Laser Resistance of Ta_2O_5/SiO_2 and ZrO_2/SiO_2 Optical Coatings under 2 μm Femtosecond Pulsed Irradiation

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(Received 14 April 2010)

Ta_2O_5/SiO_2 and ZrO_2/SiO_2 high reflecting (HR) coatings are prepared by ion beam sputtering and electron beam evaporation, respectively. The laser-induced damage thresholds (LIDTs) of these samples are investigated with 2 μm femtosecond pulse lasers (80 fs, 1 kHz). It is found that the Ta_2O_5/SiO_2 HR coating has a higher capability of laser damage resistance than the ZrO_2/SiO_2 HR coating in the 2 μm femtosecond regime. The scanning electron microscope results show that the damage sites of the ZrO_2/SiO_2 HR coating have a relatively porous structure, the loose structure of coatings will provide more sites for water molecules, and the LIDTs of HR coatings will be reduced as a result of the strong water absorption at the wavelength of 2 μm.

PACS: 42. 79. Wc, 68. 65. Ac, 42. 65. Re DOI: 10.1088/0256-307X/27/7/074215

It is well known that 2 μm lasers are widely used in eye-safe lidar, medicine, spectroscopy, remote sensing, and generation of mid-IR light sources.[1,2] The high peak power in large 2 μm femtosecond laser systems is currently limited by the damage threshold of optics[3] in the ultrashort pulse lasers used for scientific and industrial applications. However, there have been few reports on the characteristics of femtosecond laser damage at the 2 μm wavelength. Understanding of the fundamental mechanism of laser-induced damage in coatings is crucial for constructing a higher power 2 μm laser system.

In this Letter, we study the laser-induced damage of Ta_2O_5/SiO_2 and ZrO_2/SiO_2 2 μm high reflecting (HR) coatings irradiated by a continuous train of 2 μm femtosecond laser pulses. The experimental results indicate that the LIDTs of the Ta_2O_5/SiO_2 HR coating deposited by ion beam sputtering (IBS) are higher than those of the ZrO_2/SiO_2 HR coating deposited by electron beam evaporation (EBE). By means of analyzing the influence factors, including material property, electric field distribution and water absorption, it is found that water absorption plays a major role in determining the laser damage resistance of HR coating under 2 μm femtosecond pulse irradiation. We propose that the reason for this is that the porosity structure existing in the coating prepared by EBE provides sites for hiding water molecules, and water molecules will strongly absorb the 2 μm laser energy.

The ZrO_2/SiO_2 2-μm HR coating was deposited by using EBE with the coating sequence S|(4H4L)^{15}4H|Air. The Ta_2O_5/SiO_2 2 μm HR coating was prepared by IBS with the coating sequence S|(4M4L)^{14}1.5M|Air. H, M and L stand for QWOT (quarter-wavelength optical thickness) $\lambda_0/4$ of ZrO_2, Ta_2O_5 and SiO_2, respectively, and S is infrared quartz glass substrate. The reference wavelength λ_0 for the two kinds of structures is 520 nm and 515 nm, respectively. The coating deposited by IBS is well known for its superior optical quality, damage resistance, and extremely densely packed and adhesive structure. Thus, the Ta_2O_5 coating exhibits bulk-like properties and the packing density can be considered as about 1.0.[4] In contrast, the coating produced by EBE grows with a columnar and porous microstructure making it moisture sensitive. The coating collecting moisture (e.g. when exposed to air) can cause a vacuum-to-air spectral shift and change the optical properties of the coating. The calculated packing density ρ of the ZrO_2 coating is 0.71, which is derived from the vacuum-to-air spectral shift by the method mentioned in Ref. [5]. From the measured vacuum-to-air spectrum of the ZrO_2 coating shown in Fig. 1, it is found that the amount of wavelength shift $\Delta\lambda$ is 31 nm, and the wavelength of maximum transmittance measured in air λ_{air} is 600 nm.

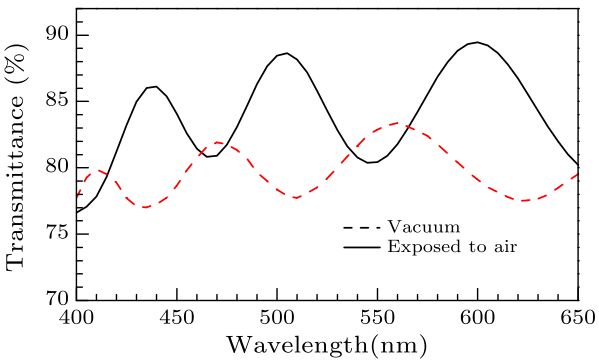

Fig. 1. Vacuum-to-air spectral shift of the ZrO_2 coating.

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Figure 2 gives the experimental setup for femtosecond laser-induced damage testing. The Ti:sapphire laser produced laser pulses of 40 fs at a wavelength of 800 nm at 1 kHz. Femtosecond laser pulsers with a central wavelength of 2 μm and pulse duration of 80 fs were generated by an optical parametric amplifier (OPA) pumped by a commercial Ti:sapphire laser system. The sample was set on a two-dimensional translation stage, and laser pulses were focused with a spherical lens of 150 mm focal length on the target plane. The focused beam measured by a CCD camera had a Gaussian spatial beam profile and the spot diameter was about 194 μm. The laser fluence was adjusted by using the absorbing filters as the attenuator. Damage testing was performed in the *s*-on-1 regime according to ISO-11254-2.[6] A constant number of 1000 laser pulses irradiated to the same site on the sample, ten sites of the sample were exposed at the same fluence and the average area of damage sites was measured by a Leica optical microscope. For the Gaussian beam, the LIDTs of the coating could be calculated by the relation between damage area and laser fluence,[7]

$$D^2 = 2\omega_0^2 \ln\left(\frac{F_0^{av}}{F_{th}}\right), \qquad (1)$$

where D is the damage crater diameter, ω_0 stands for the $1/e^2$ laser beam radius, and F_0^{av} represents the average laser fluence, F_{th} is the LIDTs of the samples. The LIDTs are determined from a plot of the square of the crater diameter versus the logarithm of the laser fluence, and calculated from linear extrapolation $D^2 \to 0$ of the data points depicted in the plot. The relative error of the LIDT determination amounts to ±10%, which is mainly due to the uncertainty in the spot size measurement and the overall energy measurement reproducibility. Figure 3 gives the relationship of the laser damage crater diameter with the laser fluence for Ta_2O_5/SiO_2 and ZrO_2/SiO_2 HR coatings. We can find that the LIDTs of the Ta_2O_5/SiO_2 HR coating deposited by IBS are about 0.679 J/cm^2, and those for the ZrO_2/SiO_2 coating deposited by EBE are about 0.459 J/cm^2.

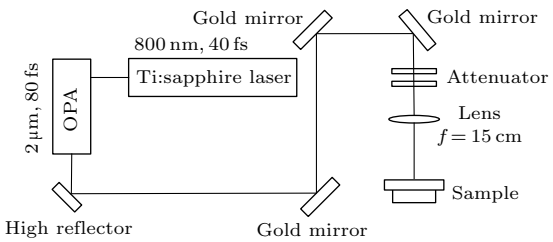

Fig. 2. Experimental setup of 2 μm femtosecond laser damage testing.

Figure 4 shows the damage morphologies of ZrO_2/SiO_2 and Ta_2O_5/SiO_2 HR coatings under the same laser fluence irradiation. It indicates that the main damage is confined to a small region at the peak of the Gaussian pulse distribution. The damage zone of HR coatings appears layered, which is explained in terms of a local intensity enhancement due to interference effects at the interface between high-low refractive index coating materials. In addition, the lateral extent of the damage crater of the Ta_2O_5/SiO_2 HR coating is smaller than that of the ZrO_2/SiO_2 HR coating. Detailed pictures of Fig. 4 are given in Fig. 5. It is found that the ZrO_2/SiO_2 HR coating deposited by EBE (Fig. 5(a)) has a relatively loose structure and lower packing density than the Ta_2O_5/SiO_2 HR coating deposited by IBS (Fig. 5(b)). The porous structure coating will hide many water molecules, which causes the strong water absorption for the 2 μm wavelength.

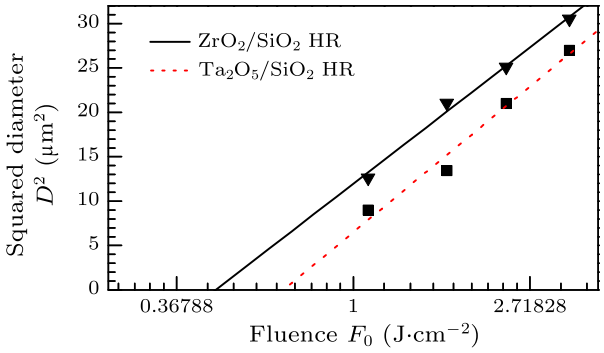

Fig. 3. The 2 μm laser damage area increases linearly with the laser fluence for Ta_2O_5/SiO_2 and ZrO_2/SiO_2 HR coatings.

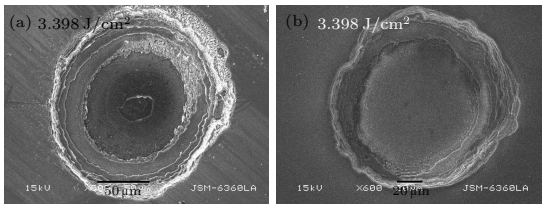

Fig. 4. Scanning electron microscope images of laser-induced damage sites on the HR coatings: (a) ZrO_2/SiO_2 coating; (b) Ta_2O_5/SiO_2 coating.

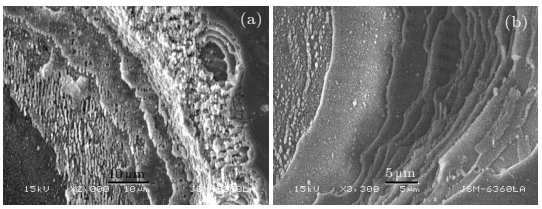

Fig. 5. Detailed view of the damage zone shown in Fig. 4.

The normalized electric field intensity distribution of the samples under the same laser irradiation is given in Fig. 6. It is found that both coatings are most likely to be damaged at the first interface between Ta_2O_5 (ZrO_2) and SiO_2. The band gaps of bulk materials Ta_2O_5, ZrO_2, and SiO_2 are 4.6 eV,[8] 5.0 eV,[8] and 7.8 eV,[9] respectively. With the excitation wavelength of 2 μm, Ta_2O_5 (ZrO_2) needs to absorb fewer photons

to excite electronics from the valence band to conduction band, so the damage would likely occur in the high-index Ta_2O_5 (ZrO_2) layer first. The ZrO_2 has a wider band gap than Ta_2O_5, so ZrO_2 needs to be excited by absorbing more photons. Additionally, Fig. 6 shows that the electric field amplitude of the first interface between ZrO_2 and SiO_2 is lower than that between Ta_2O_5 and SiO_2. The femtosecond LIDTs are closely related to intrinsic characteristics of materials, the large band gap of coating materials should have relatively higher LIDTs.[10,11] According to the discussion given above, the LIDTs of the Ta_2O_5/SiO_2 HR coating should be lower than those of the ZrO_2/SiO_2, which is not in agreement with our experimental results.

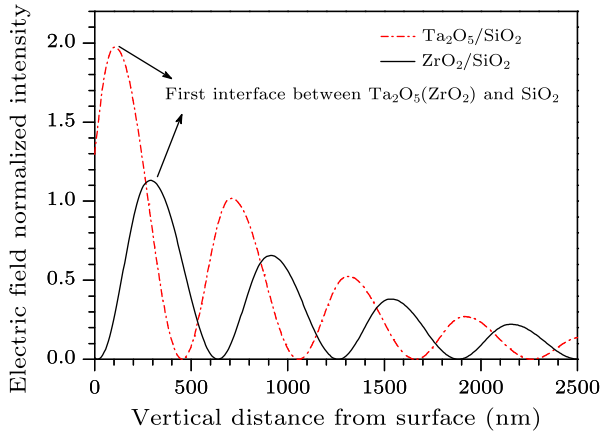

Fig. 6. Electric field intensity profile in Ta_2O_5/SiO_2 and ZrO_2/SiO_2 HR coatings normalized to the incident electric field value at the wavelength of 2 μm.

It is well known that for the stretching oscillations of O-H bindings, water has strong characteristic absorption for the 2 μm wavelength. The structure of the Ta_2O_5 coating (ρ∼1.0) produced by IBS is densely packed and adhesive, which reduces the sensitivity to moisture and results in little water absorption for the 2 μm wavelength. The ZrO_2 coating produced by EBE grows with a columnar and porous microstructure, which causes the spectral shift shown in Fig. 1. Macleod[12] considered that the columnar structure can take the form of pores running completely across the coating, and water can enter the pores more easily because of the serious capillary phenomenon. As a result, the shifts of characteristics in the multilayer coating occur due to the filling of water molecules. We have calculated the packing density ρ of the ZrO_2 coating produced by EBE is only ~ 0.71, which means that there is ~ 0.29 of water in the ZrO_2 coating. The extinction coefficient k ($\sim 10^{-3}$)[13] of water is much higher than that ($\sim 10^{-4}$)[8] of ZrO_2 and Ta_2O_5 materials at 2 μm wavelength, which causes the k value of the ZrO_2 coating to increase intensively.[14] This strong water absorption could seriously reduce the LIDTs of the ZrO_2/SiO_2 HR coating.

A rate equation shown in Ref. [15] has given the conduction band electron density for femtosecond laser irradiation. In the present work, $W_{\rm singpt}(I(t))$ is supplemented to describe the function of water absorption, and the improved rate equation can be used as follows:

$$\frac{\partial n_e(t)}{\partial t} = W_{\rm multpt}(I(t)) + W_{\rm impact}(I(t)) \cdot n_e(t) - W_{\rm rel}(n(t), t) + W_{\rm singpt}(I(t)), \quad (2)$$

where $n_e(t)$ is the electron density, $I(t)$ is the pulse intensity, and $W_{\rm multpt}(I(t))$ stands for the multiphoton ionization rate. According to the Keldysh theory, when the adiabatic parameter given by $\gamma = \omega\sqrt{m^* E_g}/eE$ is much larger than unity, which is in accordance with our experiment, $W_{\rm multpt}(I(t))$ can be calculated by

$$W_{\rm multpt} = \frac{2\omega}{9\pi}\left(\frac{m^*\omega}{\hbar}\right)^{\frac{3}{2}} \Phi\left(\sqrt{2\left\langle \frac{E_g'}{\hbar\omega}+1\right\rangle - 2\frac{E_g'}{\hbar\omega}}\right) \times \exp\left\{2\langle E_g'/\hbar\omega+1\rangle\left(1-\frac{1}{4\gamma^2}\right)\right\} \times \left(\frac{1}{16\gamma^2}\right)^{\langle E_g'/\hbar\omega+1\rangle}, \quad (3)$$

where $m^* = m_e m_h/(m_e + m_h)$ indicates the reduced mass of the electron and the hole, m_e and m_h are the effective conductivity masses of electrons and holes, respectively; ω denotes the incident laser frequency, E is the electric field amplitude of the radiation, $\langle E_g'/\hbar\omega + 1\rangle$ is the number of photons absorbed simultaneously, $E_g' = E_g[1 + (1/2\gamma^2)]$ represents the effective energy of band gap in the radiation field, E_g is the intrinsic band gap of the material, a pair of angular brackets means the integer part of the argument, and Φ describes the Dawson function given by $\Phi(z) = \exp(-z^2)\int_0^z \exp(y^2)dy$.

The impact ionization rate $W_{\rm impact}(I(t))$ is calculated by the Drude model,[16,17]

$$W_{\rm impact} = \frac{\sigma}{E_g} \cdot I(t), \quad (4)$$

where $\sigma = e^2\tau/c\varepsilon_0 n_0 m^*(1+\omega^2\tau^2)$ is the absorption cross section, $\tau = 16\pi\varepsilon_0^2\sqrt{m^*(0.1E_g)^3}/(\sqrt{2}e^4 n(t))$ is the resulting collision time which is reciprocal to the electron density, and n_0 denotes the refractive index of the material. Moreover, the Gaussian temporal pulse shape $I(t) = I_0\exp[-4\ln(2)(t/\tau_p)^2]$ is selected to describe the incident condition, in which I_0 and τ_p are the peak intensity and pulse width of the Gaussian beam, respectively. The plasma energy decay term $W_{\rm rel}(n(t))$ associated with the diffusion and recombination of electrons[18] is usually expressed by $W_{\rm rel}(n(t)) = n_e(t)/\tau_\gamma$, and τ_γ is the effective relaxation time of electrons and often applies ~ 100 fs for calculation.

$W_{\rm singpt}(I(t))$ can be considered as the single photon absorption rate caused by water molecules in the

coatings at the incident laser wavelength of 2 μm. Water molecules exist in the low-density ZrO_2/SiO_2 HR coating deposited by EBE; as a result, the low impurity level in the band gap of the coating material is produced by water molecules. Some of the electrons in the valence band are excited onto this impurity level by single photon absorption. Thus, these electrons occupying the impurity level are easier to excite to the conduction band. It is necessary to calculate the single photon absorption rate derived from Eq. (3). When the number of photons absorbed is one, which means $\langle E'_g/\hbar\omega+1\rangle$ is unity, the single photon absorption rate $W_{\rm singpt}(I(t))$ is approximately calculated by

$$W_{\rm singpt} = \frac{2\omega}{9\pi}\left(\frac{m^*\omega}{\hbar}\right)^{3/2}\Phi(2) \times \exp\left(2-\frac{1}{2\gamma^2}\right)\left(\frac{1}{16\gamma^2}\right). \quad (5)$$

In contrast, the single photon absorption rate $W_{\rm singpt}(I(t))$ of the Ta_2O_5/SiO_2 HR coating can be regarded as being approximately zero, because the structure of the coating deposited by IBS is high density. Moreover, the electron density of the ZrO_2/SiO_2 HR coating not considering water absorption is also calculated as a comparison.

Table 1. Parameters for Ta_2O_5 and ZrO_2 used in the theoretical calculation. The values for m^*, m_e, and m_h are obtained from Ref. [20], where m_0 is the free electron mass.

Material	E_g(eV)	n_0	$m_e = m_h(m_0)$	$m^*(m_0)$
Ta_2O_5	4.6	2.01	1.0	0.635
ZrO_2	5.0	1.89	1.0	0.635

The breakdown threshold is reached when the electron density in the conduction band reaches a critical electron density of $n_{cr}(\sim 1.7\times10^{20}\,{\rm cm}^{-3}$, for $\lambda\sim 2\,\mu{\rm m})$[16] considered generally as a damage criterion. The parameter values in Eqs. (2)–(5) are shown in Table 1. Figure 7 shows that the electron density of the ZrO_2/SiO_2 HR coating considering water absorption is larger than that of the Ta_2O_5/SiO_2 HR coating and the ZrO_2/SiO_2 HR coating without considering water absorption. This indicates that the ionization rate of the ZrO_2/SiO_2 HR coating produced by EBE is larger than that of the Ta_2O_5/SiO_2 HR coating produced by IBS, and the theoretical LIDTs of the $ZrO_2/SiO_2(0.459\,{\rm J/cm^2})$ HR coating are lower than that of the Ta_2O_5/SiO_2 $(0.679\,{\rm J/cm^2})$ HR coating. This law agrees with our experimental results. However, the energy level of water at the wavelength of 2 μm is so low that all excitation electrons cannot be converted to free electrons, that is, only some of the excitation electrons enter into the conduction band and convert to free electrons. Therefore, it is necessary to further analyze this conversion factor. Moreover, there are many other parameters in the calculation not to obtain the accurate value, especially for m^*, m_h and m_e. For example, the variation of m^* by a factor of 2.5 can vary the multi-photon ionization rate by 2 orders of magnitude.[19]

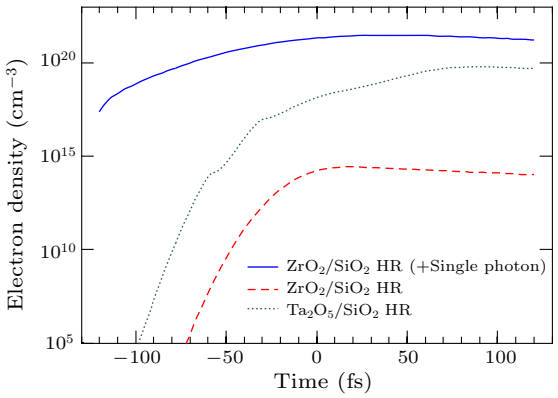

Fig. 7. Evolution of conduction-band electron density.

In summary, water absorption badly affects the laser damage resistance of the HR coating under 2 μm femtosecond laser irradiation. The coating deposited by EBE has a columnar and porous microstructure, and because of the capillary effect the porosity structure will provide more sites for water molecules. The existence of water molecules makes the coating material produce an impurity level; in this case, electrons are easier to excite to the conduction band, the ionization rate of the coating increases, and the coating material is easier to damage. Depositing optical coatings with higher density and reducing the water absorption is the next step of our work for the wavelength of 2 μm.

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