, (b) 300 °C, 191 nm, (c) 350 °C, 200 nm, and (d) 400 °C, 110 nm.

Table 1. Composition (at. %) of MgF_2 Thin Films on SiO_2/Si at Different Deposition Temperatures as Determined by ERDA

	225 °C	250 °C	300 °C	350 °C	400 °C
F	56.9	61.8	65.1	67.7	66.1
Mg	23.8	29.8	32.0	31.7	31.3
O	6.0	2.2	1.2	0.3	1.5
Ta	1.4	1.2	0.5	0.1	0.2
C	1.8	1.3	0.5	<0.1	<0.1
H	10.1	3.7	0.6	0.2	0.9
F:Mg	2.4	2.1	2.0	2.1	2.1

deposited from $\text{TiF}_4 + \text{Mg}(\text{thd})_2$,¹⁵ which proves that the TaF_5 is a better fluorine source than TiF_4 .

Refractive indices of the films were measured from the films deposited onto Si substrates. The measured values with the growth temperatures were ($\lambda = 580$ nm) as follows: 1.38 at 225–250 °C, 1.37 at 275–325 °C, and 1.36 at 350–400 °C. Our results are very close to the reported bulk value of 1.378 ($\lambda = 589$ nm) for tetragonal MgF_2 .² The lower refractive indices than the bulk, obtained with the 350 °C and the 400 °C samples, are usually a result of the porous

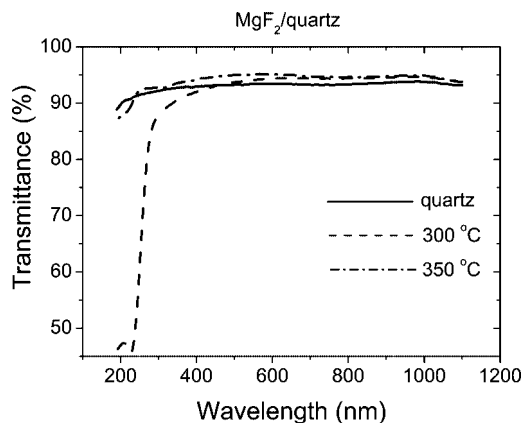


Figure 8. Transmittance spectra of a quartz substrate (solid curve), 130 nm thick MgF_2 film on quartz deposited at 300 °C (dashed), and 100 nm thick MgF_2 film on quartz grown at 350 °C (dash dot).

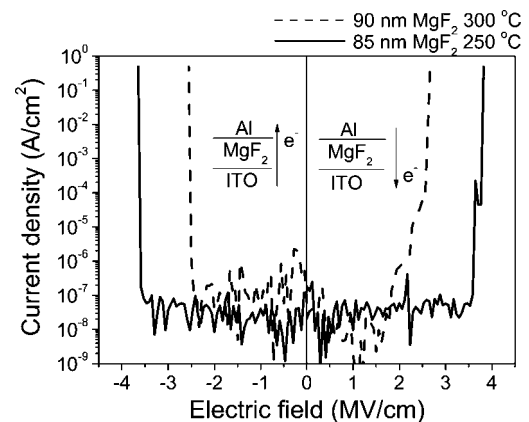


Figure 9. Leakage current densities vs electric field curves of Al/ MgF_2 /ITO capacitor structures. The films were grown at 250 °C (solid line) and 300 °C (dashed).

microstructure,³⁵ which can also be seen in Figures 5c and 5d. However, film densities of the films grown at 250–400 °C were all very close to the bulk value of 3.15 g/cm^3 for the tetragonal MgF_2 ,² as measured by XRR.

The electrical properties were measured for two films, deposited at 250 and 300 °C, in Al/ MgF_2 /ITO capacitor structures. The average permittivity obtained for a 85 nm thick film deposited at 250 °C was 4.3 at 1 MHz. The permittivity value for a 90 nm thick film grown at 300 °C was 5.0. These results are comparable with the reported value of 5.45 at 1 MHz,³⁶ as well as the permittivity of 4.9 at 10 kHz for the MgF_2 film grown by ALD at 250 °C from $\text{Mg}(\text{thd})_2 + \text{TiF}_4$.¹⁵ The leakage current density vs electric field is illustrated in Figure 9. The catastrophic breakdown occurred at -3.6 and $+3.8$ MV/cm for the film grown at

(35) Zuber, A.; Kaiser, N.; Stehle, J. L. *Thin Solid Films* **1995**, 261, 37.

(36) Jacob, M. V.; Krupka, J.; Mazierska, J.; Woods, G. S. *Mater. Sci. Eng., A* **2006**, 427, 175.

250 °C and -2.6 and $+2.7$ MV/cm for the film deposited at 300 °C. These breakdown fields are lower than what was achieved earlier in ALD of MgF_2 from $\text{Mg}(\text{thd})_2 + \text{TiF}_4$ at 250 °C, when the breakdown fields were -5.8 and $+4.4$ MV/cm for a 140 nm thick MgF_2 film.¹⁵ Hence, the ALD grown MgF_2 remains in the class of good insulators, despite its polycrystalline film structure (Figure 4). The leakage current density stayed below $<10^{-8}$ A/cm² in the film grown at 250 °C, and $<10^{-7}$ A/cm² at 300 °C before the breakdown (Figure 9).

Conclusion

Metal fluoride thin films were deposited for the first time by ALD using TaF_5 as the fluorine source. We have shown here that the novel fluorinating agent can be used for

depositing MgF_2 films, and the ALD type of film growth was verified at 300 °C. Dense and polycrystalline MgF_2 films were deposited at 225–400 °C. The films grew in columnar fashion onto silicon substrates. Films with low impurity levels and the best UV light transparency were achieved at the deposition temperature of 350 °C. Smoother and better transparency MgF_2 films were achieved at high growth temperature compared to MgF_2 films grown by ALD from $\text{TiF}_4 + \text{Mg}(\text{thd})_2$. The refractive indices were 1.36–1.38, and the permittivity of the film grown at 300 °C was 5.0. We believe that TaF_5 is an excellent choice for depositing also other metal fluorides of high quality.

CM800948K