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INTERACTION OF LASER RADIATION WITH MATTER

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Laser damage behaviour of titania coatings

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***Abstract*. A model is proposed for the generation of defects responsible for laser damage in thin titania films during repetitive exposure to nanosecond near-IR laser pulses. The model relies on the hypothesis that there is charge transfer between two point defect centres differing in photoionisation cross section, one of which has an adsorptive nature. The model's predictions agree well with the experimentally determined accumulation curve and the temperature dependence of the damage threshold at low temperatures and clarify the role of protective coatings.**

Keywords: *optical coatings, titania, laser damage, water adsorption.*

1. Introduction

The laser damage threshold of thin dielectric coatings depends on a variety of factors, such as the coating material, coating process and specific process parameters [1 – 4]. This makes it difficult to systematise available experimental data and model the laser damage behaviour of thin optical coatings [5 – 8]. In addition to the common features of the damage process (e.g., its statistical nature and the dependence of the damage threshold on the film thickness and laser pulse duration), there are some distinctive features of optical damage in a number of coatings. For example, the laser damage thresholds of single-layer titania (TiO_2) [9, 10], zinc sulphide (ZnS) [11] and hafnia (HfO_2) [12] coatings depend on whether or not there are protective overlayers. Moreover, the damage threshold of single-layer titania coatings is temperature-dependent, and the damage process has a cumulative nature [13].

It is of interest to understand the origin of the above features in the laser damage behaviour of TiO_2 coatings. Zverev et al. tentatively attributed them to the effects of film nonstoichiometry [9, 13] and gaseous environment [14]. Their assumptions were supported by later results [15 – 17], but the mechanisms underlying these effects have not yet been systematically analysed.

The objectives of this work are to model the generation of defects responsible for the damage in thin titania coatings during repetitive exposure to nanosecond near-IR laser pulses and to interpret the salient features of the process in terms of the modelling results.

The problem is approached using both earlier results and new experimental data on the structure and morphology of titania coatings. There is conclusive evidence that the laser damage threshold of thin films is structure-sensitive [2, 6, 15]. Therefore, knowledge of the film structure and morphology is critical for at least two reasons: it enables an adequate comparison of damage thresholds reported by different researchers and provides further insight into the nature of the defects responsible for laser damage in coatings.

In this study, titania films, some coated with silica, were deposited on fused quartz substrates by electron-beam evaporation. The source material for titania film growth had the form of TiO_2 tablets. The films were ~ 100 nm in thickness and were grown at an oxygen partial pressure $p_{O_2} = 1.5 \times 10^{-4}$ mbar, deposition rate of 0.45 nm s^{-1} and substrate temperature of 150 °C [10].

2. Overview of experimental data

2.1 Laser damage behaviour of titania coatings

The key features of the laser damage process in titania coatings are well known from earlier reports.

First, the process has a well-defined cumulative nature [10, 13]: when a given region is exposed to multiple nanosecond laser pulses, the damage threshold is lower than the single-shot threshold (Fig. 1). Second, the damage threshold of titania coated with a half-wave silica (SiO_2) layer is about twice that of single-layer TiO_2 coatings [9, 10]. Third, the temperature variation of the damage threshold is reversible [13]. The temperature dependence of the laser damage threshold of thin titania coatings appears crucial for understanding the nature of the defects responsible for the damage process.

The damage threshold increases with temperature and at 400 – 450 °C it is a factor of 3 – 4 higher than that under ordinary conditions (Fig. 2). Moreover, the accumulation effect disappears at these temperatures, and a single shot may be sufficient to cause material failure. Further raising the temperature has no effect on the laser damage threshold of the material. Finally, special attention should be given to the fact that heat treatment in a dry atmosphere leads to an irreversible increase in the room-temperature laser damage threshold of TiO_2 coatings [14].

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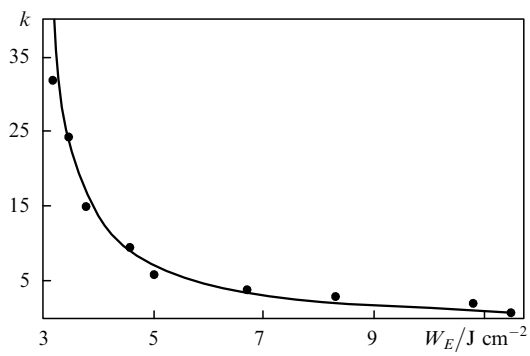

Figure 1. Accumulation curve: laser damage threshold, W_E, vs. the number of pulses, k. The solid circles represent experimental data [13] and the curve represents a theoretical fit to the data.

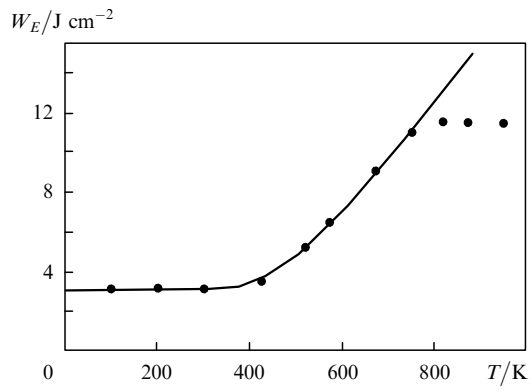

Figure 2. Laser damage threshold as a function of temperature for titania coatings. The solid circles represent experimental data [13] and the curve represents a theoretical fit to the data.

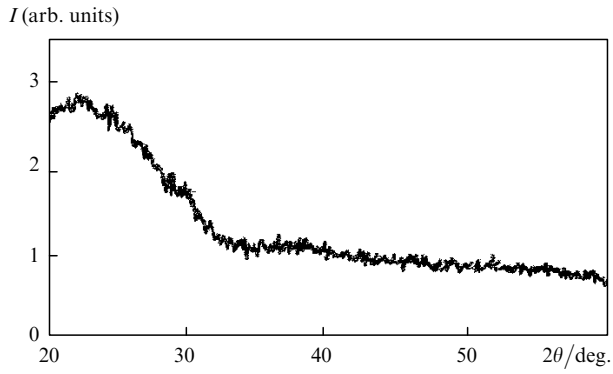

Figure 3. Typical X-ray diffraction pattern of titania coatings; θ is the diffraction angle.

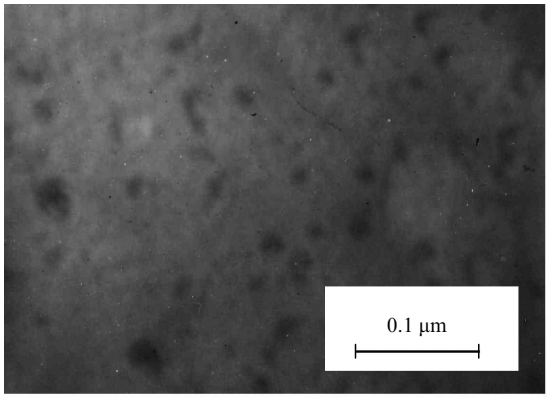

Figure 4. Transmission electron microscopic micrograph illustrating the surface morphology of a titania film.

2.2 Effect of water vapour on the properties of optical coatings

Thin layers produced by thermal or electron-beam evaporation typically have a columnar microstructure with many voids and micropores [1, 17, 18]. Porosity increases water vapour absorption when a film is transferred from vacuum to an ambient atmosphere [1, 17]. Water molecules both physi- and chemisorb at active sites on pore walls. The dissociation of the chemisorbed water leads to hydroxylation of the film surface [17]. An important point is that the physisorbed water is released at temperatures from 70 to 150 °C, whereas the chemisorbed water desorbs from the film surface between 190 and 250 °C [17]. Hydroxyls are the most tightly bound to the surface. At temperatures above 500 °C, the surface becomes hydrophobic [19].

The effect of water vapour on the optical [16, 17, 20] and mechanical [1, 16, 21] properties of thin films has been analysed in many studies. The laser damage threshold of ZnS [11], TiO_2 [9, 10, 14] and HfO_2 [12, 22, 23] films in the near-IR spectral region depends on whether such films are exposed to the ambient atmosphere or sandwiched between other layers in multilayer mirrors. The reduced laser damage threshold of the mirror in the former instance was attributed to the effect of water vapour, highlighting the important role of protective layers. As emphasised in a number of reports [1, 16, 23], the influence of water vapour on the properties of thin films depends to a significant degree on their structure and morphology.

The titania films grown in this study are amorphous (Fig. 3) and have a characteristic surface morphology (Fig. 4) with a large amount of pores, which facilitate water penetration into the coating material. The estimated packing density of the coatings is $p = 0.8$ [24].

3. A model for the generation of defects responsible for laser damage in thin coatings

3.1 Hypothesis that laser-absorbing defects have an adsorptive nature

The nature of the defects responsible for laser damage in transparent dielectric materials is a key issue in both the theoretical interpretation of laser damage and practical applications. The above experimental data suggest that the defects responsible for laser damage in TiO_2 coatings depend on the ambient atmosphere.

Characteristically, thin titania coatings contain considerable concentrations of nonstoichiometry-related native defects. The most important of them are oxygen vacancies (Ti^{III} ions) and titanium interstitials (Ti^{IV}_{irreg}), which are thought to act as electron traps [25–27]. In addition to the native defects, the properties of TiO_2 films are influenced by extrinsic defects, e.g. by those originating from adsorption [28]. The main adsorbates on titania are water and oxygen molecules and hydroxyls bonded to titanium ions [25–27]. Among the various processes that take place in the bulk and on the surface of titania, those considered below are basic to the effect under consideration. They involve the interaction

of the above-mentioned point defects and adsorbed species with near-IR radiation and conduction-band or trapped electrons [25–27]:

carrier excitation to the conduction band (donor photoionisation),

$$\mathrm{Ti}^{\mathrm{III}} + h\nu \rightarrow \mathrm{e}_{\mathrm{cb}}^{-} + \mathrm{Ti}^{\mathrm{IV}}, \tag{1}$$

electron capture at shallow ($E_{\mathrm{d}} \sim k_{\mathrm{B}}T$) surface traps,

$$\mathrm{Ti}^{\mathrm{IV}}\mathrm{OH} + \mathrm{e}_{\mathrm{cb}}^{-} \leftrightarrow \mathrm{Ti}^{\mathrm{III}}\mathrm{OH}, \tag{2}$$

electron capture at deep ($E_{\mathrm{d}} \gg k_{\mathrm{B}}T$) traps in the bulk and on the surface,

$$\mathrm{Ti}^{\mathrm{IV}} + \mathrm{e}_{\mathrm{cb}}^{-} \rightarrow \mathrm{Ti}^{\mathrm{III}}, \tag{3}$$

and photoionisation of surface traps,

$$\mathrm{Ti}^{\mathrm{III}}\mathrm{OH} + h\nu \rightarrow \mathrm{Ti}^{\mathrm{IV}}\mathrm{OH} + \mathrm{e}_{\mathrm{cb}}^{-} + \text{heat}. \tag{4}$$

Here, $\mathrm{Ti}^{\mathrm{IV}}\mathrm{OH}$ denotes a primarily hydrated titania surface; $\mathrm{Ti}^{\mathrm{III}}\mathrm{OH}$ is a hydroxyl bound to lattice $\mathrm{Ti}^{\mathrm{III}}$ ions; e_{cb}^{-} is a conduction band electron; T is the temperature; E_{d} is the depth of the energy level related to a particular defect species; and k_{B} is the Boltzmann constant.

The above suggests that the generation of defects responsible for laser damage in TiO_2 coatings involves several steps. In the first step, a defect associated with an oxygen vacancy absorbs a photon, which promotes an electron from the defect centre to the conduction band of the material, as represented by (1). In the second step, during the electron lifetime in the conduction band the electron displaces a distance $L \approx \sqrt{D\tau_{\mathrm{cb}}} \approx 10^{-5}$ nm, comparable to the film thickness ($D \approx 0.01$ cm^2 s^{-1} [29] and $\tau_{\mathrm{cb}} \approx 10^{-9}$ s [27] are the electron diffusion coefficient and lifetime in the conduction band). Some of the electrons arriving at the surface may be trapped, producing shallow ($E_{\mathrm{d}} \sim k_{\mathrm{B}}T$) levels in the band gap of the material, as represented by (2). The generation of surface defects [process (2)], which possess a larger absorption cross section in comparison with oxygen vacancies, and their subsequent photoionisation by process (4) give rise to an accumulation effect and reduce the laser damage threshold. The thermal activation processes in (2) lead to dynamic electron exchange between the shallow surface traps and the conduction band.

In the proposed model, an absorbing inclusion is treated as a point defect aggregate. The inclusion can be thought of as a heavily doped semiconductor containing two defect species: Ti^{3+} ions and hydroxyls bonded to Ti^{4+}. The formation of adsorption-related defects in the coating material is favoured by its amorphous structure and porosity. Note that nonstoichiometry-related point defects in thin films were regarded as absorbing centres in a number of studies [6, 5, 30].

3.2 Surface trap filling kinetics and accumulation curve

Consider a sample exposed to repetitive rectangular laser pulses of duration τ and intensity I, with pulse separation δ. We take $\tau_{\mathrm{tr}} \ll \tau_{\mathrm{rec}} \ll \tau \ll \delta$, where τ_{tr} is the trapping time of conduction band electrons and τ_{rec} is the photoexcited carrier recombination time ($\tau_{\mathrm{rec}} \sim 1$ ns, $\tau_{\mathrm{tr}} \sim 0.1$ ns [27]).

Rate equations that take into account two defect species differing in photoionisation cross sections (Fig. 5) must be written for two distinct time periods: during a laser pulse and between two consecutive pulses.

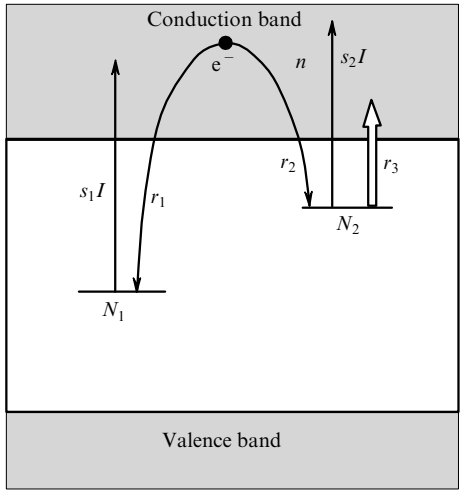

Figure 5. Electronic transitions in the model under consideration.

During a pulse, we have

$$\frac{\mathrm{d}n}{\mathrm{d}t} = s_1N_1I + s_2N_2I - r_1n - r_2n + r_3N_2, \tag{5}$$

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = r_2n - r_3N - s_2N_2I, \tag{6}$$

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = r_1N_1 - s_1N_1I, \tag{7}$$

$$n + N_1 + N_2 = N_0, \tag{8}$$

where n is the conduction band electron concentration; N_0 is the initial donor concentration; N_1 is the concentration of donors at time t; N_2 is the concentration of $\mathrm{Ti}^{\mathrm{III}}\mathrm{OH}$ surface states (2) at time t; s_1 and s_2 are the photoionisation cross sections of the defects species (1) and (4); r_1 is the probability of $\mathrm{Ti}^{\mathrm{III}}$ donor (3) formation; r_2 is the probability of surface defect (2) generation; $r_3 = C\exp[-\Delta \times (k_{\mathrm{B}}T)^{-1}]$ is the probability of the thermal ionisation energy of a $\mathrm{Ti}^{\mathrm{III}}\mathrm{OH}$ surface defect; and Δ is its ionisation energy. In what follows, we assume the number density of hydroxyls bound to the titania lattice to be constant and the absorption cross section in (4) to exceed that in (1).

At the beginning of the kth pulse, i.e., at time $t_{0\tau}^{(k)} = (k-1)(\tau+\delta)$, the conduction band electron concentration is $n_{\tau}^{(k)} = 0$ and the concentration of unionised surface states is $N_{2\tau}^{(k)} = N_{2\delta}^{(k-1)}$, i.e., the same as at the end of the $(k-1)$th interval between pulses.

Between pulses, we have

$$\frac{\mathrm{d}n'}{\mathrm{d}t} = -r_1n' - r_2n' + r_3N_2{}', \tag{9}$$

$$\frac{\mathrm{d}N_2'}{\mathrm{d}t} = r_2n' - r_3N_2', \tag{10}$$

$$\frac{dN_1'}{dt} = n'r_2, \tag{11}$$

$$n' + N_1' + N_2' = N_0'. \tag{12}$$

At the beginning of the kth interval (at the end of the kth pulse), i.e., at time $t_{0\delta}^{(k)} = k\tau + (k-1)\delta$, the concentration of unionised surface states and the conduction band carrier concentration are $N_{2\delta}'^{(k)} = N_{2\tau}^{(k)}$ and $n_\delta'^{(k)} = n_\tau^{(k)}$, where $N_{2\tau}^{(k)}$ and $n_\tau^{(k)}$ are, respectively, the concentration of unionised donors and the conduction band carrier concentration at the end of the kth pulse.

Consider first the system at low temperatures, where the thermal ionisation of surface defects ($E_d \gg k_B T$) can be neglected. The systems of Eqns (5)–(8) and (9)–(12) can be solved readily under the assumption that $n \ll N_1$, N_2 and $dn/dt \approx 0$. This implies that the electrons involved are most of the time in the ground state at local levels in the band gap of the material and the increase in conduction band electron concentration is negligible. Joining the solutions for $N_2(t)$ and $N_2'(t)$ at time $t = k\tau + (k-1)\delta$, we find the concentration of unionised shallow surface states at the end of the kth pulse:

$$N_2^{(k)} = N_0 \frac{s_1 r_2}{s_1 r_2 + s_2 r_1}\left[1 - \exp\left(-k\frac{s_1 r_2 + s_2 r_1}{r_1 + r_2} I^{(k)}\tau\right)\right]. \tag{13}$$

It is easily seen that for $k \to \infty$ the concentration of unionised surface states increases, approaching

$$N_2^{\max} = N_0 \frac{s_1 r_2}{s_1 r_2 + s_2 r_1}. \tag{14}$$

Let $I^{\text{cum}}(W_E^{\text{cum}})$ be the threshold incident intensity (fluence) for laser damage at a number of pulses $k \to \infty$. Then, for an arbitrary number of pulses, k, we have the relation stemming from the constraint of a constant absorbed energy density needed for irreversible damage development at a given pulse duration:

$$I^{(k)} N_2^{(k)} = I^{\text{cum}} N_2^{\max} = \text{const}, \tag{15}$$

where $I^{(k)}$ is the incident intensity at which damage occurs during the kth pulse.

Substituting (13) and (14) into (15), we obtain an implicit relation between the number of pulses, k, that cause the sample to fail and the incident intensity, $I^{(k)}$ (so-called accumulation curve):

$$I^{\text{cum}} = I^{(k)}\left[1 - \exp\left(-k\frac{s_1 r_2 + s_2 r_1}{r_1 + r_2} I^{(k)}\tau\right)\right]. \tag{16}$$

The accumulation curve can also be represented in the form

$$\frac{I^{(k)}}{I^{(m)}} = \frac{m}{k}\frac{\ln(1 - I^{\text{cum}}/I^{(k)})}{\ln(1 - I^{\text{cum}}/I^{(m)})}, \tag{17}$$

where $m, k \neq \infty$; $I^{(m)}$ is the incident intensity at which damage occurs during the mth pulse. In Fig. 1, the solid circles represent the experimentally determined accumulation curve from Zverev et al. [13] and the solid line shows the best fit to Eqn (17). The experimental data are seen to be well represented by this equation.

3.3 Thermal ionisation of surface states and temperature dependence of the laser damage threshold

In a steady state ($dn/dt = 0$, $dN_1/dt = 0, dN_2/dt = 0$), because of the thermal excitation of electrons to the conduction band the maximum concentration of unionised surface states is

$$N_{2T}^{\max} = N_0 \times \frac{r_2 s_1 I^{\text{cum}}}{r_1 s_2 I^{\text{cum}} + r_2 s_1 I^{\text{cum}} + r_3 s_1 I^{\text{cum}} + s_1 s_2 I^{2\text{cum}} + r_1 r_3}. \tag{18}$$

Combined with (15), this relation can be represented in the form

$$I \equiv I^{\text{cum}} = c_1 + c_2 e^{-c_4/T} + [c_3 e^{-c_4/T} + (c_1 + c_2 e^{-c_4/T})^2]^{1/2}, \tag{19}$$

where c_1, c_2, c_3 and c_4 are positive constants.

It follows from (19) that the asymptotic damage thresholds have particular values:

$$I(T \to \infty) = (c_1 + c_2) + [c_3 + (c_1 + c_2)^2]^{1/2} > I\,(T \to 0) = 2c_1. \tag{20}$$

Thus, a qualitative analysis indicates that Eqn (19) is consistent with the experimentally determined temperature dependence of the damage threshold. The best-fit curve for the temperature-dependent laser damage threshold of TiO_2 films is presented in Fig. 2.

4. Discussion

According to the above model, the accumulation effect in titania films is the consequence of the specific population kinetics of surface states that have an adsorptive nature. The formation of such states is favoured by the porous structure of the coating. The temperature dependence of the laser damage threshold is worthy of special mention. As seen in Fig. 2, the experimental data are well represented by the best-fit curve at low temperatures (below the plateau). At the same time, at high temperatures the best fit to Eqn (19) significantly deviates from the data points. This may be due to the approximations used in describing the process under consideration, primarily to the assumption that the surface hydroxyl layer experiences no changes. Indeed, as mentioned above the chemisorbed water is removed at temperatures from 190 to 250 °C. Therefore, the hydroxyl surface coverage decreases at higher temperatures because hydroxyls result from the dissociation of chemisorbed water. Note that it is at these temperatures that the laser damage threshold of titania begins to rise. Above 450–500 °C, the surface becomes essentially hydrophobic [19]. It is in this temperature range that the laser damage threshold reaches a plateau and a single shot is sufficient to cause material failure. It is therefore reasonable to assume that the discrepancy between the experimental data and theoretical fit at high temperatures arises from the absence of hydroxyls on the titania surface above 450–500 °C. This assumption is supported by the report [14] that the room-temperature laser damage threshold of titania coatings with hydrophobic surfaces exceeds that of conventional samples.

The role of protective coatings can also be understood in terms of the above model: such coatings substantially reduce the degree of titania hydration because they prevent atmospheric moisture from penetrating into the film.

5. Conclusions

The model proposed in this work describes the generation of defects responsible for laser damage in thin titania films during repetitive exposure to nanosecond near-IR laser pulses. The model's concepts enable a unified approach to the interpretation of the salient features of laser damage in coatings, such as the accumulation effect, the variation of the laser damage threshold with temperature and the effect of protective coatings. The model relies on the hypothesis that there is charge transfer between two defect centres differing in photoionisation cross section, one of which has an adsorptive nature. The model's predictions agree well with the experimentally determined accumulation curve and the temperature dependence of the damage threshold at low temperatures and shed light on the role of protective coatings.

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