Characterization of metal-oxide thin films deposited by plasma-assisted reactive magnetron sputtering

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For single layers of SiO_2, Nb_2O_5, and Ta_2O_5 that are deposited by plasma-assisted reactive magnetron sputtering (PARMS), we present measurement results for basic optical and mechanical properties, in particular, optical index, intrinsic film stress, thermal shift of spectral transmittance, and microroughness. We find high refractive indices combined with low intrinsic film roughness, moderate compressive stress, and almost a vanishing shift, indicate high potential for the production of high-performance optical coatings. The high thickness accuracy and process stability are exemplified by the measured spectral performance of multilayer stacks with about 200 single layers.

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Plasma-assisted reactive magnetron sputtering (PARMS) is a new technique for deposition of high-quality optical coatings. It has been developed to achieve process reproducibility and film thickness accuracy typical of ion-beam sputtering. Deposition rates are retained at the same range as in electron beam evaporation processes.

This study aims to characterize basic material properties of SiO_2, Nb_2O_5, and Ta_2O_5 deposited by PARMS, in particular, optical index in ultraviolet (UV)/visible (Vis)/near-infrared (NIR) area, intrinsic film stress, thermal shift of spectral transmittance, and microroughness. Each of these properties may be crucial for the suitability of a deposition technique for a specific field of application. We compare the results for the layers deposited by PARMS with those deposited by plasma ion-assisted deposition (PIAD), as well as with results of a recent study[1] on optical and mechanical properties of oxide optical coating materials deposited by a variety of state-of-the-art thin-film deposition techniques.

In addition, we present examples of complex optical coatings deposited by PARMS to demonstrate the potential of the technique in high-performance applications.

Our investigation was focused on the properties of metal-oxide films deposited by PARMS (Leybold HELIOS sputter system). SiO_2, as a low-index material, and Ta_2O_5 or Nb_2O_5, as high-index materials, were sputtered by two dual magnetrons from metal targets. An RF plasma source was used to assist complete oxidation of the thin film materials. Substrates were placed onto a load lock on a horizontally rotating turntable. Optical monitoring was used for *in situ* measurement of optical film thickness and process control. Deposition rates varied in dependence vis-à-vis particular layer thicknesses. The average rate for deposition of a multilayer stack was about 0.4 nm/s or 1.5 μm/h.

For comparison, we deposited single layers of SiO_2 and Ta_2O_5 by electron beam evaporation with ion assistance (Leybold Advanced Plasma Source)[2]. During film growth on the substrate, the film material was bombarded by argon ions with energies of about 120 eV. Deposition rates were 0.5 and 0.35 nm/s for SiO_2 and Ta_2O_5, respectively.

All layers and layer systems were deposited at mso jena onto polished fused silica and BK7 glass substrates at a diameter of 25 mm and thickness of 3 mm; for stress measurements, onto Si wafer at a diameter of 76.2 mm with thickness of 0.38 mm.

Spectrophotometry (Perkin Elmer Lambda 900 scanning spectrophotometer) was used to determine optical constants at Fraunhofer IOF. Transmittance (T) and reflectance (R) were measured at nearly normal incidence using a self-developed VN attachment, particularly, for absolute reflectance measurements. From these spectra, optical constants n (refractive index) and k (extinction coefficient) were deduced from spectra fits in terms of a Lorentzian multi-oscillator model[3]. The accuracy in n-determination was of the order of 1% relative error. From the same spectra fits, the thickness of the layers was also determined.

The thermal shift of the same samples was determined

Table 1. Overview of Samples for Measured Thickness Determined by Spectrophotometry

Process /Process ID	Material	Type	Target Thickness (nm)	Measured Thickness (nm)
PARMS				
H0058	SiO_2	single layer	370	369.5
H0061	SiO_2	single layer	2000	2019
H0057	Ta_2O_5	single layer	250	251.7
H0062	Ta_2O_5	single layer	2000	2012
H0066	Nb_2O_5	single layer	230	230.2
H0067	Nb_2O_5	single layer	2000	2002
H0074	SiO_2/Ta_2O_5	notch filter 405/488/561/639	19757	
H0078	SiO_2/Nb_2O_5	band pass 420–480	15400	
PIAD				
U651	Ta_2O_5	single layer	2000	1949
U653	SiO_2	single layer	2000	1962

at Fraunhofer IOF from transmission measurements using an OptiMon process spectrophotometer[4]. Firstly, transmission measurement was performed in atmospheric conditions at room temperature. Next, the measurement chamber was evacuated at high vacuum and heated up to a temperature of 100 °C prior to the second transmission measurement. Because of the changes in film thickness and refractive index, spectral characteristic shifts in wavelength and external values were used to quantify the thermal shift according to Ref. [1].

For stress measurements, prior deposition, the curvature of uncoated silicon wafers was determined by a Tencor system. After film deposition, measurements of the curvature were repeated, and from differences in curvature, the layer stress was calculated by Stoney's Equation[5]. In our convention, negative stress values correspond to tensile stress, while positive values relate to compressive stress.

Microroughness was determined by scanning force microscopy using a Veeco Dimension 3100. Three measurements with 1×1, 10×10, and 50×50 μm scan size and 512 sample points were performed for each sample. Results were corrected for tilt in each scan line before root mean square (RMS) roughness σ was calculated. The power spectral density function from the Fourier transform of the microtopography was derived from measurements of the three scan sizes[6].

Optical constants obtained from spectrophotometry were in reasonable agreement with typical literature values. Particularly for Ta_2O_5, the PARMS-deposited sample attained a noticeably higher refractive index than the corresponding PIAD samples. In fact, the PARMS index fell between the values typically achieved using PIAD and those reported for ion plating[1]. Similarly, for Nb_2O_5, we found higher refractive index compared to those typically achieved by PIAD. Results indicated a high packing density of the films deposited by PARMS. Extinction coefficient for SiO_2 was higher than for layers deposited by PIAD. Deposition parameters for PARMS, however, have not yet been optimized for minimum absorptance. The thickness values obtained from the spectra fit for the individual layers were identical to the target values (Table 1) within a +/–1% error corridor, thus confirming high thickness accuracy of the PARMS deposition technique.

Generally, the measurements attained an almost zero

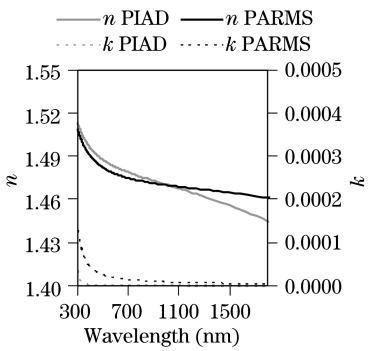

Fig. 1. Refractive index n and extinction coefficient k for single layers SiO_2 deposited by PARMS and PIAD. In the IR, absorption features in the considerably thick SQ1 substrates make the determination of silica film optical constants less reliable than in VIS/UV.

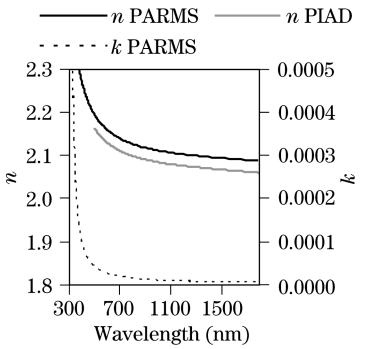

Fig. 2. Refractive index n and extinction coefficient k for single layers Ta_2O_5 deposited by PARMS and PIAD.

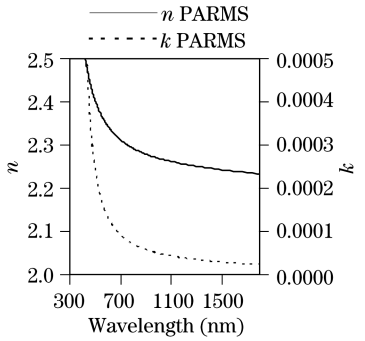

Fig. 3. Refractive index n and extinction coefficient k for single layers Nb_2O_5 deposited by PARMS.

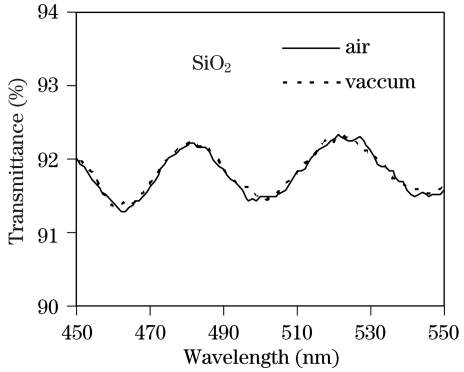

Fig. 4. Transmission of single layer SiO_2, 2000-nm thickness at room temperature and after heating in vacuum.

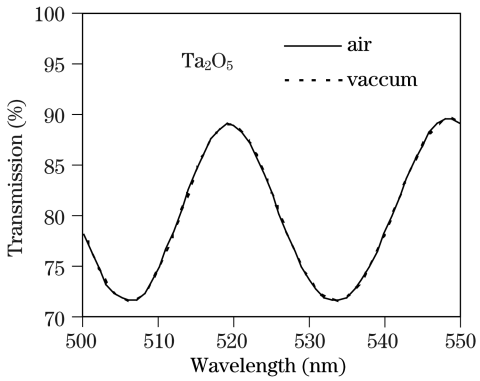

Fig. 5. Transmission of single layer Ta_2O_5, 2000-nm thickness, at room temperature and after heating in vacuum. The amplitude of the transmittance curve is reduced by the limited wavelength resolution of the spectrophotometer.

shift for all samples investigated. Even in the case of Nb_2O_5 where a slight positive shift was visible in the diagram, it was in the order of accuracy of the measurement. Low shift values indicate film morphology that should be almost free of open pores. Hence, PARMS is a promising technique for producing dense and environmentally stable interference filters, as exemplified by the temperature-stable transmission characteristics of the produced notch filter (as shown in Fig. 7).

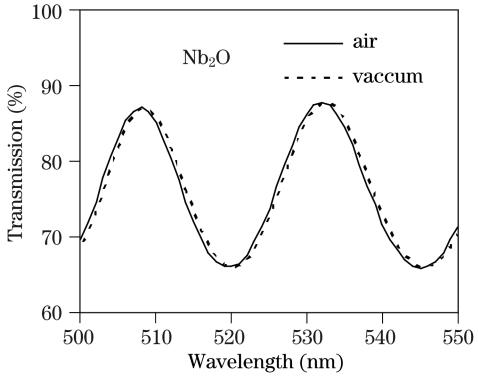

Fig. 6. Transmission of single layer Nb_2O_5, 2000-nm thickness, at room temperature and after heating in vacuum. The amplitude of the transmittance curve is reduced by the limited wavelength resolution of the spectrophotometer.

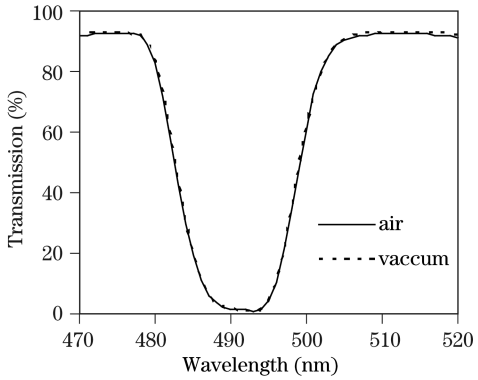

Fig. 7. Transmission of notch filter NF 405/488/561/639 at room temperature and after heating in vacuum. The residual transmittance in the blocking band is determined by the noise level of the spectrophotometer.

Table 2. Vacuum Shift and Stress for Single Layers and Notch Filter Deposited by PARMS and PIAD. Positive Sign indicates Compressive Stress

Deposition technique	Material	Thickness (nm)	Shift (%)	Stress (MPa)
PARMS	SiO_2	370	–0.14	438
PARMS	SiO_2	2000	–0.12	435
PIAD	SiO_2	2000	–0.09	
PIAD	SiO_2	744		267
PARMS	Ta_2O_5	250	–0.01	152
PARMS	Ta_2O_5	2000	0.01	132
PIAD	Ta_2O_5	2000	0.06	
PIAD	Ta_2O_5	501		–2
PARMS	Nb_2O_5	230	0.05	190
PARMS	Nb_2O_5	2000	0.08	138
PARMS	SiO_2/Ta_2O_5 multilayer	19757	0	

We found compressive stress for all single layers deposited by PARMS. The thick layers of the high-index materials tended to show lower stress as compared to the thin layers. If layers deposited by PARMS and PIAD are compared, we could observe higher stress for PARMS at both SiO_2 and Ta_2O_5. In the case of SiO_2, recently published results indicated a similar stress level for SiO_2 layers deposited by ion plating, and higher stress level for SiO_2 layers deposited by ion-beam sputtering[1]. For Ta_2O_5, we obtained significantly lower stress than what was reported for layers deposited by ion plating.

We used fused silica substrates with very high polishing quality, as confirmed by the measured RMS roughness below 0.5 nm. The microscope image (as shown in Fig. 8), however, reveals some deepening of the surface topography.

After PARMS deposition of single layers with a thickness of 200–400 nm, the surface topography and the measured RMS roughness only slightly changed as compared to the substrate. The deposition of a 2000-nm thick SiO_2 layer have resulted in an increase of RMS roughness, and a certain amount of intrinsic film roughness could be identified on the microscope image (as show in Fig. 9). In contrast, the 2000-nm thick Ta_2O_5 layer clearly showed levels surface features found on substrate at pre-coating (see Fig. 10). As a result, RMS roughness derived from the measurement over 1×1 μm was reduced. The effect, however, is restricted to small-scale surface features. At over 50×50 μm, we could still continue determining substrate properties for microtopography and RMS roughness.

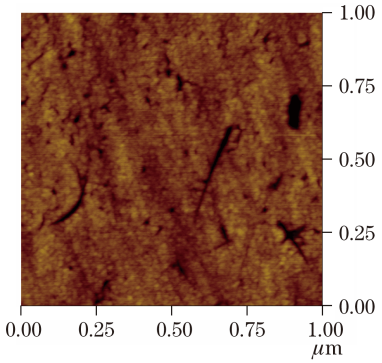

Fig. 8. Surface topography of fused silica substrate (colour scale 5 nm, $\sigma = 0.43$ nm).

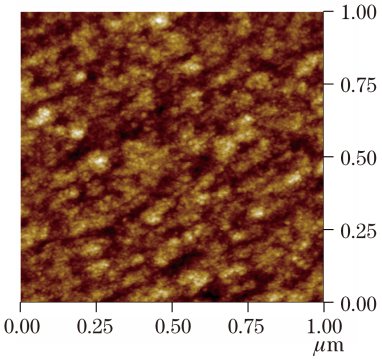

Fig. 9. Surface topography of single layer SiO_2, 2000-nm thickness, deposited by PARMS onto fused silica substrate (colour scale 5 nm, $\sigma = 0.62$ nm).

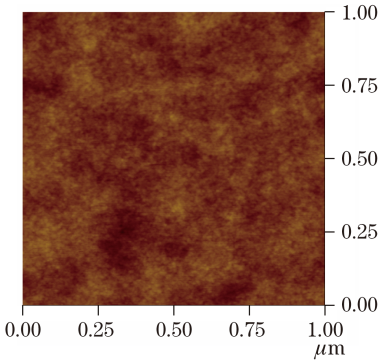

Fig. 10. Surface topography of single layer Ta_2O_5, 2000-nm thickness, deposited by PARMS onto fused silica substrate (colour scale 5 nm, $\sigma = 0.24$ nm).

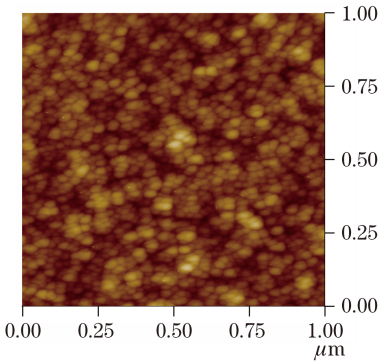

Fig. 11. Surface topography of single layer SiO_2, 2000-nm thickness, deposited by PIAD onto fused silica substrate (colour scale 20 nm, $\sigma = 1.98$ nm).

Table 3. RMS Roughness σ Derived from AFM Measurement across 1×1 and 50×50 μm

Deposition Technique	Material	Thickness (nm)	σ (nm) 1×1 (μm)	σ (nm) 50×50 (μm)
	Fused Silica	–	0.43	0.36
PARMS	SiO_2	370	0.47	0.51
PARMS	SiO_2	2000	0.62	0.50
PIAD	SiO_2	2000	1.98	1.61
PARMS	Ta_2O_5	250	0.56	0.52
PARMS	Ta_2O_5	2000	0.24	0.49
PIAD	Ta_2O_5	2000	1.77	1.11
PARMS	Nb_2O_5	230	0.45	0.44
PARMS	Nb_2O_5	2000	0.40	0.44

Layers deposited by PIAD show significantly more pronounced intrinsic roughness, as demonstrated on the example of SiO_2 in Fig. 11.

The contribution of film and substrate roughness to the measured surface topography is most clearly revealed by the power spectral density (PSD) curves, as shown in Figs. 12 and 13. For high spatial frequencies, film roughness, depending on the deposition technique, could determine surface roughness, and convergence with substrate roughness at spatial frequencies was observed between 0.1 and 1 μm^{-1}.

Data indicate that PARMS is superior to PIAD with respect to surface smoothness. The obtained roughness values are comparable to data recently reported for ion plating-deposited tantalum and hafnium oxide films[1].

The capabilities of PARMS for deposition of high-complex multilayer stacks were exemplified by a notch

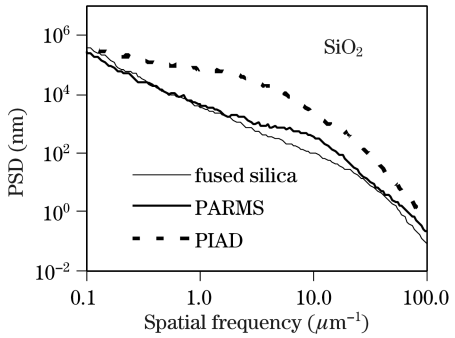

Fig. 12. PSD for SiO_2 single layer, 2000-nm thickness, deposited by PARMS and PIAD onto fused silica.

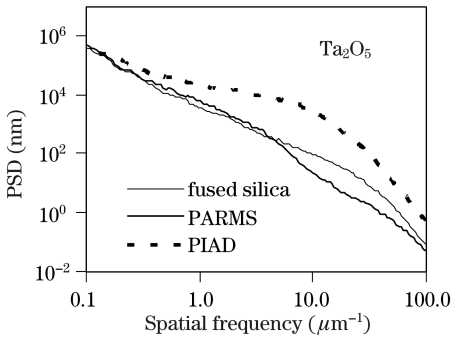

Fig. 13. PSD for Ta_2O_5 single layer, 2000-nm thickness, deposited by PARMS and PIAD onto fused silica.

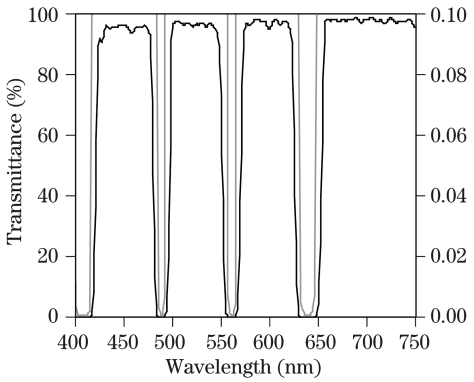

Fig. 14. Measured passband and blockband transmittance for notch filter 405/488/561/639 nm deposited by PARMS.

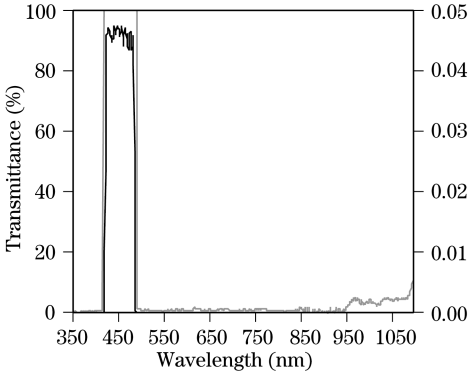

Fig. 15. Measured passband and blockband transmittance for band pass 420-480 nm deposited by PARMS.

filter and a band pass filter with broadband blocking. The notch filter was composed of 220 SiO_2/Ta_2O_5 layers, and the band pass filter of 196 SiO_2/Nb_2O_5 layers. The thicknesses of the individual layers varied between 3 and 350 nm.

In both cases, we obtained excellent agreement with the design transmittance curves. It was proven that high layer thickness accuracy could be achieved for layer stacks with more than 10-μm total thickness.

The presented results demonstrate that the PARMS technique is capable of supplying smooth high-index layers with vanishing thermal shift yet still moderate compressive stress values. Although the refractive indices were not as high as those in ion plating-deposited layers, the significantly lower mechanical stress compensates this shortcoming. Combined with high thickness accuracy, the method is found suitable for the precise manufacture of interference filters for the most demanding applications.

In conclusion, in view of the abovementioned combination of high indices, small stress, and vanishing shift for the PARMS-deposited Nb_2O_5 and Ta_2O_5 layers, the PARMS method can be considered suitable for the production of coatings with balanced optical and mechanical properties, as what has been mentioned in Ref. [1]. Finally, further optimization of the coating process parameters should be aimed at reducing compressive stress in the layer materials. Verification of the vacuum shift is deemed essential in the accurate identification of such optimal balance.

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