Comparison of laser-induced damage in Ta_2O_5 and Nb_2O_5 single-layer films and high reflectors

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Ta_2O_5 and Nb_2O_5 films are deposited on BK7 glass substrates using an electron beam evaporation method and are annealed at 673 K in the air. In this letter, comparative studies of the optical transmittance, microstructure, chemical composition, optical absorption, and laser-induced damage threshold (LIDT) of the two films are conducted. Findings indicate that the substoichiometric defect is very harmful to the laser damage resistance of Ta_2O_5 and Nb_2O_5 films. The decrease of absorption improves the LIDT in films deposited by the same material. However, although the absorption of the Ta_2O_5 single layer is less than that of the Nb_2O_5 single layer, the LIDT of the former is lower than that of the latter. High-reflective (HR) coatings have a higher LIDT than single layers due to the thermal dissipation of the SiO_2 layers and the decreased electric field intensity (EFI). In addition, the Nb_2O_5 HR coating achieves the highest LIDT at 25.6 J/cm^2 in both single layers and HR coatings.

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Ta_2O_5 and Nb_2O_5 have been widely investigated as possible candidates for corrosion barrier coatings, electrochromic films, gas sensors, and catalysts. In optical applications, Ta_2O_5 and Nb_2O_5 are used as wide transparent spectra and high-refractive (HR) index materials for optical waveguides, interference filters, anti-reflective coatings, and electroluminescent devices[1]. Ta_2O_5 and Nb_2O_5 films have especially been used as dielectric coatings in high-power laser applications. However, both films easily become substoichiometric, resulting in high absorption and low laser-induced damage threshold (LIDT). This disadvantage restricts their applications in high-power laser systems and makes them inferior to HfO_2, ZrO_2, and other materials[2]. With the improvement of post-annealing technology, the LIDT of Ta_2O_5 and Nb_2O_5 films can be increased, thus making them popular materials for study.

Despite the numerous studies conducted on laser-induced damage in films, comparing LIDT results remains difficult because test standards vary among different research teams[3,4]. Moreover, comparative studies about the LIDT of different materials are rare[5]. We believe a comparative study of Ta and Nb oxides will be useful in understanding the laser damage resistance of materials because both are the group V metals. Although simple studies have been conducted on these two materials, the effects of some important parameters such as absorption on the LIDT are not discussed[6]. Therefore, synthetic research about the properties of the two materials, including LIDT, will be meaningful and valuable. In this letter, we prepare Ta_2O_5 and Nb_2O_5 films including single-layer films (only Ta_2O_5 or Nb_2O_5) and HR coatings (Ta_2O_5/SiO_2 or Nb_2O_5/SiO_2). The films are deposited using the electron beam evaporation method, and are annealed in the air. Comparisons of the optical properties, microstructure, chemical composition, optical absorption, and LIDT are made between the two materials, as well as between single layers and HR coatings. The damage mechanisms are also discussed in detail.

All films were deposited on BK7 glass substrates by electron beam evaporation. The base pressure was 2×10^{-3} Pa, the oxygen partial pressure was 2×10^{-2} Pa, and the substrate temperature was kept at 573 K during the deposition. Both Ta_2O_5 and Nb_2O_5 single layers were deposited with an optical thickness of 6 quarter wavelength optical thickness (QWOT) at a wavelength of 550 nm. For the HR coatings, Ta_2O_5/Nb_2O_5 and SiO_2 were used as high and low refractive-index materials, respectively. The coating design of the HR structure was $(HL)^xH$, where H stands for the QWOT of Ta_2O_5/Nb_2O_5 and L stands for the QWOT of SiO_2 (the referent wavelength λ is 1064 nm). Annealing of the films was performed in the air at 673 K for 12 h.

Transmittance spectra of the films were measured using a Lambda 900 spectrophotometer. The measurement error was under 0.08%. Refractive indics and film thickness were obtained by Essential Macleod (a thin film design software). The structure of the films was analyzed using an X-ray diffractometer (XRD). The composition of the films was analyzed by X-ray photoelectron spectroscopy (XPS) using focused (300 μm in diameter) monochromatic Al-Kα ($h\nu$=1486.6 eV) radiation at a pass energy of 20 eV. Theoretical results of the electric field intensity (EFI) distributions of the films were calculated by a thin film design software (TFCalc). Optical absorption of the samples was measured by the surface thermal lensing (STL) method[7]. Damage testing was performed in the "1-on-1" regime according to ISO standard 11254-1, using a 1064-nm Q-switch pulsed laser at a pulse length of 12 ns[8]. The damage morphologies of the samples were observed using a Leica DMRXE

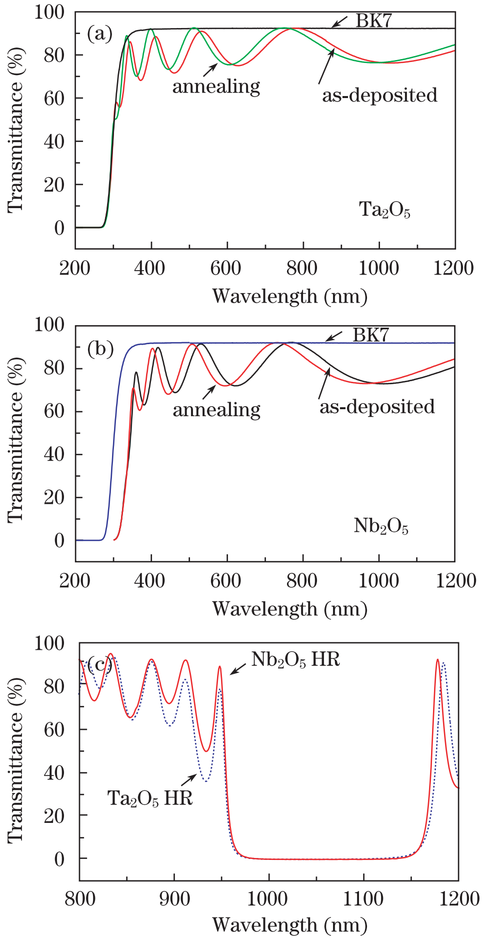

Fig. 1. Transmittance curves of (a) Ta_2O_5 single layer, (b) Nb_2O_5 single layer, and (c) HR coatings.

micropolariscope.

Figure 1 shows the transmittance curves of the Ta_2O_5 and Nb_2O_5 films. Figures 1(a) and (b) show that both the optical transmittances of the Ta_2O_5 and Nb_2O_5 single layers increase after annealing. The findings also indicate that the Ta_2O_5 single layer has better transmittance than the Nb_2O_5 single layer, especially in the short wavelength region. Figure 1(c) shows the optical transmittance of the HR coatings. The reflectances of the Ta_2O_5 and Nb_2O_5 HR coatings at 1064 nm are 99.96% and 99.90%, respectively.

The refractive index n_f is shown in Table 1. It shows that the refractive indices of both films increase after annealing. The relation between refractive index n_f and packing density P can be illustrated as

$$n_f = Pn_{\mathrm{s}} + (1 - P)n_{\mathrm{v}}, \qquad (1)$$

where n_{s} and n_{v} are the refractive indics of the solid part of the film and the voids, respectively. From Eq. (1), the packing densities of the Ta_2O_5 and Nb_2O_5 films before and after annealing are calculated, as shown in Table 1. The packing densities of the as-deposited Ta_2O_5 and Nb_2O_5 films are 0.83 and 0.85, respectively. These results indicate that there are many structural voids inside the film, which may decrease the adhesive force between aggregations in the film, resulting in structural defect. During annealing, the film structure undergoes a

Table 1. Refractive Index (n_f) at 550 nm, Thickness (d), and Packing Density (P) of the Films

Films	n_f	d (nm)	P
As-Deposited Ta_2O_5	2.055	419	0.83
Annealed Ta_2O_5	2.090	408	0.87
As-Deposited Nb_2O_5	2.153	410	0.85
Annealed Nb_2O_5	2.171	397	0.87

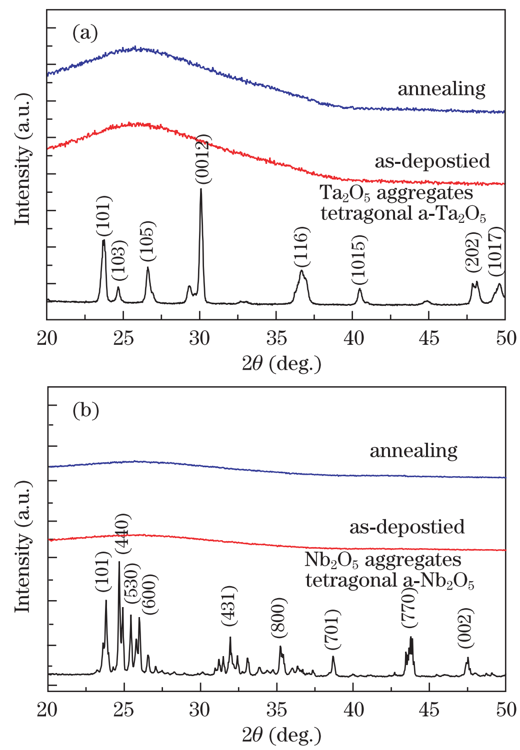

Fig. 2. XRD patterns of (a) Ta_2O_5 and (b) Nb_2O_5.

modification driven by thermal energy, accompanied by a decrease in the number of voids, thus increasing the packing densities.

Figure 2 illustrates the XRD patterns of as-deposited and annealed films. The figure demonstrates that the aggregates are tetragonal Ta_2O_5 (Card 21-1119) and tetragonal Nb_2O_5 (Card 72-1484) according to the joint committee for powder diffraction studies (JCPDS) data. The as-deposited and annealed films are both amorphous mainly due to the low annealing temperature, which is consistent with findings that Ta_2O_5 films crystallize above 973 K and Nb_2O_5 films above 773 K[9]. Although the modification during annealing decreases the voids and may form some new stable bonds, XRD results show that the amorphous structure of the films does not change. Thus, the structural defect in the phase transformation such as grain boundaries and cracks can be neglected in this study.

Figure 3(a) shows the Ta 4f XPS spectra from Ta_2O_5 films. The spectra reveal two $4f_{7/2}$ and $4f_{5/2}$ peaks at 26.4 and 28.2 eV, respectively, which shows that the composition of the films is Ta^{5+}. The O/Ta ratio is estimated from the XPS peak area together with their relative sensitivity factors. The O/Ta ratio in the as-deposited film is 2.42, indicating that the substoichiometric defect is oxygen vacancy. Although oxygen excess has also been

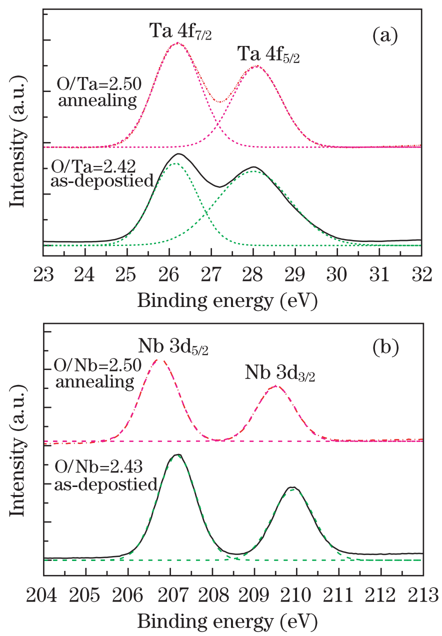

Fig. 3. XPS spectra of (a) Ta_2O_5 single layer and (b) Nb_2O_5 single layer.

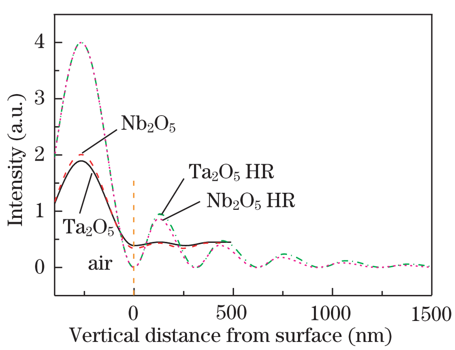

Fig. 4. EFI distributions of the films.

found as a substoichiometric defect, its appearance in Ta_2O_5 films seems unlikely[10]. After annealing above 873 K, the O/Ta ratio increases to 2.50. Figure 3(b) shows the Nb 3d XPS spectra from Nb_2O_5 films. The spectra reveal two $3d_{5/2}$ and $3d_{3/2}$ peaks at about 207 and 210 eV, respectively, according to Nb^{5+}. The O/Nb ratios are 2.43 and 2.50 for the as-deposited and annealed films. Gibbs free energy of the reaction of oxygen and nonoxidized Ta (Nb) inside the film is negative, which is favorable based on thermodynamical arguments[11]. Oxygen penetrates and reacts with the substoichiometic films during the annealing, repairing the substoichiometric defect and improving the films' stoichiometry.

Theoretical results of the EFI distributions of the films were calculated using a thin film design software (TF-Calc). Figure 4 shows that the EFI distributions in the Ta_2O_5 and Nb_2O_5 single layers are similar. The EFI in the two films slightly changes. EFI distributions in HR coatings decrease from the surface to the substrates. The highest EFI is located at the first Ta_2O_5-SiO_2 interface near the surface and the lowest EFI is located at the substrate. Each peak value appears in the Ta_2O_5-SiO_2 interfaces.

Table 2 shows the average absorption and LIDT of the

Table 2. Average Absorption and LIDT of the Films

Films	Absorption (ppm)	LIDT (J/cm^2)
As-Deposited Ta_2O_5	94.6	4.3
Annealed Ta_2O_5	40.1	7.5
As-Deposited Nb_2O_5	113.2	8.5
Annealed Nb_2O_5	63.0	13.2
Ta_2O_5 HR	137.2	17.8
Nb_2O_5 HR	142.1	25.6

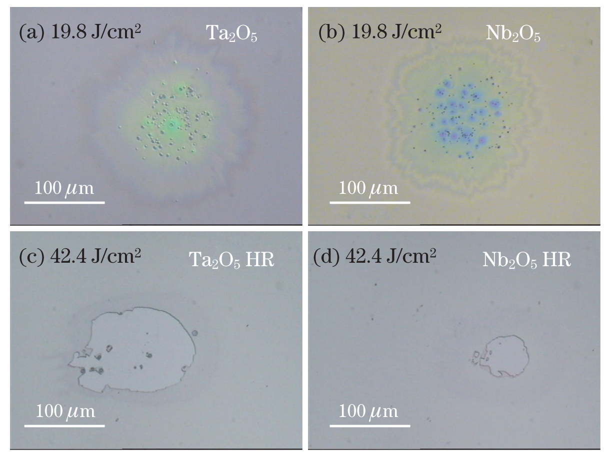

Fig. 5. Typical damage morphologies by micropolariscope of (a) Ta_2O_5 single layer, (b) Nb_2O_5 single layer, (c) Ta_2O_5 HR coating, and (d) Nb_2O_5 HR coating. (The laser energy for the damage is given in each top left corner.)

films. The absorptions of both Ta_2O_5 and Nb_2O_5 films decrease after annealing. The Nb_2O_5 single layer has a higher absorption than the Ta_2O_5 single layer, both before and after annealing. The absorption of the HR coatings is higher than that of the single layers. The decrease of absorption will be beneficial for the transmittance and the O/Ta ratio of the films deposited by the same material. For instance, when the absorption of the Ta_2O_5 single layer decreases from 94.6 to 40.1 ppm, the transmittance improves and the O/Ta ratio increases from 2.42 to 2.50 after annealing. Table 2 also illustrates that the annealed films have a higher LIDT than the as-deposited films. The Nb_2O_5 HR coating has the highest LIDT at 25.6 J/cm^2.

Figure 5 presents the typical damage morphologies of the films. Figures 5(a) and (b) display that some dispersed defect points appear in the damaged areas, and the damage enlarges from these points. However, the damage morphologies show some differences between single layers and HR coatings. In Figs. 5(c) and (d), the defect points become less evident and the flat bottom pit appears. The edges are sharp, which may indicate an explosive removal of surface layers.

Although LIDT values and damage morphologies are different for single layers and HR coatings, the damage mechanisms are still the same in nature and both are induced by defects. The defects can be divided into two kinds: structural defects such as big structural voids, nodular defects, grain boundary defects, and microcracks; substoichiometric defects, mainly oxygen vacancy. We attribute the difference in the laser damage to the following:

1) In the single layers, defect points can be seen in the damaged areas of both Ta_2O_5 and Nb_2O_5, indicating that the damage morphologies show the distinct defect-induced damage mechanism. The main defect is the substoichiometric defect as the O/Ta ratio is less than 2.50. After annealing, the substoichiometric defect disappears and the structural defect decreases, thus the LIDT improves.

2) An interesting phenomenon is that the LIDT of the Ta_2O_5 single layer is much lower than that of the Nb_2O_5 single layer, although it has a lower absorption than the latter. Abromavicius studied the LIDT of the two kinds of films, however, the absorption of the films was not examined in the research[6]. We believe that the comparison of the laser damage resistance of different materials would not be meaningful unless the films have the same absorption. In this letter, we conclude that the laser damage resistance of Nb_2O_5 is better than that of Ta_2O_5. Details about this phenomenon need to be studied further because previous studies have shown that the damage resistance is correlated with many factors such as band gap, melting point, and so on[12].

3) For the HR coatings, the damage areas show different morphologies. This can be attributed to the higher damage energy (42.4 J/cm^2) and multi-layer structure. The defect points absorb laser energy intensively to the point of melting, followed by rapid cooling. Thus, thermal stress between the high-index material (Ta_2O_5/Nb_2O_5) and the low-index material (SiO_2) contributes to flaking. In addition, the absorption of the HR coatings is higher than that of the single layers, but its LIDT improves. The increase in LIDT may be due to the low-index material SiO_2, which has excellent thermal properties. This ensures fast heat transfer from the defect points to the environment, resulting in a reduction of peak temperature and more damage-resistant films. Aside from thermal dissipation due to SiO_2 properties, the decrease of EFI will also contribute to the increase in LIDT as seen in HR coatings where the EFI decreases at the substrate and at the Ta_2O_5-SiO_2 interfaces, except at the outmost Ta_2O_5-SiO_2 interface. The LIDT of the Nb_2O_5 HR coating is higher than that of the Ta_2O_5 HR coating, which may be attributed to the better laser damage resistance of the Nb_2O_5 material.

In conclusion, the optical properties, microstructure, chemical composition, optical absorption, and LIDT of Ta_2O_5 and Nb_2O_5 films are comparatively studied in this letter. Results show that Ta_2O_5 films have better transmittance than Nb_2O_5 films, especially in the short wavelength region. The transmittance, O/Ta (Nb) ratio, and LIDT of both films can be improved by annealing. For films deposited by the same material, the decrease of absorption will improve the LIDT. However, although the absorption of Ta_2O_5 films is less than that of Nb_2O_5 films, the LIDT is lower than the latter. Damage morphologies of the HR coatings are different from those of the single layers, which may be due to the higher damage energy and multi-layer structure. In addition, the HR coatings have higher LIDT than the single layers have, and Nb_2O_5 HR coating achieves the highest LIDT at 25.6 J/cm^2 in both single layers and HR coatings.

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