

**Atomic Layer Deposition for optical applications:
metal fluoride thin films
and novel devices**

Tero Pilvi

Laboratory of Inorganic Chemistry
Department of Chemistry
Faculty of Science
University of Helsinki
Finland

Academic Dissertation

To be presented, with the permission of the Faculty of the Science of the University of Helsinki for public criticism in Auditorium A110 of the Department of Chemistry, A. I. Virtasen aukio 1, on the 5th of December 2008, at 12 noon.

Helsinki 2008

Supervisors

Professor Mikko Ritala

and

Academy Professor Markku Leskelä

Laboratory of Inorganic Chemistry
Department of Chemistry
University of Helsinki
Helsinki, Finland

Reviewers

Dr. Markku Ylilammi
Thin Film Component
VTT Micro and Nanoelectronics
Espoo, Finland

Dr. Karol Fröhlich
Institute of Electrical Engineering
Slovak Academy of Sciences
Bratislava, Slovak Republic

Opponent

Dr. Jeffrey W. Elam
Argonne National Laboratory
Energy Systems Division
Argonne, Illinois, USA

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ISBN 978-952-92-4814-8 (paperback)

ISBN 978-952-10-5133-3 (PDF version)

<http://ethesis.helsinki.fi>

Yliopistopaino

Helsinki 2008

**"The harder you work,
the luckier you get."**

ABSTRACT

Thin films of various metal fluorides are suited for optical coatings from infrared (IR) to ultraviolet (UV) range due to their excellent light transmission. In this work, novel metal fluoride processes have been developed for atomic layer deposition (ALD), which is a gas phase thin film deposition method based on alternate saturative surface reactions. Surface controlled self-limiting film growth results in conformal and uniform films. Other strengths of ALD are precise film thickness control, repeatability and dense and pinhole free films. All these make the ALD technique an ideal choice also for depositing metal fluoride thin films.

Metal fluoride ALD processes have been largely missing, which is mostly due to a lack of a good fluorine precursor. In this thesis, TiF_4 precursor was used for the first time as the fluorine source in ALD for depositing CaF_2 , MgF_2 , LaF_3 and YF_3 thin films. TaF_5 was studied as an alternative novel fluorine precursor only for MgF_2 thin films. Metal-thd (thd = 2,2,6,6-tetramethyl-3,5-heptanedionato) compounds were applied as the metal precursors. The films were grown at 175–450 °C and they were characterized by various methods.

The metal fluoride films grown at higher temperatures had generally lower impurity contents with higher UV light transmittances, but increased roughness caused more scattering losses. The highest transmittances and low refractive indices below 1.4 ($\lambda = 580$ nm) were obtained with MgF_2 samples. MgF_2 grown from TaF_5 precursor showed even better UV light transmittance than MgF_2 grown from TiF_4 . Thus, TaF_5 can be considered as a high quality fluorine precursor for depositing metal fluoride thin films. Finally, MgF_2 films were applied in fabrication of high reflecting mirrors together with Ta_2O_5 films for visible region and with LaF_3 films for UV region.

Another part of the thesis consists of applying already existing ALD processes for novel optical devices. In addition to the high reflecting mirrors, a thin ALD Al_2O_3 film on top of a silver coating was proven to protect the silver mirror coating from tarnishing. Iridium grid filter prototype for rejecting IR light and Ir-coated micro channel plates for focusing x-rays were successfully fabricated. Finally, Ir-coated Fresnel zone plates were shown to provide the best spatial resolution up to date in scanning x-ray microscopy.

PREFACE

The research studies reported in this thesis was carried out during the years 2004–2008 in the Laboratory of Inorganic Chemistry in the University of Helsinki.

First, I owe my deepest gratitude to my supervisors, professors Mikko Ritala and Markku Leskelä for their invaluable contribution and help to this study. Mikko, without your guidance this work would not have been done. Both of you had always time for me and your rapid feedback concerning my papers was just unbelievable. I had a great time during the years working in your laboratory.

Official reviewers Dr Markku Ylilammi and Dr Karol Fröhlich are warmly acknowledged for the rapid and fluent review process and their valuable suggestions to improve my thesis.

I am grateful to my co-authors for their expertise and fruitful collaboration. Many thanks go to Joan Vila-Comamala, Konstantins Jefimovs and Christian David for their valuable work in x-ray field in Switzerland. Warm thanks go to Martin Bischoff, Norbert Kaiser and Ute Kaiser for their optical studies in Germany. I am grateful also to Frans Munnik and Kai Arstila for their film composition studies. Janne Laukkanen, Jari Turunen and Matti Kaipainen are thanked for their contribution in space projects. Esa Puukilainen is thanked for his AFM measurements and Timo Hatanpää for synthesizing precursors. I am grateful also to Suvi Haukka for her chemical reaction studies.

My special thanks go to my co-workers in our laboratory, Kaupo and Jaakko, their support and advice during the years in and outside of the laboratory. I owe warm thanks to Marianna for her kind advice and SEM/EDX measurements. Warm thanks go to the rest of our ALD team: Elina, Emma, Tiina, room mate Mikko, Marko, Jakke, Viljami, Jani, Timo, Jere, Kjell, Eero and Leo, and also to all sähly players at Friday afternoon. Many thanks also to my ex-colleagues Antti and Markus for their advices in laboratory and joyful moments outside of work.

I am more than just thankful to my friends outside of academic world. Ibu, Hesse and Edi without you guys (and the countless beers), this book would have never been completed. Kissala team member Olli, your support “Anna palaa” was valuable when I was finishing last part of the thesis. Pasi, Jukka, Buge, Köpi, Happpis&Maiju, Kajsa, Ira&Sami, Eero&Ale, Timo&Laura, and rest of the friends and colleagues that are not mentioned here, thank you all for your kind support.

Last, I owe my warmest gratefulness to my parents Ritva and Rami. Your support and existence has been important during my studies. I want also thank my brother Pasi for his friendship and joyful moments outside of science world. I am thankful to my mother-in-law Marja for her support and that I was able to write most part of this thesis at Marjan Maja in Estonia. Finally, most of all I am grateful to my lovely wife Taru for her encouragement, endless support and deep love.

Helsinki, November 2008

Tero Pilvi

Tero Pilvi

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following original publications (Studies I-VII)

- I Pilvi, T., Arstila, K., Leskelä, M., Ritala, M.; Novel ALD process for depositing CaF_2 thin films; *Chem. Mater.*, 19, (2007), 3387.
- II Pilvi, T., Hatanpää, T., Puukilainen, E., Arstila, K., M., Bischoff, M., Kaiser, U., Kaiser, N., Leskelä, M., Ritala, M.; Study of novel ALD process for depositing MgF_2 thin films; *J. Mater. Chem.*, 17, (2007), 5077.
- III Pilvi, T., Puukilainen, E., Arstila, K., Leskelä, M., Ritala, M.; Atomic layer deposition of LaF_3 thin films using $\text{La}(\text{thd})_3$ and TiF_4 as precursors; *Chem. Vap. Deposition*, 14, (2008), 85.
- IV Pilvi, T., Puukilainen, E., Munnik, F., Leskelä, M., Ritala, M.; ALD of YF_3 thin films from TiF_4 and $\text{Y}(\text{thd})_3$ precursors, *Chem. Vap. Deposition*, in Press.
- V Pilvi, T., Puukilainen, E., Kreissig, U., Leskelä, M., Ritala, M.; Atomic layer deposition of MgF_2 thin films using TaF_5 as a novel fluorine source; *Chem. Mater.*, 20, (2008), 5023.
- VI K. Jefimovs, J. Vila-Comamala, T. Pilvi, J. Raabe, M. Ritala, and C. David; Zone-doubling technique to produce ultrahigh-resolution x-ray optics; *Phys. Rev. Lett.*, 99, (2007), 264801.
- VII Jefimovs, K., Laukkanen, J., Vallius, T., Pilvi, T., Ritala, M., Meilahti, T., Kaipainen, M., Bavdaz, M., Leskelä, M., Turunen, J.; Free-standing inductive grid filter for infrared radiation rejection; *Microel. Eng.* 83, (2006), 1339.

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RELATED PUBLICATIONS BY THE SAME AUTHOR

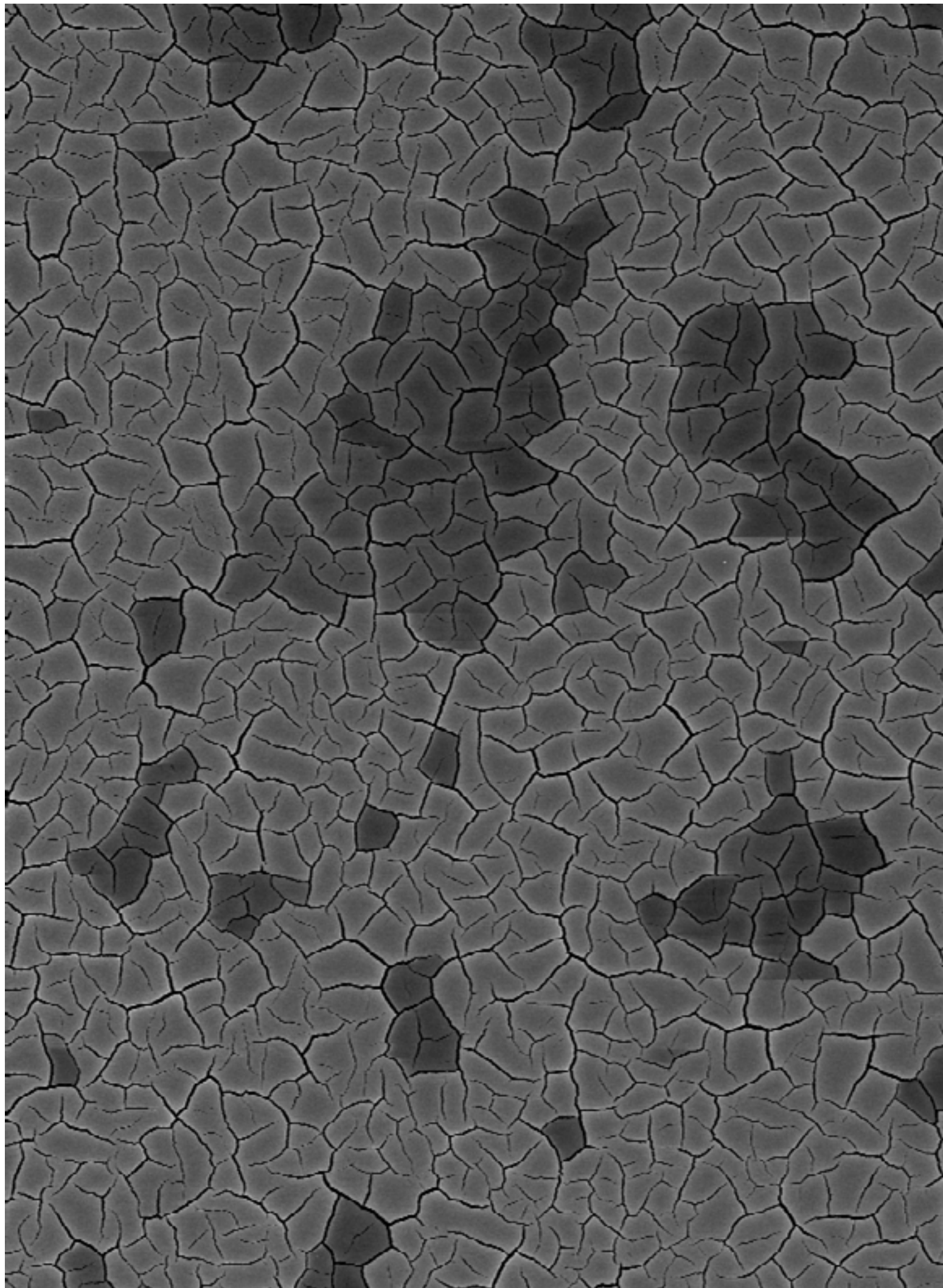
- 1 Pilvi, T., Ritala, M, Leskelä, M., Bischoff, M., Kaiser, U., Kaiser, N.; Atomic layer deposition process with TiF_4 as precursor for depositing metal fluoride thin films; *Appl. Opt.*, 47, (2008), C271.
- 2 Laakkonen, P., Turunen, J., Pietarinen, J., Siitonen, S., Laukkanen, J., Jefimovs, K., Orava, J., Ritala, M., Pilvi, T., Tuovinen, H., Ventola, K., Kaipiainen, M., Kuittinen, M.; Diffractive optics in industry and research - novel components for optical security systems; *Proc. SPIE*, 5954, (2005), 595402.

LIST OF ABBREVIATIONS AND ACRONYMS USED

α	Absorption coefficient
acac	2,4-pentanedionato (acetylacetonato), [CH ₃ C(O)CHC(O)CH ₃] [−]
ALD	Atomic layer deposition
AFM	Atomic force microscopy
E _g	Band gap
CVD	Chemical vapor deposition
EBE	Electron beam evaporation
k	Extinction coefficient
FESEM	Field emission scanning electron microscopy
FZP	Fresnel zone plate
GI-XRD	Grazing incidence X-ray diffraction
IR	Infrared
ITO	Indium tin oxide
MCP	Micro channel plate
PVD	Physical vapor deposition
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
thd	2,2,6,6-tetramethyl-3,5-heptanedionato, [(CH ₃) ₃ CC(O)CHC(O)C(CH ₃) ₃] [−]
TMA	Trimethylaluminum, Al(CH ₃) ₃
TOF-ERDA	Time-of-flight elastic recoil detection analysis
UV	Ultraviolet
VUV	Vacuum ultraviolet
λ	Wavelength
XRD	X-ray diffraction
XRR	X-ray reflection

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1 INTRODUCTION

Nowadays the push for higher density semiconductor devices, such as personal computers and mobile phones, requires smaller circuit features.¹ These can only be obtained by reducing the wavelength in the photolithographic process used to create the circuits, and by using better materials. Therefore optical components and their coatings are being forced to operate at wavelengths even in the deep ultraviolet (UV) region. As the excimer lasers extend to these wavelengths the requirements for low optical loss components increases radically.² The usage of oxide materials is limited due to their intrinsic absorption. However, fluoride compounds can be applied at these shorter wavelengths.

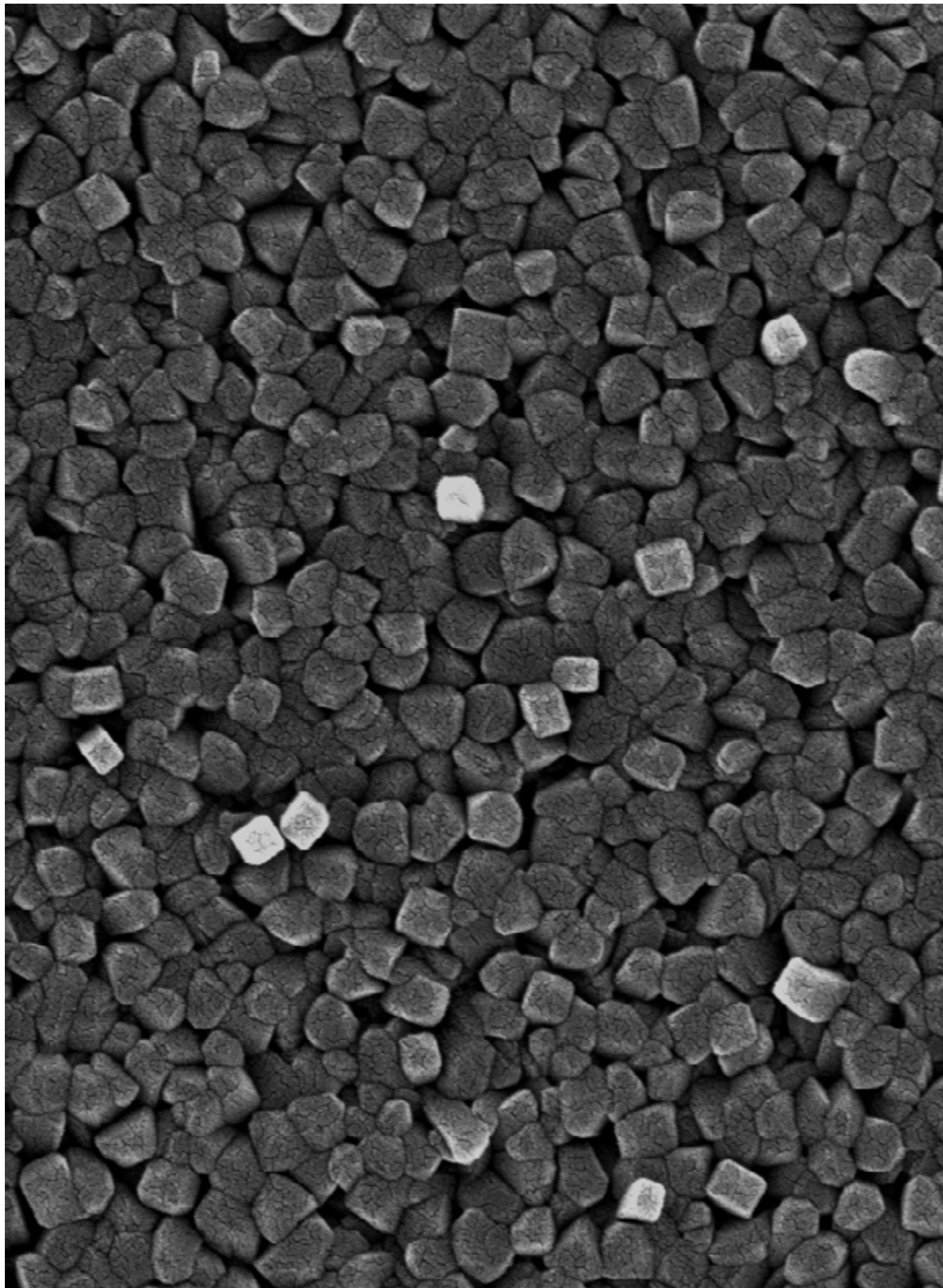
Thin films of various metal fluorides are suited for optical coatings in infrared (IR) and UV laser applications due to their excellent light transmission from the UV to IR region.³ Mainly physical vapour deposition (PVD) methods, especially evaporation techniques, have been applied for depositing these metal fluoride films.³⁻⁶ However, the main limitation of evaporated fluoride films has been that they are porous with low packing densities.⁷ Another problem in PVD methods is how to control the exact thickness of layers in multilayer stacks.⁸

Chemical vapour deposition (CVD) of fluoride films has not been adapted widely so far due to difficulties in handling the fluorine precursors, namely hazardous HF and F₂ gas.⁹ Atomic layer deposition (ALD) is a special variant of the CVD technique invented in 1974 in Finland by Suntola and co-workers to produce thin films for electroluminescent flat panel displays. In ALD,^{10,11} the film grows via saturative surface reactions, typically producing pinhole free thin films with good conformality and excellent thickness uniformity,¹² making it a perfect method-of-choice for also depositing metal fluoride thin films. The problem in depositing fluoride films by ALD has been a lack of good fluorine source. HF, obtained by thermally decomposing NH₄F, was applied as the first fluorine source in ALD for depositing CaF₂, ZnF₂, and SrF₂ films.¹³ However, HF is not an ideal choice for ALD because in addition to its unsafe chemical nature it etches glass and many oxides. Hence, there is a clear need for a better

fluorinating agent.

The aim of this study was, first, to develop novel ALD processes with better fluorine precursors for metal fluorides, and to study film growth as well as film properties. The second aim was to study the applicability of the new ALD processes in fabrication of a high reflecting multilayer stack for visible and UV region. The third and last aim was to apply already existing ALD processes for novel optical applications, especially for x-ray optics.

In this thesis, light and its interaction with matter and film/substrate systems are described. Different optical thin film materials are presented from the ALD point of view. Optical designs for one- and multilayer structures are introduced. The experimental section describes the set-up in the film growth studies and characterization methods used. Then the results on the new ALD processes of metal fluorides are reviewed and discussed. Finally, some novel optical applications of ALD are introduced with some basic background information when relevant.



2 BACKGROUND

This chapter consists of background information needed for understanding of optical thin films. As a starting point, the light itself and its spectral regions are described.

2.1 Light

The light is electromagnetic radiation (or energy) and just one portion of the various waves flying through space.¹⁴ The electromagnetic spectrum covers an extremely broad range, from radio waves with wavelengths (λ) of a meter or more, down to x-rays with wavelengths less than a billionth of a meter. A numerical equation relating the photon energy and the wavelength is¹⁵:

$$\lambda(nm) = \frac{hc}{E} = \frac{1240(eV \times nm)}{E(eV)} \quad (1)$$

where h is the Planck's constant, c is the velocity of light, and E is the energy of a photon.

Optical radiation lies between radio waves and x-rays on the spectrum, exhibiting a unique mix of ray, wave and quantum properties. At x-ray and shorter wavelengths, electromagnetic radiation is particle like what comes to ionisation and wavelike what comes to diffraction, whereas toward longer wavelengths the behaviour is mostly wavelike. The visible portion occupies an intermediate position, containing both particle and wave properties in varying processes. The relationship between the wavelength and energy of radiation is inverse, such that long wavelength radiation has lower energy than short wavelength radiation (Eq. 1).

Wavelength ranges for spectral regions starting from infrared (IR) down to x-rays are introduced in Table 1. IR light with wavelengths above 700 nm contains the least amount of energy per photon of any other range. IR radiation is unique

in that it exhibits primarily wave properties. This can make it much more difficult to focus with lenses because it refracts less and diffracts more.

Table 1. Wavelength ranges for the spectral regions from IR to x-rays.

Spectral region	Wavelength range (nm)	Energy (eV)
IR	>700	<1.8
Visible	400–700	3.4–1.8
UV	300–400	4.1–3.4
Far UV	200–300	6.2–4.1
Vacuum UV	100–200	12–6.2
Extreme UV	4–40	3.5×10^3 –160
Soft x-rays	0.35–8	1.2×10^4 – 3.5×10^3
Hard x-rays	0.01–0.35	1.2×10^4 – 3.5×10^3
Gamma rays	<0.01	$>1.2 \times 10^4$

A spectral range from short wavelength of UV to the longer IR is illustrated in Fig. 1. Visible range is about from 400 nm to 700 nm, and that is the region which human eye can detect. Wavelengths of pure colours are shown in Table 2 starting from violet (400–440 nm) and ending to red colour (630–700 nm).

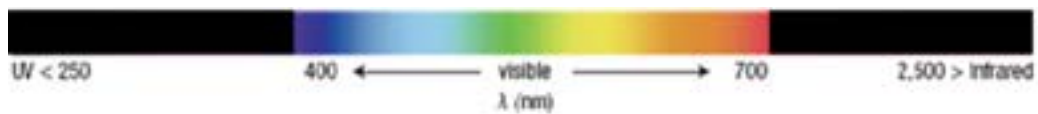


Fig. 1 Wavelengths from UV to IR region. Visible range is about from 400 to 700 nm.¹⁶

UV light can be divided to three regions, according to its anecdotal effects.¹⁴ UV-A (315-400 nm) is the least harmful and most commonly found type of UV light because it has least energy. It is often called black light, and it is applied for its relative harmlessness and its ability to cause fluorescent materials to emit visible light, thus appearing to glow in the dark. Most phototherapy and solariums use UV-A lamps. UV-B (280-315 nm) is typically the most harmful form of UV light because it has enough energy to damage biological tissues, but still not enough to be completely absorbed by the atmosphere. UV-B is known to cause skin cancer. Since the atmosphere blocks most of the UV-B light, a small change in the ozone layer could dramatically increase the danger of skin cancer. Short wavelength UV-C (100-280 nm) is almost completely absorbed in the air within a few hundred meters. When UV-C photons collide with oxygen atoms, the energy exchange causes the formation of ozone. UV-C is almost never observed in nature, since it is absorbed so quickly. Germicidal UV-C lamps are often used to purify air and water, because of their ability to kill bacteria.

Table 2. Wavelength of colours.¹⁷

Violet	Blue	Green	Yellow	Orange	Red
400–440 nm	440–480 nm	480–560 nm	560–590 nm	590–630 nm	630–700 nm

The ability to use extreme UV (EUV) and soft x-rays (1–40 nm, Table 1) in a constructive way with various optics used at longer wavelengths has been limited by fundamental physics of matter-radiation interaction.¹⁸ EUV/soft x-rays are strongly absorbed by all materials, resulting in very small near-normal reflectivity from any single interface boundary. Anyhow, x-rays are widely used in imaging. The advantages of x-ray imaging compared to imaging with visible light or electrons are the high penetration depth and the low level of diffuse scattering, which allow for the non-destructive inspection of thick, non-transparent objects.

2.2 Interaction of light with matter

The two most important properties in optical materials are refractive index (n) and extinction coefficient (k). They determine materials' suitability for optical applications, and are closely related to their dielectric properties.¹⁹ As discussed above, the light exhibits unique mix of ray, wave and quantum properties. Velocity of light is constant ($c = 3 \times 10^8$ m/s) in vacuum, but the speed of light decelerates in matter by a factor n (Fig. 2), which is also called refractive index (Eq. 2):

$$n = \frac{\text{velocity of light in vacuum}}{\text{velocity of light in matter}} \quad (2)$$

Therefore for the vacuum as well as for air $n = 1.0$, and for most of the dielectric materials $n \geq 1$. The more optically dense the material is, the more the speed of light is decelerated, and the higher refractive index is obtained. Materials can be transparent or absorbing in which the optical constant (or complex index of refraction), N , is given by (Eq. 3):

$$N = n - ik \quad (3)$$

where n is the real part of the refractive index (or often simply as the refractive index because N is real in the ideal dielectric material)²⁰, and k is the extinction coefficient, which indicates the amount of absorption loss when the electromagnetic wave propagates through the material. Both n and k are

depending on the wavelength and the absorption is zero in vacuum. The real part of the refractive index may be smaller than 1 for elements and metals. For example, n is 0.27 and k is 4.18 for pure silver ($\lambda=620$ nm).¹⁵ For a non-absorbing matter, the index of refraction is (Eq. 4):

$$n = \sqrt{\epsilon_r \mu_r} \quad (4)$$

where ϵ_r is relative permittivity, and μ_r is relative magnetic permeability, and for the most of dielectric materials μ_r is around 1 at optical frequencies. Since electrons are responsible for electronic polarizability and they can respond at optical frequencies, ϵ_r is not unity at optical frequencies.¹⁷

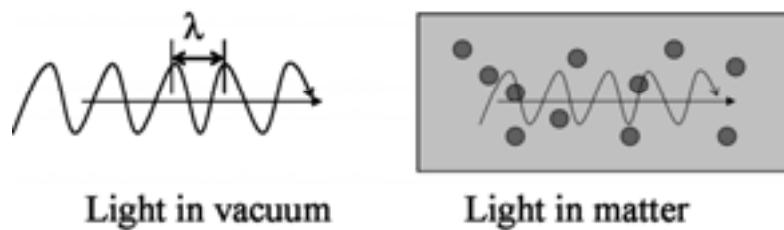


Fig. 2 Velocity of light in vacuum is constant c (left). However, velocity of light in matter (right), decelerates by a factor of n which is called refractive index.

The refractive index of a material at optical frequencies is mainly determined by the polarizability of the valence electrons.²¹ In elements with increasing atomic weight the electron population is enlarged, which results in the shielding of the positive charge of the nucleus, so that the polarizability of the valence electrons and consequently the refractive index are increased, e.g., for Si $n = 3.4$ and for Ge $n = 4.0$. Refractive index of a compound is depending on many factors, such as density and chemical bonding, and is discussed in more details later.

The extinction coefficient k is the imaginary part (Eq. 3) of the complex refractive index N . It assumes the role of an index of attenuation. If this attenuation is caused by true absorption alone, it will be termed absorption

coefficient α . The absorption constant is defined as follows (Eq. 5)¹⁹:

$$\alpha = \frac{4\pi k}{\lambda} \quad (5)$$

where α determines the wave intensity (I) transmitted through an absorbing medium (thickness x) by the exponential law of absorption, also called Lambert's law of absorption (Eq. 6):

$$I = I_0 e^{-\alpha x} \quad (6)$$

where I_0 is the intensity at $x = 0$. Real solids have typical absorption coefficient of about $\alpha = 10^{-3} \text{ cm}^{-1}$ in their transparency region, and $\alpha = 10^6 \text{ cm}^{-1}$ in the region of fundamental absorption outside the transparency band.²²

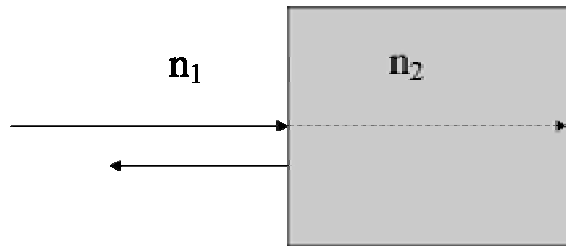


Fig. 3 Normal incident case: part of the incident light is transmitted and some part is reflected back.

When the incident light meets the matter, some part of the light transmits the matter, and some part is reflected back (Fig. 3). A phase shift in reflection is 180° if $n_2 > n_1$.²³ When light hits a transparent material, electrons in this material start to oscillate. This oscillation takes, momentarily, energy from the photon, and then gives it back. Polarization of atoms leads to a deceleration of the light propagation velocity in transparent material. Energy of the photon, and thus the wavelength of light, is the same before and after this interaction. If material contains substances which absorb photons with certain energy, i.e., light with certain wavelength of the spectrum, energy of the oscillating electrons is not returned to photon and absorption occurs. Energy of a photon makes an electron to make a transition from ground or already excited state to higher energy state. Fluorescence occurs when the excited state relax back to the

ground state with emission of photons with lower energy and longer wavelength than those of the absorbed photons.

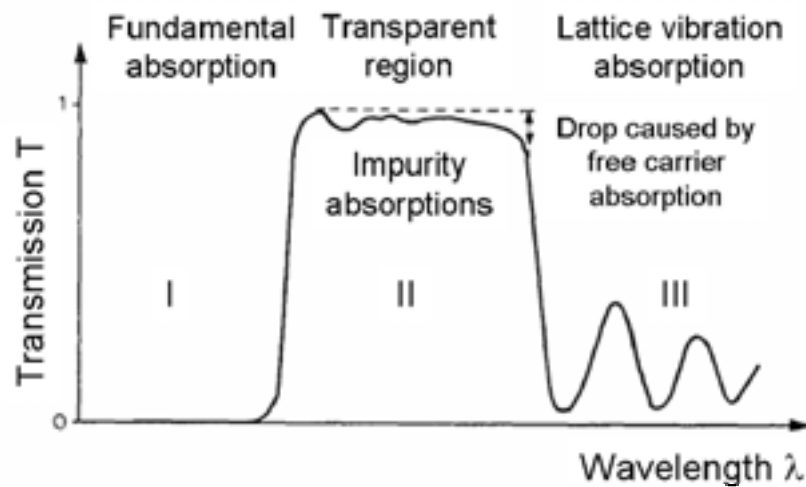


Fig. 4 Schematic curve of transmission vs. wavelength of an optical material.²¹

Fig. 4 depicts schematically the curve of transmission versus wavelength of an optical material. The desired region of high transmittance (region II) is situated between the short wavelength absorption edge (region I) and the long wavelength limit (region III). Region I depends on the electronic structure of the material (band gap), whereas region III is determined by lattice vibrations or, in the case of semiconductors, by free carrier absorption.²¹ The extent and quality of region II depends strongly on the material; on its stoichiometry and purity.

In addition to the two most important properties of materials, n and k , reflectance of material has to be added.¹⁹ Reflection of an electromagnetic radiation from the interface between two matters depends on the refractive indices of the matters and the angle of incidence.¹⁹ The optical properties of conductive materials like metals and semiconductors (at the photon energy range above the energy gap) differ from those of optically transparent matter.¹⁹ Free electron absorbs the incident electromagnetic wave in a thin surface layer and then releases the absorbed energy in form of secondary waves reflected from the surface. Thus, the light reflection comes very strong, e.g., highly conducting iridium reflects 69.7% and sodium even 99.8% of incident wave (at

580 nm). At very high photon energies, quantum effects, such as the internal photoeffects, start playing a greater role, and the optical properties of these materials become similar to those of insulators (low reflectance, existence of Brewster's angle, etc.).¹⁹ The reflectance (R) can be defined as the ratio of the reflected and incident irradiances, as illustrated in Fig. 3 (Eq. 7)²⁰:

$$\text{Reflectance} = \frac{\text{Reflected power}}{\text{Incident power}} = \left(\frac{n_1 - n_2}{n_2 + n_1} \right)^2 \quad (7)$$

where n_1 and n_2 are the refractive indices of matters 1 and 2. The last form in Eq. 7 applies only at perpendicular incidence. At the same way the transmittance (T) can be defined as the ratio of the transmitted and incident irradiances (Eq. 8)²⁰:

$$\text{Transmittance} = \frac{\text{Transmitted power}}{\text{Incident power}} = \frac{4n_1 n_2}{(n_1 + n_2)^2} \quad (8)$$

For example for glass $n_2 = 1.5$ (air $n_1 = 1.0$) Eq. 7 gives $R = 4.0\%$ and Eq. 8 gives $T = 96.0\%$.

So we can also write that transmittance is (Eq. 9):

$$T = 1 - R \quad (9)$$

Transmittance through both surfaces of glass in air would be 96.0% of 96.0%, i.e. total transmittance is around 92%. The index range of optical glasses is around 1.4–1.9 in the visible region and the transmittance through a single lens of $n = 1.9$ would be only 82%.

So far one has assumed that there is no absorption, but things go slightly more complicated when including absorption of materials in calculations. Anyhow, for any two absorbing matters, the normal incidence reflectance is (Eq. 10)¹⁹:

$$R = \frac{(n_1 - n_2)^2 + k_2^2}{(n_1 + n_2)^2 + k_2^2} \quad (10)$$

The transmitted light has the same frequency but a different velocity than the

incident light, as discussed already. Thus, the wavelengths are matching at interface (Eq. 11):

$$\lambda_2 n_2 = \lambda_1 n_1 \quad (11)$$

Therefore the wavelength changes under refraction, decreasing on going to a material of larger refractive index and vice versa.

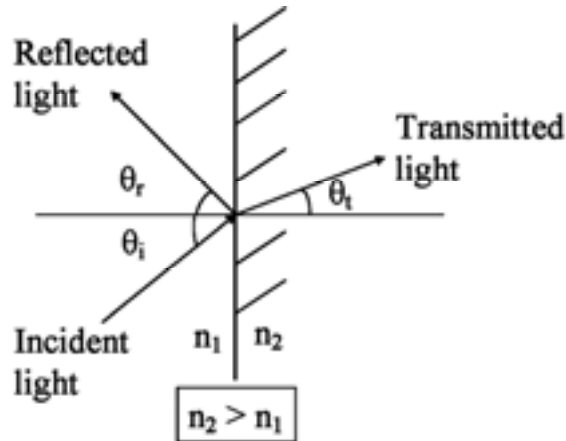


Fig. 5 Incident light is reflected and transmitted/refracted at dielectric interface.

When the light strikes a matter at an angle which is not parallel to the plane normal, the angle of reflection equals the angle of incident, $\theta_i = \theta_r$. The transmitted light is bent, or refracted (Fig. 5). This bending is described by Snell's law (Eq. 12)¹⁷:

$$n_2 \sin \theta_t = n_1 \sin \theta_i \quad (12)$$

What is called complete internal reflection can occur when the velocity in the second material is larger than in the first material ($n_2 < n_1$). In that case, the transmitted angle θ_t (Fig. 5) is larger than the incident angle θ_i . When θ_t is 90° , the incident light is at critical angle θ_c (Eq. 13):

$$\theta_c = \frac{n_2}{n_1} \quad \text{if } n_1 > n_2 \quad (13)$$

For angles exceeding θ_c , the light penetrates into the second material layer only

for a very short distance and all the light is reflected.

2.3 Interaction of light with film/substrate systems

After taking into consideration the light, its spectral regions, and its interaction with matter, one can take closer look at film/substrate systems.

When the light strikes a film, it can either be reflected (R), transmitted (T) or lost by absorption (A) or by scattering (S),²⁴ as illustrated in Fig. 6. At every interface with two materials the light is reflected again, if there is a difference in the refractive indices between these two materials.

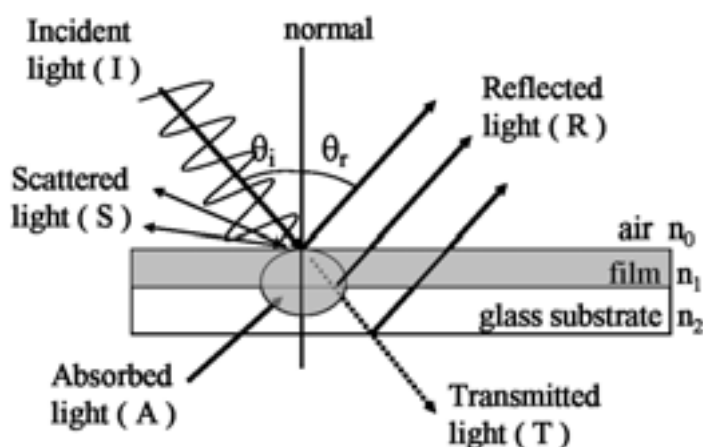


Fig. 6 The basic principle of interaction of incident light with air/film, film/glass, and glass/air interfaces. Incident beam divides into reflected, scattered, absorbed, and transmitted beams.

Sometimes there is a misunderstanding that the density of the compound is the only impressive factor in defining the refractive index, but the type of chemical bonding also influences the refractive index. Compounds with predominant ionic bonding show lower refractive indices than compounds with a high degree of covalent bonding; for example for CaF_2 ($n \sim 1.4$), for CaO ($n \sim 1.7$), and for CaS ($n \sim 2.1$) (see Table 4). The most covalently bound CaS has the highest refractive index even if it has the lowest density (order of densities is: $\text{CaO} > \text{CaF}_2 > \text{CaS}$).

The essential feature of dielectric optical thin film materials is their very low absorption ($\alpha < 10^3 \text{ cm}^{-1}$) in the relevant region of the spectrum (Fig. 4). One reason for the increased extinction in the films is often the true absorption due to small deviations from stoichiometry and contamination. In multilayer structures the spectral transmission range is determined by the absorptions of the individual coated layers. Another reason for the increased extinction in the films is scattering (S), which is an essential loss mechanism of optical components that is mainly caused by the roughness of the optical surfaces and by volume imperfections. Such imperfections include rough internal boundaries, porous microstructure, pinholes, cracks, microdust, etc.^{21, 25} Contamination becomes more important in the VUV where the extinction coefficients of water and of most organic compounds are higher by orders of magnitude compared to the visible spectral range.²⁶

The optical losses (L) are made up from (Eq. 14):

$$L = A + S \quad (14)$$

After this (Eq. 9) can be written as follows (Eq. 15):

$$T = 1 - R - L = 1 - R - A - S \quad (15)$$

In these equations (14–15): A is absorption, S is scattering, R is reflectance, and T is transmittance (see Fig. 6). L depends strongly on cleanliness, deposition method, and deposition conditions of the films.²¹ The production of high quality thin films with low loss requires glasslike or amorphous films, without internal boundaries, and with smooth surfaces.

2.4 Optical thin films

Optical thin films are widely used in many applications to control how the light is reflected, transmitted, or absorbed as a function of wavelength.²⁴ Typical layers might range in thickness from 20 nm in the UV to many times that in the IR region. As discussed earlier, for many applications the most important optical properties are the refractive index n , the extinction coefficient k , and the reflectivity. Evaluating the mechanical, chemical, and optical performance of a

coating is a major task in itself. All coatings, single or multilayer, must possess a specified degree of quality in all the three areas mentioned. Optical coatings are not generally expected to be able to withstand severe abrasive wear, while coatings on high-speed tools are.

2.4.1 Interference coating design

A high reflecting coating or a bandpass filter is a multilayer stack of alternating high and low refractive index materials. Thin film filters operate by interference of the light reflected from each interface layer as the light passes through the sample. When these light waves overlap in phase with each other, the magnitude of the wave increases, and the interference is called constructive. When the light waves are out of phase they cancel each other out, called as destructive interference.

When incident light (I) strikes a film, it can either be reflected (R), transmitted (T) or lost by absorption (A) or scattering (S),²⁴ as illustrated in Fig. 6. If one considers a light beam incident on a homogenous parallel-sided film, the amplitude and polarization state of the light transmitted and reflected can be calculated and controlled in terms of the incident angle and the optical constants of the three materials involved.

Antireflecting coatings

Fig. 6 depicts the light from the incident medium (air) of refractive index n_0 passing through thin film material of index n_1 , finally entering a substrate material (glass) of index n_2 . The refractive index of air is equal to 1.0, the refractive index of vacuum. The light transmittance through normal glass was around 92%. Complex optical systems may have many lenses conjugated together and the losses may totally be 50% or more. IR optics use very high refractive index materials such as Ge, which has a reflectance of 35% per surface. In addition to power loss, these reflections can cause “ghost” images, thus it is vital to use antireflecting (AR) coatings on the lenses.

AR coatings were first applied to military optical instrument to reduce glare from the surfaces of the large number of lenses used, e.g., in a periscope or binocular viewer,²⁷ and they were a German military secret until the early stages of World War II. These AR coatings were initially single layer of CaF_2 and later MgF_2 . The surface reflectance of 4% could be reduced to only 1% in the visible region.

AR films have typically low refractive indices (n_1), lower than the refractive index of the substrate (n_2), $n_1 < n_2$. AR coatings operate on the principle of destructive interference of the light reflected from the front and back surfaces of the AR films.²⁴ In both cases the reflection takes place of the surface of a higher refractive index material, thereby causing the same 180° phase shift upon reflection. To ensure that the relative phase shift is 180° (phase condition), the optical thickness of the film should be made one quarter wavelength so that the total difference in phase between the two beams will correspond to half wavelength, which is 180° .²⁸ As the light waves are out of phase they cancel each other out. A minimum in reflection thus occurs at wavelengths fulfilling the equation (Eq. 16)²³:

$$2nd = \left(m + \frac{1}{2}\right)\lambda \quad m = 0, 1, 2, 3, \dots \quad (16)$$

where n is refractive index of film, d is physical thickness of film, and λ is vacuum wavelength of the light. Eq. 16 can be used for calculating the minimum reflectance of a single layer as in Fig. 6 but at normal incidence for the wavelength of interest λ_0 , it simplifies to (Eq. 17):²⁹

$$R = \left(\frac{n_1^2 - n_0 n_2}{n_1^2 + n_0 n_2} \right)^2 \quad (17)$$

Eq. 17 is a useful formula for estimating how well a particular single layer coating will behave. One can calculate, e.g., the film refractive index needed for zero reflectance at the design wavelength as (Eq. 18):

$$n_1 = \sqrt{n_0 n_2} \quad (18)$$

This can be called as a amplitude condition which shows that for an AR film, the refractive index n_1 should be intermediate between the refractive indices of air and glass.²⁸ Both the phase and the amplitude condition must be fulfilled to get an ideal single layer antireflection coating. For example, with a glass $n_2 = 1.9$, and air $n_0 = 1.0$, one gets for $n_1 = 1.38$ which actually is the refractive index of MgF_2 in the visible region.³⁰ MgF_2 is the most used material for single layer AR coatings and one of the lowest index materials available. However, glasses have usually always lower refractive index than 1.9, e.g., with a glass $n_2 = 1.50$, and air $n_0 = 1.0$, one gets for $n_1 = 1.22$. Therefore more layers of other materials must be added, if the reflectance is to be minimized. Adding more layers also gives ability to achieve low reflectance over a much broader wavelength range. AR stack (dielectric stack) on a glass substrate is illustrated in Fig. 8, where the dielectric 1 is usually air.

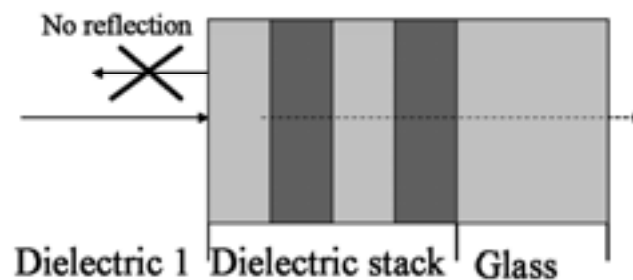


Fig. 8 Picture of antireflecting 4-layer filter on a glass substrate.

Zero reflectance with two layers on substrate is achieved when (Eq. 19)²⁸:

$$n_2 = \frac{n_1}{n_0} \sqrt{n_3} \quad (19)$$

e.g., for a glass $n_3 = 1.52$, air $n_0 = 1.00$, and for MgF_2 $n_1 = 1.38$, one gets $n_2 = 1.70$ which is a refractive index of MgO .²⁰

Multilayer stacks

Optical surfaces are coated with functional multilayer designs for a variety of purposes. The most common function is to reduce surface reflection. The materials suitable for a specific coating design are chosen according to the substrate material properties, the environment in which the coated surface will be operated, optical performance, and sometimes cost of production.

The interference effect produces many interesting results. For example, in interference filters the destructive effect is used to selectively filter light by wavelength. A quarter-wave (QW) stack consists of alternate layers of high and low n , each fulfilling equation (Eq. 20):

$$n_j d_j = \frac{\lambda_0}{4} \quad (20)$$

The multilayer is completely specified if we know n_j , k_j , and d_j for each layer, n_0 for the incident medium plus n_s and k_s for the substrate. Given the angle of incident (θ_i), the reflectance (R) and the transmittance (T) can be calculated as a function of wavelength. Modern techniques allow one to design optical coatings with quite complicated spectral characteristics, and the main problem nowadays is not to obtain a design with the required spectral properties but to find the one which is most manufacturable.³¹ Commercially available software program, namely Thinfilm, has been used in this work for analysis and optimization of optical thin film design.³² More complicated designs are beyond this thesis, but there are excellent references available.^{20, 28, 31}

The QW multilayer stack has a characteristic high reflectance (HR) region or

stopband symmetric about the design wavelength λ_0 surrounded by long and short wavelength pass regions characterized by many ripples in the passbands. The width of the HR region is determined by the ratio of the high and low refractive indices, n_H/n_L . The higher the ratio, the wider is the stopband. The maximum reflectance depends on the number of the films as well as the ratio of n_H/n_L with R increasing with the number of films (Fig. 9). The number of ripple reflectance peaks depends also on the number of layers. QW stack is a good starting design for edge filters and band pass filters of various type.³¹ Suppressing the ripple on one side of the HR region can create an edge filter, e.g., a long wavelength pass (LWP) filter transmits the long wavelengths and efficiently reflects the short ones. On the other hand a short wavelength pass (SWP) filter transmits the short wavelengths and reflects the long ones. A bandpass filter transmits a relatively narrow range of wavelengths and effectively reflects those on both sides. Usually half wavelength cavity is used and it is surrounded by QW stacks.

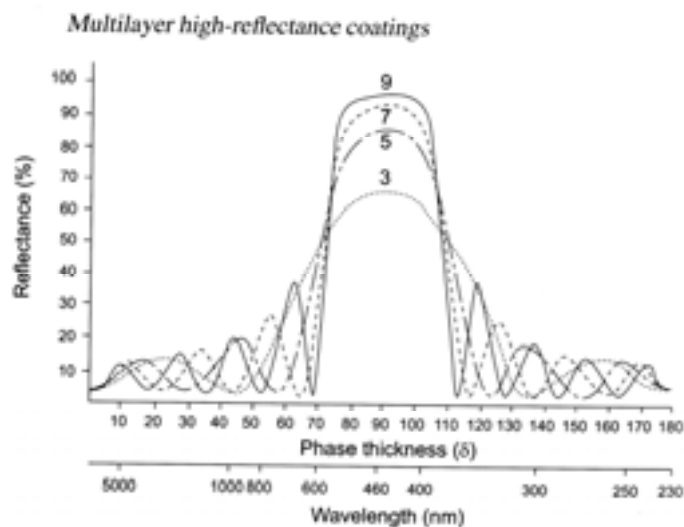


Fig. 9 Reflectance for normal incidence of alternating $\lambda_0/4$ layers of high refractive index ($n = 2.3$) and low ($n = 1.38$) dielectric materials on a glass substrate ($n = 1.52$) as a function of phase thickness or wavelength λ for $\lambda_0 = 460$ nm. The number of layers is shown as a parameter on the curves.²⁰

Once the design has been done, the wavelength characteristics can be moved by changing the layer thicknesses by the same ratio, e.g., a LWP filter with an edge at 400 nm can simply be shifted to 800 nm by making all the layers twice

as thick.

If the angle of incidence (θ_i , Fig. 6) increases, two effects are seen. First, the effective thickness of the layers becomes smaller, which causes the filter to shift to shorter wavelengths. Since the effect is inversely proportional to the film refractive index, at large angles the films are no longer matched at the same wavelength and the spectral shape degrades. The second effect at non-normal incidence is that the spectral characteristics become dependent on the polarization of the incident beam. This can be optimised and used to advantage for such components as polarizing beamsplitters. But in general, these angle effects are unfavourable.

For optimal performance of a multilayer the extinction coefficients of the individual single films should not exceed 10^{-4} . For example, in order to obtain negligible losses in multilayer AR coatings, in a film 100 nm thick one can tolerate only loss values of less than 0.01%, corresponding to a k value of 0.44×10^{-4} or an α value of 10 cm^{-1} at visible region.²¹

Nowadays reflection can routinely be reduced to 0.3% with help of multilayer AR coatings that use materials of high and low refractive index pairs. One application for AR coatings are silicon based solar cells, where the reflectance loss of 36% can be reduced by a single AR coating to 12% or significantly better by multilayer AR coatings to about 3%.³³

The high and low refractive index material pairs in film stack can be applied in colour selective coatings, in where the desired wavelength region reflects from the surface. The colours created are caused by interference in multilayers that are deposited onto glass, plastics, and non-transparent substrates, but simpler renditions can be made by selectively anti-reflecting metals; in this design fewer layers are required.³⁴ HR mirrors can also be used in applications such as decorative colour coatings in the commercial and entertainment world.

2.4.2 Optical thin film materials

One limitation in the optical thin film designing is the finite number of materials, and therefore refractive indices, available.²⁴ For multilayer stacks, the usual goal is to have two materials with as different refractive indices as possible. This gives the desired properties using the fewest number of layers in the stack. For HR coatings there are plenty of materials available, but unfortunately that is not the case in AR single layers; they are rare. In all cases, low absorption of the film is desired.

Table 3. Commonly used optical thin film materials.^{24, 35}

Material	Refractive index ($\lambda=550\text{--}600\text{ nm}$)	Transparency region (μm)
Si	4.1	1.1–14
CdS	2.5	0.5–>14
ZnS	2.35	0.38–25
TiO ₂	2.20–2.70	0.35–12
Ta ₂ O ₅	2.16	0.30–10
ZrO ₂	2.10	0.34–12
HfO ₂	2.00	0.22–12
ITO	1.95–2.00	0.4–1.5
LaF ₃	1.60–1.61	0.2–12
Al ₂ O ₃	1.59–1.63	0.20–7
ThF ₄	1.52 (at 400 nm)	0.20–15
SiO ₂	1.45	0.2–8
CaF ₂	1.43	0.15–12
MgF ₂	1.38	0.21–10

Table 3 shows some materials commonly used in optical thin film devices along with their refractive indices. It should be noted that the refractive index depends

on the film deposition method. Compounds with predominant ionic bonding show lower refractive indices than compounds with a high degree of covalent bonding. CdS has a high refractive index of 2.5 and for ZnS $n = 2.35$. Sulphides are applied as the high index component at the longer wavelengths, because nearly all the commonly used metal oxide compounds absorb light at wavelengths $> 8 \mu\text{m}$.³⁴

Oxides. Oxides are an important class of optical coating materials because they generally form hard, abrasion resistant, chemically and environmentally stable films with a good variety of refractive indices and spectral ranges of high transmission.³⁵ Oxygen atoms form partially covalent bonds with metals that account for the unique thermal stability of oxide compounds with quite high refractive indices, but also for relatively narrow spectral ranges of transparency.³⁶ For example, TiO_2 ($n \sim 2.5$) has a high refractive index in the visible range (Table 3), but unfortunately it begins to absorb light below 450 nm, rendering it useless for UV optics applications. The band gap and the variety of possible crystal phases of TiO_2 are properties responsible for its useful reactivity in photocatalysis where incident light of energy greater than the 3 eV band gap of TiO_2 generates holes and electrons. These carriers produce the oxidation and reduction reactions on the surface of TiO_2 layers responsible for the photocatalytic activity. These properties make TiO_2 useful for applications such as self-cleaning and defogging windows.

The coating materials used to make optical thin film filters for the visible region are TiO_2 and SiO_2 . But as TiO_2 absorbs light also in the 900-1100 nm region due to water absorption, Ta_2O_5 may be a better choice for wavelengths over 900 nm. Ta_2O_5 is a high refractive index material ($n = 2.16$) that has superior optical behaviour to TiO_2 in that it exhibits lower water absorptions in the near IR. Therefore it is applied for wavelength division multiplexing filters and other demanding applications.

ZrO_2 and HfO_2 and their silicates are very common thin film materials in microelectronic applications due to their high permittivity values. ZrO_2 is also a useful optical material because of its great hardness, high UV transmission, and high laser-induced damage threshold (LIDT) values.³⁷ LIDT is the fluency at which irreversible damage is created.³⁸ Absorption of ZrO_2 does not become

significant until close to 250 nm of wavelength. HfO_2 can also be applied in laser damage resistant coatings for the UV region.³⁷ HfO_2 and ZrO_2 both can be useful as UV coatings, but their refractive indices are just around 2.0 (Table 3), so they require a greater number of high-low refractive index material pairs in high reflection coating design in the visible region than, e.g., TiO_2 or Ta_2O_5 .

Indium tin oxide (ITO) is the most common example of a transparent conductive oxide, while others are doped ZnO and SnO_2 . ITO, in which around 10% Sn is generally added to In_2O_3 , has a large band gap and is transparent between 400 nm and 800 nm. Refractive index of ITO is around 2.0. It begins to reflect light at longer wavelengths so that at about 2.0 μm it behaves like metal and reflects > 90%.²⁷ The transition wavelength between transmission and reflection is determined by the added carrier concentration in these films. The first application for ITO was to defrost aircraft windows by sending a current through the coating. ITO is also applied in transparent contacts, liquid crystal displays, touch screens, solar cells, and anti-fogging windows. ITO is applied in thermal control and architectural glass and windshields for its wavelength selective ("green house") properties to admit the visible wavelengths of the sun light but prevent the heat escape.³⁹ This can serve to reduce heating requirements during cold weather, so the use of solar energy is maximized.

Generally the high refractive index oxide compounds begin to absorb at around 300 nm, e.g., TiO_2 absorbs at as long wavelengths as 450 nm. Therefore, when a thin film coating is needed for use below 350 nm, the number of candidate oxides are quite limited, SiO_2 and Al_2O_3 being the most common exceptions.⁴⁰ SiO_2 is one of the most desired optical materials together with MgF_2 due to its wide transmittance region of 0.2–8 μm .

Fluorides. Today research and development in UV coatings focuses on the stringent requirements for optical components used in the new generations of wafer-steppers for the semiconductor industry working at 193 nm (ArF-Excimer) and 157 nm wavelength (F_2 -Excimer).³⁵ The materials of choice for this application are metal fluorides which exhibit sufficiently low absorption for the vacuum UV region. As opposed to the oxides, fluoride compounds are characterized by the formation of mostly ionic bonds due to the high electronegativity of fluorine. Generally metal fluorides are dielectric materials

which are optically transparent over a wide range of wavelengths. Several fluorides have a wide band gap around 10 eV and they are suitable for applications in the wavelength range even below 200 nm.

LaF₃ is a promising vacuum ultraviolet (VUV) transparent material. As LaF₃ thin films exhibit extremely good moisture resistance, they are very useful, e.g., for protecting optical components.⁴¹ Even if LaF₃ has a low n value of 1.6 (Table 3), it is still the highest among VUV transparent films. Therefore LaF₃ can be used in multilayer stacks for constructing a high-low refractive index pair with, e.g., MgF₂.⁴²⁻⁵¹

CaF₂ has a low refractive index of 1.4, and it belongs to those few materials that have a lower refractive index than a bare glass. CaF₂ is optically transparent over a wide wavelength range from mid-IR to VUV,⁵² which makes bulk CaF₂ useful for optical components such as UV laser systems, lenses, prisms and windows.^{53, 54} In addition, CaF₂ can be applied for optical multilayers and filters.^{13, 55}

MgF₂ is the lowest refractive index material in Table 3 ($n \sim 1.4$). It is capable for use in a wide wavelength region from 157 nm to around 10 μm .⁵⁶ Therefore improvements in its deposition are constantly under investigation. MgF₂ has been used as a low n material together with a high n material such as TiO₂,⁵⁷ Sc₂O₃,⁵⁸ CeO₂,⁸ Al₂O₃,^{59,60} and LaF₃.⁴²⁻⁵¹ in optical multilayers which can be used, e.g., as the high reflectance mirrors for ArF excimer laser irradiation and as narrow band pass filters.⁴² MgF₂ thin films have also been applied in multilayers with conducting materials, e.g. with Ag⁶¹⁻⁶⁴ for flat panel displays and electromagnetic shielding, and with ITO for solar cells.⁶⁵ MgF₂ is also widely used for enhancing the reflectance of aluminum mirrors in the vacuum UV region.^{7, 66-70} To avoid the aluminum oxidation, aluminum has to be covered with a protective film. However, the cover layer can decrease the reflectance of Al, especially in deep UV range, but MgF₂ has good transmittance down there also.

The operational lifetimes of optical systems employing high power excimer lasers are limited by the LIDTs of the coated components in the system. Fluoride compounds satisfy laser damage requirements, and the candidate materials can be: AlF₃ and MgF₂ for low refractive index material, and LaF₃ and

GdF₃ for high refractive index material.²⁹

Semiconductors. Si and Ge are the most used semiconductors and can be applied as high refractive index films in the IR region.³⁵ Si is also used in multilayer stacks in the EUV/x-ray region.

Metals. In EUV region nearly all materials usually absorb light strongly, making it difficult to focus or otherwise manipulate light in this wavelength range. Telescopes that form images with EUV light use multilayer mirrors that are constructed of hundreds of alternating layers of high-mass metal, such as molybdenum and tungsten, and a low-mass spacer such as silicon. Each layer pair is designed to have a thickness equal to half wavelength of light to be reflected. Metallic mirror is omnidirectional, which means it reflects light from every angle, but it also absorbs a significant portion of the incident light, whereas dielectric mirror does not contain free electrons and therefore can reflect light more efficiently.

Al, Au, and Ag are highly reflecting metals (>90%), but they require abrasion and chemical resistant dielectric overcoating because of their softness and vulnerability to scratching. Hard metals like Rh, Ni, and Cr do not require protection, but they reflect only <70%.³⁵ Metal films are applied as reflectors, semitransparent beam splitters, transparent conductive films, absorbers, and in multilayer reflector stacks in the EUV/x-ray region. Al is widely used as a reflector in the IR, visible and UV region. Protected silver films yield very high reflecting mirrors for the visible and near IR region but still Al is most frequently used in mirror coatings due to its superior long-term stability compared with Ag.⁷¹ Semitransparent silver films can be used as transparent heat reflectors and transparent conductive films.

Above percolation thickness, the optical behaviour of metal films is similar to the corresponding bulk materials, and they are transparent to visible and reflective for IR radiation as long as thickness is below about 20 nm.²² In this thickness interval, transparent metal films can be applied as neutral beamsplitters, solar control coatings, thermal insulating coatings, transparent electrodes, and heating layers.^{22, 35}

2.4.3 Common deposition techniques

Generally physical vapor deposition (PVD) methods and especially evaporation have been the earlier work horse for fabricating optical coatings, but other techniques are increasing their importance.

Every deposition technique has its own influence on film structure and on the resulting properties. Therefore coating engineers are forced to make compromises in adopting techniques that appear to be suitable for their current specific coating needs.⁷² In the PVD methods the vaporized material is transported through a reduced atmosphere and condensed on a non-heated or heated and generally rotated substrate where the coating is formed.⁷³

The production of coatings for the deep and vacuum UV (DUV/VUV) region is still dominated by the thermal evaporation of a small class of fluoride materials including LaF_3 and MgF_2 as the most prominent ones.²⁵ However, these materials tend to form coatings with a columnar microstructure containing various defects and especially voids, which may absorb contaminants from the environment.

If CaF_2 is taken as an example thin film material, mainly PVD techniques have been used for the film deposition, e.g., electron-beam evaporation (EBE),⁷⁴⁻⁷⁹ thermal evaporation,^{41,80-84} r.f. magnetron sputtering,⁸⁵ pulsed laser deposition,⁵³ and molecular beam epitaxy (MBE),^{52,86-100} The sequence of deposition processes yielding stable, harder and more adhesive coatings is said to be as follows: resistance heated evaporation < e-beam evaporation < sputtering < ion assisted deposition.³⁴

Chemical vapor deposition (CVD) is a material synthesis method where the constituents of a vapour phase participate heterogeneous reaction sequences to form a solid film on a solid substrate.⁷³ CVD of metal fluoride thin films has not been adopted widely so far due to difficulties in handling the fluorine precursors, namely hazardous HF or F_2 gas.⁹ A few CVD processes have been reported for depositing MgF_2 films,^{9,101-103} LaF_3 films,^{104,105} CaF_2 films,¹⁰⁶ and YF_3 thin films.¹⁰⁷ Generally for interference optical thin film production, PVD technologies are dominant, while CVD methods are rarely used.¹⁰⁸

2.5 Modern optics

So far just classical thin film interference optics has been discussed, but new modern optics is now briefly introduced with some practical examples. Generally classical optics is understood as 2-D films, whereas the modern optics as 3-D structures. The field of modern optics including diffractive and reflective devices is growing fast at the moment and new applications based on micro and nano optics are actively developed.

Mesh structure. One example of the modern optics is a conductive grid or mesh structure with tiny holes. These nanoholes in films may be fabricated, e.g., by focused ion beam (FIB) milling.¹⁰⁹ Surprisingly the transmittance of the light can be enhanced through these nanohole arrays (Fig. 10). Experimental studies have shown extraordinary light transmittance through arrays of subwavelength holes in silver and gold films.¹¹⁰ Transmittance efficiencies at peak wavelengths were significantly higher than the fraction of light that impinged on the holes, and orders of magnitude higher than predicted by the earlier theory. The extraordinary transmittance results from a combination of waveguiding effects within holes and electromagnetic waves at the surface of the metal, such as surface plasmons.¹¹¹ For the surface plasmons to be formed, the spacing between the holes in the mesh must be comparable to the wavelength of the light hitting the mesh. The increased light transmittance has number of potential applications including higher sensitivity surface spectroscopy.

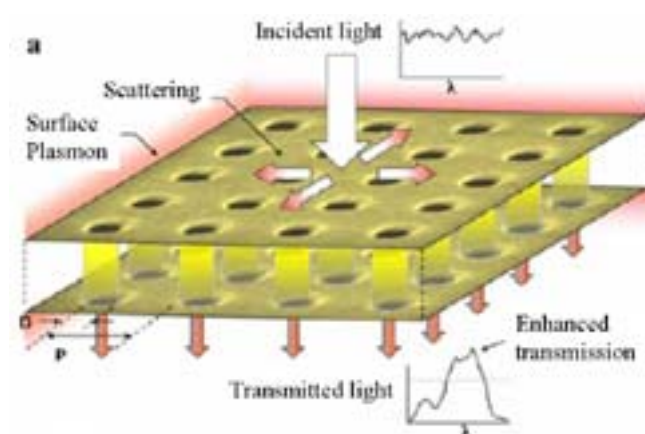


Fig. 10 Nanohole arrays in a metal film. The diagram illustrates incident light scattering into surface plasmon modes and enhanced transmittance at selected wavelengths.¹¹¹

In addition to the enhanced light transmittance, the grid structure can also be used for rejecting some part of the spectral range. For example, a inductive grid filter for rejecting IR radiation while passing part of the visible light as well as x-rays through has been fabricated,^{VII} and will be discussed in more details in Chapter 4.4.

When a matrix of hollow glass tubes is fused together, and drawn longer and narrower, the result is a micro channel plate (MCP). MCPs are used for focusing x-rays, and if the walls of the holes are coated with a thin metal layer with high density, MCP can focus the x-rays much more efficiently, but producing a smooth and conformal coating inside the micropores is a difficult task and will be discussed more in Chapter 4.5.

Metamaterials. More recently, metamaterials has been a hot topic.^{109,112} The metamaterials are artificially designed subwavelength composites possessing extraordinary optical properties that do not exist in nature. Natural materials all have a positive refractive index, but the metamaterials with negative refractive indices refracts light opposite way to the natural materials. The metamaterials can alter the propagation of electromagnetic waves, resulting in negative refraction, subwavelength imaging, and cloaking. Negative refraction was reported in bulk metamaterials composed of silver nanowires with a separation distance much smaller than wavelength at optical frequencies (Fig. 11).¹¹² A porous alumina template was prepared by electrochemical anodization, into which silver nanowires were electrochemically deposited.

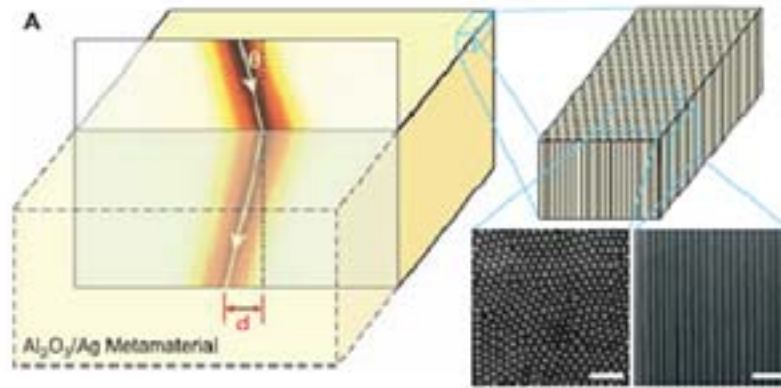


Fig. 11 Negative refraction in bulk metamaterial was achieved at visible frequencies. (Left) Schematic of negative refraction from air into silver nanowires metamaterials. (Right) Nanowires embedded in an alumina matrix, as well as SEM images showing the top and side view of the nanowires (60 nm wire diameter and 110 nm centre to centre distance). The scale bars indicate 500 nm.¹¹²

Another recent example of metamaterials is so called fishnet structure that was fabricated by evaporation and FIB (Fig. 12).¹⁰⁹ The stack consists of alternating layers of 30 nm Ag and 50 nm MgF₂, and the dimensions of the structure correspond to the diagram in Fig. 12a. The structure was fabricated so that the 3-D fishnet metamaterial can achieve a negative refractive index near the visible region ($\lambda=1450\text{--}2200\text{ nm}$)

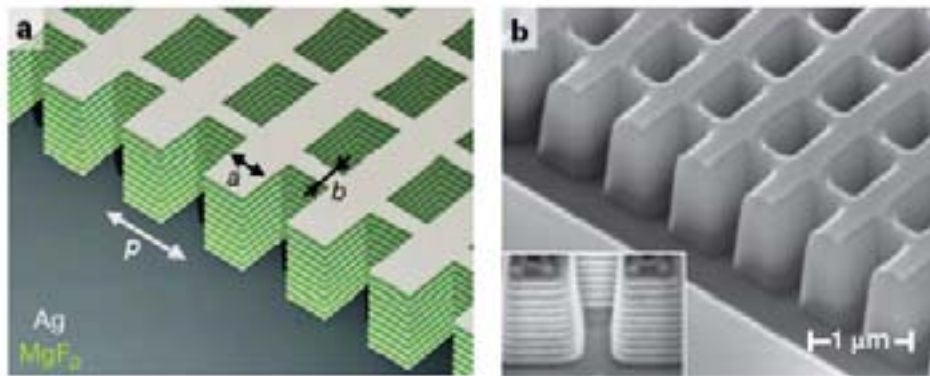


Fig. 12 Diagram of the 21-layer fishnet structure (a) with a unit cell of $p=860\text{ nm}$, $a=565\text{ nm}$ and $b=265\text{ nm}$. Cross-sectional SEM image of the fabricated fishnet structure is also shown (b).¹⁰⁹

2.6 ALD and optical thin films

Due to the certain difficulties in PVD and CVD methods (Chapter 2.4.3), atomic layer deposition (ALD) technique is considered as an option for depositing optical thin films in this section. In addition to the ALD method itself, optical film materials are introduced with some practical applications.

Because the evaporation distribution is not geometrically (and perhaps compositionally) uniform, the properties of the coating can vary spatially over the substrate holder.¹¹³ Applications such as thick metal mirror production are not affected, but a uniform layer can be critical in the production of demanding broadband and multiple-band antireflection coatings, narrow bandpass filters, polarizing coatings, and hot/cold mirrors. On the other hand, conformal films are needed for modern 3-D optics devices.

In ALD, the film growth takes place in a cyclic manner.¹² In the simplest case, one cycle consist of four steps: (1) exposure of the first precursor, (2) purge or evacuation of the reaction chamber, (3) exposure of the second precursor, and (4) purge or evacuation. This cycle is repeated as many times as necessary to obtain the desired film thickness. As the film growth proceeds in a self-limiting manner, each cycle deposits exactly the same amount of material. The ALD process is schematically shown in Fig. 13 (left). Many ALD processes may be performed over a relatively wide temperature range,^{12,114} and several low temperature ALD processes were published recently.¹¹⁵

Controlling the film thickness in ALD is easy, because the film grows via alternate saturative surface reactions. Surface controlled self-limiting film growth results in conformal and uniform films (Fig. 13 right). Other strengths of ALD are repeatability and dense and pinholes free films. The main drawback in ALD is its slowness, but batch ALD offers higher throughput and potentially lower cost than using single wafer cluster tools.¹¹⁶ Other challenges for ALD and especially for optical thin films are: high deposition rate ALD processes, fabricating artificial optical materials, and depositing highest and lowest refractive index materials.¹¹⁷

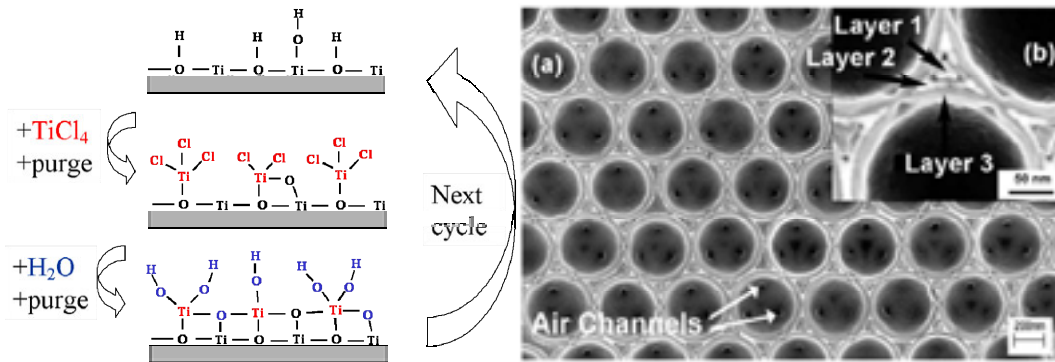


Fig. 13 Principle of ALD film deposition cycle schematically illustrated by an example of the growth of TiO_2 from TiCl_4 and H_2O precursors (left). Ion milled cross section of the opal photonic crystal (PC) with three-layer structure (right). The PC was fabricated by infiltration of opal template consisting of 466 nm silica spheres with 10 nm ZnS:Mn (layer 2) and 26 nm TiO_2 (layer 1), removing the silica template with HF, and backfilling with 10 nm TiO_2 (layer 3).¹¹⁸

General properties of selected optical materials deposited by the ALD technique are introduced in Table 4. The materials are listed in the decreasing order of refractive index. In addition to growth temperatures, transmittance regions are given for some materials. Optical properties of thin films are highly influenced by the deposition processes and the growth temperature. Therefore refractive indices given in Table 4 are only meant as guidance values. Detailed information is found from references included in Table 4.

Table 4. Selected ALD materials for optics

Material	Growth temperature (°C)	Transmittance range (μm) from ref. ^{20, 22}	Refractive index n ($\lambda \sim 550\text{--}640$ nm)	Ref.
La ₂ S ₃	300–500		2.7–2.8	119
TiO ₂	100–600	0.4–3	2.3–2.8	120–124
In ₂ S ₃	300–400		2.5–2.7	125
Cr ₂ O ₃	330–465	<0.6–8	2.4–2.7	126
ZnS _{1-x} Se _x	400, 500		2.3–2.5	127, 128
NiO	300		2.4	129
Nb ₂ O ₅	150–350	0.38–8	2.2–2.4	130
ZnS	320, 500	0.4–15	2.3	13, 131, 132
ZrO ₂	150–500	0.34–12	1.8–2.3	133–136
SrS _{1-x} Se _x	380		2.1–2.2	128
Ta ₂ O ₅	80–500	0.3–10	1.9–2.2	137
CaS	325–400		2.1	138
BaS	180–400		2.1	139, 140
In ₂ O ₃	300–500		2.1	141, 142
SrS	120–460		2.0–2.1	140, 143
Si ₃ N ₄	227–627	0.25–9	2.0–2.1	144
SrTa ₂ O ₆	200–350		1.9–2.1	145
HfO ₂	150–500	0.25–12	1.8–2.1	146–148
ZnO	177		2.0	149
AlN	500		2.0	150
Sc ₂ O ₃	175–500	0.35–13	2.0	151
Gd ₂ O ₃	300–400		1.9–2.0	152
LaGaO ₃	325–425		1.9–2.0	153
SnO ₂	50–600		1.6–2.0	154, 155
Y ₂ O ₃	200–600	0.25–12	1.8–1.9	156, 157
Ga ₂ O ₃	370		1.8–1.9	158
ITO	300–500	0.4–1.5	1.8–1.9	142, 159
PrSiO _x	200–400		1.8–1.9	160
LaAlO ₃	325–400		1.7–1.9	161
La ₂ O ₃	150–250	0.35–2	1.6–1.9	162
CaO	205–300		1.7–1.8	163
MgO	325–425	0.21–8	1.7	164
Al ₂ O ₃	100–500	0.2–7	1.6–1.7	131, 165, 166
polyimide	170		1.6	167
LaF ₃	225–350	0.2–12	1.6	III
YF ₃	175–325		1.5–1.6	IV
ZnF ₂	260–320		1.5	13
Window glass	as a reference		1.5	24
SiO ₂	150–300	0.2–9	1.4	168
SrF ₂	260–320	<0.6–>12	1.4	13
CaF ₂	300–450	0.15–12	1.4	13,I
MgF ₂	225–400	0.2–10	1.3–1.4	II,V

Thin films with a low density and a predominant ionic bonding (fluorides > oxides > sulphides) show lower refractive indices than films with a high density as well as high degree of covalent bonding, as discussed earlier. Therefore not surprisingly, La_2S_3 has the highest refractive index of 2.7–2.8 together with TiO_2 ($n \sim 2.3$ –2.8) in Table 4. The refractive index of TiO_2 generally increases with crystallization and densification of the film.¹²¹ For example, refractive indices of ALD TiO_2 films grown from $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ and H_2O increased with the growth temperature: 2.3 at 150 °C, 2.4 at 200 °C, and saturation level of 2.5 was reached at 225 °C.¹²¹ The increase of refractive index of TiO_2 film with the deposition temperature was also observed with TiCl_4 – H_2O process, where the refractive index increased from 2.4 (150 °C) to 2.6 (450 °C).¹²⁰

In addition to pure compounds, refractive indices and crystalline structures can be tailored by mixtures of different oxides.^{116,169-171} For example, in the composite of $\text{TiO}_2/\text{Al}_2\text{O}_3$ the crystalline material (TiO_2) can be modified to appear as optically amorphous.¹⁷¹ In the future, deposition of this kind of artificial materials with amorphous structure or tailored refractive indices will likely be increasing.

Ta_2O_5 has also high refractive index and high transmittance region of 0.3–10 μm (Table 4). The refractive index measured for ALD Ta_2O_5 film grown from TaCl_5 and H_2O increased from 2.0 to 2.2 with an increase with the deposition temperature from 80 to 300 °C.¹³⁷ The observed absorption coefficient α was below 100 cm^{-1} with the film deposited at 80 °C. However, α increased monotonically for two orders of magnitude when the growth temperature was increased to 500 °C. The reason for the increased effective absorption was a high amount of light scattering from the rough surface of the film.

Refractive index of 2.2 was obtained for ZrO_2 film grown from ZrCl_4 and water precursors at 500 °C,¹³³ whereas refractive index of 2.1 was observed with HfO_2 thin films grown from HfCl_4 and H_2O at 500 °C.¹⁴⁶ Refractive index of 2.1 was also obtained for HfO_2 grown from $\text{Hf}(\text{N}(\text{CH}_3)(\text{CH}_2\text{CH}_3))_4$ and H_2O precursors at temperature between 150 and 325 °C.¹⁴⁸ Nitrides (Si_3N_4 and AlN) have indices around 2.0. Nitride compounds in general find application in mechanical and decorative applications rather than optical applications.

Al_2O_3 is the most popular ALD material due to its excellent ALD process based on trimethylaluminium (TMA) and water.¹⁶⁵ Refractive index of $n \sim 1.7$ was obtained for an amorphous Al_2O_3 film deposited at 100–500 °C.

SiO_2 is one of the most desired optical materials together with MgF_2 due to its high transmittance region of 0.2–9 μm . Unfortunately there has not been a good ALD process for depositing high quality SiO_2 films until recently.¹⁶⁸

Polymer substrates are continually replacing glass optics in a number of applications: critical (medical, scientific, military) as well as commercial.¹⁷² Some polymeric materials used in the optical industry are: polycarbonate (PC), polymethylmethacrylate (PMMA), and polyetherimide. Polyimide grown by ALD at 170 °C had a refractive index of 1.6 (Table 4). The refractive indices of polymers used in optical components are said to range from around 1.4 to 1.6.¹⁷²

CaF_2 has a low refractive index of 1.4, and belongs to those few materials (SiO_2 , SrF_2 and MgF_2 in Table 4) that has a lower refractive index than a bare glass. MgF_2 has the lowest refractive index material in Table 4 ($n \sim 1.4$). More about ALD metal fluoride films (LaF_3 , YF_3 , CaF_2 and MgF_2) are discussed in Chapter 4.1.

Multilayer structures have been fabricated by ALD for different purposes and applications. ALD could be a very promising method to meet the requirements for the deposition of multilayer structures where the exact film thickness is essential. Encouraging results have been observed with ALD multilayers, e.g., HR multilayer fabricated by alternating $\text{TiO}_2/\text{Al}_2\text{O}_3$,¹¹⁶ $\text{ZnS}/\text{Al}_2\text{O}_3$,¹³¹ $\text{Ta}_2\text{O}_5/\text{MgF}_2$ (Chapter 4.3) and $\text{LaF}_3/\text{MgF}_2$ (Chapter 4.3). A reflectance of about 90% was demonstrated with a 9-layer stack of $\text{ZnS}/\text{Al}_2\text{O}_3$ at visible region.¹³¹

Besides the ALD materials introduced in Table 4, ALD metals can also be applied in optical applications, e.g., for focusing x-rays and in x-ray mirrors. For example, $\text{W}/\text{Al}_2\text{O}_3$ nanolaminate deposited by ALD may be important for x-ray mirrors and low thermal conductivity thermal barrier and tribological coatings.^{173,174} The fabrication of lightweight and flexible x-ray mirrors is possible using ALD structures even on polymer substrates, and high reflectivity values of 74–78% at $\lambda = 1.54 \text{ \AA}$ were reached with $\text{W}/\text{Al}_2\text{O}_3$.¹⁷⁵ These x-ray

mirrors could be very useful for x-ray focusing, adaptive x-ray mirrors and future x-ray observatory missions in space.

Thanks to nanostructure trench filling capability, ALD opens a path for innovative nanostructured optical devices and integrated optical devices.¹⁷⁰ High performance optical retarders based on all dielectric immersion nanogratings have been fabricated by the aid of ALD.^{169,176} Optical phase retarders or wave plates can be key elements in many optical applications. All-dielectric nanolaminate materials deposited by ALD were utilized to fill trenches of the nanogratings to form immersion nanogratings (Fig. 14). Unfilled high aspect ratio nanostructures are mechanically weak and thus susceptible to scratch damage.¹⁷⁰ Furthermore, using the dielectric filling material versus air adds additional design freedom for choosing the refractive index contrast with the material comprising the immersion grating. The refractive index of the nanolaminate material was tailored and controlled precisely by controlling the ratio of TiO_2 and SiO_2 . By changing the ratio of $\text{TiO}_2/\text{SiO}_2$, the refractive index of the nanolaminate material could be varied from 1.46 to 2.35. An antireflective coating consisting of four layers of TiO_2 and SiO_2 was also deposited by ALD on the top of the retarder (not shown). TiO_2 was deposited from titanium ethoxide and water, whereas SiO_2 was fabricated from a silanol and water. Two nanogratings fully filled by ALD Ta_2O_5 can also be integrated together as illustrated in Fig. 15.

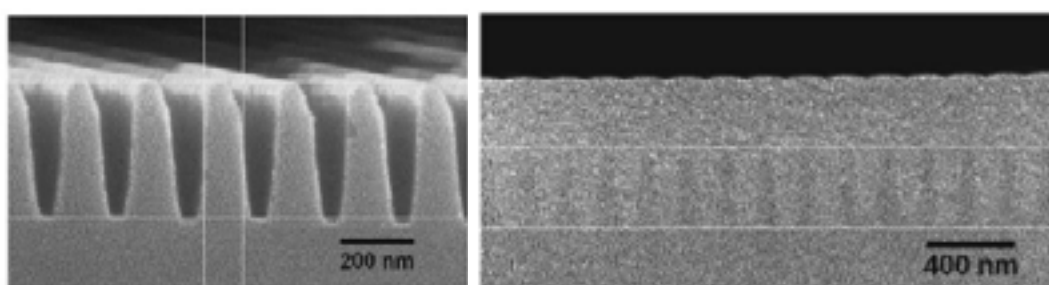


Fig. 14 Cross-sectional SEM image of the nanograting before (left), and after filling with nanolaminate $\text{TiO}_2/\text{SiO}_2$ by ALD (right). The grating has depth of ~ 390 nm with a period of 200 nm.¹⁶⁹

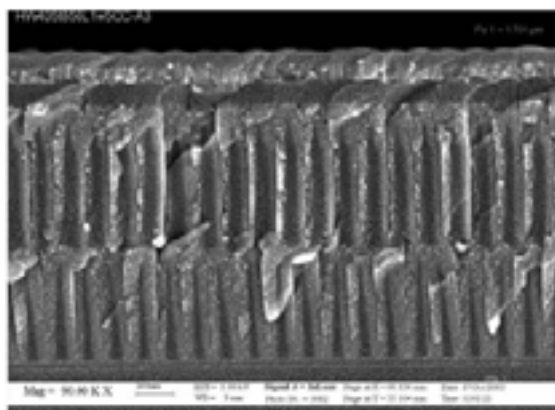


Fig. 15 Cross-sectional SEM image of a two-layer monolithically integrated half-wave plate with two fully trench-filled nanostructure grating layers.¹⁷⁶

ALD can also be applied for shape engineering due to the conformal film growth onto a template.¹¹⁷ Lens arrays which are used in microdisplays, digital imaging, and telecommunication can be fabricated by the aid of ALD.¹⁷⁷ A method for forming a microlens array based on conformal ALD growth of SiO_2 around template posts is shown in Fig. 16.

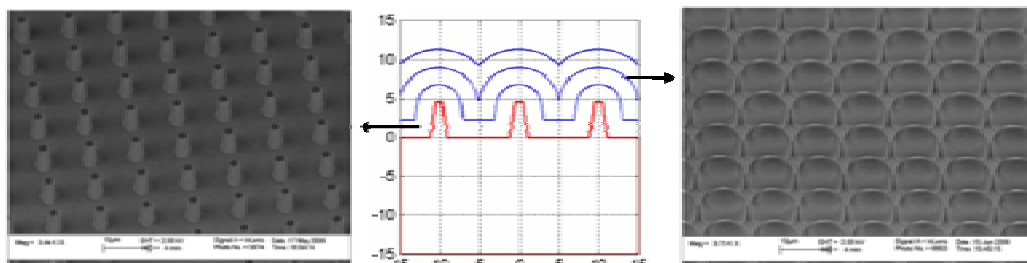


Fig. 16 SEM image of a microlens template (left) which is represented with the red bottom line in the simulation example of the constant-speed surface contour growth (middle). SEM image of the final microlens arrays with a diameter and a pitch size of $10\ \mu\text{m}$ after $4.8\ \mu\text{m}$ thick SiO_2 deposition by ALD onto the template (right).¹⁷⁷



3 EXPERIMENTAL

In this chapter, the methods used for thin film growth studies and for the characterization of the deposited films are presented. More specific information including, when relevant, precursor synthesis, properties and pulsing sequences can be found in the original publications (I-VII).

Film deposition

CaF_2 ,^I MgF_2 ,^{II,V} LaF_3 ,^{III} YF_3 ,^{IV} and Ta_2O_5 (Chapter 4.2) thin films were grown in a hot-wall flow-type F-120 reactor (ASM-Microchemistry Ltd., Helsinki, Finland). Ir thin films for inductive grid filters was also coated with the F-120 reactor,^{VII,178} whereas Ir films for micro channel plates as well as Fresnel zone plates were deposited with SUNALE™ R150 reactor (Picosun, Espoo, Finland).^{179,VI} The pressure in both reactors was below 10 mbar. The films were mainly deposited onto $5 \times 5 \text{ cm}^2$ Si(100,111) substrates with native SiO_2 . Other substrates were $2.5 \times 5 \text{ cm}^2$ quartz, $5 \times 5 \text{ cm}^2$ glass (borosilicate and sodalime), and $5 \times 5 \text{ cm}^2$ ITO (Indium tin oxide) film on glass.

Film characterization

The films were characterized by many different methods. Adhesion of the films was tested with a simple Scotch tape test. Thicknesses and refractive indices of the films were determined from optical reflection and transmission spectra obtained with a Hitachi U2000 spectrophotometer in the wavelength range of 190–1100 nm. A fitting program, described elsewhere,³² was used in analyzing the spectra. In some cases the spectra were measured with a Lambda850 spectrometer in the wavelength range of 140–800 nm.^{II,III}

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^{IV-V} or with a

Bruker-axs D8 Advance x-ray diffractometer.^{I-III}

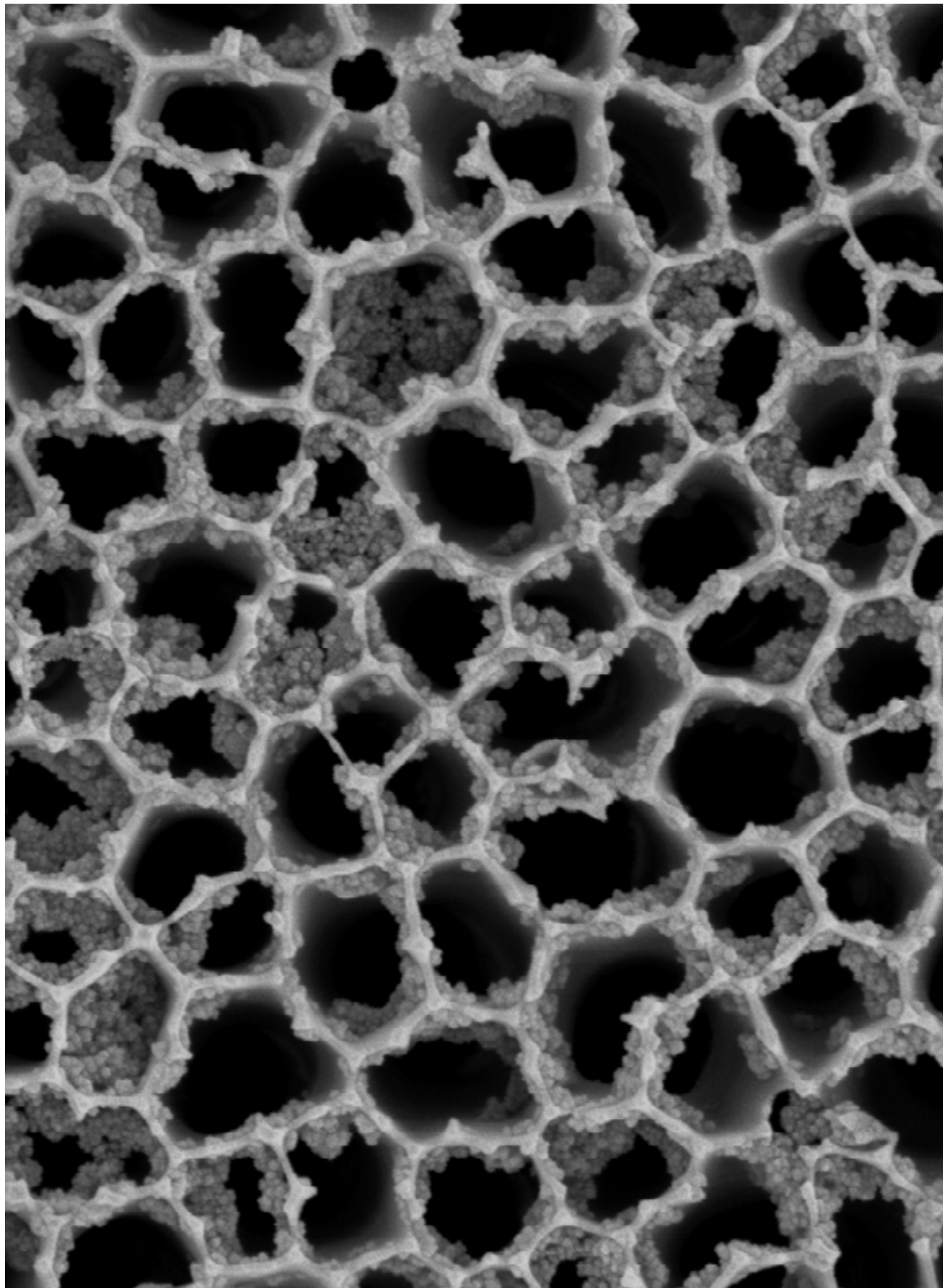
Film morphology was studied with atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) was used only in case of MgF₂ deposited from TiF₄ + Mg(thd)₂.^{II} TEM studies were done by using a JEOL JEM 3010 equipment operated at 300 kV, with a point-to-point resolution of 0.21 nm. AFM studies were done by using a Veeco Instrument Nanoscope V. Samples were measured in tapping mode in air using a phosphorus doped silicon probe (RTESP) delivered by Veeco Instrument with a scanning frequency 0.3–1.0 Hz. Roughness values were calculated as root-mean-square values (R_q). Several wide scans were performed from different parts of the samples to guarantee the uniformity of the film surface. Final images were measured from a scanning area of $2 \times 2 \mu\text{m}^2$ and no image processing except flattening was done. For SEM studies a Hitachi S4800 FESEM equipment was used. The samples were coated a thin metal alloy using a Cressington 208HR sputter coater.

Composition of the films was analyzed by time-of-flight elastic recoil detection analysis (TOF-ERDA) using 24 MeV $^{127}\text{I}^{5+}$,^{I-III} and 35 MeV $^{34}\text{Cl}^{7+}$ projectile beam.^{IV-V} More details from ERD analysis is found elsewhere.¹⁸⁰

Electrical properties, permittivity and current density, were measured at room temperature on Al/metal fluoride/ITO/glass capacitor structures with Al dot electrode area of $2.04 \times 10^{-7} \text{ m}^2$. About 100 nm thick Al dots were deposited on top of the metal fluoride films by e-beam evaporation (EBE) through a shadow mask. Permittivity of the films was measured using a HP 4284A precision LCR-meter at 10 kHz. A Keithley 2400 SourceMeter was used to measure leakage current densities.

Inductive grid filters (Chapter 4.4) were done in collaboration with the University of Joensuu (Finland). The filters were fabricated in Joensuu excluding Ir coating made by ALD. Micro channel plates (MCPs) (Chapter 4.5) were fabricated together with Oxford Instruments (Espoo, Finland), the University of Joensuu (Finland), and the University of Leicester (England). Fresnel zone plates (Chapter 4.6) were done in collaboration between the Universitat Autònoma de Barcelona (Spain) and the Paul Scherrer Institut in Villigen (Switzerland). The

silicon structures were patterned in Switzerland and later scanning transmission x-ray microscopy experiments were carried out at the PoLLux Beamline of the Swiss Light Source at the Paul Scherrer Institut.



4 RESULTS AND DISCUSSION

The main results of the thesis are summarized in this chapter. More details about ALD processes and experimental work can be found in the corresponding publications (I-VII).

4.1 Novel ALD processes of metal fluorides

Fluoride ALD processes have been largely missing, which is mostly due to lack of a good fluorine precursor. $\text{TiF}_4^{\text{I-IV}}$ and TaF_5^{V} were applied as novel fluorine precursors in these studies. They are both solids with relatively low vapor pressure at room temperature and can thus be quite safely handled and removed from reactor exhaust gases. Both fluorine sources also have the properties required for an ALD precursor, e.g., sufficient volatility as well as high reactivity and good thermal stability.¹² It must be emphasized that it is uncommon to use metal compound as non-metal precursor source in ALD.^{12, 114} Thus, the key question in these reactions is how completely the reaction can be, i.e., how the ligands and especially metal atoms can be eliminated from the final film.

TiF_4 precursor was used for the first time as a fluorinating agent for depositing CaF_2^{I} , MgF_2^{II} , $\text{LaF}_3^{\text{III}}$ and YF_3^{IV} thin films by ALD. TaF_5 was used as an alternative novel fluorine source only for depositing MgF_2 thin films.^V Because of the larger size of Ta (ionic radii of 0.64 Å) compared to Ti (0.42 Å),¹⁸¹ tantalum may be less readily incorporated as an impurity into MgF_2 thin films. This decrease in metal impurities would lead to increase of desired UV light transmittance of the films.

4.1.1 Film growth

Growth characteristics of ALD metal fluoride thin films were studied on silicon substrates. Uncommonly high growth rates for thermal ALD processes were

obtained,¹⁸² especially in the case of LaF₃ thin films; 1.8–5.2 Å/cycle (Fig. 17 and Table 6). Other growth rates (Å/cycle) were 0.5–1.6 for CaF₂, 1.1–1.7 for YF₃, 0.7–1.6 for MgF₂ (from TiF₄), and 0.4–1.1 for MgF₂ (from TaF₅) (Fig. 17).

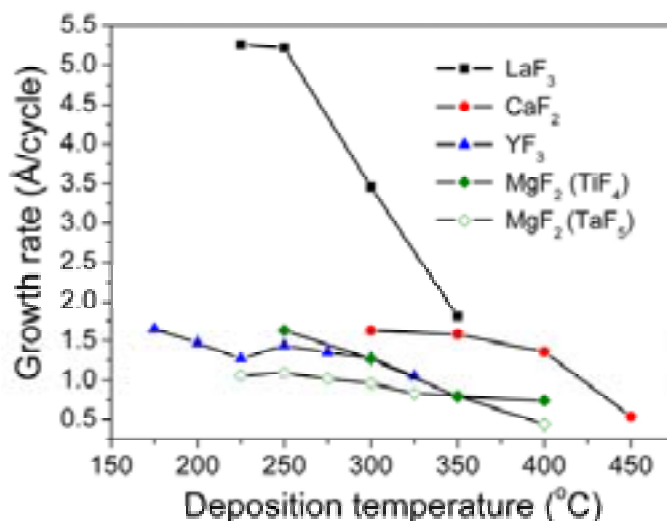
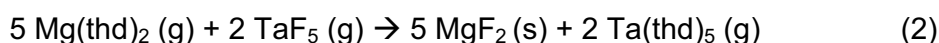
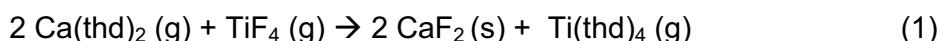


Fig. 17 Growth rates of fluoride thin films on Si as a function of deposition temperature.

Explanation for these high growth rates may be found from a unique film growth mechanism. While the detailed reaction mechanism remains unidentified at the moment, the following net reactions (1, 2) are suggested:



In the reaction of Ca(thd)₂ and TiF₄ (1), a solid CaF₂ is formed as well as volatile Ti(thd)₄. With this suggested reaction (1), 4 times higher growth rate was reached for CaF₂^I than that published before for ALD of CaF₂ with HF as the fluorine source.¹³ The same type of reaction using TiF₄ as a fluorinating agent can be applied for depositing MgF₂,^{II} LaF₃,^{III} and YF₃^{IV} thin films. Even if this ALD process was quite general, it was not successful in all cases, for example Al(thd)₃, Gd(thd)₃ and Pb(thd)₂ did not react with TiF₄ forming fluoride. In reaction (2) volatile precursors form solid MgF₂^V and volatile Ta(thd)₅.

In ALD, the overall reaction is divided into two half reactions occurring during

the two pulses. As an example, the stepwise growth mechanism of CaF_2 film is suggested in Fig. 18. The reaction scheme starts with $\text{Ca}(\text{thd})_2$ pulse (Fig. 18a). The preceding TiF_4 pulse has left TiF_x adsorbed on the surface of the previously deposited CaF_2 . The incoming $\text{Ca}(\text{thd})_2$ first reacts with TiF_x forming solid CaF_2 as well as volatile $\text{Ti}(\text{thd})_4$. After $\text{Ca}(\text{thd})_2$ has consumed all TiF_x on the surface, $\text{Ca}(\text{thd})_2$ still adsorbs on top of the formed solid CaF_2 , and the surface becomes now covered by adsorbed $\text{Ca}(\text{thd})_x$. Then during the TiF_4 pulse (Fig. 18b), TiF_4 reacts with $\text{Ca}(\text{thd})_x$, and volatile $\text{Ti}(\text{thd})_4$ and solid CaF_2 are formed. After TiF_4 has consumed all the $\text{Ca}(\text{thd})_x$ on the surface, TiF_x adsorbates cover the top of the freshly deposited CaF_2 surface. This leads back to the start of the scheme (Fig. 18a). In summary, different from the most other thermal ALD processes, metal fluoride is formed in both half reactions during one ALD cycle. This kind of reaction mechanism could explain the high growth rates of the fluoride films. A similar mechanism can be suggested for all other fluorides also.

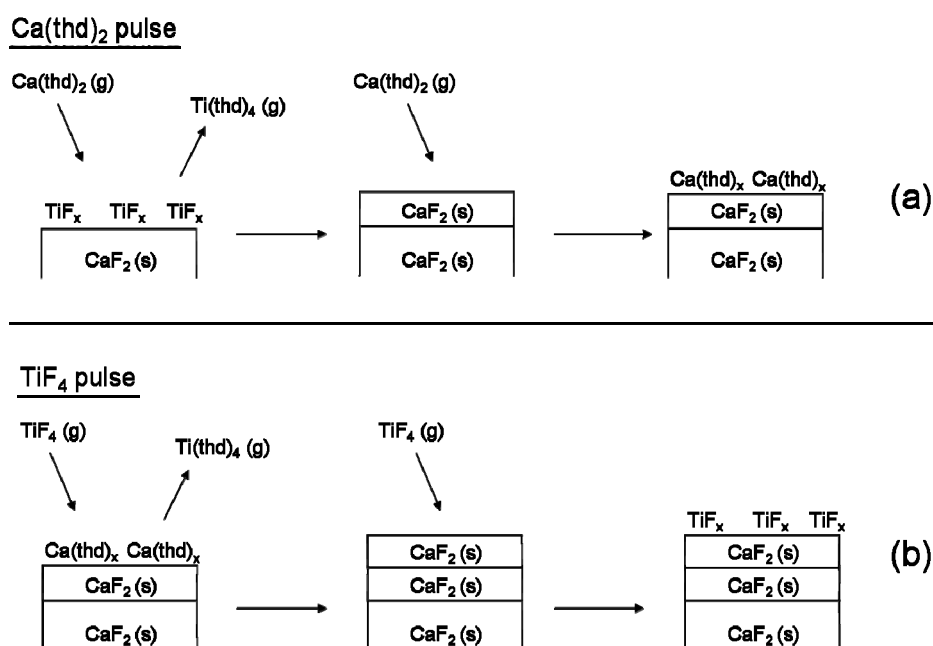


Fig. 18 Suggested reaction mechanism in ALD of CaF_2 during a) $\text{Ca}(\text{thd})_2$ pulse, and b) TiF_4 pulse. N_2 purges are always applied after each precursor pulses. CaF_2 is formed in both half reactions.¹

Common to all metal fluoride thin films grown by ALD was that the growth rate decreased with increasing deposition temperature (Fig. 17 and Table 6). This was also observed in ALD of fluoride thin films using HF as a fluorine source.¹³

One explanation could be that the adsorption density of TiF_x may decrease at elevated temperature.¹

4.1.2 Crystallinity and density

Because most of the films are polycrystalline, the films consist of crystalline grains, which are separated by grain boundaries that are less dense and may be impurity-enriched.²² This is the reason why film properties may differ significantly from bulk properties.

Table 5. Densities and crystalline structures of fluoride thin films on Si. Densities were determined by XRR or ERDA*.

Material	ALD process	Growth temperature (°C)	Density (g/cm ³)	Ref. density (g/cm ³)	Crystalline structure
MgF_2	$\text{Mg}(\text{thd})_2 + \text{TiF}_4^{\text{II}}$	250–400	2.4–2.8	3.15 ³⁰	Crystalline, tetragonal
	$\text{Mg}(\text{thd})_2 + \text{TaF}_5^{\text{V}}$	225–400	2.9–3.1		Crystalline, tetragonal
CaF_2	$\text{Ca}(\text{thd})_2 + \text{TiF}_4^{\text{I}}$	300–450	2.9–3.1	3.18 ³⁰	Crystalline, cubic
LaF_3	$\text{La}(\text{thd})_3 + \text{TiF}_4^{\text{III}}$	225–350	3.3–4.5	5.9 ³⁰	Crystalline, hexagonal
YF_3	$\text{Y}(\text{thd})_3 + \text{TiF}_4^{\text{IV}}$	175–200	2.6–3.8*	5.1 ¹⁸³	Amorphous
		225–325	4.2–4.8*		Crystalline, orthorhombic

The trend that film density increased with the growth temperature was similar to all fluoride films (Table 5). One reason for this might be that the films grown at high deposition temperatures are also much purer.

Diffraction patterns of all fluorides are illustrated in Fig. 19. The following phases were obtained: tetragonal for MgF_2 , cubic for CaF_2 , orthorhombic for YF_3 , and hexagonal for LaF_3 . Interestingly, the most intense reflection of MgF_2 film grown from TaF_5 at 400 °C was (111), whereas for MgF_2 film grown from TiF_4 at the same temperature it was (110) reflection. As an exception, YF_3 films could be deposited below 225 °C, and the films were amorphous when deposited at 175–200 °C. However, YF_3 thin films were polycrystalline when the substrate temperature was 225 °C and above.

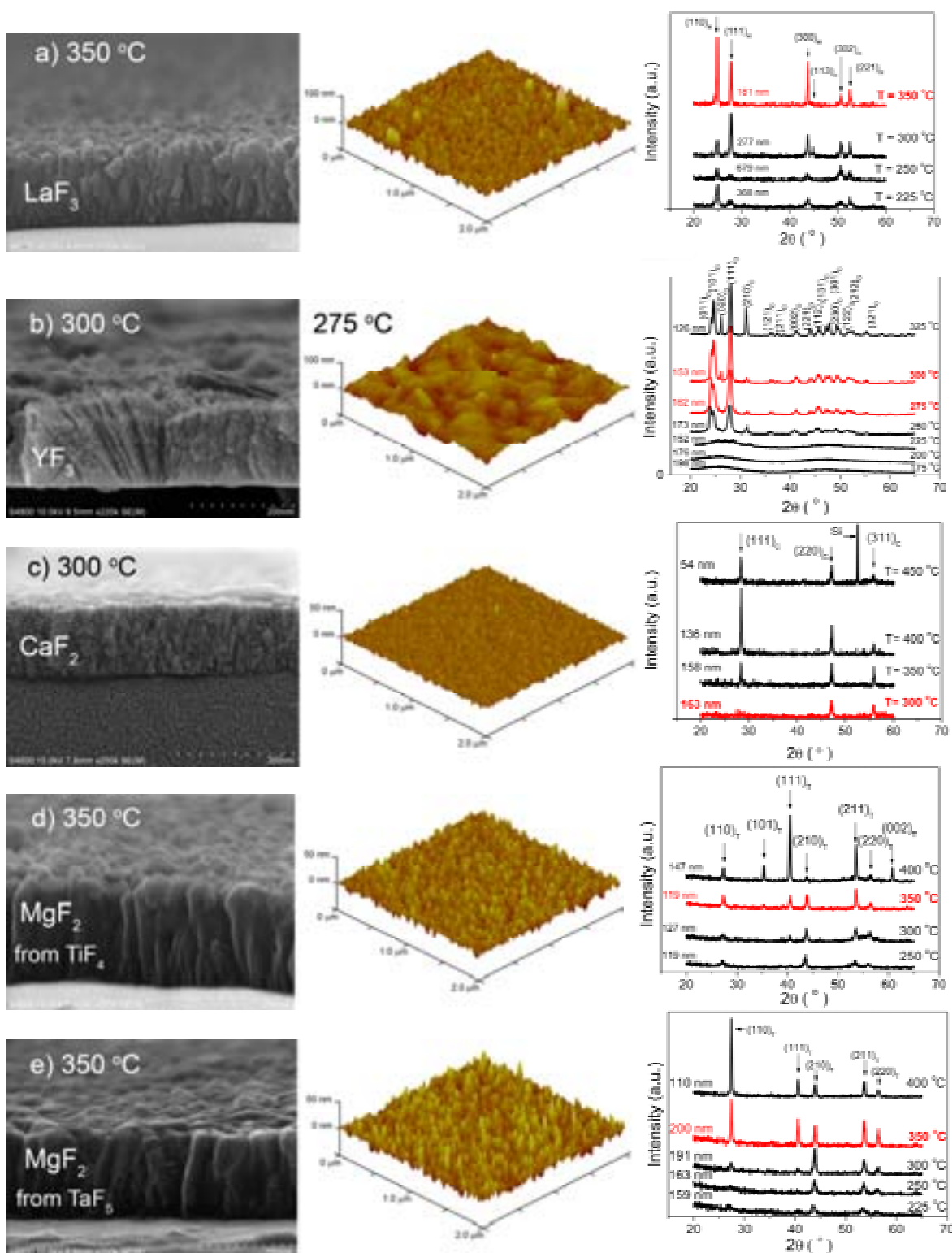


Fig. 19 Cross-sectional SEM images (left), AFM images (middle), and GI-XRD patterns (right) of fluoride films on Si for a) LaF_3 , b) YF_3 , c) CaF_2 , d) MgF_2 (from TiF_4), and e) MgF_2 (from TaF_5).

4.1.3 Morphology and surface roughness

The morphology of the film was analyzed by AFM and cross-sectional SEM (Figs. 19 and 20). The growth mode of LaF_3 at 350 °C is columnar (Fig. 19a), whereas at 250 °C the structure was between columnar and granular.^{III} Columnar type of film growth was also observed with MgF_2 samples (Fig. 19d and e). On the other hand, YF_3 seems to have lamellar type of growth at 275–300 °C (Fig. 19b), and CaF_2 grows granularly at 300 °C (Fig. 19c).

The surface roughness of the fluoride films on the silicon substrates increased usually with an increase in the deposition temperature as seen in Table 6 and Fig. 20. Smooth films were typically observed only at the lower growth temperatures, but unfortunately they had also high impurity contents. MgF_2 film deposited from $\text{Mg}(\text{thd})_2$ and TiF_4 at 400 °C and YF_3 film deposited at 350 °C had noteworthy high rms-roughness values of 23.0 and 17.0 nm, respectively.

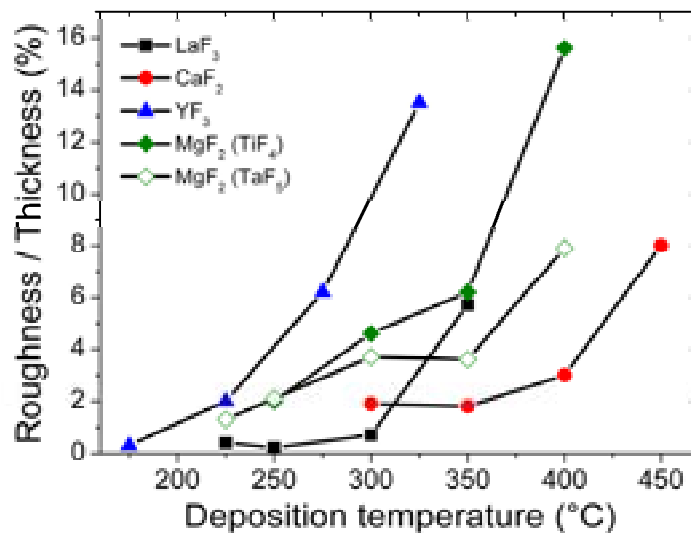


Fig. 20 Roughness (nm) divided film thickness (nm) %-values as a function of growth temperature (°C).

Table 6. Properties of metal fluorides films on Si. Film thickness was measured by spectrophotometry, roughness by AFM, and impurities by TOF-ERDA or ERDA*.

Material	ALD process	Growth T (°C)	Growth rate (Å/cycle)	Thickness (nm)	Rms roughness (nm)	Total impurity content (at. %)	Stoichiometry (F/metal)
LaF ₃	La(thd) ₃ +TiF ₄ ^{III}	225	5.2	368	1.6	29.4	2.6
		250	5.2	679	1.4	26.8	2.7
		300	3.5	277	2.0	16.5	2.6
		350	1.8	181	10.3	3.5	2.8
CaF ₂	Ca(thd) ₂ +TiF ₄ ^I	300	1.6	163	3.1	2.1	2.0
		350	1.6	158	2.8	1.7	2.0
		400	1.4	136	4.1	2.1	2.0
		450	0.5	54	4.3	9.2	2.0
YF ₃	Y(thd) ₃ +TiF ₄ ^{IV}	175	1.7	198	0.5	31.5*	3.1
		225	1.3	152	3.0	17.9*	3.1
		275	1.4	162	10.1	18.5*	3.0
		325	1.1	126	17.0	3.0*	3.1
MgF ₂	Mg(thd) ₂ +TiF ₄ ^{II}	250	1.6	163	3.3	19.6	2.2
		300	1.3	127	5.8	5.6	2.1
		350	0.8	102	6.3	0.6	2.0
		400	0.7	147	23.0	0.3	2.0
	Mg(thd) ₂ +TaF ₅ ^V	225	1.1	159	2.1	19.3*	2.4
		250	1.1	163	3.4	8.4*	2.1
		300	1.0	191	7.0	2.8*	2.0
		350	0.8	200	7.1	0.6*	2.1
		400	0.4	110	8.7	2.6*	2.1

4.1.4 Composition

Good stoichiometry as well as purity of fluoride films is important because impurities increase absorbance of the film, especially in the UV range. Contamination becomes more important in the VUV where the extinction coefficients of water and of most organic compounds are higher by orders of magnitude compared to the visible spectral range.²⁶ CaF_2 thin films had a good stoichiometry with F/Ca ratio value of 2.0 in all the films grown in the temperature range of 300–450 °C (Table 6). LaF_3 thin films were fluorine deficient with F/La ratio of 2.6–2.8. However, these ratios were still closer to stoichiometric than those reported for some PVD methods,^{184,185} which shows that LaF_3 films with exact stoichiometry are difficult to reach. YF_3 thin films had F/Y ratios between 3.0 and 3.1, whereas MgF_2 thin films deposited from $\text{Mg}(\text{thd})_2 + \text{TiF}_4$ had F/Mg ratios of 2.0–2.2. On the other hand, MgF_2 films grown using TaF_5 as a fluorinating agent were slightly fluorine rich with F/Mg ratio between 2.0 and 2.4.

Total impurity contents in the films seem to decrease with increasing substrate temperature, except for CaF_2 films (Table 6). The impurity content of CaF_2 stayed around 2.0 at. % at 300–400 °C, but due to decomposition of the $\text{Ca}(\text{thd})_2$ precursor at 450 °C the content increased up to 9.2 at. %. At lower deposition temperatures, especially in the case of LaF_3 (225–250 °C) and YF_3 (175 °C) samples, a lot of impurities were detected with total values around 30 at. %. High amounts of impurities could be caused by an incomplete reaction. High growth rates of these films also support that conclusion. The lowest total impurity contents (at. %) were usually obtained at higher growth temperatures: 1.7 for CaF_2 at 350 °C, 0.6 for MgF_2 grown from TaF_5 at 350 °C, 0.3 for MgF_2 grown from TiF_4 at 400 °C, 3.5 for LaF_3 at 350 °C, and 3.0 for YF_3 at 325 °C. Metal/F ratio was improved especially for MgF_2 thin films when the total impurity content decreased. The detected impurities were H, C, O and Ti or Ta depending on the used fluorine source. Unfortunately the highest purity was correlated with the poorest morphology in the YF_3 and MgF_2 samples.

4.1.5 Optical properties

It should be kept in mind that the depositions and characterizations of the films in this thesis have not been done in clean room environment, which might have affected the light transmittance of the films caused by impurity particles. In addition, the optical as well as other properties of thin films differ from the pure bulk materials. For example, the transparency of vacuum deposited thin films is often slightly worse than that of bulk materials.²¹ A small packing density causes a reduction of the refractive index of the films. Light transmittance depends heavily on the impurities; especially in the UV range.⁴⁰ Measuring the absorption is a straightforward way to confirm the purity of the film.

Generally the refractive indices were close to the bulk values at the visible region (Table 7). However, lower than the bulk values were obtained at higher deposition temperatures. This is mainly due to increasing roughness and porosity of the polycrystalline film microstructure,¹⁸⁶ as shown by SEM and AFM (Fig. 19). Generally the absorption for the fluoride films was negligible, except for YF_3 films the absorption coefficients of $0\text{--}500\text{ cm}^{-1}$ were obtained ($\lambda = 1.0\text{ }\mu\text{m}$). Therefore, slightly higher than bulk indices were observed at lower growth temperatures caused by high amount of impurities, especially oxygen in YF_3 films.

The transmittance curves were measured down to 190 nm only from films having a combination of high purity with reasonably low roughness. For these measurements the films were deposited onto high transmittance quartz substrates. Comparisons made with YF_3^{IV} and $\text{MgF}_2^{\text{II,V}}$ showed that the purer film grown at higher temperature seemed to be better choice. Only the highest transmittance samples of these are illustrated in Fig. 21. The highest transmittances were obtained with MgF_2 films due to their low total impurity contents of 0.6 at. % (Table 6). MgF_2 and CaF_2 have lower refractive indices than the bare quartz substrate; therefore, their transmittance curves are above the quartz curve (Fig. 21). MgF_2 thin film deposited from $\text{Mg}(\text{thd})_2 + \text{TaF}_5$ onto quartz substrate had the highest light transmittance down to the UV region. This proves that TaF_5 must be considered as an excellent fluorine source for ALD, and even better than TiF_4 . On the other hand, $\text{YF}_3/\text{quartz}$ sample had the weakest light transmittance in the near UV region. This is mainly due to light

absorption by high amount of impurities, as discussed already above. However, YF₃ had the reasonable light transmittance at 500–1100 nm.

Table 7. Refractive indices of fluoride thin films on Si determined by spectrophotometry.

Material	ALD process	Growth temperature (°C)	Refractive index n ($\lambda = 580$ nm)	Ref. refractive index n ($\lambda = 589$ nm)
LaF ₃	La(thd) ₃ +TiF ₄ ^{III}	225–350	1.58–1.61	1.61 ³⁰
YF ₃	Y(thd) ₃ +TiF ₄ ^{IV}	175–325	1.51–1.59	1.55 ¹⁸³
CaF ₂	Ca(thd) ₂ +TiF ₄ ^I	300–450	1.42–1.44	1.43 ³⁰
MgF ₂	Mg(thd) ₂ +TiF ₄ ^{II}	250–400	1.34–1.42	1.38 ³⁰
	Mg(thd) ₂ +TaF ₅ ^V	225–400	1.36–1.38	

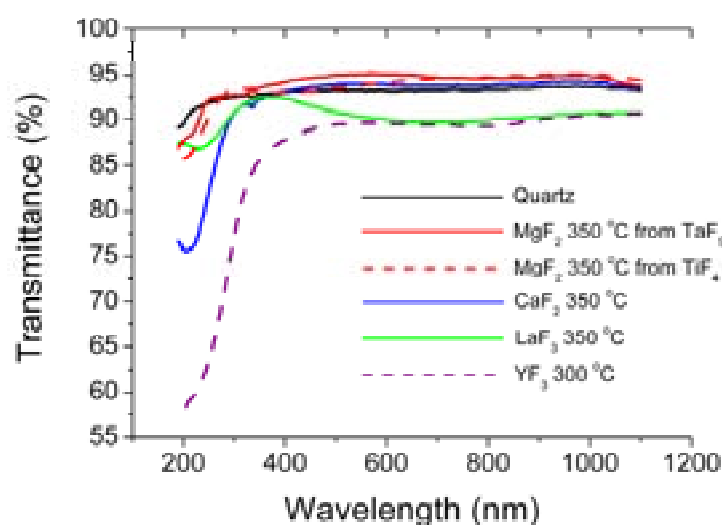


Fig. 21 Transmittance spectra of metal fluoride thin films on quartz, and a spectrum of bare quartz substrate in a wavelength range of 190–1100 nm. Film thicknesses were 100 nm for MgF_2 (from TaF_5), 155 nm for MgF_2 (from TiF_4), 143 nm for CaF_2 , 110 nm for LaF_3 , and 127 nm for YF_3 .

4.1.6 Electrical properties

Metal fluorides are dielectric materials with high band gap values of (eV): 12.8 for MgF_2 ,¹⁸⁷ 12.1 for CaF_2 ,⁵² 10.3 for YF_3 ,¹⁸⁸ and 10.3 also for LaF_3 .¹⁸⁹ Electrical behaviour of the metal fluoride thin films was measured from Al/fluoride/ITO capacitor structures on glass and results are introduced in Table 8.

Table 8. Electrical properties of the fluoride films.

Material	ALD process	Growth T (°C)	Thickness (nm)	Permittivity (at 10 kHz)	Ref. permittivity	Breakdown field (MV/cm)
LaF ₃	La(thd) ₃ + TiF ₄ ^{III}	250	85	12.3	14.0 ¹⁹⁰	−1.8, +2.3
CaF ₂	Ca(thd) ₂ + TiF ₄ ^I	350	200	6.6	6.81 ³⁰	−0.31, +0.43
YF ₃	Y(thd) ₃ + TiF ₄ ^V	200	93	5.8	13.6 (at 1 kHz) ¹⁹¹	−3.9, +4.9
		300	88	6.2		−2.4, +2.5
MgF ₂	Mg(thd) ₂ + TiF ₄ ^{II}	250	140	4.9	5.45	−5.8, +4.4
	Mg(thd) ₂ + TaF ₅ ^{IV}	250	85	4.4	(at 1 MHz) ¹⁹²	−3.6, +3.8
		300	90	5.1		−2.6, +2.7

LaF₃ thin film has the highest permittivity of 12.3, whereas MgF₂ films have the lowest permittivity in the range of 4.4–5.1. All average permittivity values were in good agreement with the bulk or relevant reported values. MgF₂ together with YF₃ films exhibit the highest leakage values before the catastrophic breakdown. For CaF₂ film the leakage level stayed below $<10^{-7}$ A/cm² before the catastrophic breakdown, which is better than 10^{-6} A/cm² reported for an evaporated CaF₂ film.⁸⁰ Leakage current densities for CaF₂ were also significantly better than those achieved earlier with ALD CaF₂ grown from Ca(thd)₂ and HF in a similar capacitor structure and with almost the same film thickness.¹³ On the other hand, CaF₂ seems to be the poorest insulator with the lowest breakdown fields of -0.31 and +0.43 MV/cm (Table 8). Both LaF₃ and

YF₃ thin films had leakage levels below 10⁻⁵ A/cm² before the breakdowns. MgF₂ film deposited from TiF₄ had high breakdown fields of -5.8 and +4.4 MV/cm, which are incredibly better than 0.2 MV/cm observed earlier for a 292 nm thick MgF₂ film deposited by thermal evaporation.⁸⁰ Anyhow, MgF₂ film grown using TiF₄ as a fluorine precursor had a leakage level below <10⁻⁵ A/cm² before breakdown, whereas MgF₂ films grown from TaF₅ at 250 and 300 °C had lower leakage levels of 10⁻⁸ A/cm² and 10⁻⁷ A/cm² before breakdown, respectively. And as expected, YF₃ film with the amorphous film structure (Table 5) grown at 200 °C is a better insulator (-3.9 and +4.9 MV/cm) than the highly crystalline 300 °C sample (-2.4 and +2.5 MV/cm) where the current can leak along the grain boundaries. The leakage current density stayed below 10⁻⁵ A/cm² within both samples before the breakdown.

In a summary, results in Table 8 prove that most ALD grown metal fluoride films remain in the class of good insulators, despite polycrystalline structure of these films (Table 10).

4.2 High reflecting coating / bandpass filter

To study the applicability of the new fluoride processes in fabricating of high reflecting optical coating, the multilayer stack was built up from quarter-wave layers of MgF₂ and Ta₂O₅ for visible region, and another stack of MgF₂ and LaF₃ for UV region. Reflection over as high as 99% can be achieved in narrow bands with quarter-wave stacks, which exhibit very low absorption, and therefore are qualified for high-energy laser applications.³⁴

It has been shown already that ALD can be applied in preparation of multilayer stack for optical applications.¹³¹ However, multilayer stack of oxide and fluoride films or just fluoride films has never been fabricated by ALD. It is an interesting and difficult task; alternating oxide and fluoride coatings can be problematic because oxygen must be present for the oxide compound but, simultaneously, oxygen incorporation or substitution in the fluoride layer must be avoided to maintain low optical absorption.¹⁹³

The multilayer coatings were built up from quarter-wave layers so that the layers had optical thicknesses:

$$nd=\lambda/4 \quad (23)$$

where n is refractive index of the layer, and d is the geometric thickness of the layer. The wavelength λ was chosen to be 550 nm at visible region and 248 nm for UV region.

Visible region. High reflecting (HR) coating for visible area were grown by ALD using Ta_2O_5 as a high- n (H) and MgF_2 as a low- n (L) material. Their combination provides a high index ratio, and thereby a minimum number of layers required to achieve a desired performance. Ta_2O_5 was deposited from $\text{Ta}(\text{OEt})_5$ and H_2O , whereas MgF_2 was grown from $\text{Mg}(\text{thd})_2$ and TaF_5 . The deposition temperature was 250 °C. Refractive indices determined from test ALD runs were 2.18 for Ta_2O_5 and 1.42 for MgF_2 . When using these refractive indices, values of 67 nm for Ta_2O_5 and 97 nm for MgF_2 were evaluated for the geometric thicknesses from Eq. 25. Once the exact growth rates were determined from the test ALD runs, the numbers of deposition cycles were chosen so that the target film thicknesses could be achieved. The optical performance was examined by comparing the measured reflectance spectrum with that calculated for the ideal design structure.

A reflectance spectrum of nine-layer structure (HLHLHLHLH) is depicted in Fig. 22. This kind of structure acts as a HR coating as discussed above. The main interest lies in the HR region of 450–720 nm. The side band regions where the reflectance exhibits several maxima and minima are not that important. The measured reflectance was about 96%, whereas the design reflectance was 97%. Higher reflectance could be obtained by just simply depositing more layers. As shown in Fig. 22 (left), the measured curve (squares) has been slightly shifted to longer wavelengths than the design curve (solid line). A reason for this is that the growth rate of MgF_2 was slightly more than estimated from the test run. However, as illustrated in Fig. 22 (right), fitted curve (dashed line) with increased thickness of MgF_2 layers it fit properly together with the measured one (squares). Due to the increased thickness of the MgF_2 layers (97 nm $\rightarrow$ 103 nm), 1% of the reflectance is lost from 97% to 96% at the same time.

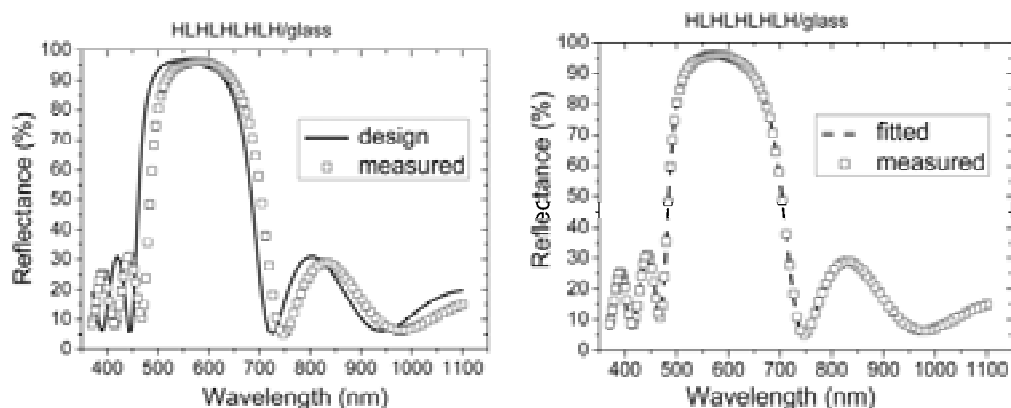


Fig. 22 Designed (solid line), measured (squares), and fitted (dashed line) reflectance spectra of a nine-layer structure HLHLHLHLH/glass. H is Ta_2O_5 film and L is MgF_2 .

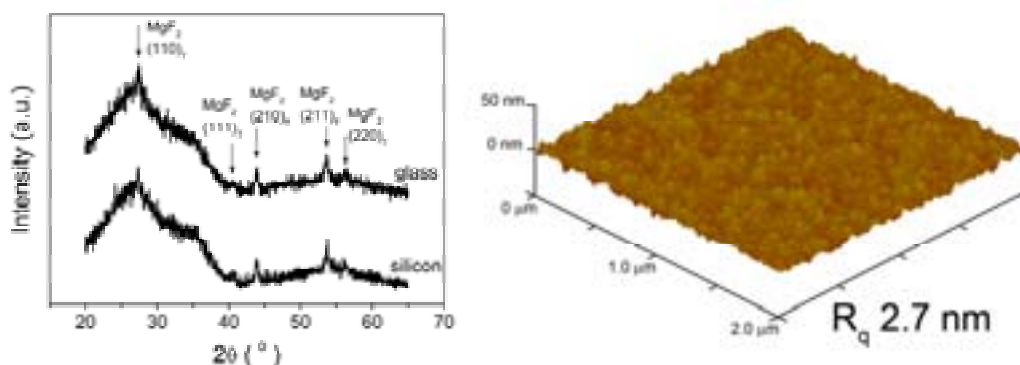


Fig. 23 GI-XRD patterns (left) and AFM image (right) of HLHLHLHLH structure grown onto silicon (AFM image, right) or glass at 250 °C. H is Ta_2O_5 film and L is MgF_2 .

Crystalline structure of the stack structure was measured as well as the surface roughness (Fig. 23). Ta_2O_5 grown from $\text{Ta}(\text{OEt})_5$ and H_2O at 250 °C stays amorphous, whereas MgF_2 is polycrystalline. Rms-roughness of the 9-layer sample was only 2.7 nm.

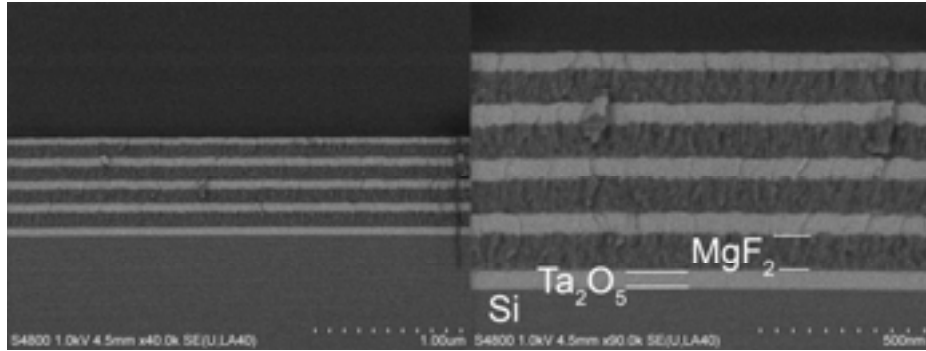


Fig. 24 Cross-sectional SEM image of HLHLHLHLH multilayer structure grown onto silicon at 250 °C.

Cross-sectional SEM images (Fig. 24) show that the layers are separated by sharp interfaces. The films pose also good thickness uniformities across the whole sample. Fig. 25 illustrates how the stack looks visually.



Fig. 25 Photograph of HLHLHLHLH multilayer stack deposited on glass (left) and on Si (right). The samples lie on a white paper. H is Ta_2O_5 film and L is MgF_2 .

UV region. The same design was used for preparing four-layer HR stack for UV region. This time instead of use of Ta_2O_5 , LaF_3 was used as a high-n material (H) due to its better UV light transmittance. LaF_3 was deposited by using $\text{La}(\text{thd})_3$ and TiF_4 as precursors, whereas MgF_2 (L) was grown from $\text{Mg}(\text{thd})_2$ and TiF_4 . The deposition temperature was 275 °C. 248 nm was chosen as a central wavelength. Refractive indices determined from test ALD runs were 1.62 for LaF_3 and 1.43 for MgF_2 . With these refractive indices, values of 38 nm for LaF_3 and 43 nm for MgF_2 were evaluated for the geometric thicknesses from Eq. 23, (Table 9).

Table 9. Film thicknesses and refractive indices used for LaF_3 and MgF_2 films in reflectance spectra (Fig. 44).

Material	Design		Fitted	
	d (nm)	n (580 nm)	d (nm)	n (580 nm)
LaF_3	38	1.62	35	1.60
MgF_2	43	1.43	36	1.40
LaF_3	38	1.62	35	1.60
MgF_2	43	1.43	39	1.40

A reflectance spectrum of four-layer structure (HLHL) on silicon is depicted in Fig. 26. This time the main interest lies in the HR region of around 190–250 nm. The measured reflectance (squares) as well as the ideal design (solid line) was about 80% (Fig. 26). Higher reflectance could be obtained by just simply depositing more layers. As illustrated in Fig. 26 left, the measured curve has been shifted to shorter wavelengths than the designed one (solid line) because the growth rates of the fluorides as well as the refractive indices were slightly less than determined from the test runs. However, fitted curve (dashed line), which used parameters are shown in Table 9, fits together with the measured curve, as shown in Fig. 26 right. Even the reflectance stayed around 80%.

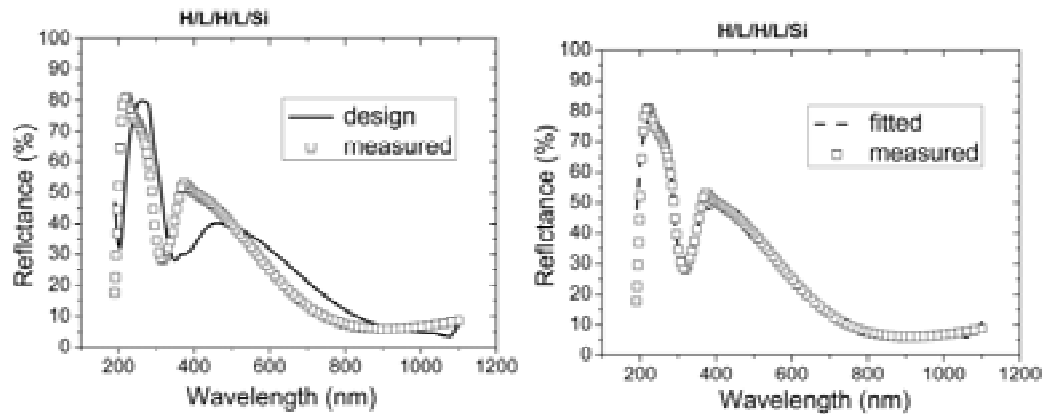


Fig. 26 Designed (solid line), measured (boxes), and fitted (dashed line) reflectance spectra of a four-layer structure HLHL/Si. H is LaF_3 film and L is MgF_2 .

4.3 Anti-tarnishing coating

To show that ALD method can also be used for protecting silver mirror coatings a thin film of Al_2O_3 was deposited by ALD on top of a 100 nm thick Ag film evaporated by e-beam. 5 x 5 cm² glasses were used as substrates in this experiment. About 5 nm thick Al_2O_3 film was fabricated from TMA and H_2O precursors at 250 °C. A reference Ag/glass sample was also heated in the same ALD reactor at 250 °C for the same time as the ALD process took place, but of course without ALD coating. Since then the samples have been aged for three years and 10 months in normal room atmosphere (Fig. 27). Silver mirror coating with Al_2O_3 film is still bright, but the Ag layer without protective thin film is tarnished. This experiment simply shows that the ALD method has potential for depositing anti-tarnishing films and could especially be applied for components with complex shapes and topographies.



Fig. 27 Photo of already tarnished Ag/glass (left), and bright Al_2O_3 /Ag/glass (right). The samples have been aged almost four years at room atmosphere. Mirrors show Finnish cloudy summer sky taken with a digital camera without flash and the photo has not been processed in any way.

4.4 Inductive grid filters

The fabrication process of a freestanding inductive grid filter prototype for rejecting IR light is presented here.^{VII} The idea of the inductive grid filter is simple: it behaves like a metal grid in a door of a microwave oven that passes shorter visible light through but keeps longer harmful microwaves inside the oven. This concept is widely used also in the mirrors of radio telescopes. For rejecting microwave radiation, the grid structures or holes need only be on the order of one decimetre, but for rejecting IR radiation, the fabricated structures have to be scaled down in submicron size. Inductive grid filters are aimed to be used in front of x-ray detectors that will operate at cryogenic temperatures in space and should be protected from IR radiation to avoid heating.

The thickness of the grid affects the absorption of IR radiation, while the effective area of the holes of the grid is responsible for the transmission in the short wavelength region. To allow x-rays to pass through the filter, the metal grid must be freestanding and supported only by its edges, otherwise x-rays would be blocked by the substrate.

Development of inductive grid filters has been challenging and a few techniques have been tried out for fabricating these filters. The inductive grid fabrication process steps starting from Si wafer substrate and finishing to freestanding Ir grid are schematically shown in Fig. 28. Briefly, Si substrate was covered with layers of SiN_x, Cr, SiO₂, PMMA, and Cu (Fig. 28 A). After that the grid filter was manufactured with low energy electron beam lithography (B), etching (C), Ir-coating of deep grooves by ALD using Ir(acac)₃ and O₂ precursors at 300 °C (D), etching again (E-F), and removing etch stop layers (G) and the mask (H). The final grid structure after preparation was: period of 400 nm, linewidth of ~80 nm, and thickness of ~400 nm. More details about the manufacturing process are found in the corresponding article (VII).

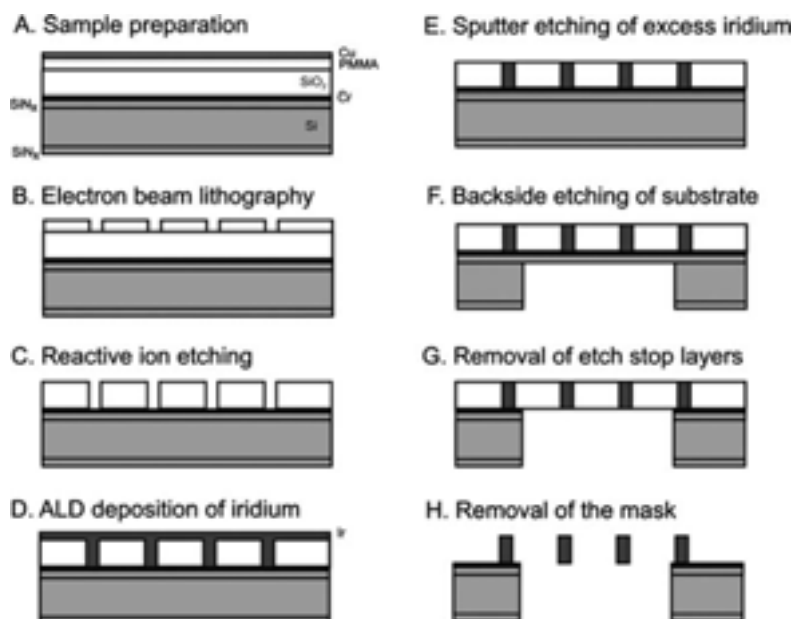


Fig. 28 Fabrication steps of a freestanding inductive grid.^{VII}

SEM images of the grid are illustrated in Fig. 29. The ball-like residues shown originate from an unknown source of particle contamination, most likely they are residues of etched layers. However, their presence does not significantly affect the performance of the filter because they just block only part of the open area.

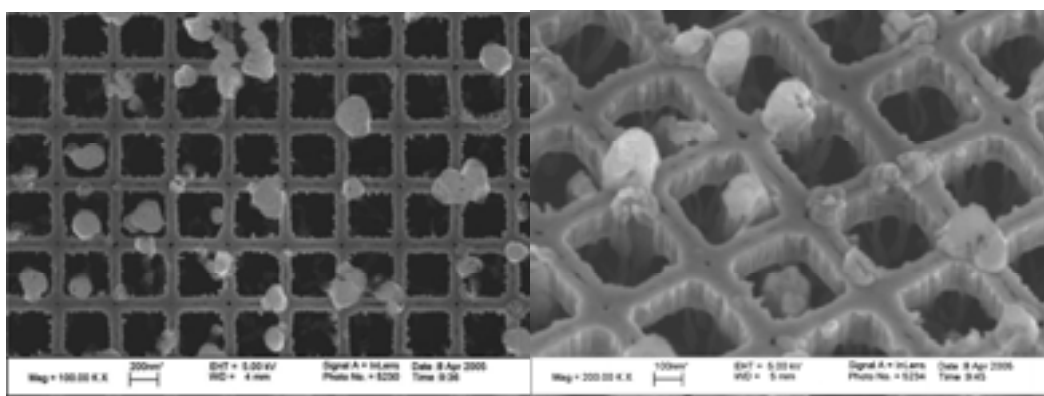


Fig. 29 SEM images of iridium grid filter taken from front side (left),^{VII} and slightly tilted (right).¹⁷⁸

Transmittance spectrum of the grid was measured in the wavelength range of 200–2000 nm (Fig. 30). One can see that the peak of the measured curve

(dashed) is lower and slightly shifted towards longer wavelengths than calculated curve (solid). This is mainly caused by the ball-like residuals on top of the filter (Fig. 29). Calculation of the transmittance curve is beyond this thesis and can be found in more details elsewhere.^{VII} The correspondence between experimental and theoretical results is not perfect; still it represents relatively high rejection of the IR light. In the IR region the transmittance reduces strongly and is only 0.5% at 2000 nm. In the visible region the transmittance curve reaches a peak, around 34% at 540 nm. Going down to the shorter wavelengths absorption of the metal continues to increase, which leads to a decrease of the transmittance. The transmittance could not be measured in the region of 1–100 nm, but a transmittance of 40% was calculated with the same parameters as used in Fig. 30.

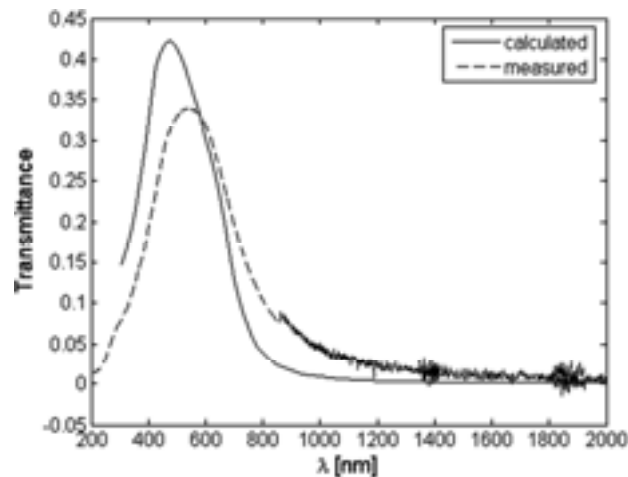


Fig. 30 Calculated (solid curve) and measured (dashed) zeroth order transmittance spectra of a free-standing Ir grid with the following parameters: period of 400 nm, linewidth of ~80 nm, and thickness of ~400 nm.^{VII}

As a conclusion, a method for fabrication of a freestanding grid filter for IR radiation rejection was developed. The first freestanding iridium grid filter prototype was fabricated and it was capable of suppressing IR radiation by a factor of 100 while keeping the transmittance in the x-ray region at around 40%. Unfortunately, the fabrication method is quite unique and difficult, which makes it hardly repeatable. However, ALD was successful in its part; the problems were in other fabrication steps.

4.5 Micro channel plates

In this section, micro channel plates (MCPs) used for focusing x-rays are shortly introduced. MCPs are made from a matrix of hollow glass tubes fused together. Normally the MCPs have circular channels, typically 5 μm to 12 μm in diameter, but for the x-ray optics purposes square type of channels are mostly used because of better filling factor. MCPs are planned to be applied in the optics of imaging x-ray fluorescence spectrometer MIXS onboard of European Space Agency's BepiColombo Mercury Orbiter to be launched in 2013.¹⁷⁹ Fluorescent x-rays that come from the surface of Mercury to the curved MCPs, are reflected by the metal coated channel walls, and thereby focused onto a detector. The device mimics the eye of a lobster where millions of micro channels focus the light (Fig. 31). The advantage of the MCP optics is that it is much lighter than the more conventional x-ray optics.

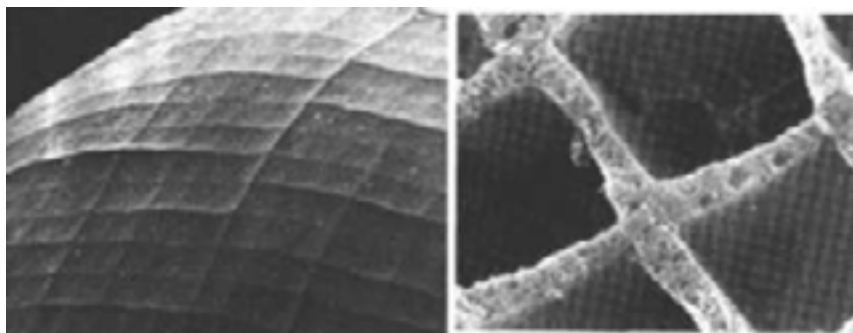


Fig. 31 Left: The eye of a lobster, viewed with a microscope. Right: close-up image of a small area of the eye. The eye consists of millions of square “channels”, each channel measure about 20 microns across.¹⁹⁴

The performance of x-ray mirrors is severely limited when the grazing angle is greater than a few degrees or when the energy of x-ray is greater than 2 keV. This applies also to MCP based x-ray optics so that the efficiency at larger grazing angle or at higher energy can be increased by coating the MCPs with metal layers of a high density, and thus with a high critical angle for total reflection of x-rays. But producing smooth and conformal coating inside the

pores is a difficult task for, e.g., sputtering because the metal does not penetrate deep in the holes in this method. Fortunately, conformal metal film with high density might be deposited by the ALD technique, but it is still a big challenge because of the long and narrow channels.

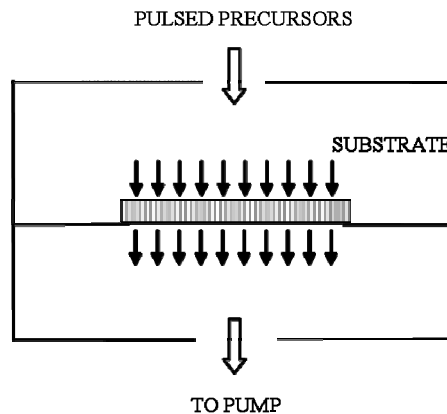


Fig. 32 Schematic picture of the novel flow through type ALD reactor.¹⁹⁵



Fig. 33 Photos of un-coated (left) and Ir-coated (right) MCPs. One euro coin is just shown as a reference.¹⁷⁹

The MCPs test samples with 20 μm square pores were up to 2.8 mm thick with a size of about 10 x 10 mm², so aspect ratios were up to 140:1. The MCPs were coated with about 10–20 nm of Ir metal by ALD in a SUNALE™ (Picosun, Espoo, Finland) reactor at 350 °C using the novel reactor geometry where the precursors are forced to flow through the porous substrate (Fig. 32). About 1 nm

thick Al_2O_3 film, deposited by ALD from TMA and water, was used as a seed layer. The metal precursors were $\text{Ir}(\text{acac})_3$ and O_2 . The normal pulse times were 2×1.5 s for Ir and 0.7 s for oxygen with purging times of up to 120 s. $\text{Ir}(\text{acac})_3$ pulses were doubled to ensure sufficient amount of Ir-precursor. A special sample holder with two or three places for the samples was used. One challenge is to seal the MCPs well enough that no bypass routes are available around the MCP. Reference Si pieces were placed above and under the through-porous samples to confirm Ir thicknesses by XRR.

The MCPs were successfully coated with Ir thin film as shown in Fig. 33. Ir film thickness was measured from a cross-section of MCP by energy dispersive x-ray spectroscopy (EDX) (Fig. 34). Ir was found to be slightly thicker at top (17 nm) compared to the bottom of the channel (13 nm), but this is believed not to attenuate reflectivity of the Ir-coated channels.

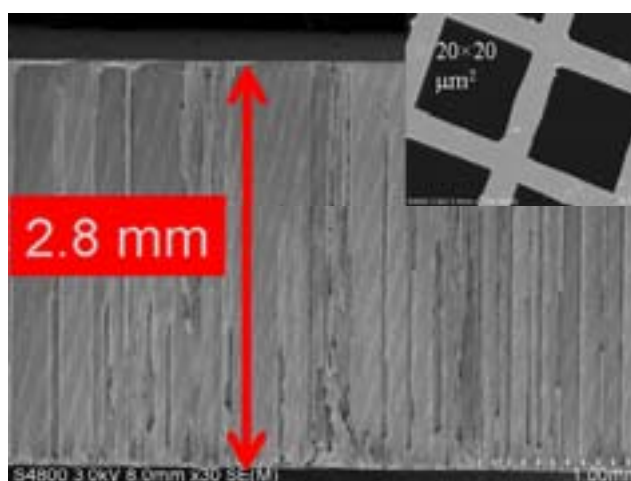


Fig. 34 The cross-sectional SEM image of Ir-coated MCP, insert illustrated also SEM image of top of the MCP.¹⁷⁹

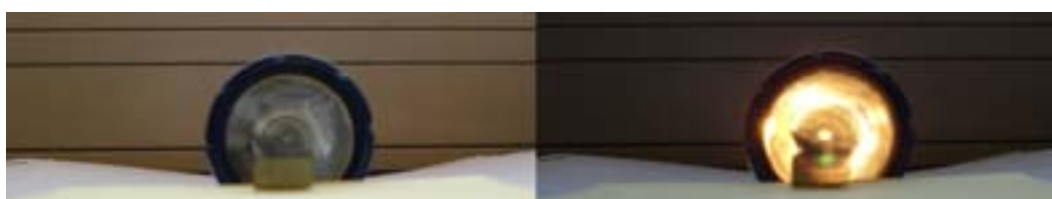


Fig. 35 The Ir-coated MCP seems visually opaque (left), but when the flashlight behind the MCP is on (right), the light can clearly pass through the channels of the MCP.

Photos of Ir-coated MCP were taken when the flashlight behind the MCP is off (Fig. 35 left) and on (Fig. 35 right). When the flashlight is off the MCP seems visually opaque, but when the flashlight is on the MCP clearly passes light through the channels.

Taken together, encouraging results were observed with Ir-coated MCPs where Ir metal was deposited by ALD. The fabrications of the metal coated MCPs are truly challenging and one problematic part from ALD point of view is how to deposit a thin conformal metal layer along every channel, and even more challenging seems to be preparation of MCPs themselves. However, ALD might be the only method, which can be used for coating MCPs. Unfortunately x-ray reflectivity test results are underway, but production of the final MCPs is still to be started at the moment.

4.6 Fresnel zone plates

X-ray microscopy has emerged as a technique to observe structures which are not accessible with conventional optical microscopy. X-ray microscope applications are ranging from semiconductor package inspection and failure analysis to advanced materials research, medical implants, and MEMS technology. In addition, x-ray microscopy has advantages in respect to electron microscopy due to the longer penetration depth and chemical sensitivity of the x-ray radiation. Key elements in x-ray microscopes are the x-ray lenses. These are used in a scanning transmission x-ray microscope to focus the incoming beam on the sample or in a full-field transmission x-ray microscope to project a magnified image of the sample on a spatially resolving detector (Fig. 36).¹⁹⁶ Since the refractive index of matter in the x-ray range is very close to unity, refractive optics and mirrors are not available for high-resolution x-ray imaging.

Diffraction optics, i.e., Fresnel zone plate (FZP) lenses are the optical elements which offer the highest spatial resolution.¹⁹⁷ FZPs are circular diffractive transmission gratings with a radially increasing line density (Fig. 37). The outermost ring width (Δr) determines the resolution (δ_{res}) reached by the microscope (Eq. 24), and thus should be as small as possible, typically below 50 nm.¹⁹⁶

$$\delta_{\text{res}} = 1.22 \times \Delta r \sim \Delta r \quad (24)$$

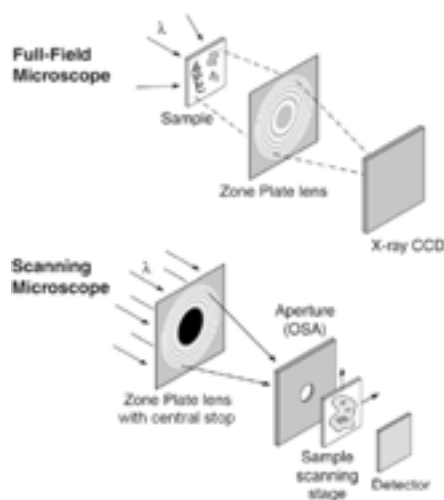


Fig. 36 Schematic view of a full-field x-ray microscope and scanning x-ray microscope.

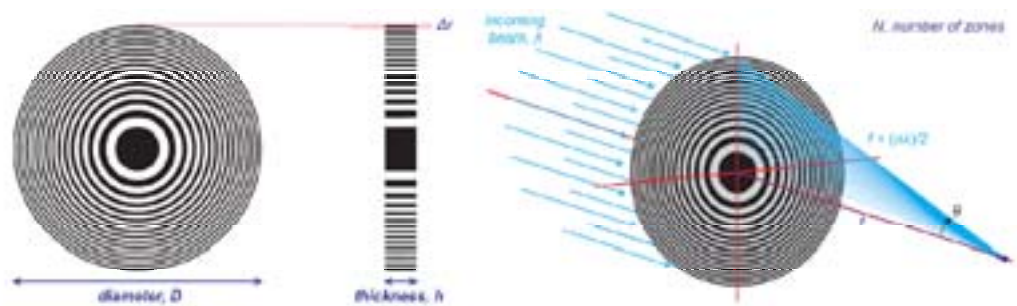


Fig. 37 Fresnel zone plates as a diffracting element.¹⁹⁸

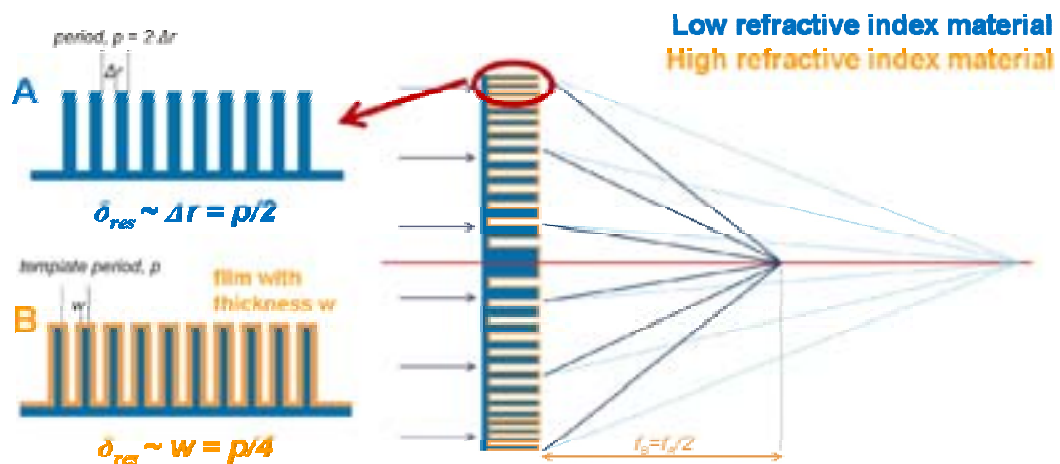


Fig. 38 Zone-doubling technique of FZP. Resolution is doubled and the manufacturing is much easier. Si operates as low- n (blue) and Ir as high- n material (orange).

There has been little progress in reducing outermost zone widths over the past ten years. This is related to an intrinsic limitation of e-beam lithography, which is the main technique to create practically all these FZPs worldwide. While lithography tools are capable of writing with nanometres spot sizes, the range of secondary electrons created in the resist layer determines the obtainable structure sizes. The exposed pattern is thus blurred, which has a particularly detrimental consequence when writing dense patterns of lines such as gratings or FZPs. While isolated line widths down to 10 nm can be obtained by high resolution e-beam lithography, writing the periodic structures seems to be

limited to pitches of around 40–50 nm. As a consequence, no FZPs with lines and spaces below 20–25 nm can be written in a straightforward way, and the smallest lines resolved are 15 nm wide.¹⁹⁷

We have developed a novel technique for a fabrication of ultrahigh resolution FZP lenses,^{VI} which is based on the coating of a template structure with a metal layer of iridium (Fig. 38). The template was fabricated from single silicon crystal, which serves as a low- n material (Fig. 38A). As Ir has a much higher x-ray refractive index than Si, a doubling of the effective zone density and subsequent improvement of the resolution by a factor of two compared to the template structure is achieved (Fig. 38B). Manufacturing steps of FZP are introduced in Fig. 39. The method is very reproducible as it only requires a single lithography step and allows the fabrication of structures with quite high aspect ratios, which increases the efficiency of ultrahigh resolution optics. Low voltage e-beam lithography and a highly anisotropic reactive ion etch process were applied to fabricate the silicon template structure (Fig. 39, 1–3). The height of the template was 170 nm. Finally a highly conformal 20 nm thick Ir thin film was deposited by ALD onto the template (Fig. 39, 4) using $\text{Ir}(\text{acac})_3$ and O_2 as precursors at 350 °C.¹⁹⁹ The method was used to fabricate Ir-coated FZPs with line widths down to 15 nm. A successfully fabricated FZP is shown in Fig. 40.

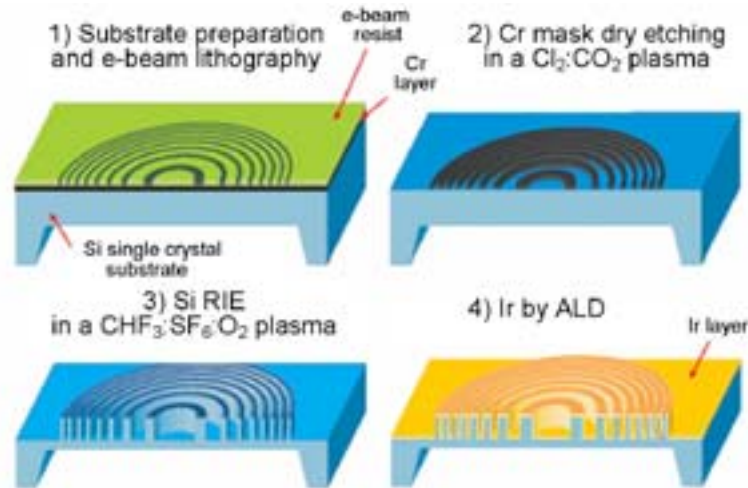


Fig. 39 Manufacturing steps of Ir-silicon Fresnel zone plate. The silicon template had 80 nm periods and a duty cycle of 0.25 at the outer regions. Finally a 20 nm thick Ir layer was deposited by ALD.¹⁹⁸

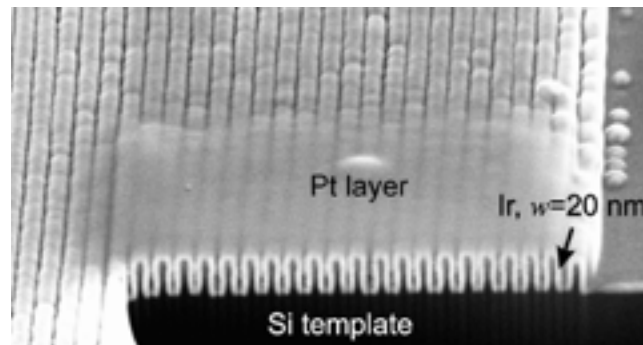


Fig. 40 A cross-sectional SEM image of a Ir Fresnel zone plate with 20 nm wide outermost zones prepared by depositing Ir by ALD onto a silicon template. A thin Pt layer was locally deposited to achieve a clean focused ion beam cross section.^{VI}

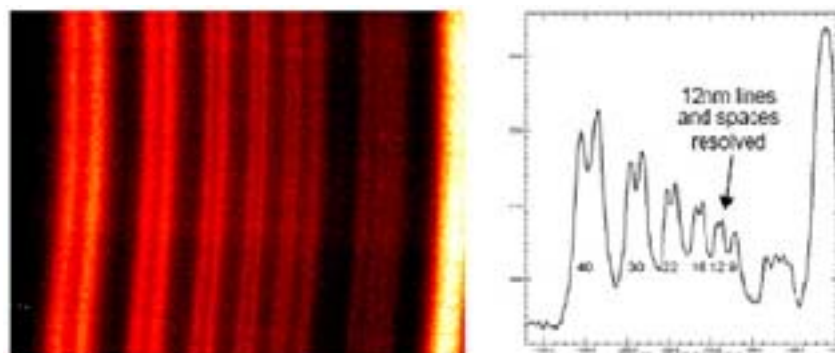
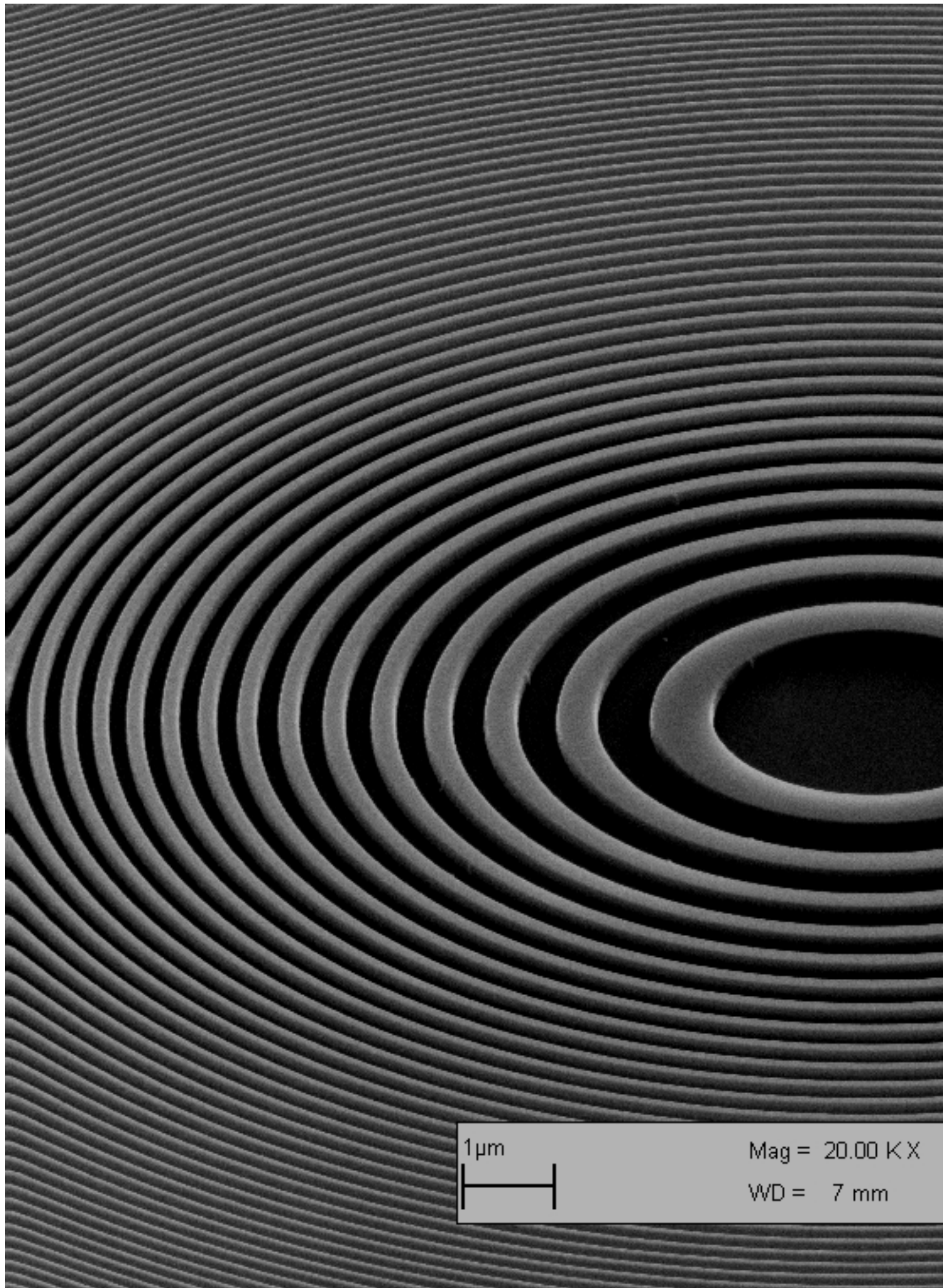


Fig. 41 Scanning x-ray microscope image of a test object consisting of a cross section of a GaAs/InGaAs structure with line pairs from 40 nm to down 9 nm thicknesses (left). Lines and spaces down to 12 nm can be resolved. Horizontal cross section through the image (right) shows the separation of 12 nm lines. Photon energy of 1 keV was used.

The imaging properties of the devices were experimentally tested in a scanning x-ray microscope using another FZP as a test object. A resolution of 15 nm was achieved. More recently, a test object consisting of a cross section of GaAs/InGaAs structure was imaged. The structure consisted of layer pairs of 40 nm down to 9 nm in thickness, each separated by a spacer of the same thickness (Fig. 41, left). Line pairs down to 12 nm could be resolved (Fig. 41, right), which represents the best resolution achieved to date in x-ray microscopy. However, the method still has a potential to push the limits of x-ray microscopy even down to the sub-10 nm level, and these studies are currently in progress.



1 μm



Mag = 20.00 K X

WD = 7 mm

5 SUMMARY AND CONCLUSIONS

Thin films of various metal fluorides can be applied in many optical applications due to their excellent light transmission in a broad wavelength area. The problem in depositing fluoride films by ALD has been a lack of good fluorinating agent. Several ALD processes were developed to deposit metal fluoride thin films from metal-thd compounds and novel fluorinating agents of TiF_4 and TaF_5 at 175–450 °C. The fluoride films of MgF_2 , LaF_3 and YF_3 were deposited for the first time by ALD. In addition, for CaF_2 a four times higher growth rate was obtained than that published for ALD of CaF_2 with HF as the fluorine source.

Especially MgF_2 is a desired film material worldwide due to its low refractive index and high light transmittance down to vacuum UV region. Therefore, among the fluorides deposited the highest transmittances as well as the lowest refractive indices below 1.4 ($\lambda=580$ nm) were obtained with MgF_2 samples. MgF_2 grown from the TaF_5 precursor showed even better light transmittance at UV region than MgF_2 grown from TiF_4 . Therefore, TaF_5 must be considered as a high quality fluorine precursor for depositing fluoride thin films. Most fluoride thin films were reasonable insulators despite their polycrystalline structure. The highest permittivity of 12 was obtained for LaF_3 , whereas MgF_2 films grown from TiF_4 had the highest breakdown fields.

Metal fluoride films were also used for fabricating high reflectance dielectric mirrors. Stack samples were fabricated by deposition of a 9-layer structure with alternating high-n Ta_2O_5 and low-n MgF_2 films, and a 4-layer structure of LaF_3 and MgF_2 films. In both cases the layers were separated by sharp interfaces and had good uniformities across the substrates. Therefore high reflectance of 96% ($\lambda = 570$ nm) was obtained with $\text{Ta}_2\text{O}_5/\text{MgF}_2$ sample. This proves that the novel ALD fluoride processes can be applied also together with oxides in multilayer structures, and higher reflectance is achievable by just depositing more layers into the stack.

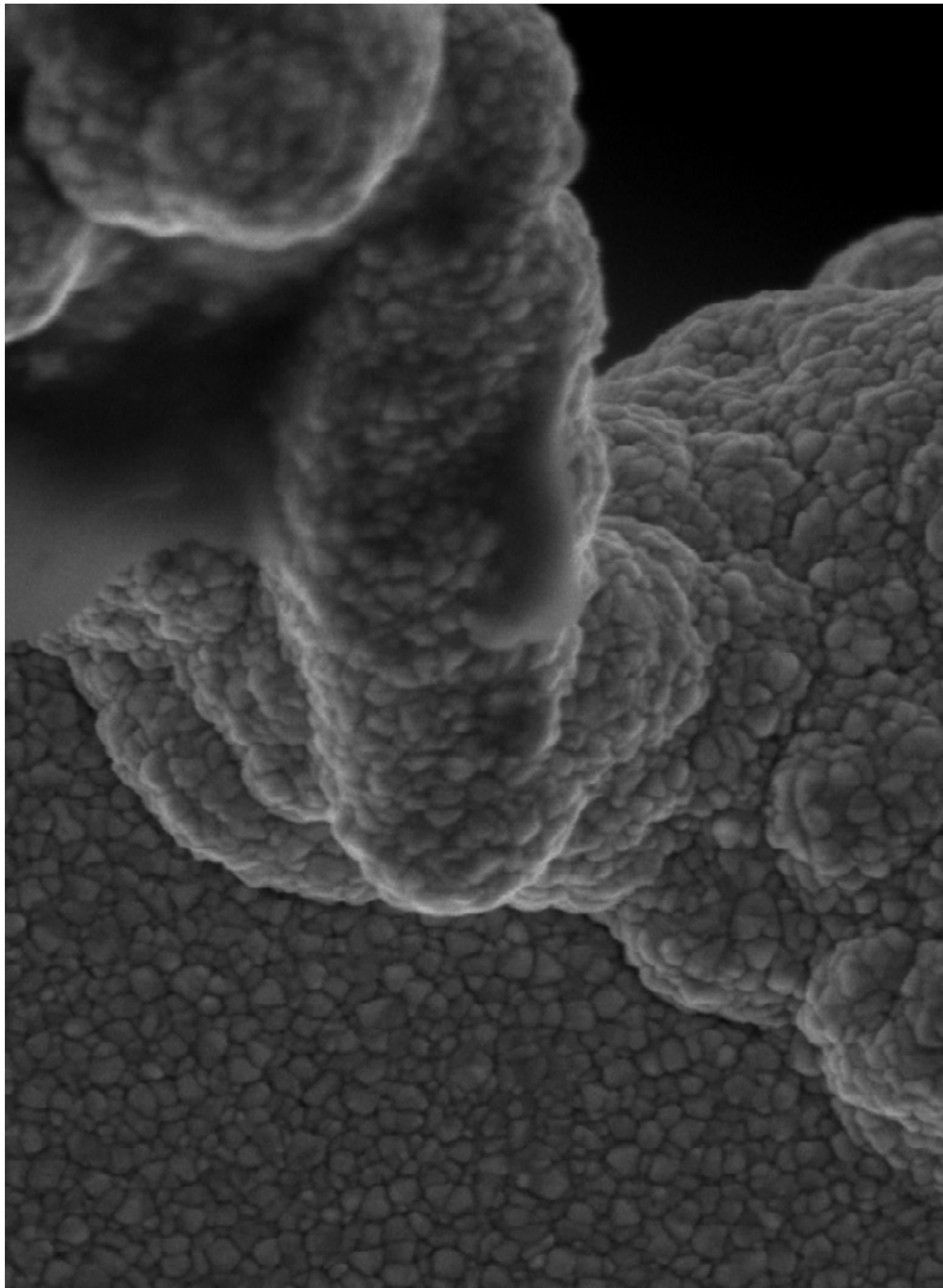
It was also shown that a thin ALD Al_2O_3 film could be applied as an anti-tarnishing layer on top of the silver mirror coating. The sample was aged at

normal room atmosphere for almost 4 years without visible tarnishing.

One aim of this thesis was to fabricate novel optical devices. The first freestanding iridium grid filter prototype for rejection of infrared light was fabricated and characterized successfully. Unfortunately, the fabrication method is difficult, which makes it hardly repeatable, but ALD was successful in its part. Micro channels plates (MCPs), which are applied for focusing x-rays, were Ir-coated effectively by ALD. The ALD technique might be the only method to deposit a conformal, highly reflective metal layer onto the narrow channels of the MCP. There is still place for an improvement to obtain highly uniform ALD coating along the channels. However, production of the final MCPs is to be started at the moment and hopefully they will have a safe trip to Mercury.

A novel technique was developed to fabricate Fresnel zone plates (FZPs) that frees us from the present limitations of e-beam lithography and thereby simplifies FZP preparation and improves the spatial resolution of x-ray microscopy. Line pairs down to 12 nm could be resolved with the Ir-coated FZP, which represents the best resolution achieved up to date in x-ray microscopy. However, the method has a potential to push the resolution limits of x-ray microscopy even down to the sub-10 nm level.

Developments in optical coating materials, deposition techniques, process parameter control and equipment are continuing processes. Therefore, novel coating materials and optical devices will definitely be seen in the near future. For example, ALD of artificial fluoride materials with amorphous structure or tailored refractive index will be the future task. Anyhow, the aims of this thesis were achieved successfully. The novel ALD processes were introduced to deposit fluoride thin films, which can be applied in fabrication of high reflecting mirrors. In addition to the novel fluoride thin films, power of ALD was shown for protecting silver mirror coating from tarnishing. Also novel devices for x-ray optics, like grid filters and MCPs, were successfully developed. Finally, receiving the happy end to the book, the best spatial resolution was achieved up to date in x-ray microscopy with the Ir-coated Fresnel zone plate.



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