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Comparative study of ALD SiO$_2$ thin films for optical applications

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Abstract: We have investigated the suitability of atomic layer deposition (ALD) for SiO$_2$ optical coatings and applied it to broadband antireflective multilayers in combination with HfO$_2$ as the high refractive index material. SiO$_2$ thin films were successfully grown using tris[dimethylamino]silane (3DMAS), bis[diethylamino]silane (BDEAS) with plasma activated oxygen as precursors, and the AP-LTO 330 precursor with ozone, respectively. The amorphous SiO$_2$ films show very low optical losses within a spectral range of 200 nm to 1100 nm. Laser calorimetric measurements show absorption losses of 300 nm thick SiO$_2$ films of about 1.5 parts per million at a wavelength of 1064 nm. The films are optically homogeneous and possess a good scalability of film thickness. The film surface porosity - which correlates to a shift in the transmittance spectra under vacuum and air conditions - has been suppressed by optimized plasma parameters or Al$_2$O$_3$ sealing layers.

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Introduction

One of the challenges for using dielectric coatings in optical multilayer stacks is the realization of low absorption and low scattering losses. Furthermore, films have to be prepared with a precise control of optical thickness combined with a uniform thickness distribution. Commonly, thin films applied in precision optics are deposited by physical vapor deposition (PVD) [1–4]. However, this method requires great technical efforts to meet strict tolerances, e.g. in film thickness, and *in situ* film growth monitoring is often necessary to ensure good reproducibility.

Atomic layer deposition (ALD) is an alternative and very promising method that inherently offers a high reproducibility, large-area thickness uniformity and conformal coating on structured substrates with high aspect ratio [5, 6]. ALD is a special form of chemical vapor deposition (CVD), in which the gaseous precursors are exposed to the substrate sequentially and independently from each other. The precursor pulses are separated by purging cycles. Due to this cycle-based process the reaction does not take place in the gas phase, but is only surface limited. Since the substrate surface has a limited number of reaction surface sites, the reaction saturates after a certain precursor exposure. The surface-controlled ALD growth mechanism enables an excellent scalability of film thickness within a sub-nanometer range as well as high repeatability without *in situ* monitoring. Using atomic layer deposition, the resulting film thickness is precisely controlled by the number of ALD cycles.

ALD optical coatings were introduced using Al_2O_3 as low refractive index material and ZnS [5], HfO_2 [7] or TiO_2 [6, 8] as high refractive index material. However, highly precise optics require a higher refractive index contrast between the dielectrics. Silicon dioxide is one of the most applied low-index materials in optical interference coatings. Thin SiO_2 films deposited by ALD are widely studied for application in microelectronics such as gate oxide films in semiconductor devices [9, 10]. In semiconductor industry very thin continuous films of typically less than 4 nm are required [11]. For that reason, the growth during the early stages of deposition is critical for applications in semiconductor devices. In optical applications conversely, nucleation plays a minor role, since rather thick layers are needed (up to several hundred nm). To fulfill the stringent requirements on thickness control a linear and reproducible film growth as enabled by ALD is demanded.

Deposited dielectric ALD films are typically amorphous when they are prepared at low substrate temperatures (< 250°C) [12]. The formation of an amorphous film is accompanied by low surface roughening, for that reason low scattering losses can be expected. Furthermore, optically homogeneous films without refractive index gradients are expected, since ideally in every ALD cycle the same reaction takes place.

There is an evident lack of investigation on the optical properties, e.g. transmittance or optical homogeneity, of relatively thick SiO_2 ALD films. Before applying silicon dioxide films in multilayer stacks, fundamental questions on optical film quality have to be investigated. We present a thorough investigation of optical properties of silicon dioxide thin films synthesized by atomic layer deposition using common Si-precursors, namely 3DMAS [11, 13], BDEAS [14–16] and the AP-LTO®330 precursor [17–19]. The optical properties (refractive index, optical losses, and vacuum-to-air shift) and film stresses obtained in four different SiO_2 ALD processes are compared. To confirm the possibility of utilizing SiO_2 in optical coatings, a broad band antireflection coating was designed and successfully produced using SiO_2 and HfO_2 as low and high refractive index material, respectively.

Experimental

Atomic layer deposition

ALD depositions of SiO_2 were carried out at substrate temperatures of 200°C (unless noted otherwise) using four different processes, see also Table 1:

(1) SiO_2 thin films were grown from tris [dimethylamino] silane (3DMAS) and plasma activated oxygen. The films were deposited in a commercial Oxford Instruments open load ALD system (OpAL) equipped with an inductively coupled plasma (ICP) RF generator, operating at 13.56 MHz. The pulsing time of 3DMAS, which was heated to 30°C, was 400 ms. A "hold precursor" step of 4 s after the 3DMAS pulse was introduced to ensure surface-saturated reactions. The excess 3DMAS and by-products were purged for 4 s. Oxygen plasma was pulsed for 3 s, where the oxygen flow rate was set 50 sccm and the plasma power to 300 W. This step was followed by 4 s of purging. The process pressure was approximately 400 mTorr. A detailed description of film growth experiments was reported earlier [20].

(2) Furthermore, SiO_2 films were deposited using bis [diethylamino] silane (BDEAS) as silicon source in an Oxford Instruments FlexAl reactor, see also [15]. Oxygen plasma with a plasma power of 200 W was used as oxidizing agent. The pressure during the O_2-plasma was 25 mTorr. The pulsing sequence was: 125 ms BDEAS pulse followed by a hold precursor step of 2 s (closed chamber), 5 s purge, 5 s plasma pulse and 2 s purge. The process pressure was approximately 14 mTorr. In the following, this process is hereafter referred to as BDEAS-I.

(3) SiO_2 films from BDEAS and O_2-Plasma were additionally deposited in a Sentech SI ALD LL system. During the oxygen plasma pulse the plasma power was set to 200 W and the oxygen flow rate to 200 sccm. The ALD cycle consists of 140 ms BDEAS pulse, 1860 ms purge, 1000 ms oxygen plasma pulse and 1000 ms purge. The chamber pressure was 150 mTorr. This process is hereafter referred to as BDEAS-II.

(4) Depositions using the AP-LTO®330 precursor [17] were carried out in combination with O_3 as the oxygen source. A Picosun Oy Sunale R200 ALD tool was used in a single wafer showerhead mode with optional stop-flow set-up. The AP-LTO®330 precursor was kept at 20°C and pulsed for 100 ms by its own vapor pressure followed by a hold precursor step of 10 s. The excess precursor and by-products were purged for 5 s. After the subsequent O_3 pulse of 2 s the reactant was trapped in the chamber for 10 s before purging the chamber for 8 s.

Table 1. Process parameters of SiO₂ depositions.

	tool/ location	precursor	reactant	ALD cycle (in s) [precursor pulse / hold step / purge / reactant pulse / hold step / purge] (total)
(1)	OpAL / Jena	3DMAS	O_2-plasma	[0.4 / 4 / 4 / 3 / - / 4] (15.4)
(2)	FlexAL / Eindhoven	BDEAS	O_2-plasma	[0.125 / 2 / 5 / 5 / - / 2] (14.125)
(3)	SI ALD LL / Stuttgart	BDEAS	O_2-plasma	[0.140 / - / 1.860 / 1 / - / 1] (4)
(4)	Sunale R200 / Espoo	AP-LTO 330	O_3	[0.1 / 5 / 10 / 2 /10 / 8] (35.1)

A double-sided broadband antireflective coating was deposited in an OpAL reactor using SiO_2 from 3DMAS and HfO_2 from tetrakis[dimethylamido] hafnium (TDMAH). For HfO_2 thin films the TDMAH was pulsed for 400 ms and subsequently purged for 8 s, an oxygen plasma pulse of 5 s was used to oxidize the film followed by 15 s purging.

Characterization

The film growth behavior of SiO_2 films from 3DMAS was investigated on Si (100) substrates. In addition the growth behavior was tested on dielectric sublayers, for this purpose we used Si substrates pre-coated with thin Ta_2O_5 layers (by PVD) due to availability. The film thickness was determined by X-ray reflectometry (XRR) using a D8 advance type (Bruker AXS) X-ray diffractometer. Film morphology and crystal structure were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurement, respectively.

For characterization of optical properties SiO_2 films with a thickness of about 300 nm have been grown using the afore-mentioned ALD processes on fused silica (Lithosil® Q1), BK7 and B270 substrates. The optical performance of the SiO_2 layers, i.e. transparency and optical homogeneity, was examined by evaluating the transmittance and reflectance spectra that were recorded in a wavelength range from 200 nm to 1100 nm using a PerkinElmer Lambda 950 spectrophotometer equipped with a self-developed VN-attachment [21]. The measurement accuracy of the spectrophotometer is $\pm$ 0.2% in the UV and $\pm$ 0.1% in the VIS. From these spectra, the optical losses and the refractive indices *n* were determined. Additional absorption measurements with detection limits of a few hundred ppb (parts per billion) were done using laser calorimetric measurements at a wavelength of 1064 nm [22].

Vacuum-to-air-shift (VAS) was calculated from the shift of the maximum of transmission spectra taken under ambient and under high vacuum conditions (less than 10^{-5} mbar) [23]. The density of silica films that were deposited from 3DMAS at different substrate temperatures was identified from XRR spectra. Film stress measurements were performed using a TENCOR®FLX 2320 for 300 nm thick SiO_2 coatings that were deposited on 3" double-sided polished silicon wafers.

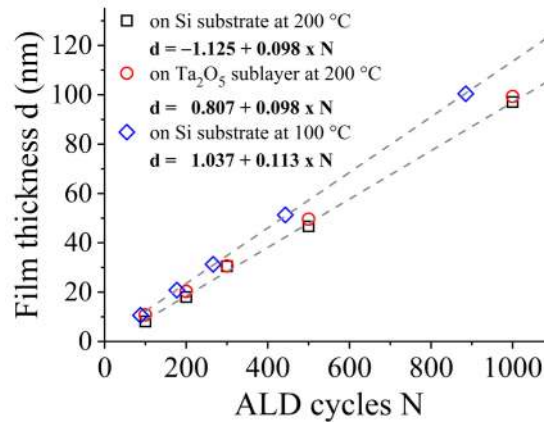**Results and discussion**

SiO_2 single layers

Fig. 1. Thickness calibration curve of SiO_2 films on Si substrates and Ta_2O_5 sub-layers prepared using 3DMAS at 100°C and 200°C substrate temperature.

For all ALD processes a linear film growth rate of SiO_2 thin films is verified by the linear relation of performed ALD cycles and resulting film thickness. Figure 1 shows exemplarily the thickness calibration curve of SiO_2 deposited using 3DMAS. At 200°C substrate temperature the determined growth rate is 0.98 Å/cycle, that is comparable to observed growth rates using BDEAS-I (1.14 Å/cycle), BDEAS-II (1.23 Å/cycle) and the AP-LTO®330 precursor (1.85 Å/cycle). Deposition of SiO_2 from 3DMAS at 100°C results in a slightly increased growth rate of 1.13 Å/cycle. A higher growth rate at lower deposition temperatures

was also found for BDEAS-I. This has been attributed to decreased precursor chemisorption at higher temperatures due to a lower –OH density after the plasma step [15].

ALD nucleation and growth is generally affected by different substrate materials [24, 25]. For application of ALD SiO_2 layers in optical multilayer stacks, the linear film growth needs to be demonstrated also on dielectric coatings. Figure 1 shows that SiO_2 films have the same constant growth behavior on Ta_2O_5 pre-coated Si substrates. In conclusion, the thickness of SiO_2 layers in e.g. dielectric layer stacks can be controlled easily by counting ALD cycles. Slightly deviating growth behavior of SiO_2 on Si and the dielectric sub-layer can be attributed to a substrate depending delay in thin film nucleation in the initial stages of the growth [26].

The crystallinity of the SiO_2 thin films is shown exemplarily for the layers deposited with the 3DMAS precursor (see Fig. 2). The single diffraction peak in the XRD pattern is attributed to the silicon substrate, suggesting that the SiO_2 layer is amorphous. This assumption is confirmed with SEM micrographs that show a dense SiO_2 thin film without visible crystallites.
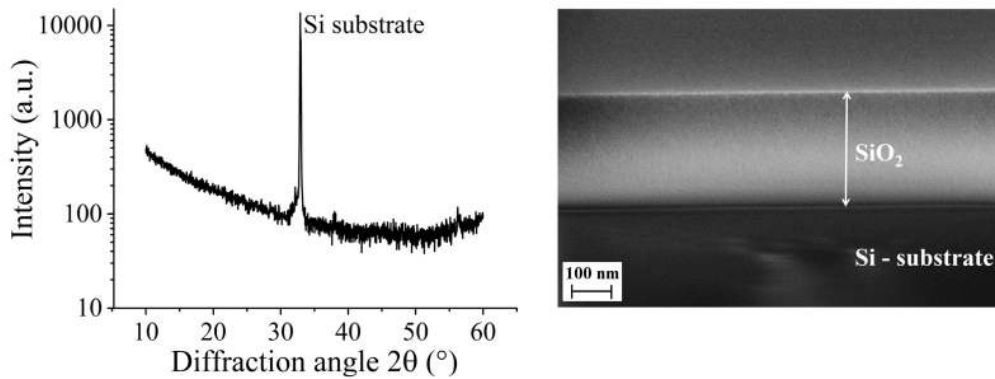

Fig. 2. XRD pattern (left) and SEM micrograph (right) of 300 nm as-deposited SiO_2 on Si substrate using 3DMAS at a substrate temperature of 200°C.

Intensity losses of transmitted light due to scattering or absorption are referred to as optical losses. Fused silica substrates were used for investigations of optical losses due to their low absorption down to the UV spectral range. Optical losses are subsequently calculated from transmittance T and reflectance R measurements of deposited SiO_2 thin films (100% - T - R). Figure 3 depicts the losses of SiO_2 coated and uncoated fused silica substrates. The optical losses of the prepared samples using the 3DMAS, BDEAS-I, BDEAS-II or the AP-LTO®330 precursor are in good agreement with those from the bare substrate in a wavelength range from 200 nm to 1100 nm. The deposited silicon oxide films show no significant absorption or scattering losses in this range. Laser calorimetric measurements revealed that absorption losses of samples with 300 nm SiO_2 films prepared using 3DMAS are less than 3.9 parts per million (ppm) at 1064 nm. The bare fused silica substrates have absorption losses of ca. 2.4 ppm. The extinction coefficient of the deposited SiO_2 corresponds to $k \approx 0.4 \cdot 10^{-6}$. These SiO_2 layers with very low absorption losses might be considered for applications in laser optics.
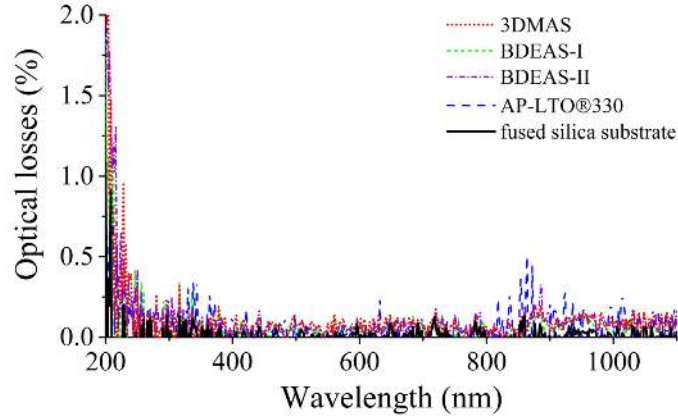
Fig. 3. Optical losses (100% - T – R) of uncoated fused silica substrate and of SiO_2 coated fused silica substrate using 3DMAS, BDEAS or the AP-LTO®330 precursor.

The deposited films from 3DMAS and BDEAS are optically homogeneous, confirmed by the matching spectra of the coated sample and the bare fused silica substrate in all half-wave positions (not shown). If there would be a small inhomogeneity in the samples prepared with the AP-LTO®330 precursor this cannot be evaluated reliably with the measurement technique used in this study since the refractive index contrast between the uncoated substrate and the SiO_2 is extremely low. Therefore, the oscillations in the reflectance and transmittance spectra cannot be resolved with the given measurement accuracy. The refractive index of this layer is nearly identical with that of the substrate material.
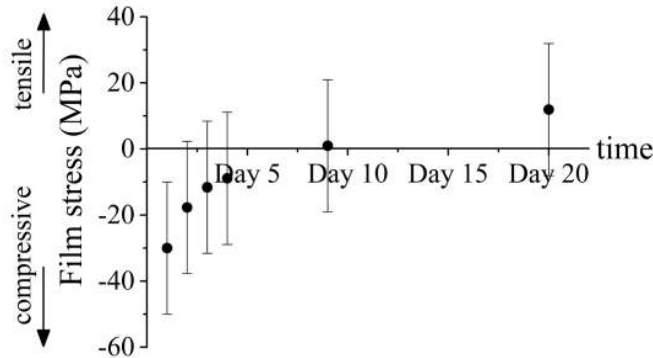

Fig. 4. Film stress of a 300 nm SiO_2 layer prepared with 3DMAS at 200°C over a time period of 20 days.

SiO_2 films deposited at 200°C using 3DMAS have slight compressive stress in the range of - 30 MPa. An evaluation of film stress values over a period of 20 days has shown that this stress relaxed towards tensile stress with time when the sample was stored under ambient conditions (see Fig. 4). For comparison, stress values after long term are about 40 MPa, 10 MPa and 20 MPa, for SiO_2 films deposited using 3DMAS, BDEAS-I and the AP-LTO®330 precursor, respectively. Films prepared from 3DMAS at a deposition temperature of 100°C have tensile stress of about 110 MPa after long term. ALD is known to produce dense, pinhole-free layers [27]. However, the stress value relaxation indicates that the film is not highly densified and exhibits open pores [28]. If the pores are filled with water under ambient conditions, the film composition can change. As a result the effective refractive index is increased due to infiltration of water and hence the transmittance spectra of the film will be influenced. This effect can be measured as a vacuum to air shift (VAS).

The transmittance spectra of SiO$_2$ films, synthesized with 3DMAS, BDEAS-I and BDEAS-II, measured under ambient conditions and vacuum conditions show that the maximum positions of the spectra are shifted considerably (Fig. 5(a)). The films exhibit a negative vacuum-to-air shift of −2.1%, −1.8% and −1.3%, respectively, which can be attributed to a decrease in film refractive index under vacuum conditions [23]. Only the film deposited using the AP-LTO 330 precursor shows nearly no vacuum-to-air shift, see Fig. 5(a).

The occurring vacuum-to-air-shift (VAS) is a drawback for application in extreme environments, as for instance in space applications. The changed refractive index of the SiO$_2$ layers under vacuum conditions would alter the performance of the optical system. It should be noted that the substrate temperature during deposition, which was varied between 100°C and 300°C, has no influence on the density of the SiO$_2$ films deposited with 3DMAS and consequently the VAS could not be reduced by changing the substrate temperature (not shown). Considering the example of SiO$_2$ prepared using 3DMAS, we present two possibilities to reduce the shift. First, we adjusted the oxygen plasma parameter, and second, an alumina sealing layer was applied.
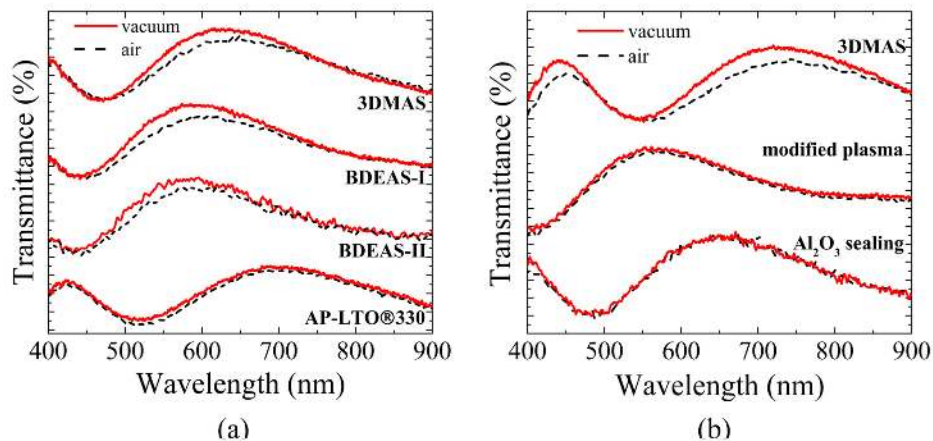

Fig. 5. Transmission spectra measured in air and vacuum for SiO$_2$ films with film thickness in a range of 290 nm and 360 nm prepared on glass substrates at (a) 200°C substrate temperature using 3DMAS, BDEAS or the AP-LTO®330 precursor and (b) 100°C substrate temperature using standard 3DMAS process, 3DMAS process with modified plasma parameters, and standard 3DMAS process applying an additional 3 nm Al$_2$O$_3$ sealing. The spectra are offset for clarity.

The material properties of thin films prepared by PEALD depend on the radical flux as well as on the flux and energy of the ions during the plasma step [29–32]. The flux of the radicals and ions increase with higher plasma powers and the dose also increases with a longer plasma time. The ion energy is mostly determined by the pressure, i.e. the ion energy will be higher at lower pressures. Denser films are expected by increasing the plasma power, decreasing the pressure (using a lower oxygen flow rate) and by applying a longer plasma pulse time, since the surface will be exposed to a higher reactivity. In the developed process, the plasma power is already at its system-dependent maximum value of 300 W. The oxygen flow rate is reduced from 50 sccm to 10 sccm. Additionally, the plasma pulse time is increased to 8 s. With these process modifications the shift can be drastically reduced to ≤- 0.5%, see Fig. 5(b). A reduced pressure is required for higher ion energy. Consequently, this process needs an additional 10 s pump-down time before the plasma ignition to provide a low and stable oxygen pressure during the plasma pulse. The lengthened cycle time leads to lower deposition rates (~9 nm/h instead of ~27 nm/h).

Another and more effective way to prevent the VAS is to seal the porous SiO$_2$ layer with an ultra-thin Al$_2$O$_3$ film that prevents water penetration. Aluminum oxide has excellent

sealing properties and it is widely used as protective or barrier layer against moisture [12, 33–35]. The sealing layer should be as thin as possible to have the lowest possible influence on the refractive index of the overall layer system. ALD is a preferable method to deposit such very thin layers of Al_2O_3. Aluminum oxide films were deposited using trimethylaluminium (TMA) and oxygen plasma with a plasma power of 300 W and an oxygen flow rate of 50 sccm. The pulsing time was 50 ms for TMA and 3 s for the O_2-plasma. Deposited 300 nm SiO_2 films were coated with 1.5 nm and 3 nm Al_2O_3 films. The VAS cannot be prevented by a 1.5 nm sealing layer. In contrast, an Al_2O_3 layer of 3 nm is sufficient to prevent water molecules to fill pores of the SiO_2 sub-layer as the layer system shows no vacuum-to-air shift under the tentative conditions (see Fig. 5(b)). This result was verified in several reproduction runs.
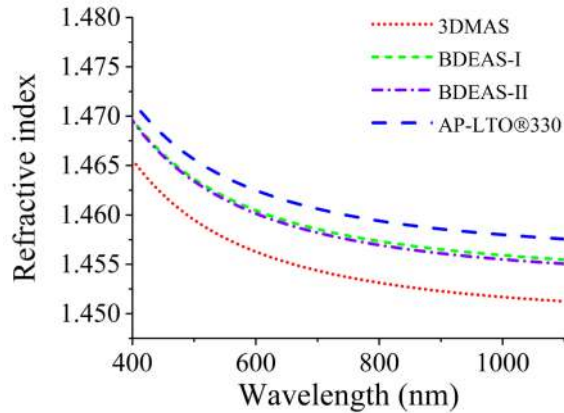

Fig. 6. Refractive index under ambient conditions of SiO_2 layers prepared at 200°C substrate temperature by using 3DMAS, BDEAS and the AP-LTO®300 precursor.

The determined refractive index under ambient conditions of SiO_2 layers deposited using 3DMAS, BDEAS and the AP-LTO®330 precursor is illustrated in Fig. 6 and listed in Table 2. Deviation of refractive indices originates among others from different film densities. The SiO_2 film obtained with 3DMAS has the lowest refractive index that correlates well to the highest measured VAS, which is due to higher porosity compared to the other precursors.

Table 2. Comparison of results for SiO_2 films deposited at 200°C substrate temperature.

	process	Growth rate (Å/cycle)	optically homogeneous	optical losses (200 – 1100nm)	VAS	n @ 550nm
(1)	3DMAS	0.98	yes	very low	−2.1%	1.458
(2)	BDEAS-I	1.14	yes	very low	−1.8%	1.462
(3)	BDEAS-II	1.23	yes	very low	−1.3%	1.462
(4)	AP-LTO 330	1.85	N/A	very low	no	1.464

Broad band antireflection coating

The possibility to apply atomic layer deposited SiO_2 films in optical coatings was demonstrated with an 8-layer broadband antireflection coating (BBAR) using SiO_2 and HfO_2 as low and high refractive index material, respectively. The broad band antireflection coating was designed using commercially available software FilmWizard™ (SCI). The total thickness of the designed BBAR (Table 3) is 391 nm. The design includes a 3 nm thin Al_2O_3 sealing layer to protect the coating from water penetration. Due to its low thickness this extra sealing layer has barely an influence on the spectral transmittance of the BBAR and the multilayer has been optimized to taking into account the top Al_2O_3.

Table 3. Individual layer thickness of the BBAR coating and necessary ALD cycles to obtain the particular thickness.

Layer	Material	Thickness (nm)	ALD cycles
Substrate	N-SF8		
1	HfO_2	18.6	108
2	SiO_2	19.1	162
3	HfO_2	40.5	244
4	SiO_2	10.4	83
5	HfO_2	153.5	949
6	SiO_2	19.5	166
7	HfO_2	29.8	177
8	SiO_2	97.3	868
sealing	Al_2O_3	3.0	26

High refractive index N-SF8 glass substrates of 1 mm thickness were used as substrate material. The influence of the reflection at the substrate's backside surface is suppressed by a double-sided coating. HfO_2 thin films prepared at 100°C substrate temperature show better mechanical properties compared to HfO_2 thin films deposited at 200°C, hence the BBAR is deposited at a fixed substrate temperature of 100°C. The required number of ALD cycles to reach the particular layer thicknesses of the design (see Table 3) are calculated from the linear equation coefficients taken from the corresponding thickness calibration curves. The double-sided coating is accomplished side by side. To prevent backside coating, the substrates were placed in home-made substrate holders. Figure 7 shows the simulated and the measured transmittance spectra of the substrates with a double-sided BBAR coating. With this double-sided BBAR coating an average transmittance of about 97% can be reached in a spectral range from 390 – 1100 nm.
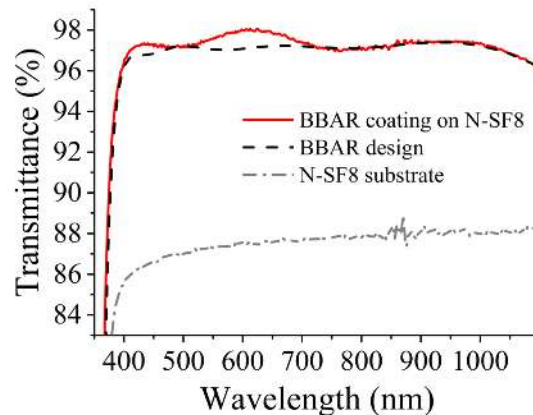

Fig. 7. Simulated and measured transmittance spectra of uncoated and BBAR double-sided coated N-SF8 samples.

Repeated measurement of the transmittance spectra 6 months after deposition shows a good long term stability of the BBAR. As seen in Fig. 8 the transmission spectra of the BBAR double-sided coated N-SF8 sample do not shift (even 6 months after deposition) if the measurement is done under air or vacuum conditions. This implies that the additional 3 nm Al_2O_3 thin film is sufficient to suppress the vacuum-to-air shift. Theoretical modelling has shown that a failure of the protective Al_2O_3 sealing layer and subsequently a change of the optical properties of the top SiO_2 layer due to VAS would result in a lower transmittance of about 0.5% in the whole spectral range.
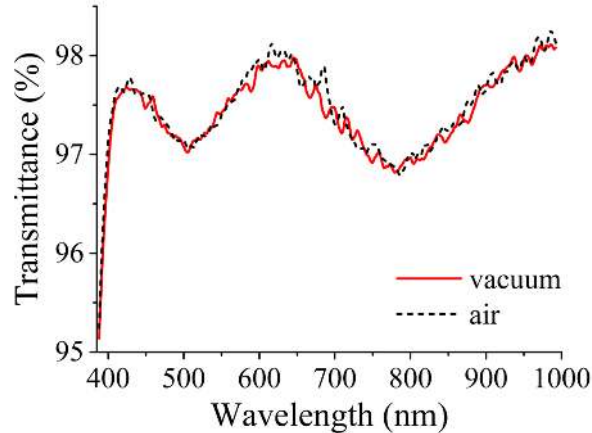
Fig. 8. Transmittance spectra of BBAR double-sided coated N-SF8 sample measured under air conditions and under vacuum conditions 6 months after deposition. No vacuum-to-air shift of transmittance spectra occur.

Conclusion

This comprehensive study on the optical properties of atomic layer deposited SiO_2 shows that various precursors and different ALD tools can be applied to produce silicon dioxide thin films with a high optical quality. We have demonstrated the optical performance of SiO_2 films deposited using 3DMAS, AP-LTO®330 and BDEAS. The grown SiO_2 thin films have low absorption or low scattering losses within a spectral range from 200 nm to 1100 nm. The optical losses are well below 0.5% in a spectral range from 230 nm to 1100 nm. Spectrophotometric measurements reveal a high optical homogeneity of deposited silicon dioxide films. Conclusively, using atomic layer deposition we were able to realize low-loss films with a good thickness control, making ALD an excellent technology for depositing optical elements. In this contribution, we demonstrated the application of ALD SiO_2 films as low-refractive index material in a BBAR with an average transmittance of 97% in a wavelength range from 390 – 1100 nm. The rather long deposition times can be shortened by simultaneous double-sided coating. For application in extreme environment it is worthwhile to check other precursor combinations to reduce the vacuum-to-air shift of SiO_2 thin films.

Regarding the results of this work, a wide range of potential optical application especially in the UV spectral range is attributed to SiO_2 ALD films such as low index material in dichroic mirrors, anti-reflection coating and optical band pass filter. Due to the conformity of ALD thin films prospectively functionalized optical coatings can be deposited on highly curved lenses and on diffractive optical elements.