Atomic layer deposition process with TiF$_4$ as a precursor for depositing metal fluoride thin films

Tero Pilvi,¹,* Mikko Ritala,¹ Markku Leskelä,¹ Martin Bischoff,² Ute Kaiser,³ and Norbert Kaiser⁴

¹Department of Chemistry, P.O. Box 55, University of Helsinki, FI-00014 Helsinki, Finland
²Institute of Applied Physics, Friedrich-Schiller-University, Max-Wien-Platz 1, 07743 Jena, Germany
³Central Facility of Electron Microscopy, Electron Microscopy Group of Materials Science, University of Ulm, Albert Einstein Allee 11, D-89069 Ulm, Germany
⁴Fraunhofer Institut für Angewandte Optik und Feinmechanik, Albert-Einstein-Straße 7, D-07745 Jena, Germany

*Corresponding author: Tero.Pilvi@helsinki.fi

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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. © 2008 Optical Society of America

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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-
heptanedionato = C\textsubscript{17}H\textsubscript{19}O\textsubscript{2}), Ca(thd)\textsubscript{3} (Volatex Oy, Porvoo, Finland), and La(thd)\textsubscript{3} (Volatex Oy) were used as metal precursors and TiF\textsubscript{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 spectrosopy.

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 \textsuperscript{127}I\textsuperscript{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\textsubscript{2} ALD process is shown in Fig. 1. The growth rate of CaF\textsubscript{2} film saturates to approximately 1.6 Å/cycle after a 2.5 s Ca(thd)\textsubscript{2} pulse length and after a 0.5 s TiF\textsubscript{4} pulse length. Although the detailed reaction mechanism remains unknown at this point, the net reaction is believed to be

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2 \text{Ca(thd)}_2(g) + \text{TiF}_4(g) \rightarrow 2 \text{CaF}_2(s) + \text{Ti(thd)}_4(g).
\]

Quite similar growth behavior was observed also with MgF\textsubscript{2} [11] and LaF\textsubscript{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\textsubscript{2} film (Fig. 3) supports XRD results on crystallization of the film deposited at

![Fig. 2. GI-XRD patterns of MgF\textsubscript{2}, CaF\textsubscript{2}, and LaF\textsubscript{3} thin films deposited on silicon at 350 °C.](image-url)
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.

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
reference spectrum of bare quartz (solid curve) in the wavelength range of 175–800 nm. MgF₂ 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 MgF₂ sample can be the lower impurity content: 0.6 versus 1.7 for CaF₂ and 3.5 at. % for LaF₃ (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 TiF₄ was used as a novel fluoride precursor. The films were polycrystalline and MgF₂ grew more columnarly than LaF₃ and CaF₂ on silicon. Good stoichiometry was obtained at 350 °C–400 °C with low impurity levels. MgF₂ 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.

References