Comparison of laser-induced damage in Ta$_2$O$_5$ and Nb$_2$O$_5$ single-layer films and high reflectors

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Ta$_2$O$_5$ and Nb$_2$O$_5$ 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$_2$O$_5$ and Nb$_2$O$_5$ films. The decrease of absorption improves the LIDT in films deposited by the same material. However, although the absorption of the Ta$_2$O$_5$ single layer is lower than that of the Nb$_2$O$_5$ 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$_2$O$_5$ HR coating achieves the highest LIDT at 25.6 J/cm$^2$ in both single layers and HR coatings.

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Ta$_2$O$_5$ and Nb$_2$O$_5$ have been widely investigated as possible candidates for corrosion barrier coatings, electrochromic films, gas sensors, and catalysts. In optical applications, Ta$_2$O$_5$ and Nb$_2$O$_5$ 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$_2$O$_5$ and Nb$_2$O$_5$ 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$_2$O$_5$ and Nb$_2$O$_5$ 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$_2$O$_5$ and Nb$_2$O$_5$ films including single-layer films (only Ta$_2$O$_5$ or Nb$_2$O$_5$) and HR coatings (Ta$_2$O$_5$/SiO$_2$ or Nb$_2$O$_5$/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$^{-5}$ Pa, the oxygen partial pressure was 2×10$^{-2}$ Pa, and the substrate temperature was kept at 573 K during the deposition. Both Ta$_2$O$_5$ and Nb$_2$O$_5$ 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$_2$O$_5$/Nb$_2$O$_5$ and SiO$_2$ were used as high and low refractive-index materials, respectively. The coating design of the HR structure was (HL)$^2$H, where H stands for the QWOT of Ta$_2$O$_5$/Nb$_2$O$_5$ and L stands for the QWOT of SiO$_2$ (the referent wavelength $\lambda$ 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 indices 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-K$_\alpha$ ($h\nu=1486.6$ 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-switched pulsed laser at a pulse length of 12 ns$^{[8]}$. The damage morphologies of the samples were observed using a Leica DMRXE.
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Figure 1 shows the transmittance curves of the Ta$_2$O$_5$ and Nb$_2$O$_5$ films. Figures 1(a) and (b) show that both the optical transmittances of the Ta$_2$O$_5$ and Nb$_2$O$_5$ single layers increase after annealing. The findings also indicate that the Ta$_2$O$_5$ single layer has better transmittance than the Nb$_2$O$_5$ single layer, especially in the short wavelength region. Figure 1(c) shows the optical transmittance of the HR coatings. The reflectances of the Ta$_2$O$_5$ and Nb$_2$O$_5$ 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

$$n_f = Pn_s + (1 - P)n_v,$$

where $n_s$ and $n_v$ are the refractive indices of the solid part of the film and the voids, respectively. From Eq. (1), the packing densities of the Ta$_2$O$_5$ and Nb$_2$O$_5$ films before and after annealing are calculated, as shown in Table 1. The packing densities of the as-deposited Ta$_2$O$_5$ and Nb$_2$O$_5$ 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 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$_2$O$_5$ (Card 21-1119) and tetragonal Nb$_2$O$_5$ (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$_2$O$_5$ films crystallize above 973 K and Nb$_2$O$_5$ 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$_2$O$_5$ 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
found as a substoichiometric defect, its appearance in T\textsubscript{a}_2O\textsubscript{5} films seems unlikely\cite{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\textsubscript{2}O\textsubscript{5} films. The spectra reveal two 3d\textsubscript{5/2} and 3d\textsubscript{3/2} peaks at about 207 and 210 eV, respectively, according to Nb\textsuperscript{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\cite{11}. Oxygen penetrates and reacts with the substoichiometric 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 (TFCalc). Figure 4 shows that the EFI distributions in the T\textsubscript{a}_2O\textsubscript{5} and Nb\textsubscript{2}O\textsubscript{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 T\textsubscript{a}_2O\textsubscript{5}-SiO\textsubscript{2} interface near the surface and the lowest EFI is located at the substrate. Each peak value appears in the T\textsubscript{a}_2O\textsubscript{5}-SiO\textsubscript{2} interfaces.

Table 2 shows the average absorption and LIDT of the films. The absorptions of both T\textsubscript{a}_2O\textsubscript{5} and Nb\textsubscript{2}O\textsubscript{5} films decrease after annealing. The Nb\textsubscript{2}O\textsubscript{5} single layer has a higher absorption than the T\textsubscript{a}_2O\textsubscript{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 T\textsubscript{a}_2O\textsubscript{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\textsubscript{2}O\textsubscript{5} HR coating has the highest LIDT at 25.6 J/cm\textsuperscript{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$_2$O$_5$ and Nb$_2$O$_5$, 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$_2$O$_5$ single layer is much lower than that of the Nb$_2$O$_5$ 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. 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$_2$O$_5$ is better than that of Ta$_2$O$_5$. 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.

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$_2$O$_5$/Nb$_2$O$_5$) 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$_2$O$_5$-SiO$_2$ interfaces, except at the outmost Ta$_2$O$_5$-SiO$_2$ interface. The LIDT of the Nb$_2$O$_5$ HR coating is higher than that of the Ta$_2$O$_5$ HR coating, which may be attributed to the better laser damage resistance of the Nb$_2$O$_5$ material.

In conclusion, the optical properties, microstructure, chemical composition, optical absorption, and LIDT of Ta$_2$O$_5$ and Nb$_2$O$_5$ films are comparatively studied in this letter. Results show that Ta$_2$O$_5$ films have better transmittance than Nb$_2$O$_5$ 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$_2$O$_5$ films is less than that of Nb$_2$O$_5$ 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$_2$O$_5$ HR coating achieves the highest LIDT at 25.6 J/cm$^2$ in both single layers and HR coatings.

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References