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Effects of oxygen flow on properties of La$_2$Ti$_2$O$_{7-x}$ films

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Abstract

In order to obtain the relationship between the properties and the oxygen flow rate of La$_2$Ti$_2$O$_{7-x}$ film, the films were prepared by electron beam evaporation with various oxygen flow rates on Si and quartz substrates. The effects of oxygen flow on the properties of La$_2$Ti$_2$O$_{7-x}$ film were analyzed by XRD, XPS, optical constant and laser damage test. The result shows that the La$_2$Ti$_2$O$_{7-x}$ film lose oxygen and lead to the transition of Ti$^{4+}$ to Ti$^{3+}$ in oxygen-free environment. When the oxygen flow rate is greater than 4 sccm, the content of Ti$^{4+}$ is stable. The refractive index of La$_2$Ti$_2$O$_{7-x}$ films decreases with the increase of oxygen flow rate and stabilizes at oxygen flow rate greater than 4 sccm. The extinction coefficient of film deposited in oxygen-free environment is less than 10$^{-4}$. As the oxygen flow rate increases, the film absorption is further improved to reach 10$^{-5}$ at wavelengths longer than 350 nm. The laser damage threshold of films increased with increasing oxygen flow and the maximum value is 18.35 J cm$^{-2}$.

1. Introduction

Thin films have been widely used in the fields of optics, electronics and material chemistry. Oxide film is an important optical film used in high-energy laser system. Weak absorption and high resistance to laser-induced damage are usually required. However, an important problem for oxide films is that it is easy to lose oxygen in preparation [1–4], which causes the chemical mismatch to affect the performance of the film. The effects of the oxygen content on their optical properties for high refractive index oxide film materials such as TiO$_2$, HfO$_2$, Ta$_2$O$_5$ and ZrO$_2$ were investigated [5–10]. Meanwhile, LaTiO$_3$ films also has a high refractive index [11], excellent stability and the wide transmission range of 360 to 7000 nm [12]. It has been regarded as a potential optical thin film material. However, for this material, the researchers’ main research focused on metal-insulator transition, spin–charge-orbital ordering and high-temperature superconductivity [13–17] due to its perovskite structural. The research on structural, optical properties of amorphous LaTiO$_3$ films is scarce. Junhong Su studied the influence of deposition temperature on optical and laser-induced damage properties of LaTiO$_3$ films [12]. Philippe Combette investigated the morphological, structural, dielectric and pyroelectric of LaTiO$_3$ thin films as function of growth conditions [18]. But regrettably, the effect of oxygen flow on the optical properties of the LaTiO$_3$ films is not exhaustive, which is unfavorable to the preparation of high quality films and limits its applications.

As we know, the oxygen atmosphere is an important factor in the preparation of the oxide film. Therefore, in this paper, the effects of oxygen flux on the structural, optical and laser damage properties of non-crystalline La$_2$Ti$_2$O$_{7-x}$ films prepared on Si and fused quartz substrates using electron-beam evaporation were investigated.

2. Experimental

La$_2$Ti$_2$O$_{7-x}$ films were deposited by electron beam evaporation (ZKS500–1/3) on Si and fused quartz substrates. The films were deposited using the La$_2$Ti$_2$O$_7$ pellets (purity 99.99%, provided by Beijing nonferrous metal research institute) as starting material. Si and fused quartz substrates were cleaned ultrasonically in alcohol solution before deposition. During deposition, the base pressure was 3 × 10$^{-3}$ Pa, the working pressure was
about $1 \times 10^{-2}$ Pa, the electron-beam current was 110 mA, e-beam voltage was 8KV, and the deposited temperature kept at 150 °C with various oxygen flows of 0, 1, 2, 4 and 8 sccm, respectively.

Refractive indexes, extinction coefficient and physical thickness of La$_2$Ti$_2$O$_7$ films were measured by ellipsometry (J.A.Woollam M-2000UI, American) and the thickness were controlled at about 160 nm. Transmission spectra of samples were measured by spectrophotometer (Hitachi U-3501, Japan). The structures of films were characterized by x-ray diffraction (XRD, X’Pert PRO MPD) with 2θ angle in the range of 10–90°. The elemental composition and the element’s chemical states of samples were investigated by x-ray photoelectron spectroscopy (XPS, PHI5400) with a Mg Kα radiation source ($h\nu = 1253.6$ eV). The laser induced damage threshold (LIDT) of thin films was tested according to ISO standard 11254–1 using 1064 nm Q-switch pulsed laser with a pulse length of 10 ns on the laser damage testing equipment developed by our research group. In the test, the diameter of the laser beam was 0.8 mm and the image distinguish method was used for damage testing. The damage threshold was fitted with zero probability damaged.

3. Result and discussion

3.1. X-ray diffraction analysis

As shown in figure 8, the LIDT of the film increases slightly with the oxygen flow rate, which are 16.03, 16.23, 17.5, 18.18 and 18.35 J cm$^{-2}$, respectively. XRD is a common method to study the crystal phase of materials. The XRD spectra of the films prepared at oxygen flow rates of 0 and 8 sccm are shown in figure 1. By searching PDF card library, it was found that the diffraction angles corresponding to the three strong peaks of the compounds (La$_5$Ti$_5$O$_{17}$, La$_2$Ti$_2$O$_7$ and LaTiO$_3$) formed by La, Ti and O are all between 20° to 50°. At the same time, it can be seen from figure 1 that no diffraction peaks appear in the range of 10-90°. Thus, it can be drawn that the samples are all amorphous.

3.2. XPS spectrum analysis

La, Ti, O and contamination C are all elements in the film prepared at an oxygen flow rate of 8 sccm. The XPS survey spectra were calibrated using the C1s (284.61 eV) peak and illustrated in figure 2. The peak of Ti2p3 of 458.11 eV is close to the value of 458.33 eV in TiO$_2$ [19]. The peak of La3d5 is 832.25 eV corresponding to 832.50 eV of La$_2$O$_3$ [20]. It indicated that the film is mainly composed by La$^{3+}$, Ti$^{4+}$ and O$^{2-}$. Since the starting material is La$_2$Ti$_2$O$_7$ pellets, the film should be La$_2$Ti$_2$O$_7$ without losing oxygen in the preparation process.

At the same time, it is known that the La oxides has only one compound state of La$_2$O$_3$ and the Ti oxide has a variety of valence states, in the XPS analysis, valence changes of Ti element was mainly analyzed. XPS spectrum of the Ti element in the film deposited at different oxygen flows are shown in figure 3.

It can be seen that the Ti diffraction peak shows a normal distribution basically when the oxygen flow rate is 4 and 8 sccm. However, when the oxygen flow rate is less than 4 sccm, especially when the oxygen flow rates are 0 and 1 sccm, it is obvious that there is a left-side shoulder peak. For the further analysis of the valence and content of Ti, the XPS-peak-differenating analysis was carried out. The results show that the Ti elements on the main peaks is Ti$^{4+}$ which the binding energy is 458.11 eV corresponding to the value of 458.33 eV in TiO$_2$ [19].

Figure 1. XRD spectra of samples prepared at different oxygen flow.
Meanwhile, the Ti elements on the left-side shoulder peak is Ti$^{3+}$ which the binding energy is 456.21 eV corresponding to the value of 456.80 eV in Ti$_2$O$_3$ [21]. The values of Ti$^{3+}$/Ti$^{4+}$ were calculated by the peak area ratio of different valence states. The results are shown in Table 1.

| Oxygen flow (sccm) | 0   | 1   | 2   | 4   | 8   |
|-------------------|-----|-----|-----|-----|-----|
| Ti$^{3+}$/Ti$^{4+}$ | 0.089 | 0.046 | 0.028 | 0.017 | 0.015 |

Table 1. Value of Ti$^{3+}$/Ti$^{4+}$ prepared at different oxygen flow.

Figure 2. XPS spectra of all elements.

Figure 3. XPS spectrum of the Ti element.
As can be seen from table 1, the proportion of Ti$^{4+}$ gradually increases with the increase of oxygen flow. This means that a partial Ti$^{4+}$ transformed into Ti$^{3+}$ when the oxygen flow reduced gradually during the deposition. Correspondingly, the oxygen loss in the film decreases as the oxygen flow increases. According to the calculation of the molecular content ratio, the X in La$_2$Ti$_2$O$_{7-x}$ are 0.015, 0.017, 0.027, 0.044 and 0.082 deposited at different oxygen flow. At the same time, it can be observed that when the oxygen flow rate is 0, 1 and 2sccm, the difference of Ti$^{3+}$/Ti$^{4+}$ ratio is relatively large among them, when the oxygen flow rate is 4 and 8sccm, the change slightly and the components tend to be stable. This indicates that oxygen supplementation exceeding 4sccm can compensate for the oxygen lost in film formation of La$_2$Ti$_2$O$_{7-x}$ film to achieve component stability.

3.3. Optical properties

Optical constants are important performance parameters for optical films. A Si/Cauchy/roughness model was established to fit the optical constant of the film. Refractive index and extinction coefficient of La$_2$Ti$_2$O$_{7-x}$ films prepared at different oxygen flows were measured. The results are shown in figure 4.

As can be seen from figure 4(a), the refractive index decreases with the increase of wavelength and follows a normal dispersion in the wavelength range of 350–1600 nm. For different oxygen flows, the refractive index decreased as oxygen flow increased. Specifically, when the oxygen flows were 0, 1, 2, 4 and 8sccm the refractive indices at wavelength of 1064 nm were 1.9724, 1.9721, 1.951, 1.912 and 1.9144, the thickness were 159.67, 168.07, 162.04, 172.61, 173.84 nm, respectively. In the meantime, there are two distinct index changing regions, one region is that the oxygen flow rate are 0, 1 and 2sccm, the other is that oxygen flow rate are 4 and 8sccm. The refractive index varies very small within each region, but it is apparent between the two regions. This shows that when the oxygen flow rate is less than 2sccm, the oxygen atmosphere has a weak influence on the refractive index. When the oxygen flow rate is higher than 4sccm the refractive index will be affected greatly. Continuously increasing the oxygen flow rate to 8sccm, the oxygen in the environment tends to balance, thereby obtaining a stable composition and a stable refractive index. From this, it can be concluded that the refractive index of the film tends to be stable when the oxygen flow rate above 4sccm. From figure 4(b), it shows that when the oxygen flow rate is 8 sccm the extinction coefficient of the film is less than $10^{-5}$ at a wavelength longer than 320 nm, while when the oxygen flow rate is 4 sccm the extinction coefficient is less than $10^{-5}$ at a wavelength longer than 400 nm. The smaller the oxygen flow rate, the longer wavelength of the film extinction coefficient is less than $10^{-5}$. Especially, when the oxygen flow rate is 0 sccm, the extinction coefficient is still greater than $10^{-5}$ even at 800 nm, indicating that the absorption of the films prepared under this condition is obviously greater than that of others. This shows that the larger the oxygen flow rate, the shorter the extinction coefficient of the film less than $10^{-5}$ and the longer optical transparency zone. At the same time, the wavelength is greater than 450 nm the extinction coefficient of all samples are less than $10^{-5}$ showing the low absorption of the films prepared under all conditions.

Combined with XPS analysis results, it can be conclude that the changes of refractive index and extinction coefficient of the film are closely related to the oxygen loss and keep the uniformity. The smaller the oxygen flow rate, the more significant oxygen loss in the film, so that the larger the refractive index, the greater the absorption.

The transmittance spectra of samples at different oxygen flow rate are shown in figure 5. It can be observed that the transmittance of all samples is greater than 80% when the wavelength is greater than 330 nm. Except for the wavelength range of 424–480 nm, the transmittance of the samples is about 75%. The closest transmittance between the film and the substrate is 93.44% and 93.47% at the wavelength of 584 nm. The difference between them is only 0.03%. These indicate that the La$_2$Ti$_2$O$_{7-x}$ films has excellent optical transparency in visible region.

![Refractive index and extinction coefficient](image)
Compared to TiO$_2$ film, the transmittance is lower than 60% at the wavelength of 400 nm \cite{22}. This indicates that the absorption of La$_2$Ti$_2$O$_{7-x}$ films is less than that of TiO$_2$ film.

3.4. Laser damage property
The group of experiments was performed at a pulsed laser with energy of 120 mJ. Figure 6 shows the full view and an enlarged 2.5 times image of the surface damaged of La$_2$Ti$_2$O$_{7-x}$ films prepared at 150 °C and the oxygen flow rate at 0 sccm. Figure 7 shows an enlarged 20 times image of the surface damaged morphologies of the film prepared at the oxygen flow rate of 0, 1, 2, 4 and 8 sccm, respectively.

Figure 7 shows that the area of the damage spot and its serrated edge morphology have little change, but the shedding area in the damage spot decreased slightly with the increase of oxygen flow. This shows that the oxygen flow rate has no significant effect on the laser damage mechanism and effect difference of the La$_2$Ti$_2$O$_{7-x}$ film.

The LIDT of the film increases slightly with the oxygen flow rate, which are 16.03, 16.23, 17.5, 18.18 and 18.35 J cm$^{-2}$, respectively. This trend is same as that of TiO$_2$ film \cite{22}. It can be explained that during the deposition process, the loss of oxygen results in a decrease in the absorption of larger sub stoichiometric components. The result is consistent with the researchers’ study of the oxygen partial pressure on the ZrO$_2$ film \cite{23, 24}. The film is destroyed due to the thermo mechanical coupling effect, while the thermal absorption of the metallic film is larger than that of the dielectric film. Therefore, LIDT of LaTiO$_3$ film decreased when the oxygen lost.

According to the research literature, the LIDT of TiO$_2$ film is about 9 J cm$^{-2}$ \cite{22}, the LIDT of ZrO$_2$ film is about 18.5 J cm$^{-2}$ \cite{24}. In contrast, La$_2$Ti$_2$O$_{7-x}$ film has a higher LIDT and better process stability. At the same time, the conclusion of this paper is consistent with the results of other researchers \cite{22–24}, that is, the more fully oxidized the film, the less the sub stoichiometric composition, and the higher LIDT of the film.
4. Conclusion

In the oxygen-free condition, the Ti$^{3+}$ accounts for nearly 25% of the Ti element in the film and the deposited film is obviously deoxygenated. With supplement of oxygen increases, the proportion of Ti$^{3+}$ decreased gradually. When the oxygen flow rate increased to 4sccm, the Ti$^{3+}$ accounted for nearly 10% of Ti element, the oxygen loss improved significantly. Continuous increase in oxygen flow, the film composition changes little. The refractive index of La$_2$Ti$_2$O$_7$$_{-x}$ films decreases with the increase of oxygen flow rate. When the oxygen flow rate is larger than 4sccm, the refractive index is basically stable. When the oxygen flow rate is greater than 8sccm, the absorption coefficient of the film can be reduced to $10^{-5}$ while the wavelength is more than 350 nm with a wide range of transparent. The oxygen flow rate has no significant effect on the laser damage of the La$_2$Ti$_2$O$_7$$_{-x}$ film. The LIDT of La$_2$Ti$_2$O$_7$$_{-x}$ film increased with the increase of oxygen flow. The highest LIDT of La$_2$Ti$_2$O$_7$$_{-x}$ film is 18.35 J cm$^{-2}$, which is higher than that of TiO$_2$ film about 9 J cm$^{-2}$.

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