Tunable optical properties of amorphous Tantala layers in a quantizing structure

THOMAS WILLEMSEN,1,2,* MARCO JUPÉ,2 LAURENT GALLAIS,3 © DOMINIC TETZLAFF,4 AND DETLEV RISTAU1,2

1Institute of Quantenoptics Quest, Leibniz Universität, 30167 Hanover, Germany
2Laser Zentrum Hannover e.V., Hollerithallee 8, 30419 Hanover, Germany
3Aix Marseille Univ, CNRS, Centrale Marseille, Institut Fresnel, Marseille, France
4Institute of Electronic Materials and Devices, Leibniz Universität, 30167 Hanover, Germany
*Corresponding author: t.willemsen@lzh.de

Received 17 August 2017; revised 27 September 2017; accepted 3 October 2017; posted 3 October 2017 (Doc. ID 304631); published 30 October 2017

Plasma deposition techniques like ion-beam-sputtering (IBS) are state of the art to manufacture high quality optical components for laser applications. Besides the well optimized process and monitoring systems, the coating material selection is integral to achieve optimum optical performances. Applying the IBS technology, an approach is presented to create novel materials by the direct application of binary oxides in a quantizing structure. By reducing the physical thickness of the high refractive index material to a few nm, within a classical high-low index stack, the electronic confinement can be changed. Optical characterizations of the manufactured samples with decreasing quantum well thicknesses result in an increasing blue shift of the absorption gap and offer a method to approximate the effective mass of the high refractive index material in conjunction with theoretical models. Laser-induced damage threshold tests of coating samples prepared with different well thicknesses indicate an increase of the measured threshold values with optical gap energy. © 2017 Optical Society of America

OCIS codes: (310.0310) Thin films; (310.3840) Materials and process characterization; (310.6860) Thin films, optical properties.

https://doi.org/10.1364/OL.42.004502

During the last years, industrial and fundamental research applications imposed increasing demands on optical coatings to fulfill the new technological challenges of high end lasers. In terms of losses, defect distributions, and laser-induced damage thresholds, plasma deposition techniques like ion-beam-sputtering (IBS) are well approved to deposit complex optical components. In combination with the best suited broad band monitoring systems and in situ re-optimization tools, challenging designs with the necessary layer accuracy to a few atomic mono layers can be manufactured [1–3]. This accuracy requires detailed knowledge of optical and electronic properties of the sputtered material to achieve the best optical performances. In general, only a limited spectrum of well characterized coating binary materials is applied for high quality optics production. In this context, the ion-beam-co-sputter technique can enable alternative prospects for optical designs [4]. In particular, dielectric ternary composite layers with improved electrical and optical properties can be deposited to increase the laser-induced damage threshold (LIDT) of optical components [5,6]. In semiconductor materials, a different concept has been successfully applied. If the thickness (quantum well) of the crystalline material is small enough, in the range of a few nm, then the electronic states are changed [7,8]. This well-established principle is mainly applied for the fabrication of diode lasers [9]. Amorphous structures lack a microscopic periodic long range order and have no well-defined band gaps in the solid, in contrast to crystalline materials. However, a defined optical gap between the ground and excited state imposes a necessary condition for the creation of a well structure. In a previous study of amorphous layer structures, so-called nanolaminates were investigated, indicating a shift of the optical gap for Hafnia embedded in silica [10]. Nevertheless a detailed study of the samples to exclude a blue shift because of increased silica content and a microscopic analysis of the layer structures could not be performed.

This Letter reports on the manufacturing and characterization of dielectric quantized amorphous Tantala nanolaminates applying IBS technology. A method is presented to tune the electronic confinement parameters correlated to theoretical models. The geometric layer structures of the nanolaminates are analyzed by transmission electron microscopy (TEM), as well as the influence of different total contents of the high refractive index material with respect to the change of the optical gaps. Resulting LIDT values are measured in a 10,000 to 1 procedure at a center wavelength of 800 nm.

The description of the quantization of the introduced dielectric nanolaminates requires consideration of energetic states of the quasi free electrons in the conduction band, as well as the corresponding hole in the valence band (compare depicted principle in Fig. 1). The reduction of the thickness leads to the generation of new states for both the electrons and holes, which are related by the quantum well thickness \( L_{\text{well}} \). The high refractive index material H with a lower optical gap (quantum well) changes the carrier confinement, while the low refractive
The range of (0.01 stated in units of the rest mass of an electron, and it is usually in direct proportion to the eigenvalues \(E\) energy values

\[ \text{effective mass} = m_e \]

whereby \(x\) defines the position, and \(\sigma\) and \(\gamma\) are the presented parameters of Eqs. (1) and (2), respectively. The tunneling into the barriers broadens the quantum well \(L_{\text{well}}\) by \(L_{\text{eff}} = L_{\text{well}} + \frac{2}{\gamma}\).

All presented dielectric nanolaminates are manufactured by applying an IBS process. Because the process parameters are very reproducible, layers smaller than 2 nm are produced by varying the time. Thicker layers are controlled with an optimized broadband optical monitoring system (BBM) [1]. Samples are characterized applying high resolution spectrometric transmittance and reflectance measurements (PerkinElmer —Lambda1050) close to the normal angle of incidence (AOI). On the basis of the obtained absorption coefficient \(\alpha(\omega)\), a Tauc approximation is applied to determine the optical gap. In detail, by plotting the square root of the product of the absorption coefficient \(\alpha(\omega)\) and the frequency of light \(\omega\) versus the photon energy, the optical gap is defined as the intersection point with the photon energy at an absorption coefficient of zero [12]. Additionally, the layer structures of nanolaminates are analyzed by applying TEM (Tecnai G2 F20 TMP). Mass-thickness contrast in brightfield TEM imaging is applied to analyze the thickness of the layer. For further investigations, the samples are tested with respect to their LIDT according to ISO 21254 [13]. Under an AOI of 6°, the samples are irradiated at p-polarized laser pulses, characterized by a central wavelength of \(\lambda_e = 775\ nm\), with a pulse duration of \(\tau_p = 130\ fs\), a repetition rate of 1 kHz, and an effective beam diameter of \(d_{\text{beam}} = 97\ \mu m\). The LIDT value at the threshold of 0% is depicted after the sample is irradiated by 10,000 pulses.

Table 1 summarizes the properties of manufactured nanolaminates. Five different Tantala and silica stacks (\(LH^4\))L are manufactured by varying the layer thickness of the high refractive index material down to 0.5 nm and keeping the thickness of the low refractive index barriers with 20 nm, as well as the total design thickness of the samples with (382 ± 10) nm constant in every sample. The thickness is selected to about 3 QWOT at \(\lambda_e = 800\ nm\) to ensure a precise calculation of the refractive indices (±1%) by applying Sellmeier formalism. The nanolaminate sequences can be considered as single layers. Coating stacks containing nanolaminate wells that are 8-nm thick causes optical gap values comparable to single high refractive index materials of Tantala of 4.30 eV [14]. A clear change in the optical gap is obvious for manufactured samples with index quantum wells smaller than 4 nm. For instance, a blue shift of the optical gap up to 123% is observed for 0.5-nm \(Ta_5O_2\) wells with respect to single \(Ta_5O_3\) films. These shifts indicate a change in the electron confinement for Tantala layers smaller than 4 nm (insets in Fig. 2). A maximum change of the index of refraction \(\Delta n_{\text{ref}} = 0.18\) is reached with respect to a varying optical gap.

**Table 1. Properties of Manufactured Nanolaminates**

<table>
<thead>
<tr>
<th>Well</th>
<th>Design</th>
<th>Optical Gap [eV]</th>
<th>Refractive Index at 800 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>(LH)(^4)L</td>
<td>4.31 ± 0.05</td>
<td>1.65</td>
</tr>
<tr>
<td>4</td>
<td>(LH)(^4)L</td>
<td>4.35 ± 0.05</td>
<td>1.57</td>
</tr>
<tr>
<td>2</td>
<td>(LH)(^6)L</td>
<td>4.50 ± 0.05</td>
<td>1.52</td>
</tr>
<tr>
<td>1</td>
<td>(LH)(^7)L</td>
<td>4.65 ± 0.05</td>
<td>1.49</td>
</tr>
<tr>
<td>0.5</td>
<td>(LH)(^8)L</td>
<td>5.30 ± 0.05</td>
<td>1.47</td>
</tr>
</tbody>
</table>

*Each well thickness measurement was performed with Tantala, respectively. Every barrier of \(L = SiO_2\) remained constant at 20 nm.
validate the electronic quantization in amorphous
Transmittances of the nanolaminates are shown in the insets.
SiO$_2$ higher and is kept constant in the calculations. The barrier of
the electron holes is expected to be one order of magnitude
With respect to the effective electron mass, the effective mass
and the effective mass of the electrons. In a simplified model,
[Eq. (1)], depending on the length $L_{\text{well}}$ of the quantum well
and the effective mass of the electrons. In a simplified model,
the effective mass is inversely proportional to the optical gap.

![Fig. 2](image2.png)

**Fig. 2.** Determined optical gap values are correlated to calculations applying different effective masses $m^*$ as fit parameters. Transmittances of the nanolaminates are shown in the insets.

The increase of the optical gap of the high refractive index material is calculated by applying Schrödinger formalism [Eq. (1)], depending on the length $L_{\text{well}}$ of the quantum well and the effective mass of the electrons. In a simplified model, the effective mass is inversely proportional to the optical gap. With respect to the effective electron mass, the effective mass of the electron holes is expected to be one order of magnitude higher and is kept constant in the calculations. The barrier of SiO$_2$ is set to 7.5 eV [15]. A good correlation between the predicted and determined optical gap values of the manufactured samples is reached. The effective electron mass of Tantala can be approximated in between (0.7–0.9) $m_e$ (Fig. 2).

In the following, three main conditions are considered to validate the electronic quantization in amorphous Ta$_2$O$_5$-SiO$_2$ nanolaminates. First, a blue shift caused by higher silica content has to be excluded. The total thickness of the presented samples in Table 1 is kept constant, while the content of silica is increased for shorter quantum wells, in correlation with varying Tantala content. Three additional nanolaminates with an absolute constant thickness of (33 ± 1) nm of Tantala are compared (Fig. 3). The barrier layers are selected to reach a constant total physical design thickness $d_{\text{phy}} = (377 ± 5)$ nm. The blue shift is similar to a decreasing quantum well thickness of Tantala, with respect to the samples presented in Fig. 3.

Second, the electrons tunnel into the barriers approximating an exponential decay and broaden the wells by $L_{\text{eff}}$ according to Eq. (3). For the following study, an effective electron mass of 0.8$m_f$, a well thickness of $L_{\text{well}} = 1$ nm, and a barrier limit of $E_0 = 7.5$ eV were assumed. This results in an effective well of $L_{\text{eff}} \approx 1.16$ nm. The electron confinement is expected to stay constant by lowering the barriers above the calculated effective well. Four additional samples are compared and characterized. The barriers are lowered from 20 nm down to 1 nm, while the wells are kept constant with 1 nm (Table 2). The total design thickness is kept constant for samples with barriers of 20, 10, and 5 nm. As a crosscheck, the absolute content of 34-nm Ta$_2$O$_5$ is equal for the sample applying 1 nm and 10 nm barriers. The optical gap remains constant according to the theoretical predictions. The index of refraction could be improved by $\Delta n_{\text{eff}} = 0.3$ for decreasing silica content with respect to the 20 nm and 1 nm barriers. The tunable index of refraction in combination with a constant optical gap depicts a major advantage compared to ternary composites. The composition ratio of the sputtered materials determines both the index of refraction and the optical gap [14].

The third condition requires a strict amorphous layer structure with steep interfaces. The possible formation of ternary composites at the barriers and wells must be prevented. A classical high-low stack of Ta$_2$O$_5$ and SiO$_2$ was manufactured with various sequences of nanolaminates and then prepared for TEM inspection (Fig. 4). The thicknesses determined by TEM of the Ta$_2$O$_5$ and SiO$_2$ layers was (1.3 ± 0.5) nm and (20 ± 0.5) nm, respectively, and matched the designed layer dimensions. A clear Ta$_2$O$_5$ layer structure is visible, indicating the good quality of the interfaces.

![Table 2](image1.png)

**Table 2.** Variation of Barriers with Constant Wells of 1 nm

<table>
<thead>
<tr>
<th>Barrier [nm]</th>
<th>Design</th>
<th>Optical Gap [eV] for H = Ta$_2$O$_5$ Refractive Index at 800 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>(LH)$^{17}$L</td>
<td>4.65 ± 0.05</td>
</tr>
<tr>
<td>10</td>
<td>(LH)$^{14}$L</td>
<td>4.62 ± 0.05</td>
</tr>
<tr>
<td>5</td>
<td>(LH)$^{10}$L</td>
<td>4.60 ± 0.05</td>
</tr>
<tr>
<td>1</td>
<td>(LH)$^{6}$L</td>
<td>4.67 ± 0.05</td>
</tr>
</tbody>
</table>

![Fig. 3](image3.png)

**Fig. 3.** Transmittance measurement of different samples with a constant thickness of Tantala. Silica is used as low refractive index material. $d_{\text{phy}}$ depicts the total physical design thickness.

![Fig. 4](image4.png)

**Fig. 4.** Brightfield TEM cross-section image of a dielectric nanolaminate showing the alternating layer structure of Ta$_2$O$_5$ (bright contrast areas) and SiO$_2$ (dark contrast areas).
A promising application can result in the implied change of the electron confinement in dielectric nanolaminates. The power compatibility of optical components can be increased by substituting high refractive index layers affected by high field intensities with a certain stack of nanolaminates, comparable to refractive index steps down (RISED) concept applied for ternary composites [16]. In the following, 10,000 LIDT tests for the nanolaminate samples (Table 1) were performed and compared to a single Tantala layer. The LIDT values were decoupled from the possible different intensity distributions $|E|^2$ in the films and normalized to the maximum LIDT value and summarized as relative LIDT (Fig. 5). A clear increase of the damage threshold can be observed for shorter well thicknesses, corresponding to higher optical gaps. A similar increase of the threshold fluence results with respect to ternary composites [6,14,17–19]. In future studies, nanolaminate structures will be implemented in designs for complex optical components required for ultra-short pulse applications to improve the LIDT in the fs regime. A detailed comparison between ternary composites and nanolaminates has to be included with respect to the evolution of the optical gap and index of refraction as well as the LIDT. In practical applications, nanolaminates offer the possibility to tune the optical gap without applying a complex zone target system in the coating machine. Empirical studies in the fs regime indicate that plenty of interlayers are not influencing the LIDT for high quality coating processes [4]. In ternary composites, the index of refraction and optical gap are determined by the selected composition of the sputtered target materials, which depends on the position of the zone target assembly, especially the deposition of complex optics, like chirped mirrors, which require several switches of the zone target. Small positioning errors for ternary composites have huge impacts on the sensitive target parameters of the group delay dispersion.

In conclusion, a novel approach is presented to generate amorphous dielectric materials with adjustable optical properties required for the precise production of high quality optical components. Binary layer structures are created by embedding a high refractive index material (quantum well) in a matrix of a low refractive index material (barrier). A quantization resulting in a new electric and optical confinement could be observed by selecting the thickness of the well material to be smaller than 4 nm. In good correlation with theoretical models, the quantized nanolaminates offer a method to determine the effective electron mass of the quantum well material itself. The observed increase of the LIDT of the manufactured Tantala samples illustrates the high potential of quantized nanolaminates in high power coatings.

**Funding.** Deutsche Forschungsgemeinschaft (DFG) (Cluster of Excellence 201 Quest); Volkswagen Foundation (Hymnos (ZN3061)).

**Acknowledgment.** The authors thank the LNQE for TEM.

**REFERENCES**