Comparison of TiO_2 and ZrO_2 Films Deposited by Electron-Beam Evaporation and by Sol-Gel Process *

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TiO_2 and ZrO_2 films are deposited by electron-beam (EB) evaporation and by sol-gel process. The film properties are characterized by visible and Fourier-transform infrared spectrometry, x-ray diffraction analysis, surface roughness measure, absorption and laser-induced damage threshold (LIDT) test. It is found that the sol-gel films have lower refractive index, packing density and roughness than EB deposited films due to their amorphous structure and high OH group concentration in the film. The high LIDT of sol-gel films is mainly due to their amorphous and porous structure, and low absorption. LIDT of EB deposited film is considerably affected by defects in the film, and LIDT of sol-gel deposited film is mainly effected by residual organic impurities and solvent trapped in the film.

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In high-power laser applications, one of the factors preventing its development is the lower laser-induced damage threshold (LIDT) of dielectric coatings.[1] Advances in laser technology research are also concentrated on new deposition processes[2] and film materials[3] for laser coatings. The most important optical parameters of coatings are the refractive index, the extinction coefficient and surface roughness, LIDT, etc.[4] Electron-beam (EB) evaporation and sol-gel method are two commonly used technologies for depositing high LIDT dielectric coatings. The EB evaporated optical films have good optical properties and chemical stability.[2] The sol-gel method offers several advantages over EB techniques, such as preparing large aperture optical films, simplicity and precise control of film stoichiometry.[5] TiO_2 and ZrO_2 are two hard, durable, and laser-damage-resistant materials of high refractive index and are widely used to produce multilayer coatings in the visible spectral region.[6]

In this Letter, we compare the optical properties, structure, surface roughness, absorption and LIDT of these two coating materials by the above-mentioned two deposition process.

In our experiment, all the films are deposited on high-quality BK7 substrates super-polished and cleaned ultrasonically in alcohol solution before deposition. The film thickness is about 500 nm. The samples studied in our experiment are outlined in Table 1. The preparation process of sol-gel films can be seen in Ref. [7]. TiO_2 and ZrO_2 are used as starting materials, respectively. The EB films are prepared with the following process parameters. The substrate temperature is kept at 300°C during deposition. The base pressure is 2×10^{-3} Pa, and oxygen partial pressures are 3×10^{-2} Pa and 1×10^{-2} Pa during deposition for TiO_2 and ZrO_2, respectively. The deposition rates of TiO_2 and ZrO_2 are 1.33 nm/s and 0.67 nm/s, respectively. The samples are annealed at 400°C in air for 24 h after deposition.

Table 1. Samples and preparation conditions.

Sample No	Deposition method	Annealing
Ti-1	Sol-gel	As-deposited
Ti-2	EB	As-deposited
Ti-3		400°C
Zr-1	Sol-gel	As-deposited
Zr-2	EB	As-deposited
Zr-3		400°C

The transmittance spectra of the films are measured with a Lambda 900 spectrometer. Optical constants of the films are determined from the transmittance spectra by the envelope method.[8] Based on the Bruggeman effective-medium approximation,[9] the relationship between packing density and refractive index of the films can be obtained. The film structure is characterized by Fourier-transform infrared (IR) spectrometry with a NEXUS FT-IR instrument and x-ray diffraction (XRD, RGAKU/MAX-3C type). The rms surface roughness is measured by the total integrated scattering method.[10] The surface thermal lensing (STL) technique[11] is used to measure the absorption of films at 1064 nm. LIDT is tested using a 1064 nm, 12 ns pulse laser in the one-on-one mode with the ISO standard 11254-1.[12] The surface defects and damage morphologies are observed with a Leica-DMRXE microscope.

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Table 2 shows the calculated optical constants and packing density of the films. It is known that the buck anatase and ZrO_2 crystal have the refractive index 2.49 ($\lambda = 589\,\mathrm{nm}$)[13] and 2.10 ($\lambda = 550\,\mathrm{nm}$),[6] respectively. It is found that the refractive index, packing density and extinction coefficient of sol-gel films are lower than those of the EB films. The high refractive index and packing density of the EB films show that they have more bulk-like features than the porous sol-gel films. A low extinction coefficient indicates a low absorbance, since the absorbance α and extinction coefficient k read the relation $\alpha = 4\pi k/\lambda$, where λ is the wavelength.

Table 2. Calculated optical constants ($\lambda = 550\,\mathrm{nm}$) and packing density.

Sample	Ti-1	Ti-2	Ti-3	Zr-1	Zr-2	Zr-3
Refractive index n	2.14	2.24	2.25	1.73	1.95	1.97
Packing density	0.77	0.83	0.84	0.64	0.81	0.83
Extinction coefficient k (10^{-4})	0.50	5.50	3.40	0.00	0.11	0.05

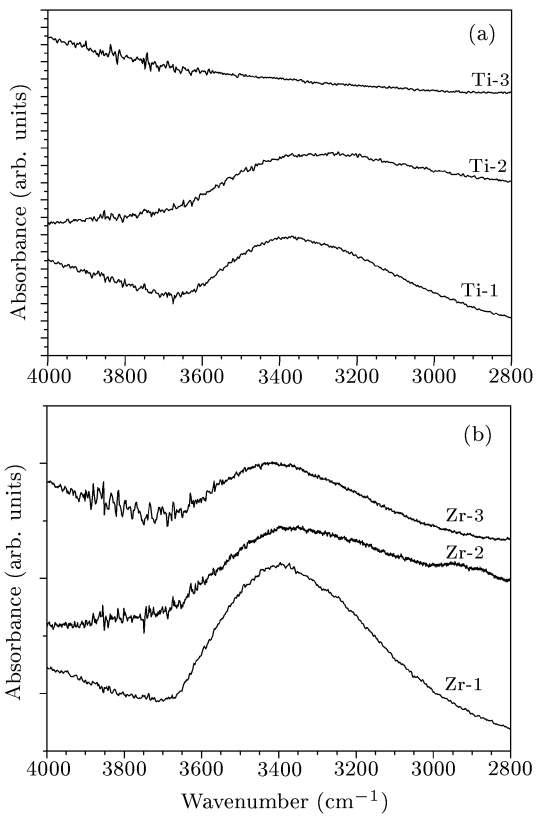


Fig. 1. IR absorption spectra of samples.

Figure 1 shows the IR absorption spectra of the samples. The absorption peak in the range 3000–3600 cm^{-1} is caused by the vibration of OH group in the film. It is found that the OH group presents in both the physical and chemical deposited films. The OH group in the EB film is caused by presence of H_2O in its column structure.[14] In the sol-gel films, the OH group is related to the residual organic impurities and solvent besides H_2O.[7] The peak area can qualitative indicate the concentration of OH groups. It can be found that the peak area in the sol-gel films is larger than those in the EB samples.

Figure 2 shows the XRD spectra of the samples. It is well known that TiO_2 mainly presents three forms in the film: amorphous, anatase and rutile;[13] and ZrO_2 also has three crystal phases: monoclinic, cubic and tetragonal.[6] Figure 2 shows that the sol-gel coatings are of amorphous structures. The diffraction peaks of anatase A (101), and cubic and monoclinic ZrO_2 C (111), M (110) etc, can be found in both the as-deposited and annealed EB samples, verifying that the films are polycrystalline structures.

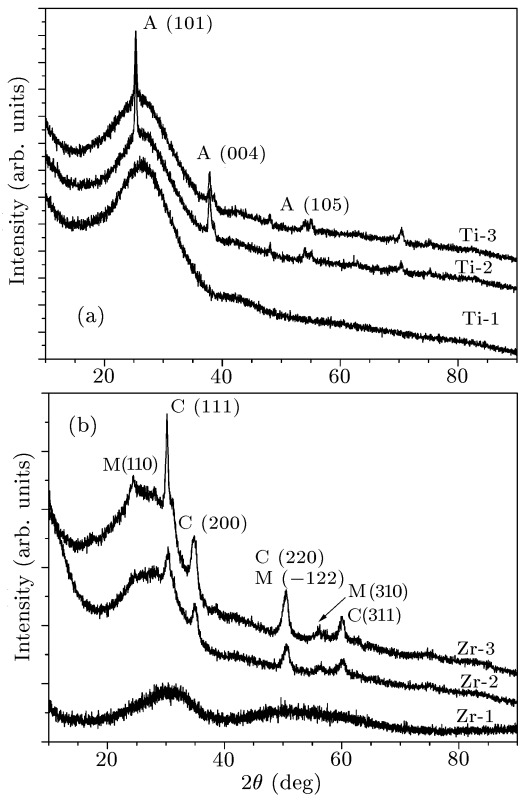
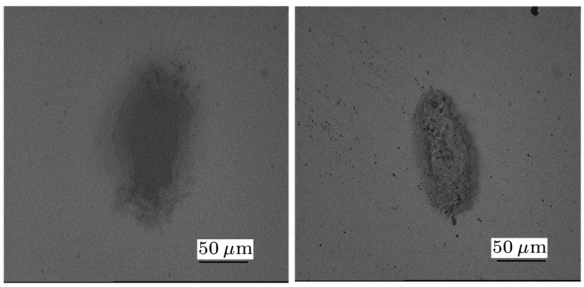


Fig. 2. XRD spectra of samples.

Table 3 shows the measured surface defect density, rms roughness, absorption and LIDT of the samples. It can be seen that the sol-gel coatings have lower surface defect density, roughness, absorption and higher LIDT than those of the EB films. Compared with the absorption and LIDT results of the samples, a good relation, for which the sample has low (high) absorption will have high (low) LIDT, is established.

The typical laser damage morphologies of the samples are shown in Fig. 3. In the sol-gel sample Zr-1, the film is only slightly melted and has no clear edge of damage region, and has no apparent evidence of surface defect induced damages. In the EB sample

Zr-3, it can be found that the film within the damage region seems to be taken off completely down to the substrate so that a large damage area and a clear boundary are left, and the crater develops around several black spots, which are impurities or defects in the film.



(a) Zr-1 11.6 J/cm^2 (b) Zr-3 9.0 J/cm^2

Fig. 3. Optical micrographs of typical damage. (a) Zr-1 11.6 J/cm^2, (b) Zr-3 9.0 J/cm^2

Table 3 Measured surface defect density ρ, rms roughness σ, absorption A and LIDT.

Sample	Ti-1	Ti-2	Ti-3	Zr-1	Zr-2	Zr-3
ρ (/mm^2)	18	77	83	22	41	81
σ (nm)	1.69	2.70	3.23	1.20	2.99	3.13
A (ppm)	123.7	204.5	151.6	55.7	106.1	86.1
LIDT (J/cm^2)	6.0	4.0	5.0	11.0	6.0	8.0

From the above discussion, it can be concluded that the high OH group concentration and amorphous structure in the sol-gel coating result in their low refractive index and low packing density. The film microstructure is related to energetic conditions during the film growth. The low temperatures sol-gel deposited atoms have low energy or mobility, and the film will contain more microvoids or pores. These voids create a low packing density that results in a low refractive index film. During annealing, thermal energy provides the mobility of the atoms and ions, so the loose columns become denser after annealing, which increases the refractive index and packing density of the film. This is the reason why OH disappears in Ti-3 compared with Ti-2, as seen in Fig. 1(a).

It is widely known that laser-induced damages in optical films are often a problem of defects, located on the surface and bulk of coatings.[15] Thus, surface and coating quality are major factors that limit performance. The amorphous structure of sol-gel film also contributes its high LIDT. It can be explained by the increase of surface roughness and inhomogeneity in films due to the crystallization of materials. The inhomogeneity is potential source of laser damage because they may act as defects that become initiation sites for laser damage. The porous structure of sol-gel films tends to be more favourable to energy relaxation, which also contributes to film's high LIDT. Tables 2 and 3 also show that the low absorption of the sol-gel film is another factor for its high LIDT. Since the EB films always have non-stoichiometry defects[16] and more surface defects, which are the absorption centres and damage initiation of high-power laser coating.

In conclusion, the film structure, OH group concentration and absorption have significant influence on optical properties and LIDT of films. The sol-gel films have lower refractive index, packing density and roughness than EB films due to their amorphous structure and high OH group concentration in the film. The high LIDT of sol-gel films is mainly due to their amorphous and porous structure, and low absorption. LIDT of the EB film is considerably effected by defects in the film, and LIDT of the sol-gel deposited film is mainly affected by residual organic impurities and solvent trapped in the film.

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