Novel ALD Process for Depositing CaF_2 Thin Films

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Metal fluorides, like CaF_2, are interesting dielectric materials which are optically transparent over a wide wavelength range down to the vacuum ultraviolet regime. In addition, CaF_2 has a low refractive index and is therefore an attractive material for optical filters. In this study thin films of calcium fluoride were deposited by atomic layer deposition (ALD) at a temperature range of 300−450 °C using TiF_4 as a new convenient fluoride precursor. $Ca(thd)_2$ was used as a calcium precursor. Films were analyzed by X-ray diffraction/reflection (XRD/XRR), field emission scanning electron microscopy (FESEM), time-of-flight elastic recoil detection analysis (TOF-ERDA), and UV−vis spectrophotometer. The growth rate of the film was 1.6 Å/cycle, which is 4 times higher than that published before for CaF_2 ALD. All films were polycrystalline and the impurity levels were low. The refractive index was 1.43 and the permittivity 6.6. This novel ALD process using the new fluoride precursor TiF_4 is likely more general and applicable also to other metal fluorides.

Introduction

Calcium fluoride is a wide band gap material ($E_g = 12.1$ eV) which is optically transparent over a wide wavelength range from mid-infrared to vacuum ultraviolet.[1] Due to its wide transmission range, CaF_2 is useful for optical components such as UV laser systems, lenses, prisms, and windows.[2,3] In addition, CaF_2 has a low refractive index and is therefore useful for optical multilayers and filters.[4,5] Optical filters consist of alternating layers of high and low refractive index materials, and a larger difference in refractive indices means that fewer layers are needed for a given optical performance.

Lattice mismatch between CaF_2 and Si is only 0.6% at room temperature[6] and 1.6% at 600 °C,[7] so CaF_2 thin films can be used as growth templates for crystalline silicon[8,9] and as buffer layers for epitaxial layers on silicon, e.g., $Fe_3Si/CaF_2/Si(111)$,[10] α-Fe/CaF_2/Si(111),[11,12] Fe/Cu/CaF_2/Si(111),[13] $CeO_2/CaF_2/Si(111)$,[14] ZnO/CaF_2/Si(111),[15] diamond/Ir/CaF_2/Si(111),[16] Cu/CaF_2/Si(111),[17] Al,Cu/CaF_2/Si(111),[18] Co/CaF_2-(110)/Si(001),[19] and $MnF_2/CaF_2/Si(111)$.[20] Epitaxial CaF_2 thin films have been deposited not only onto Si but also onto copper.[21]

Selective adsorption using CaF_2 masks on a stepped Si(111) has been observed for a variety of molecules, e.g., ferrocene, and is emerging as a general method for growing one-dimensional nanostructures of transition metals and other materials using chemical vapor deposition (CVD).[22] CaF_2 buffer layer has also been used between a glass support and a Pd film in hydrogen sensor to reduce the internal stresses and to improve the mechanical stability of the sensor.[23]

Mainly physical vapor deposition techniques have been used for the production of CaF_2 thin films, e.g., molecular

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beam epitaxy (MBE),[1,7,8,10,24−35] electron-beam evaporation (EBE),[17,36−40] thermal evaporation,[9,41−45] r.f. magnetron sputtering,[46] and pulsed laser deposition.[2] Purdy et al.[47] have used CVD technique for depositing CaF_2 films. Some other fluorides have also been prepared by CVD methods either from fluorinated metal precursors (e.g., hexafluoroacetylacetonate)[47−53] or by use of separate fluorinating agents NF_3,[50,54−57] HF,[58] or SF_6.[59,60] Atomic layer deposition (ALD) method is one of the CVD techniques and it is becoming more popular especially in depositing thin films for microelectronic applications.[61] However, only one study of CaF_2 ALD[4] has been reported prior to this paper. In that case $Ca(thd)_2$ and HF were used as precursors.

Benefits of the ALD method compared to the other methods are film uniformity, precise thickness control, excellent step coverage, and high reproducibility.[62] Films can also be deposited routinely even onto curved substrates. The problem in depositing fluoride thin films by ALD has been a lack of a good fluoride source. The previously used fluoride precursor HF was obtained by thermally decomposing NH_4F,[4] but HF is an aggressive chemical which for example etches silicates and is therefore not ideal for ALD. Hence, there is a clear need for a better fluoride precursor.

In this paper, a novel method for depositing CaF_2 thin films by ALD is described based on a relatively safe fluoride precursor TiF_4, which fulfills the main requirements for ALD precursor, i.e., sufficient volatility, high reactivity, and good thermal stability.[62] TiF_4 is a solid at room temperature and can thus be readily and safely handled and removed from the reactor exhaust gases. So far only one study has been reported using TiF_4 in ALD, but in that case TiF_4 was used as a titanium source for TiO_2, not as a fluoride precursor.[63] In the present work $Ca(thd)_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionato = $C_{11}H_{19}O_2$) is used as a cation precursor. $Ca(thd)_2$ has been used a few times in ALD processes, e.g., for depositing CaF_2,[4] CaS,[64] and $CaCO_3$[65] at temperatures between 200 and 450 °C. The present process is suggested and hoped to proceed with the following overall ligand exchange reaction:

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

The reaction of $Ca(thd)_2$ and TiF_4 results in a solid CaF_2 deposit and volatile $Ti(thd)_4$. Possibly also other volatile byproducts may form, e.g., $TiF_x(thd)_{4-x}$, where x is 0−3. The key question is how completely the thd ligands and Ti atoms can be eliminated from the film.

Experimental Section

Film Deposition. The films were grown in a hot-wall flow-type F-120 ALD reactor (ASM-Microchemistry Ltd.) between 300 and 450 °C. The overall pressure in the reactor was about 1 kPa. CaF_2 thin films were deposited mainly onto 5 × 5 cm^2 native SiO_2-covered Si(100) and Si(111). Other substrates were 5 × 5 cm^2 borosilicate glass, sputtered indium tin oxide (ITO) film, and 2 × 5 cm^2 quartz substrates. $Ca(thd)_2$ (Volatec Oy, Finland) was evaporated from an open glass boat at 190 °C and TiF_4 (Strem Chemicals Inc.) at 145 °C inside the reactor. $Ca(thd)_2$ and TiF_4 pulse times were 0.5−3.5 and 0.5−2.0 s. Nitrogen (99.9995% NITROX UHPN 3000 nitrogen generator) was used as a carrier and a purge gas. And 0.5−1.0 s nitrogen purge periods were used after both precursor pulses to separate the precursors in the gas phase and to remove the gaseous reaction byproducts.

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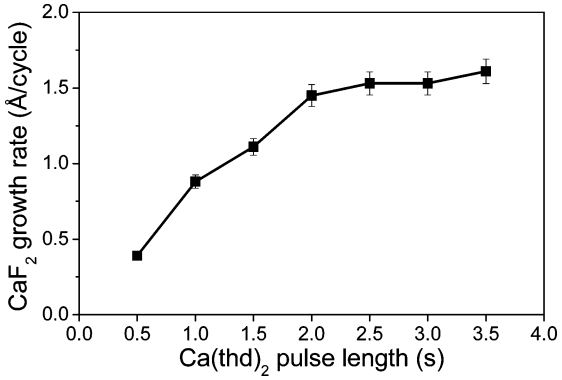

Figure 1. Growth rate of CaF_2 films on silicon as a function of $Ca(thd)_2$ pulse length at 350 °C. TiF_4 pulse and purge times were 1.0 s.

Film Characterization. Film thicknesses, densities, and crystal structures were evaluated from XRR and grazing incidence (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.

Thicknesses and refractive indices of the CaF_2 thin films were determined from reflection (or transmission) spectra obtained with a Hitachi U2000 spectrophotometer in the wavelength range of 370−1100 nm. A fitting program developed and described by Ylilammi and Ranta-aho[66] was used to analyze the spectra. The error in the thickness measurements was estimated to be ±5%.

Film morphology was studied by a Hitachi S4800 FESEM. Before SEM analysis the samples were sputter-coated with Pd/Pt alloy (Cressington 208HR Sputter Coater). Composition and impurity levels of the films were analyzed by TOF-ERDA using 24 MeV $^{127}I^{5+}$ projectile ion beam.[67]

Al/CaF_2/ITO/glass capacitors were prepared by depositing ca. 100 nm thick Al top electrode dots with an area of 2.04×10^{-7} m^2 on the top of CaF_2 films by EBE through a shadow mask. Permittivities of the films were measured using a HP 4284A precision LCR-meter at 10 kHz. A Keithley 2400 SourceMeter was used for measuring leakage current densities. All electrical properties of the films were measured at room temperature.

Results and Discussion

Film Growth. CaF_2 film growth characteristics were mainly studied on silicon substrate. Self-limitation of the new ALD process was proven at 350 °C by varying $Ca(thd)_2$ pulse time (Figure 1). In these experiments the TiF_4 pulse as well as the purge times were 1.0 s. As seen in Figure 1, the growth rate saturates to about 1.6 Å/cycle after 2.5 s $Ca(thd)_2$ pulse length. This is significantly longer pulse time compared to that of the earlier published CaF_2 ALD process[4] where the pulse length was only 0.2 s, but now the growth rate is also 4 times higher. From the crystal structure and lattice parameters (for a cubic CaF_2 $a = 5.46$ Å)[68] one may estimate a thickness of 2.73 Å for a monolayer of cubic CaF_2. So the growth rate of 1.6 Å/cycle corresponds to about 0.6 monolayer of CaF_2.

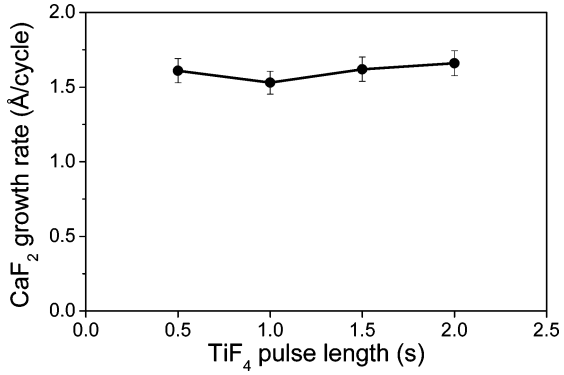

Figure 2. Growth rate of CaF_2 films as a function of TiF_4 pulse length at 350 °C. $Ca(thd)_2$ pulse time was 2.5 s and purge time 0.5 s.

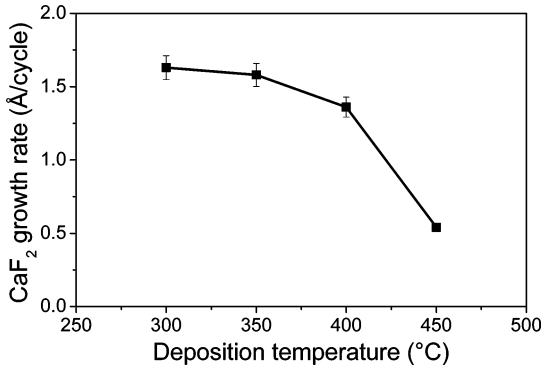

Figure 3. Growth rate of CaF_2 films as a function of deposition temperature. $Ca(thd)_2$ pulse length was 2.5 s whereas TiF_4 pulse and purge times were 0.5 s.

Figure 2 shows the CaF_2 growth rate as a function of the TiF_4 pulse length at 350 °C. The $Ca(thd)_2$ pulse length was 2.5 s. Saturation of the growth rate was achieved already with 0.5 s pulse time of the anion precursor TiF_4. Purge times were also varied (not shown here) and 0.5 s was found to be sufficient.

The influence of the temperature on the growth rate was investigated by varying the reactor temperature while keeping all the other growth parameters constant (Figure 3). Pulse lengths of 2.5 s for the $Ca(thd)_2$ and 0.5 s for the TiF_4 were applied. The purge times were 0.5 s. Poor quality films were obtained at 250 °C including weak adhesion between the film and the silicon substrate. The highest growth rates of about 1.6 Å/cycle were achieved at 300−350 °C. While going to higher deposition temperatures, the growth rate decreased first slowly to 1.36 Å/cycle at 400 °C and then rapidly to 0.54 Å/cycle at 450 °C. Decreasing growth rate with increasing deposition temperature was also observed earlier in the CaF_2 ALD from $Ca(thd)_2$ and HF.[4]

The highest growth rate in the present process is 4 times higher than that obtained by the HF-based process. Accordingly, the adsorption density of $Ca(thd)_2$ must also be 4 times higher. Reaching such a high adsorption density likely requires that some of the thd ligands are removed already during the $Ca(thd)_2$ pulse, as suggested in Figure 4 a. The preceding TiF_4 pulse has left TiF_x adsorbed on the surface of a previously deposited CaF_2. The incoming $Ca(thd)_2$ first reacts with TiF_x forming solid CaF_2 and volatile $Ti(thd)_4$. After $Ca(thd)_2$ has consumed all TiF_x on the surface, $Ca(thd)_2$ still adsorbs on top of the freshly formed solid CaF_2

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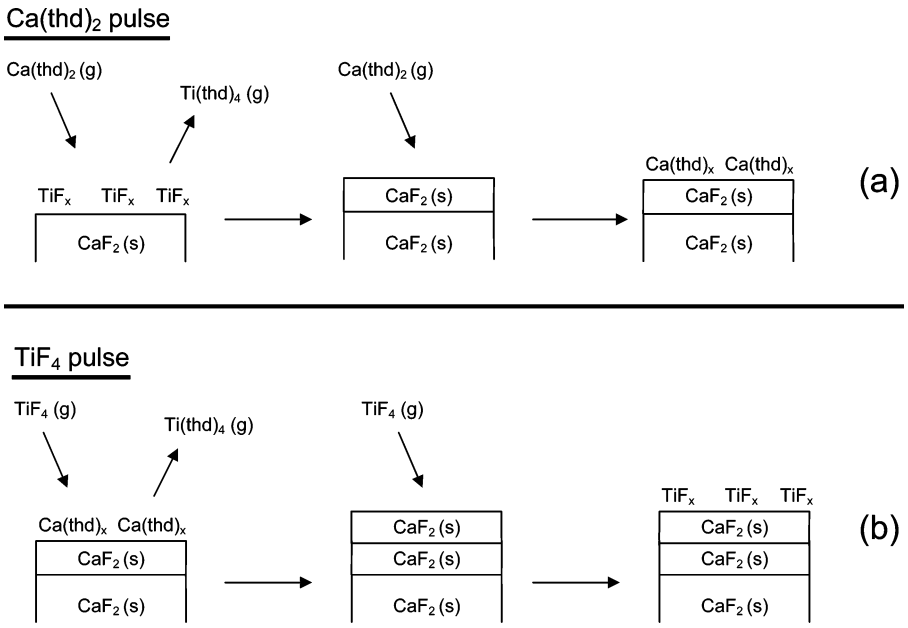

Figure 4. Suggested reaction schemes in CaF_2 ALD during (a) $Ca(thd)_2$ pulse and (b) TiF_4 pulse.

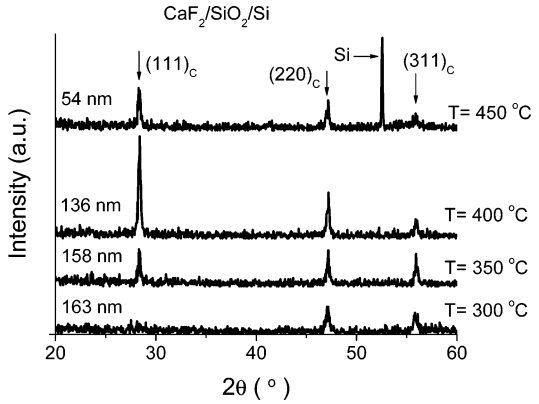

Figure 5. GI-XRD patterns of CaF_2 thin films grown at temperatures between 300 and 450 °C.

and the surface becomes covered by adsorbed $Ca(thd)_x$. Then during the TiF_4 pulse TiF_4 reacts with $Ca(thd)_x$ and volatile $Ti(thd)_4$ and solid CaF_2 are formed, as reaction scheme (b) in Figure 4 depicts. Once TiF_4 has reacted with all $Ca(thd)_x$ on the surface, TiF_x adsorbates are formed on top of the deposited solid CaF_2. This leads to the same situation as where scheme (a) started. In summary, CaF_2 is formed in both subreactions during one ALD cycle. Such a mechanism could explain the high, 1.6 Å/cycle, growth rate of the CaF_2 film. On the other hand, when the deposition temperature is increased, the adsorption density of TiF_x may decrease, leading to the decrease of the growth rate. $Ca(thd)_2$ has been reported to be stable up to as high temperature as 590 °C, but some decomposition was detected already at 450 °C when depositing $CaCO_3$ on soda lime glass.[65] One possibility for the high growth rate could also be that TiF_x catalyzes $Ca(thd)_2$ decomposition as long as TiF_x remains on the surface.

Film Properties. All the films were polycrystalline calcium fluoride as determined by XRD. Figure 5 depicts the diffraction patterns obtained from CaF_2 thin films grown between 300 and 450 °C. The films were randomly oriented and showed (111), (220), and (311) reflections at all

Table 1. Composition (at. %) of CaF_2 Thin Films Deposited at Different Temperatures as Determined by TOF-ERDA

	300 °C	350 °C	400 °C	450°C
F	65.7	65.5	65.4	60.2
Ca	32.2	32.8	32.5	30.6
O	0.8	0.7	0.7	5.5
Ti	0.8	0.8	0.7	0.2
C	0.1	<0.1	0.5	1.0
N	<0.1	<0.1	<0.1	<0.1
H	0.2	0.1	0.2	1.3
B	<0.1	<0.1	0	1.0
F:Ca	2.0	2.0	2.0	2.0

temperatures; only at 300 °C the (111) reflection was missing. Crystallinity of the films increased with the deposition temperature. It must be noted that the film grown at 450 °C is much thinner than the others, which likely explains the decrease in XRD intensities.

Film morphology was analyzed by SEM (Figure 6 and 7). In line with XRD, SEM images illustrated polycrystalline film structure, though with just small grains in the film deposited at 300 and 350 °C (Figures 6a and 6b). Larger grains were seen in the films grown at higher temperatures (Figures 6c and 6d). The grain size looks larger at 400 °C than at 450 °C (Figures 6c and 6d), but this is again most probably due to the larger film thickness, 136 nm vs 54 nm. A cross-section SEM image of CaF_2 film on silicon substrate is illustrated in Figure 7. Small granular grains can be seen in the film deposited at 300 °C. MBE deposited CaF_2 films were reported to have a granular structure on silicon.[7] Evaporated CaF_2 and LiF films were also reported to grow granularly on amorphous substrates, whereas MgF_2 and LaF_3 films were mentioned to have columnar structure.[44]

Densities of the films deposited between 300 and 450 °C were 2.9−3.1 g/cm^3 as measured by XRR. These are very close to the CaF_2 bulk density of 3.18 g/cm^3.[68] Roughnesses of the films deposited at 350 °C were correlated with the film thicknesses: 0.8 and 1.7 nm for 7.4 and 40 nm thick films, respectively.

Purity of the optical films is very important because impurities can cause absorbance to the film. In this work

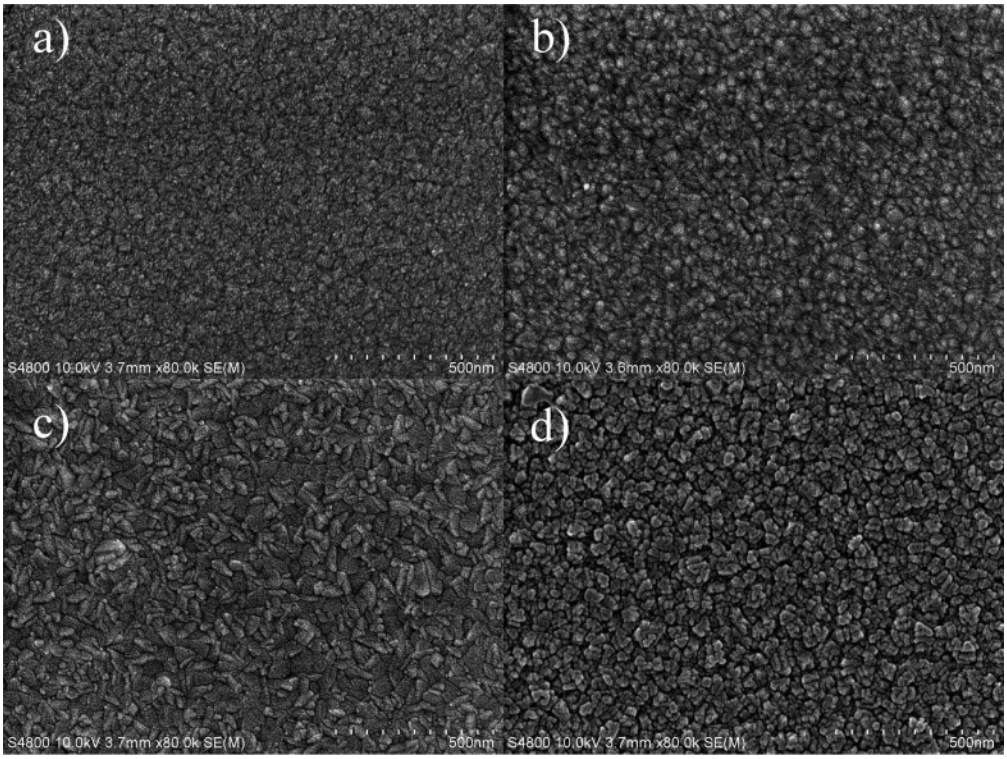

Figure 6. SEM images of CaF_2 thin films. Deposition temperatures and thicknesses of the films were (a) 300 °C, 163 nm, (b) 350 °C, 158 nm, (c) 400 °C, 136 nm, and (d) 450 °C, 54 nm.

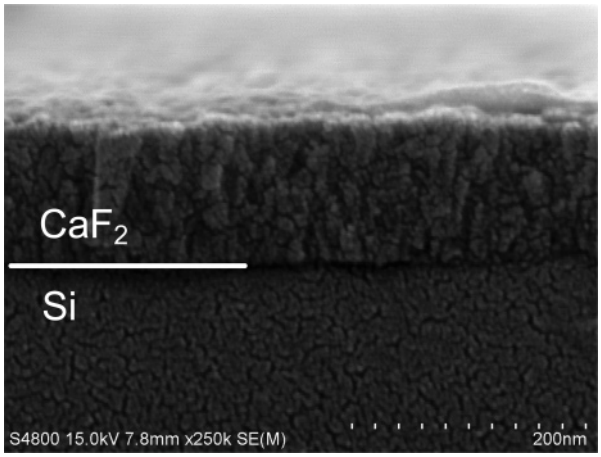

Figure 7. Cross-section SEM image of $CaF_2/SiO_2/Si$. Deposition temperature and thickness of the film were 300 °C and 163 nm.

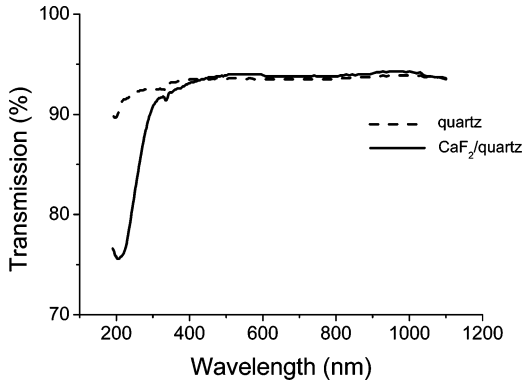

Figure 8. Transmission spectra of a quartz substrate and a CaF_2 film on quartz. Thickness of the CaF_2 film deposited at 350 °C was 143 nm.

film compositions were analyzed by TOF-ERDA (Table 1). The reported concentrations are averages found in the films excluding the surface and interface regions. F:Ca stoichiometry was approximately 2.0. All impurity levels of the films were less than 1.0 at. % when the deposition temperature was 400 °C or less. At 400 °C the carbon content increased from 0.1 to 0.5 at. %, which was also achieved in the earlier CaF_2 ALD process as measured by the Rutherford backscattering method.[4] $Ca(thd)_2$ precursor was apparently slightly decomposing at 450 °C because oxygen and carbon impurities increased substantially. Boron impurities most likely come from the borosilicate glass substrate. The low impurity contents in the films indicate that the suggested ligand exchange reaction (1) is indeed efficient and goes close to a completion.

Refractive indices of the films were evaluated from the reflection spectra because most of the films were deposited onto silicon. Low refractive index of 1.43 (at $\lambda = 580$ nm) was obtained in films deposited between 300 and 450 °C. This is very close to the bulk value of the cubic CaF_2, 1.434 at 589 nm.[68]

Figure 8 depicts a transmission spectrum of a 143 nm CaF_2 film on quartz (solid line) and a reference spectrum of a bare quartz substrate (dash line). In the wavelength range of 450−1100 nm the transmission of the CaF_2 film is at the same level as the quartz substrate, but transmission drops considerably below 400 nm. Though the impurity levels of the films were reasonably low according to TOF-ERDA, these levels were obviously not low enough for high UV transmission.

Electrical characteristics of the films were measured from $Al/CaF_2/ITO$ capacitor structures where the CaF_2 film was about 200 nm thick. The average permittivity obtained for

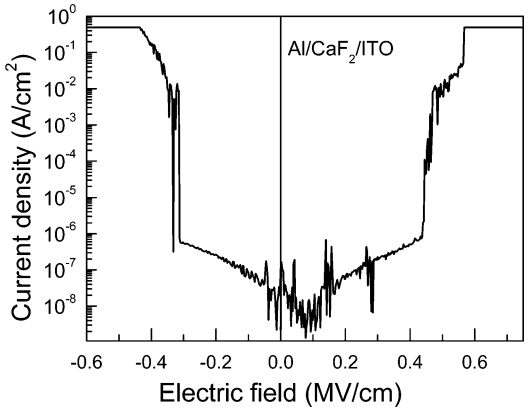

Figure 9. Leakage current density vs electric field curves of Al/CaF_2/ITO capacitors. Thickness of the CaF_2 film grown at 350 °C was 200 nm.

the CaF_2 film grown at 350 °C was 6.6, which is close to the bulk value of 6.81[68] and 7.0 reported earlier for ALD-made CaF_2 films.[4] Leakage current density of the film versus electric field is illustrated in Figure 9. Breakdown occurred at electric fields of −0.31 and +0.43 MV/cm. This is better than +0.0013 MV/cm achieved earlier with ALD CaF_2.[4] Before the breakdown the leakage current density was less than 10^{-7} A/cm^2, which is better than 10^{-6} A/cm^2 reported for an evaporated CaF_2 film.[41] Leakage current density values were also significantly better than those earlier achieved with ALD[4] in a similar capacitor structure and with almost the same film thickness. Anyhow, it still looks like that the CaF_2 film is not a good insulator even though it is a wide band gap material. This is probably due to the impurities and the polycrystalline structure of CaF_2 film.

Conclusion

We have proven here that the suggested novel ALD process for depositing CaF_2 thin films works better than the earlier CaF_2 ALD process. The films were deposited from a new relatively safe fluoride precursor TiF_4 and $Ca(thd)_2$ between 300 and 450 °C. The growth properties were studied and the highest growth rates of about 1.6 Å/cycle were achieved at 300−350 °C. The CaF_2 films seemed to grow granularly on SiO_2/Si at 300 °C. The films were polycrystalline and their densities were close to the bulk value. The grain size of the films enlarged with increasing deposition temperature as expected. The impurity levels were low and the F:Ca ratio was approximately 2.0. Low refractive index of 1.43 was achieved at all deposition temperatures, but the transmission decreased rapidly with decreasing wavelength in the UV range. The electrical properties were also studied and the permittivity of the CaF_2 film grown at 350 °C was 6.6. Leakage current densities less than 10^{-7} A/cm^2 were obtained in the Al/CaF_2/ITO capacitors before breakdown. We believe that this novel ALD process using the new fluoride precursor TiF_4 is a useful method also for the preparation of other metal fluoride thin films with good quality.

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