Atomic layer deposition process with TiF_4 as a precursor for depositing metal fluoride thin films

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A novel atomic layer deposition process for the preparation of fluoride thin films in a temperature range of 225 °C–400 °C is introduced. The crystallinity, morphology, composition, thicknesses, refractive indices, and transmittance of the films are analyzed. Low impurity levels are obtained at 350 °C–400 °C with good stoichiometry. Refractive indices of 1.34–1.42 for MgF_2, 1.43 for CaF_2, and 1.57–1.61 for LaF_3 films are obtained.

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1. Introduction

Metal fluorides are interesting materials due to their good ultraviolet (UV) light transparency. Mainly physical vapor deposition methods have been used for the production of fluoride thin films [1–3]. Some fluorides have also been prepared by chemical vapor deposition (CVD) methods either from fluorinated metal precursors [4–6] or by use of separate fluorine precursors [7,8]. Atomic layer deposition (ALD) is one of the CVD techniques in which the film is grown by means of saturative surface reactions between alternately supplied precursors. Distinguishing it from the other CVD methods, in ALD the source vapors are pulsed into the reactor one at a time, separated by purging the reactor with an inert gas, e.g., nitrogen. Each precursor exposure step saturates the surface with a monolayer or more usually a submonolayer of that precursor. This results in a unique self-limiting film growth mechanism. One ALD cycle is repeated as many times as necessary to obtain the desired film thickness. Potential benefits of the ALD method compared with the other methods are film uniformity, excellent step coverage, precise thickness control, and high reproducibility [9].

The problem in depositing fluoride films by ALD has been the lack of a good fluoride source. The previously used fluoride precursor HF [10] etches glass and is not ideal for ALD. In this study, the films were deposited using a new relatively safe fluoride precursor TiF_4, which has a low vapor pressure, is a solid at room temperature, and can thus be readily and safely handled and removed from the reactor exhaust gases. It also fulfills the main requirements for an ALD precursor, i.e., good thermal stability, sufficient volatility, and high reactivity [9].

We present here a novel ALD process for depositing MgF_2, CaF_2, and LaF_3 thin films. Further examples can be seen in [11,12]. In this paper we evaluate the optical and structural properties of these fluoride thin films and compare them at a film growth temperature of 350 °C.

2. Experiment

A. Film Deposition

The films were grown in a hot-wall flow-type F120 ALD reactor (ASM-Microchemistry, Helsinki, Finland). All the films were deposited in a temperature range of 225 °C–450 °C. The pressure in the reactor was approximately 10 mbars. The films were deposited mainly on quartz and Si with native SiO_2. $Mg(thd)_2$ (thd = 2,2,6,6-tetramethyl-3,5-

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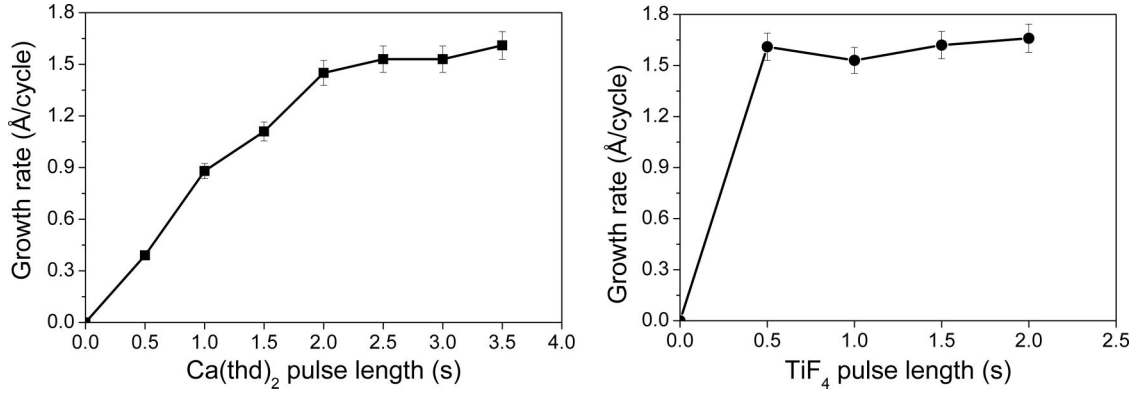

Fig. 1. Growth rate of CaF_2 films on silicon as a function of the $Ca(thd)_2$ and TiF_4 pulse lengths at 350 °C. The TiF_4 pulse and purge times were 1.0 s (on the left), and the $Ca(thd)_2$ pulse time was 2.5 s and the purge times were 1.0 s (on the right) [12].

heptanedionato = $C_{11}H_{19}O_2$), $Ca(thd)_3$ (Volatec Oy, Porvoo, Finland), and $La(thd)_3$ (Volatec Oy) were used as metal precursors and TiF_4 (Strem Chemicals, Newberryport, Massachusetts) as a fluoride precursor.

B. Film Characterization

Thicknesses and refractive indices of the films were determined from reflection and transmission spectra obtained with a Hitachi U2000 spectrophotometer in the wavelength range of 190–1100 nm. We used a fitting program, developed and described in [13], in analyzing the spectra. The error in the film thickness measurements was estimated to be ±5%. Another spectrometer used was a Lambda 850.

Film thicknesses, densities, and crystal structures were evaluated from x-ray reflection (XRR) and grazing-incidence x-ray diffraction (GI-XRD) patterns measured with a Bruker-axs D8 Advance x-ray diffractometer. Film thicknesses were analyzed by XRR only from the thinnest samples up to 40 nm; otherwise they were measured with UV–vis spectroscopy.

Film crystalline structure and morphology was studied with transmission electron microscopy (TEM) and scanning electron microscopy (SEM). For TEM studies a JEOL JEM 3010 was used and operated at 300 kV, with a point-to-point resolution of 0.21 nm. TEM cross-sectional sample preparation was carried out using standard techniques including mechanical polishing and Ar-ion thinning. For SEM studies Hitachi S4800 FESEM equipment was used. Before the SEM analysis, the samples were sputter coated with a thin Pd/Pt alloy (Cressington 208HR Sputter Coater). Composition and impurity levels of the films were analyzed by time-of-flight elastic recoil detection analysis (TOF-ERDA) by use of a 24 MeV $^{127}I^{5+}$ projectile ion beam [14].

3. Results and Discussion

A. Film Growth

Characteristic to ALD is that the film is grown through sequential saturative surface reactions. As an example, self-limitation of the novel CaF_2 ALD process is shown in Fig. 1. The growth rate of CaF_2 film saturates to approximately 1.6 Å/cycle after a 2.5 s $Ca(thd)_2$ pulse length and after a 0.5 s TiF_4 pulse length. Although the detailed reaction mechanism remains unknown at this point, the net reaction is believed to be

$$2\,Ca(thd)_2(g) + TiF_4(g) \rightarrow 2\,CaF_2(s) + Ti(thd)_4(g). \quad (1)$$

Quite similar growth behavior was observed also with MgF_2 [11] and LaF_3 thin films (results unpublished).

B. Film Properties

All the films passed the tape adhesion test. The films were polycrystalline as determined by GI-XRD. The crystallinity of the films increased with the deposition temperature as expected. XRD results obtained at 350 °C are shown in Fig. 2.

A TEM image of a MgF_2 film (Fig. 3) supports XRD results on crystallization of the film deposited at

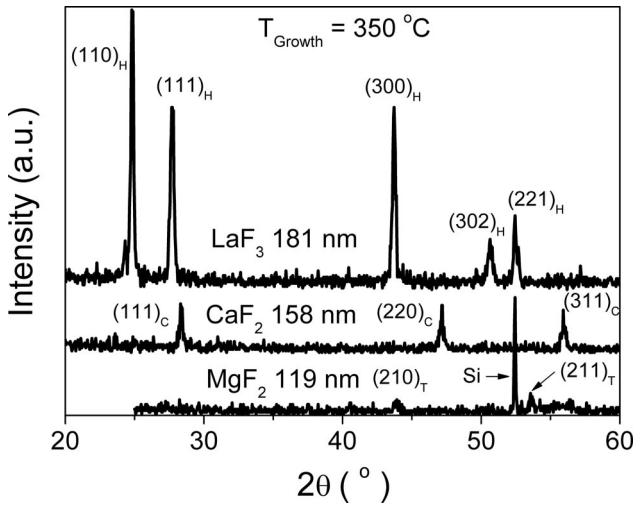

Fig. 2. GI-XRD patterns of MgF_2, CaF_2, and LaF_3 thin films deposited on silicon at 350 °C.

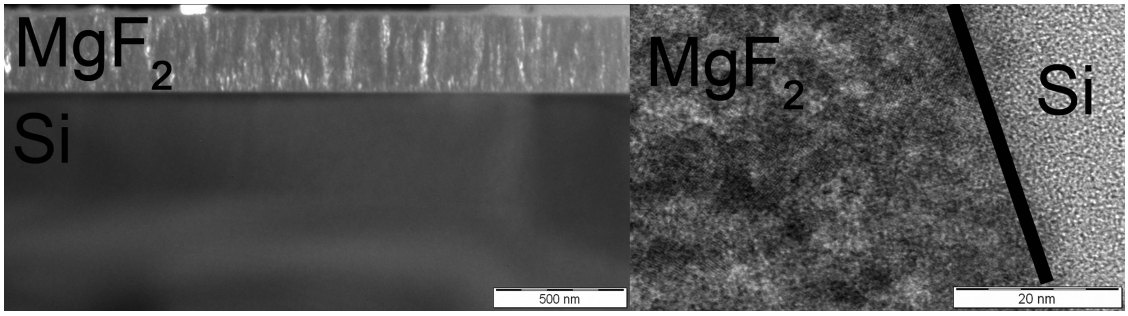

Fig. 3. Cross-sectional TEM images of approximately 280 nm thick MgF_2 thin film deposited on Si at 250 °C.

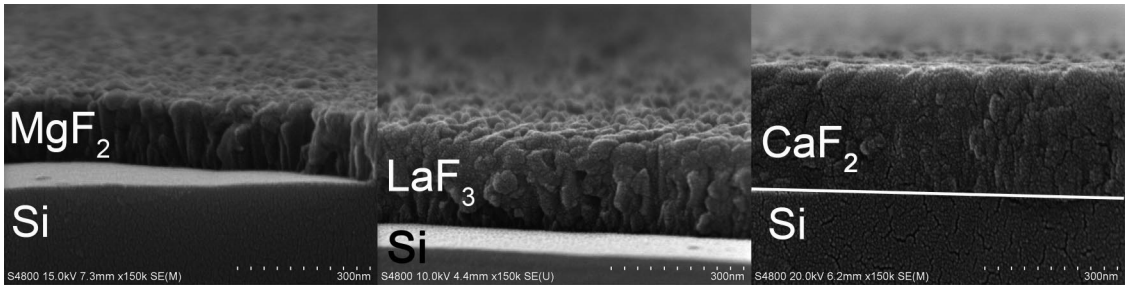

Fig. 4. Cross-sectional SEM images of MgF_2, LaF_3, and CaF_2 thin films deposited on Si at 350 °C.

250 °C. The structure of the film is columnar, but the columns are not uniform as seen in a dark-field image (Fig. 3, left). A high-resolution image of a near interface region between MgF_2 film and silicon shows clearly a polycrystalline film structure (Fig. 3, right).

The morphology of the films was analyzed from the cross-sectional SEM images (Fig. 4). MgF_2 grew more columnarly (left) than LaF_3 (center) or CaF_2 (right) at 350 °C. The results are in good agreement with evaporated MgF_2 thin films, which were reported to have columnar structure on silicon [15] and amorphous substrates [16]. As seen in Fig. 4, the LaF_3 thin film had the highest surface roughness of the fluoride films deposited at 350 °C.

Film compositions were determined by TOF-ERDA (Table 1). UV optics materials must have low levels of transition metal impurities or other elements that absorb in the UV range. It was reported that the impurity contents must be below 0.5% and in some cases even below 0.1% by weight [17]. The reported contents (Table 1) are averages found in the bulk of the films excluding the surface and interface regions. Total impurity contents (at. %) in the films decreased usually with increasing deposition temperature [11,12]. These low impurity levels indicate that the ligand exchange reaction (1) in the ALD process is efficient and proceeds close to completion.

Table 1. Compositions (at. %) of MgF_2, CaF_2, and LaF_3 Thin Films Deposited at 350 °C as Measured by TOF-ERDA

	MgF_2	CaF_2	LaF_3
F	66.7	65.5	70.9
Mg, Ca, La	32.7	32.8	25.6
O	0.3	0.7	1.4
Ti	0.2	0.8	0.5
C	<0.1	<0.1	0.9
N	<0.1	<0.1	0
H	<0.1	0.1	0.8
B	0	<0.1	0
F:metal	2.0	2.0	2.8

Refractive indices were evaluated from reflection spectra because most of the films were deposited on silicon. Refractive indices of 1.34–1.42 for MgF_2, 1.43 for CaF_2, and 1.57–1.61 for LaF_3 were obtained at $\lambda = 580$ nm.

Figure 5 depicts transmission spectra of MgF_2 (dotted curve), CaF_2 (dashed curve), and LaF_3 (dashed–dotted curve) films grown on quartz at 350 °C, and a

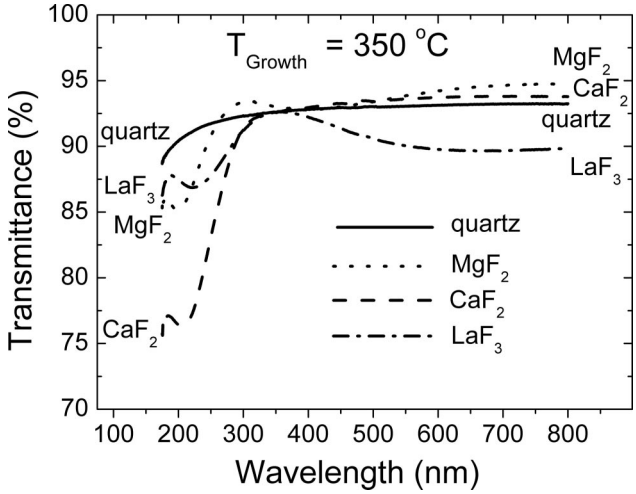

Fig. 5. Transmission spectra of a quartz substrate and 155 nm MgF_2 film, 143 nm CaF_2 film, and 106 nm LaF_3 film on quartz deposited at 350 °C.

reference spectrum of bare quartz (solid curve) in the wavelength range of 175–800 nm. MgF_2 film had the best transmittance values of 93% at 300 nm and 86% at 260 nm. The main reason for the best performance of the MgF_2 sample can be the lower impurity content: 0.6 versus 1.7 for CaF_2 and 3.5 at. % for LaF_3 (Table 1). Although the impurity levels in the films were quite low according to TOF-ERDA, they are not low enough for really high transmission in the deep UV.

4. Conclusion

Novel ALD processes for depositing fluoride thin films have been introduced. The films were grown between 225 °C and 450 °C. $Mg(thd)_2$, $Ca(thd)_2$, and $La(thd)_3$ were used as metal precursors, and TiF_4 was used as a novel fluoride precursor. The films were polycrystalline and MgF_2 grew more columnarly than LaF_3 and CaF_2 on silicon. Good stoichiometry was obtained at 350 °C–400 °C with low impurity levels. MgF_2 film had the best transmittance of the fluoride films deposited at 350 °C. In summary, the results demonstrate that ALD can be a suitable method for depositing optical fluoride thin films.

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