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Very thick mixture oxide ion beam sputtering films for investigation of nonlinear material properties★

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Abstract. Currently, optical coating technology is facing a multitude of new challenges. Some of the new requirements are addressed to the spectral behavior of complex coatings, but in addition, the power handling capabilities gain in importance. Often, both demands are combined in the same component, for example in chirped mirrors for ultra-short pulse applications. The consequent demands on the accuracy of the layer thicknesses and the stability of the refractive indices require a deposition by sputtering processes. For high end components, Ion Beam Sputtering (IBS) is often the method of choice. Utilizing the Co-sputtering technique, IBS additionally allows a higher flexibility in the possible coating materials by mixing two pure oxides into one ternary composite material. These composite materials are also advantageous for researching third order nonlinear effects, which can limit the functionality of optics at high powers. The layer thicknesses required for this fundamental research often exceed 100 µm, which therefore makes low stress and absorption in the layer materials mandatory. A reduction of these decisive properties can be achieved by a thermal treatment of the sample. Usually, this is performed by a post-deposition annealing. Alternatively, the coating temperature can be increased. This is rarely done for IBS processes, but it can be assumed, that the effect is comparable to that of ex-situ annealing. In this work, different ternary mixtures of Al_2O_3/SiO_2, HfO_2/Al_2O_3 as well as Nb_2O_5/Al_2O_3 were investigated for their layer stress and absorption, applying both, in-situ temperature treatment as well as post manufacturing annealing. It is observed that suitable thermal treatment as well as material composition can significantly reduce layer stress and absorption in the deposited layer. This enabled the manufacturing of layers with thicknesses of over 180 µm as well as the measurement of nonlinear properties of the deposited materials.

1 Introduction

In the past years, deposition processes were developed to most flexible technologies for numerous applications. The current research in optics manufacturing can be partitioned in two major trends of development. The first direction is the achievement of most complex designs with respect to the optical performances. These studies are driven by the need for the management of broad spectra or the filtering and separation of narrow wavelength bands with high contrast ratios [1]. The requirements on the film thickness accuracy and the stability of the index of refraction are very high in these applications and in addition, a huge number of layers as well as also increasing total film thicknesses are necessary. With respect to these demands in accuracy, the coatings are manufactured by sputtering processes. Because of its high reproducibility and the achievable coating quality, IBS is often considered for high end applications [2]. The second trend is the management of quality aspects for high end laser optics. Often, the power handling capability or losses are critical parameters which limit the applicability of the component [3]. Especially with respect to losses and for improvement of the damage threshold, oxidic mixture materials were applied successfully [4]. In these cases, the mitigation of crystallization effects and the modification of the electronic band structure are of main importance. The flexibility of present technological approaches allows for infinite variation of the properties of ternary oxides between the properties of the original binary oxides, which are combined in the composite material. Indeed, the application of the Co-sputter technique allows to manufacture a broad spectrum of materials which can also be used for fundamental studies. Examples for such fundamental investigations are third order nonlinear effects in dielectric materials [5]. It is assumed that the lifetime of the Kerr-effect is strongly increasing close to the resonance of the electronic band gap. For the investigation of this behavior, the band gap of the material has to be tuned by varying the content of the materials, and the material has to be transparent for the third harmonic of the Ultra Short Pulse (USP) laser source at its fundamental wavelength of approximately 800 nm [6]. In the final experiment, the spectral broadening by self-phase modulation is used. In addition, the nonlinear refractive index of the layer has to be measured by an improved z-scan

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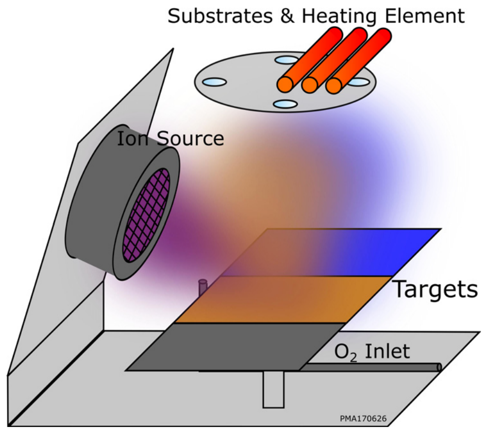


Fig. 1. Schematic of the IBS coating plant. From the ion source, an ion beam (violet) sputters two of the three target materials (blue and brown). The atoms deposit on the substrates and create a layer of mixed composition. Oxygen is provided for the process to produce oxidic layers.

approach. Both measurements require a propagation length of more than 0.1 mm, and this demand defines the minimum film thickness. As a consequence, the film stress and especially the absorption of thick layers have to be minimized in the deposition process. After the coating process, a temperature treatment can be used for a final reduction of optical losses and of layer stress [7, 8]. In the present study both, the optimization of the losses and stress are presented. Thereby, the variation of the material content, the thermal treatment and the growth temperature is discussed. Finally, the measurement of nonlinear properties presented for an exemplary layer.

2 Coating procedure

The samples are manufactured by the IBS-Co-sputter technique using 25 mm fused silica substrates with a thickness of 1 mm. Generally, IBS is employed to manufacture highly precise layer stacks of best quality, but the area deposition rate of the process is relatively limited. However, for the manufacturing of multiple micrometer coatings, the deposition speed can be increased to nearly one nm s^{-1} for a smaller deposition area by optimizing the substrate position. In this work, the co-sputter technique is applied. This technology uses a target translation mount which is equipped with three targets of different materials, allowing to deposit two different ternary composite types without a change of the target materials. The ratio of material content of the coatings is varied by the lateral motion of the target relative to the ion beam. The relative positioning of ion source, targets and samples is presented in Figure 1. The coverage of the ion beam on the respective neighboring targets and the sputter efficiency of the material define the composition of the material flux which results in layers with composed of a mixture of both oxides produced from the target materials. In this work, only single layers are investigated. All processes are reactive, and the sputtered particles oxidize during the deposition, if a sufficient flux of oxygen is supplied. The oxygen flux used for the Al_2O_3/SiO_2-layers was 50 sccm. Hafnium shows a strong dependency on the oxygen flux, therefore this behavior was investigated in more detail (see Fig. 2(b)). In the coatings presented in this work, an argon plasma generated by a Veeco RF high power ion source is used. The ions are then extracted and neutralized before they hit the target. The applied acceleration voltage is 1500 V for extraction and the ion beam current is 400–500 mA. The diameter of the ion beam on the targets is approximately 10 cm and the pressure during the coating is in the range of 5×10^{-4} mbar. A heating system is rarely used in IBS processes, but as the substrate temperature can be important for layer-stress and absorption minimization, a powerful heater is implemented (see Fig. 1).

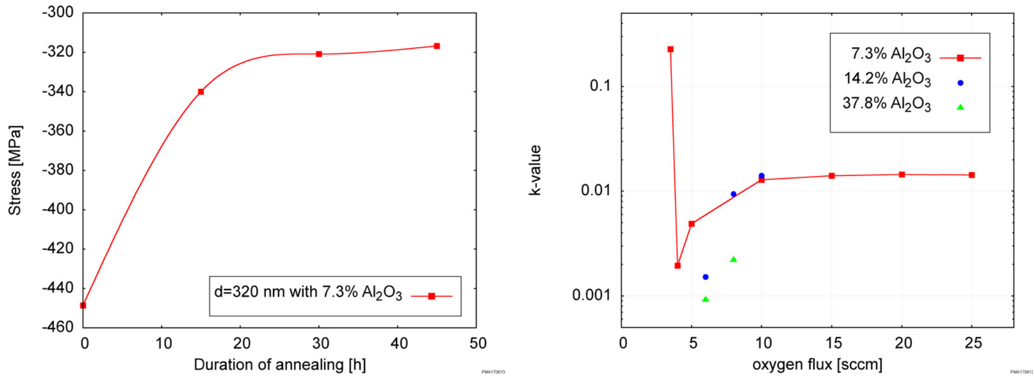
3 Mechanical and optical properties of IBS films

There are mainly two parameters, which limit the thickness which can be reached for high quality optical layers. The first parameter is the mechanical stress caused by the deposition of the layer on the substrate. For a stress level exceeding the limits, the layer will either delaminate from the substrate surface and shatter, or the stress will break the substrate, if the bond between layer and substrate is sufficiently high. An example is depicted in Figure 3. To measure the stress of coated substrates in this work, a commercial zygo “Verifire ZPX” interferometer is used. It allows measuring the surface curvature of the sample before and after the coating. From the two measured values and material parameters (Young’s modulus and Poisson number of the substrate material as well as substrate and layer thickness) the stress can be calculated using Stoney’s equation [10].

The second parameter of importance is the absorption in the layer material. Especially for ultra violet wavelengths, optical layer materials may exhibit significant absorption which becomes critical for high propagation length in thick layers. To manufacture high quality optical layers with the required thicknesses, it is therefore necessary to reduce the absorption in the layer material. To determine the absorption in the deposited layers, a commercial PerkinElmer “Lambda 1050” spectrometer is used to measure the transmission spectrum. Applying the software “Spektrum” [11], the transmission data is fitted, and the absorption is calculated.

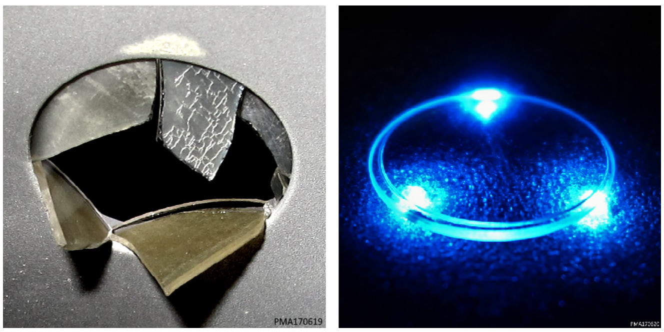
The post-process annealing was done under normal atmospheric conditions, and one thermal cycle consisted of slow heating to a set temperature, maintaining this temperature for a set time, and a slow returning to room temperature. For stress measurement, several of these cycles were performed, to see the temporal stress development. The temperatures used for the annealing are 330 °C for the Al_2O_3/SiO_2-mixtures and 150 °C for HfO_2/Al_2O_3. If in-situ heating was applied, the samples were heated during the whole coating process to approximately 330 °C. The mixture compositions were determined by EDX-analysis [12].

The results for stress and absorption of Al_2O_3/SiO_2 and HfO_2/Al_2O_3 mixtures are presented in Figures 2 and 4, respectively. In (a), the layer stress for both mixtures ($92 \pm 5\%$ $Al_2 O_3$ and $8 \pm 1\%$ SiO_2 as well as $64 \pm 3\%$ $Al_2 O_3$ and $36 \pm 2\%$ SiO_2) is presented, while (b) and (c) feature



(a) (b)

Fig. 2. The layer stress (a) and absorption at 266 nm (b) in HfO_2/Al_2O_3-layers.



(a) (b)

Fig. 3. Two coated optics with a diameter of 25 mm. (a) An optic destroyed during the coating by the layer stress. (b) A high quality optical layer with a thickness of 182 μm, low stress and low losses (illuminated for better layer visibility). With fitting thermal treatment, the stress induced breakage can be avoided.

the spectral absorption values for the different compositions. The plots in Figure 4 illustrate a consistent influence of in-situ heating compared to ex-situ annealing. Ex-situ annealing reduces the layer stress in samples manufactured in the coating process without heating to almost zero. When the sample is heated during the coating, the initial stress value is lower, but annealing after the deposition reduces the stress less than for the unheated samples. The reason for this remaining layer stress is thermal stress, which results from the temperature difference between the coating process and room temperature. Although the two different mixtures of the coating materials show the same qualitative behavior, it has to be noted that a higher SiO_2-content in the layer results in a lower initial stress value after the coating. Especially in the cases without in-situ heating, the initial stress for the two mixtures is strongly different. This can most probably be explained by the preventing of crystallization effects caused by the higher silica content. The initial stress of the 64% Al_2O_3/36% SiO_2-mixture is also low, when compared to single SiO_2-layers and Al_2O_3-layers [8,9].

The absorption values behave slightly different. The absorption losses of the samples deposited without heating are reduced after annealing. Nevertheless, these coatings do not reach loss values as low as the absorption levels observed for the in-situ heated samples. On the other hand, the heated samples do not show significant changes under ex-situ annealing.

The qualification of HfO_2/Al_2O_3-layers produces slightly different results, as can be seen in Figure 2. Ex-situ annealing does not reduce the stress to a completely relaxed state, although this may result from changes in the annealing temperature. Additionally, a strong influence of the oxygen content on absorption during the coating was observed. For the applied deposition process, a minimum of absorption was determined for an oxygen flux of 4 sccm. Measurements for changed ternary compositions show a similar characteristic, whereby higher Al_2O_3-contents cause lower absorption values.

4 Nonlinear properties

With the samples generated by applying the gained knowledge on layer stress and absorption, it was possible to measure the nonlinear refractive index of the deposited material. The measurements were performed with an interferometric set-up based on the z-scan technique [13]. The set-up consisted of an Mach-Zehnder-interferometer with the sample placed in a focussed beam inside of a telescope in one arm of the interferometer. After passing the sample, the beam is collimated again and superimposed with the undisturbed beam from the second arm. The resulting interference pattern is recorded by a digital camera (Basler Pulse puA1600-60um) and used to calculate the wave front-curvature of the beam which was influenced by the sample. Moving the sample through the focus changes the intensity and therefore the strength of the Kerr-Lens created, which is then visible as a change in the curvature of the wave front. The measurements were performed using a Nd:$YV0_4$-laser emitting at 1064 nm with a pulse length of 12 ps. The system was able to reach pulse energies of up to 150 μJ.

To determine the nonlinear refractive index, the procedure is modeled utilizing the ABCD-matrix formalism combined with the distributed lens approximation [14], and the so simulated curve is fitted to the measured values. For the fitting of the obtained data one needs to know the

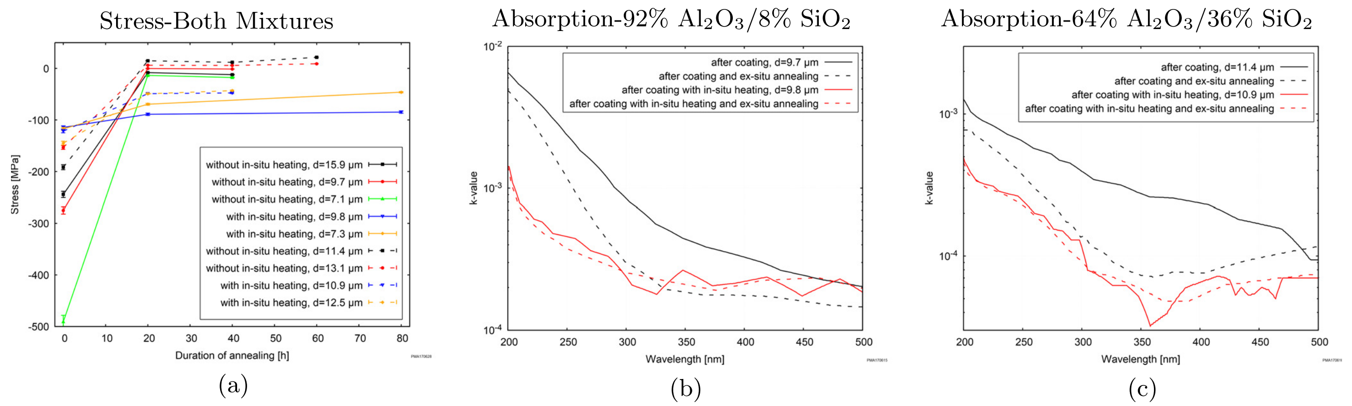


Fig. 4. Stress and absorption for different mixtures of Al_2O_3 and SiO_2. (a) The influence of different thermal treatments on the layer stress for 92% Al_2O_3/8% SiO_2 (solid) and 64% Al_2O_3/36% SiO_2 (dashed). (b) The effect on the spectral absorption for 92% Al_2O_3/8% SiO_2. (c) The same for 64% Al_2O_3/36% SiO_2.

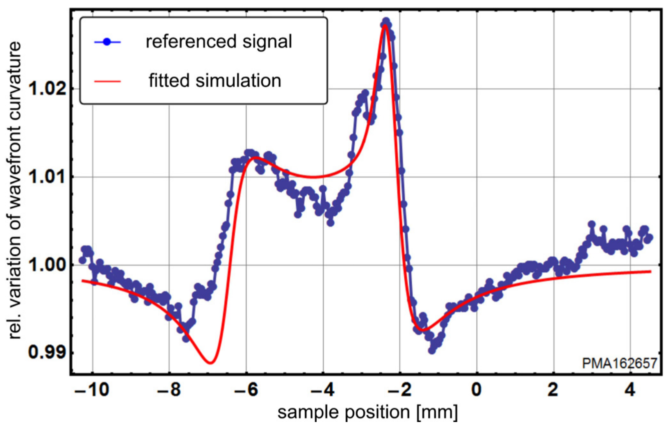


Fig. 5. Measured and simulated relative variation of the wavefront curvature caused by the variation of the Kerr-Lens in the sample during movement along a focused beam.

thickness and the refractive index of the considered substrate and layers on the sample, the laser wavelength, the focus diameter in the telescope (28 μm), the M^2 -parameter of the beam (1.04), the focal length of the telescope lenses (5 cm), and the distance between the second lens and the recording camera.

When using substrates of sufficient thickness, the produced curve shows two peaks. One of the peaks is caused by the used substrate material, and one by the deposited layer. These two peaks then allow the determination of the nonlinear refractive indices of substrate material as well as deposited layer in one measurement. A measurement of a thick substrate with a deposited layer and the fitted simulation are presented in Figure 5. The sample used for the measurement was a 85 μm thick layer of $91 \pm 5\%$ Nb_2O_5 and $9 \pm 1\%$ Al_2O_3, which was manufactured with regards to the findings from the investigations presented before. The determined nonlinear refractive index is 21.6×10^{-16} cm^2 W^{-1}, which is higher than the value (7.3×10^{-16} cm^2 W^{-1}) known from niobium oxide bulk material [15]. This difference may result from the deposition process or the differing compositions of bulk material and layer.

5 Conclusion

In summary, the present study illustrates the complexity of parameters which have to be respected when manufacturing thick optical layers. We show that applying ex- and in-situ thermal treatments can significantly reduce the layer stress and the absorption in the deposited material. With these optimizations, it is possible to manufacture high quality optical layer with thicknesses of over 180 μm, which are suitable to investigate nonlinear properties.

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