Properties of pulsed laser deposited optical coatings

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Abstract

Hafnia and yttria films for optical applications were prepared by pulsed laser ablation with oxygen ion bombardment of the growing films. The influence of the laser and ion beam parameters on the refractive index and microstructure of the films was investigated. The optical quality of the films with respect to absorption and laser damage was characterized at the Nd:YAG-laser wavelength by measuring the laterally resolved absorptivity and the laser damage thresholds. Both hafnia and yttria films prepared at low ion energy and intensity (150 eV, 50 μA/cm²) were amorphous and had a high bulk-like refractive index and packing density. At high ion energy and intensity (700 eV, 400 μA/cm²) the films became polycrystalline with high refractive index and packing density at relatively high growth rates above 10 to 20 nm/min or relatively low refractive index and packing density at low growth rates. Films with high laser damage threshold at 1.06 μm wavelength could only be prepared with strong oxygen bombardment. Highly reflective multilayer systems of only one material with alternately high and low refractive index were prepared by varying the parameters of oxygen ion bombardment during deposition. Their reflectivity and laser damage threshold at 1.06 μm as well as their microstructure were investigated.

1. Introduction

Pulsed laser deposition is now a widely used method in research for the deposition of thin films. The method might also be of interest for the preparation of optical coatings if the characteristics of the method, such as high instantaneous growth rates, relatively high kinetic energies of particles and high cleanliness, would result in improved optical quality compared to corresponding films prepared by conventional methods. Several authors [1–3] reported on the preparation of optical oxide and fluoride coatings by pulsed laser deposition, and have shown that relatively high refractive indices and, hence, high packing densities of the coatings can be achieved with that method.

In recent papers [4–6], we have shown that yttria, hafnia and zirconia films with high bulk-like refractive indices can be prepared by pulsed laser deposition and that oxygen ion bombardment of the growing films is needed for the preparation of films with low absorption and high laser damage thresholds at the Nd:YAG-laser wavelength. Moreover, we found that the refractive indices of those films are related to the growth rate (determined by the laser power density and the laser pulse repetition rate), the ion energy and the ion current density. High bulk-like refractive indices were obtained by using relatively low ion bombardment (150 eV ion energy, 50 μA/cm² ion current density), while the refractive indices strongly decrease with increasing ion bom-
barrlement, that is increasing ion energy and current density. Microstructural investigations revealed that high refractive-index films are amorphous with a high packing density, and low refractive-index films are polycrystalline with a low packing density. Furthermore, we have shown that multilayer systems with respect to refractive index consisting of one material can be prepared by controlling the ion beam parameters during the deposition [5,6]. Since films with high laser damage thresholds could only be prepared with strong oxygen ion barrlement [4], we will present in this paper the results of optical investigations of yttria and hafnia films prepared with strong oxygen ion bombardment using 700 eV ion energy and 400 μA/cm² ion current density. Moreover, we will report on further investigations concerning the preparation of multilayer systems of one material for optical applications.

2. Experimental details

The experimental set-up used for the preparation of yttria and hafnia films by pulsed laser deposition was illustrated elsewhere [4]. It consists of a high vacuum chamber that can be evacuated to a base pressure of 5 × 10⁻⁵ Pa. For the ablation of particles from sintered targets the beam of an excimer laser operating at 248 nm wavelength and having 20 ns pulse duration was used. The beam was focused onto the target surface to a cross-section of 4 mm² and moved in spirals with a constant vector velocity across a target area of 30 mm diameter. The target–substrate distance was 70 mm.

The growing films were bombarded with an oxygen ion beam produced by means of an r.f. ion source. The ion energy and current density were 150 eV and 50 μA/cm², respectively, for low ion bombardment and 700 eV and 400 μA/cm² for strong ion bombardment. Prior to deposition the substrates were cleaned chemically and strongly oxygen ion bombarded for about 5 min in order to remove macroscopic and microscopic impurities. All films were prepared without substrate heating. However, with strong ion bombardment maximum substrate temperatures up to 100°C were measured.

The film growth was controlled by means of an in-situ ellipsometer operating at 678.3 nm wavelength and 70° angle of incidence. Films for optical investigations were deposited onto SiO₂-substrates and with an optical thickness of a quarter of the Nd:YAG-laser wavelength, i.e. 266 nm.

The laterally resolved absorptivity at 1.06 μm wavelength was measured by means of photothermal deflection spectroscopy. The laser damage thresholds \( D_0 \) and \( D_1 \) were determined using a Nd:YAG-laser of 10 ns pulse duration, where the laser beam was focused to a cross-section of 37 μm diameter. Each sample was irradiated with a lateral matrix of laser shots, where one row consisted of 50 laser shots of the same energy, which was varied in appropriate steps. Two different values \( D_0 \) and \( D_1 \) are given, both characterizing the laser damage threshold. The lower value \( D_0 \) represents the energy density at which just one of the 50 laser shots of the same energy leads to damage of the film visible in an optical microscope using 150 times magnification. \( D_1 \) is the energy density at which all laser shots lead to film destruction. Consequently, \( D_0 \) is a measure for the predominantly defect induced laser damage and \( D_1 \) is a measure for the predominantly intrinsic absorption induced damage.

The cross-sectional TEM studies were carried out in a high resolution electron microscope operating at 400 kV acceleration voltage. For these investigations the films were deposited on silicon substrates. Perpendicular to the sample surface a wedge was cut out, which afterwards was thinned by means of an Ar⁺-ion beam of 5 keV energy and 1 mA/cm² current density.

3. Results and discussion

3.1. Single layers

As shown in Fig. 1, the refractive index of yttria and hafnia films prepared by pulsed laser deposition with strong oxygen ion bombardment of the growing films varies with the growth rate of the films, which is determined by the laser power density and the laser pulse repetition rate. At relatively high growth rates above 20 nm/min the films were found to have high bulk-like values of refractive index and, hence, high packing densities. Investigations by transmission electron microscopy revealed that those films
have a polycrystalline microstructure, in contrast to films prepared with low oxygen ion bombardment (up to 150 eV ion energy and 50 \( \mu \text{A/cm}^2 \) ion current density), which had the same high values of refractive index at high and low growth rates but were amorphous. With decreasing growth rates the refractive indices of the films decrease from 2.10 down to 1.80 in the case of hafnia and from 1.96 down to 1.70 in the case of yttria. Those low-refractive index films of both materials were found to be polycrystalline, too. However, to account for the low values of refractive index, the packing density has to be small in comparison to the corresponding high-refractive index films.

In Fig. 2a–d the laterally resolved absorptivity as well as the laser damage thresholds (see figure captions), both measured at 1.06 \( \mu \text{m} \) wavelength, of various hafnia films prepared by pulsed laser deposition with strong oxygen ion bombardment are presented. The upper figures (Fig. 2a and b) were obtained from high-refractive index films deposited at relatively high growth rates, the lower ones (Fig. 2c and d) from low-refractive index films deposited at low growth rates. In both cases the laser power density increases from Fig. 2a to b and c to d.

Fig. 2. Laterally resolved absorptivity and laser damage thresholds \( D_0 \) and \( D_1 \) at 1.06 \( \mu \text{m} \) wavelength of various excimer laser deposited hafnia films prepared with strong oxygen ion bombardment (700 eV ion energy, 400 \( \mu \text{A/cm}^2 \) current density; \( n \) – refractive index, \( S_0 \) – laser power density, \( r \) – growth rate, \( f \) – laser pulse repetition rate). (a) \( D_0 < 10 \text{ J/cm}^2; D_1 = 26 \text{ J/cm}^2 \ n = 2 \times 10^5, S_0 = 1 \times 10^8 \text{ W/cm}^2, r = 45 \text{ nm/min}, f = 150 \text{ Hz}; \) (b) \( D_0 = 12 \text{ J/cm}^2; D_1 = 25 \text{ J/cm}^2 \ n = 2.10, S_0 = 1.3 \times 10^8 \text{ W/cm}^2, r = 60 \text{ nm/min}, f = 150 \text{ Hz}; \) (c) \( D_0 = 11 \text{ J/cm}^2; D_1 = 34 \text{ J/cm}^2 \ n = 1.85, S_0 = 8 \times 10^7 \text{ W/cm}^2, r = 8 \text{ nm/min}, f = 150 \text{ Hz}; \) (d) \( D_0 = 20 \text{ J/cm}^2; D_1 = 88 \text{ J/cm}^2 \ n = 1.85, S_0 = 1 \times 10^8 \text{ W/cm}^2, r = 6 \text{ nm/min}, f = 12 \text{ Hz}. \)
Comparing only films of equal refractive index deposited at different laser power densities, i.e. Fig. 2a with b and Fig. 2c with d, we can see that the number of absorption peaks within the films strongly decreases with increasing laser power density. The average height of those peaks increases, and the basic absorptivity, that is the absorptivity of the regions between the absorption peaks, remains about constant. Simultaneously, the lower more defect induced laser damage threshold $D_0$ increases, which is not surprising since the probability to hit an absorption defect by the laser shots decreases with decreasing number of absorption peaks. On the other hand, the higher more intrinsic absorption induced laser damage threshold $D_1$ does not increase since it is a measure for the laser damage threshold of the regions with basic absorptivity and is therefore determined mainly by the basic absorptivity of the films.

Comparing hafnia films of different refractive index deposited at the same laser power density and ion beam parameters but at different growth rates controlled by the laser pulse repetition rate, i.e. comparing Fig. 2a with d, we can see that decreasing growth rates result in decreasing number and average height of the absorption peaks. Consequently, the laser damage threshold $D_0$ increases considerably. The increase of $D_1$ with decreasing growth rate is, however, in contrast to the increasing basic absorptivity.

The findings can be interpreted by distinguishing between the effects related to the pulsed laser ablation process itself and the ion bombardment of the growing films. One of the main characteristics of the hafnia and yttria films which is due to the pulsed laser ablation process is their high bulk-like refractive index associated with a high packing density. According to a model proposed by Metev [7] such high packing densities should be attributed to the high instantaneous growth rates in the order of $10^5 \text{ nm/s}$ during the pulses of ablated species arriving at the substrate and the relatively high kinetic energies of the ablated species, leading to a layer by layer growth mode and a dense amorphous microstructure.

Using sufficiently high ion energies and current densities, ion bombardment of the growing films induces crystallization processes in the films, resulting in the transformation from the amorphous to a polycrystalline microstructure. The packing density of that polycrystalline structure, however, is apparently high at relatively high mean growth rates and, consequently, still determined by the characteristics of the pulsed laser ablation process. If the mean growth rate becomes too low, the ion bombardment causes changes in the film growth mode towards island-like growth and with it the formation of smaller crystallites and a number of voids, resulting in a lower packing density. The influence of the ion bombardment should mainly be related to the supply of additional energy and momentum into the growing films causing higher mobility of the film surface atoms, creating sites that are energetically favoured for the nucleation of crystallites and resputtering of loosely bound species. Consequently, the main parameter that determines whether dense amorphous and crystalline or relatively loosely packed films are produced was found to be the ratio of bombarding ions to incoming particles from the target and therefore the energy supplied per film volume.

The absorption and the laser damage thresholds of the hafnia films can be discussed in a quite similar way. As we have shown previously [4], hafnia films deposited by pulsed laser ablation without oxygen ion bombardment are oxygen deficient and show high basic absorption, that is oxygen ion bombardment is needed for the preparation of stoichiometric films with low basic absorption. Though such low absorbing hafnia films were already obtained with the low oxygen ion bombardment, films with high laser damage thresholds could only be prepared by using strong ion bombardment. Consequently, the influence of the oxygen ion bombardment of the growing films on absorption and laser damage thresholds should be attributed both to improvements of stoichiometry of the films and to the observed phase transformations.

Moreover, we observed that the absorption peaks are mainly related to the particulates originating from the pulsed laser ablation process. The number of particulates, like the number of absorption peaks, decreases with increasing laser power density, which might be explained by a reduced generation of such particulates or a more effective destruction immediately after their ejection in the laser plasma formed above the target surface. Hence, the increase of the laser damage threshold $D_0$ with increasing laser power density is associated with the decrease in the
number of particulates. The particulates should be oxygen deficient (since the whole target surface showed such deficiency after the first cycle of laser irradiation) and therefore relatively well absorbing. Oxygen ion bombardment does, in dependence of energy, intensity and duration of bombardment, at least partly compensate the oxygen deficiency and in this way lead to decreasing absorption peak heights. Hence, it reduces the influence of the absorption peaks on the laser damage thresholds. Since at low growth rates the compensation is more effective, \( D_0 \) is higher at low growth rates and otherwise constant parameters.

In summary, one can say that with respect to absorption and laser damage thresholds the use of high laser power densities but relatively low growth rates, which have to be controlled by the laser pulse repetition rate, combined with strong oxygen ion bombardment are of advantage for the preparation of both high- and low-refractive index hafnia films, where the growth rate must be sufficiently high for high-refractive index films according to Fig. 1.

3.2. Multilayers of one material

On the basis of the variation of the refractive indices of yttria and hafnia films prepared by oxygen ion beam assisted pulsed laser deposition with deposition parameters, multilayer systems of one material with alternating refractive indices were prepared and investigated. Since the difference between high- and low-refractive index films is relatively small, many sublayers are needed for highly reflecting multilayer systems.

In Fig. 3 the spectral dependencies of the reflectivity of two multilayer systems of yttria designed for 532 nm (Fig. 3a) and 1064 nm (Fig. 3b) wavelength are shown. Both systems consist of 41 sublayers of 133 nm and, respectively, 266 nm optical thickness. The high-refractive index sublayers were deposited with low oxygen ion bombardment using 150 eV ion energy and 50 \( \mu A/cm^2 \) ion current density and, simultaneously, at a relatively high growth rate of 45 nm/min, whereas the low-refractive index sublayers were deposited with strong oxygen ion bombardment using 700 eV ion energy and 400 \( \mu A/cm^2 \) ion current density and at a relatively low growth rate of 10 nm/min. The growth rate was altered by altering only the laser pulse repetition rate (using 150 Hz and 25 Hz) at constant laser power density of \( 7.5 \times 10^7 \) W/cm\(^2\). Additionally, the theoretical curves of these multilayer systems were calculated using the refractive indices measured on the corresponding single layers. As can be seen in Fig. 3, good agreement between the measured and calculated curves was obtained. Slight deviations should be due to small inaccuracies in thickness and refractive index of the sublayers. It should be noted that similar multilayers of yttria and hafnia were prepared using strong oxygen ion bombardment for the high-refractive index and the low-refractive index sublayers, where only the growth rate was altered accord-
ing to Fig. 1. All systems were prepared without interruptions between the individual sublayers.

The measurement of the laser damage thresholds of these highly reflecting multilayer systems succeeded, unfortunately, only for the 532 nm system \(D_0 = 12 \text{ J/cm}^2, D_1 = 58 \text{ J/cm}^2\). All yttria and hafnia systems designed for 1.06 μm wavelength showed too low mechanical stability, they flaked off the whole sample area due to the first laser shot of the laser damage measurement. We attribute this to the high intrinsic stresses of the films, which accumulate in such thick multilayer systems. Remarkably, the 532 nm multilayer systems consisting of 41 sublayers had relatively high laser damage thresholds, whereas 1.06 μm systems consisting of only 15 sublayers were easily destroyed, showing that the thicknesses of the sublayers play an important role, too. The film systems were never detached at the substrate–film-boundary, which indicates that the adherence between substrate and first sublayer is strong due to the ion bombardment prior to deposition. Hence, either the adherence between two sublayers is relatively weak or in the films itself, presumably in films with low packing density, are mechanically weak regions. We were, however, not able to clarify where the failures actually occur.

For microstructural investigations we prepared a multilayer system consisting of 11 alternately high- and low-refractive index sublayers of yttria on a silicon substrate. Both types of sublayer were deposited with strong oxygen ion bombardment using merely different repetition rates for the alteration of the growth rate and, with it, of the refractive index. While the first 6 sublayers were deposited without interruption, we made pauses of several minutes after the deposition of each of the remaining sublayers in order to see the influence of the interruption of the deposition process on the boundaries between the sublayers. Transmission electron micrographs of the cross-section of this multilayer system are shown in Fig. 4. The individual sublayers are well distinguishable. The high-refractive index sublayers are relatively dark in appearance, while the low-refractive index sublayers are richer in contrast and show a number of light regions. As can be seen, both types of sublayer are polycrystalline. Moreover, high refractive index films seem to grow in dense columns perpendicular to the substrate with relatively large crystallites and nearly no space between them, whereas the crystallites of low refractive index films are more randomly oriented and smaller with a number of voids between them. Though there exist distinct boundaries between the sublayers with sharp transition zones confirming our observations with the
in-situ ellipsometer that the refractive index changes abruptly in response to the altering ion beam parameters and/or growth rates [5], the crystallites sometimes grow into the next sublayer, both from high- to low- and from low- to high-refractive index sublayers.

At the substrate–film-boundary a layer of approximately 4 nm of oxidized silicon and an amorphous layer of approximately 3 nm thickness can be observed, after which the crystalline film formation only begins. These layers might be due to ion induced mixing of silicon with oxygen and yttria in the beginning of the deposition and might contribute to the above mentioned good adherence.

In consequence of the interruptions of the deposition process thin layers that are light in appearance have formed between the corresponding sublayers. This can be seen particularly clearly after the 7th and the 9th layer, that is at the transition from high- to low-refractive index films. Such thin layers ought to be avoided because the laser damage thresholds and the adherence will be deteriorated.

The results presented in this paper show that highly reflecting multilayer systems consisting of one material with different refractive indices can be prepared by ion assisted pulsed laser deposition, if the deposition parameters are varied during deposition. Thereby it is important that the deposition process itself does not essentially influence the properties of already deposited sublayers.

4. Conclusions

Oxide films with refractive indices and therefore packing densities as high as the corresponding bulk material can be prepared by excimer laser deposition. Those films deposited at low oxygen ion bombardment are amorphous, whereas strong oxygen ion bombardment results in crystalline films with bulk-like refractive indices provided the growth rate is high enough. Moreover, strong oxygen ion bombardment is necessary to improve the quality of oxide films with regard to absorption and laser damage thresholds. High laser power densities are needed to minimize the number of particulates and with it the number of absorption peaks inside the films, which, however, could not be eliminated completely.

At low growth rates controlled preferably by the pulse repetition rate strong oxygen ion bombardment leads to a strong decrease in the refractive index and the packing density of oxide films. This effect can be used for the preparation of multilayers with respect to refractive index consisting of only one material. Further work must be directed to the reduction of the intrinsic stress of the oxide films, which led to relatively low mechanical stability of the multilayer systems prepared so far.

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