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Correlations between the oxygen deficiency and the laser damage resistance of different oxide films

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ABSTRACT

Ta_2O_5, ZrO_2 and HfO_2 films are deposited on BK7 substrates by electron beam evaporation method. The effects of oxygen deficiency on the optical properties and laser-induced damage threshold (LIDT) are investigated by the combination of experimental methods and first principles calculations. The results show that the oxygen deficiency weakens the transmittance, whereas it enhances the absorption of all the films. Once the oxide vacancy appears, the band gaps decrease greatly, which seriously decrease the LIDT. The calculated negative vacancy energies indicate that, when the oxygen vacancy exists, Ta_2O_5 is most easily to be damaged, next is ZrO_2 and the last is HfO_2. It is consistent with the LIDT results that Ta_2O_5 increases 64.8%, ZrO_2 increases 19.4% and HfO_2 increases 12.9% when the oxygen vacancy is eliminated.

1. Introduction

The laser-induced damage in optical films is one of the most important research subjects in the field of high power laser systems. In numerous reports, point defects have been regarded as the main source of the nanosecond laser damage of films. For oxide films, oxygen deficiency is the most serious defect, which has been found and proved in Ta_2O_5, Nb_2O_5, TiO_2, ZrO_2, and so on [1–4]. However, up to present, evaluation of the relationship between laser damage threshold and point defects was limited because of lack of non-destructive detection techniques workable at the nanometric scale. Thus, new ways should be explored. Earlier, it was found that the first principles calculations may be a proper approach to study such characteristics as band gap, energy and electronic structure of minimal volume (or periodic minimal volume) [5–7]. Although the calculated results frequently deviate from the experimental ones, we believe that this is a door to study the correlations between the defects in minimal volume and the laser damage resistance. However, systematic researches on this subject are scarcely reported.

In addition, many studies put forward in comparison of the laser damage resistance of different films. Scott published a review of the laser-induced damage threshold (LIDT) of UV coatings such as CaF_2, MgF_2, ThF_4, SiO_2, Al_2O_3, ZrO_2 and HfO_2, which intended to provide the relevant data available in this field [8]. Akhtar fabricated 19 types of oxides, fluorides and mixtures of various dielectrics, and provided the LIDT for some of these films [9]. Szymanowski and our earlier work both studied the optical properties and laser-induced damage of Ta_2O_5 and Nb_2O_5 films [2,10,11]. These investigations mainly focused on the comparison of the experimental LIDT, or the possible damage mechanism from the data. If one can obtain and associate the defect characteristics in the minimal volume of different materials with their laser damage resistance, it may be more meaningful for understanding the substaintial laser damage mechanism.

In the present study, we firstly make a comparison of such film properties as optical parameters, microstructures, absorption and LIDT in Ta_2O_5, ZrO_2 and HfO_2 with and without oxygen vacancy. Then, the attempt is produced to find the correlations between oxygen deficiency and laser damage resistance using the combination of first principles calculations and laser damage experiments. It is expected to be a new step in exploration of the nanosecond laser-induced damage mechanisms.

2. Experimental details

The Ta_2O_5, ZrO_2 and HfO_2 aggregates with the purity of 99.99% were used as the starting materials. All the films were deposited

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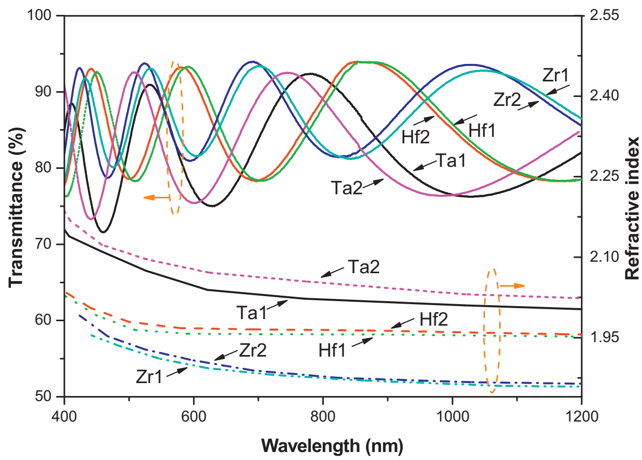

Fig. 1. Transmittance and refractive index of the films.

on BK7 substrates by conventional electron beam evaporation. For improving the LIDT, the substrates were chemically treated and carefully cleaned, and optimized parameters are used for deposition and annealing of each film. The base pressure was 2×10^{-3} Pa and oxygen partial pressure was 2×10^{-2} Pa during deposition. Annealing of Ta_2O_5 films was performed in the air at 673 K, whereas annealing of ZrO_2 and HfO_2 films was produced in the air at 473 K. In the following, the as-deposited films are denoted as M1 (M is the metal element in the oxide), and the films after annealing are denoted as M2. Transmittance spectra were measured using a Lambda 900 spectrophotometer and the wavelength accuracy of the device during spectra recording was within 0.08%. The refractive indices were calculated by Essential Macleod (a thin film design software). The film thickness was measured with WYKO NT1100 profilometer. The microstructure was analyzed by an X-ray diffractometer (XRD). The optical absorption of samples was measured by surface thermal lensing (STL) method [12]. The sensitivity of the measurement is 1 ppm. Damage testing was performed in the "1-on-1" regime according to ISO standard 11254-1, using 1064 nm Q-switch pulsed laser at a pulse length of 12 ns [13,14]. The LIDT was defined as the incident pulse energy density (J/cm^2) when the damage occurs at 0% damage possibility.

3. Calculation method

The band gaps and vacancy energies were calculated by a first-principle pseudopotential method within the local density approximation. The program of CASTEP (Cambridge Serial Total Energy Package) is used [15]. As the calculated results are influenced obviously by the material structure, the monoclinic structure is chosen in the calculation for all the oxides. The ICSD number of Ta_2O_5 is 280396, ZrO_2 is 41010 and HfO_2 is 57385. The $2 \times 2 \times 1$ supercells are built for all the oxides. The energy cutoff is set at 340 eV, and the K-point grid is set to $3 \times 3 \times 3$.

4. Results and discussion

4.1. Optical properties, absorption and LIDT

Fig. 1 shows the transmittance curves and refractive indices of the films before and after annealing. It is seen that optical transmittance of all oxide films increases after annealing, which can be attributed to the absorption decrease. In addition, Fig. 1 also shows that the transmittance curves shift to the short wavelength after annealing, which indicates the film thickness decreases as listed in

Table 1
Refractive indices (n_f), thickness (d), average grain sizes (D) and absorption of the films.

Films	Annealing (K)	n_f (at 550 nm)	d (nm)	D (nm)	Absorption (ppm)
Ta1	–	2.07	426	–	90.8
Ta2	673	2.09	414	–	39.2
Zr1	–	1.91	552	7.5	49.8
Zr2	473	1.92	541	8.3	32.1
Hf1	–	1.96	448	10.2	38.2
Hf2	473	1.97	442	11.6	29.5

Table 1. The refractive indices also increase after annealing for all the films.

The microstructure of the films is revealed by XRD measurements as shown in Fig. 2. It is found that Ta_2O_5 films are amorphous, ZrO_2 films are tetragonal, and HfO_2 films are monoclinic [16,17]. After annealing, the microstructures of all the films are unchanged. The average grain sizes of ZrO_2 and HfO_2 films are calculated by Scherrer's equation. The crystallite size grows up slightly after annealing.

Table 1 also shows the average absorption of the films detected by STL method. It is obtained that the absorption of as-deposited films is much higher than that of annealing ones. It is consistent with the optical transmittance results (Fig. 1). The STL absorption is always caused by oxygen deficiency in Ta_2O_5, Nb_2O_5, ZrO_2, etc., which is mainly induced by the extreme high temperatures and vacuum in deposition processing [11,18]. After annealing, absorption decreases significantly in all oxides under consideration. It can be attributed to the elimination of oxygen deficiency.

Fig. 3 reveals the LIDT results of the films. It shows that after annealing the LIDT increases for all the films. The LIDT increases by 64.8% for Ta_2O_5 films, 13.3% for ZrO_2 films and 12.9% for HfO_2 films. It clearly indicates that the remover of oxygen vacancies increases LIDT.

4.2. Calculated band gaps and vacancy energies

Previous studies showed that the calculated results were influenced greatly by the material structure when using the first-principle pseudopotential method. The band gap results were nearly 7 times of differentiation between the orthorhombic structure and hexagonal structure of Ta_2O_5 [19]. Therefore, the same structure of oxides used in the first-principle method may be more proper to make a comparison of the band gaps and vacancy energies [20]. In this study, we choose the monoclinic structure in the

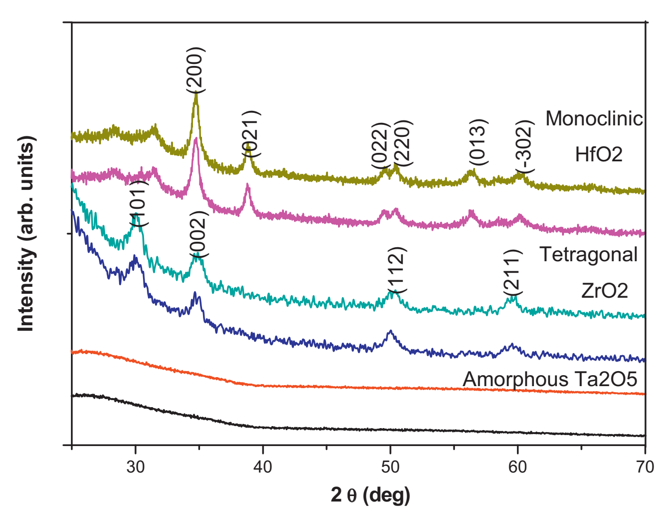

Fig. 2. XRD curves recorded from the films.