Optical characteristics of NUV-VIS-NIR transparent Zr-Si-B-N hard films for protection of optical and laser devices

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Abstract. Optically transparent Zr–Si-B-N films on quartz plates were manufactured by direct current magnetron sputtering of multiphase ZrB2·50%ZrSi2 ceramic cathode. Structural investigations have been carried out using X-ray diffraction analysis, scanning electron microscopy, and glow-discharge optical-emission spectroscopy. The dependences of optical properties including transmittance, reflectivity, and refractive index, vs. wavelength were determined by spectrophotometry. Films exhibited amorphous structure, average mechanical properties (hardness of 11 GPa, elastic modulus of 135 GPa, elastic recovery of 53%) and demonstrated transmittance up to 90% and reflectivity ~15%.

Introduction

With the advent of high-power and high-energy laser systems, interest has increased in the development of thin optical films that are resistant to the intense effects of a high-power laser. In [1-3], the mechanisms of laser damage to films for air and vacuum media were revealed. In a vacuum environment, when exposed to a laser, the material melts, while in an air environment, higher thermal conductivity leads to deformation of the material and peeling of the coating in areas damaged by the laser as a result of heating the material. To attenuate the laser power, composite polymer films [4,5] and films based on organic dyes [6] obtained by centrifugation are usually used. However, defects and contamination of such films are critical factors for the laser-induced damage threshold (LIDT) [7]. To eliminate this disadvantage, the ion-beam sputtering (IBS) method, which is related to physical deposition methods (PVD), is used for deposition of optical films [8]. For example, the LIDT of a multilayer optical film increases by 20 times due to the application of the top layer by the IBS method [9]. Note that the recent use of ion sputtering processes in combination with ion cleaning of the substrate surface significantly improved the morphology of film and their structure, which has reduced the absorption in films and increased the LIDT. This category of methods also includes the magnetron sputtering (MS) method, which makes it possible to obtain low-defect dense films with high adhesion strength [10, 11]. The MS method is used to obtain coatings with high oxidation resistance and thermal stability [12, 13], which will increase the stability of optical films when exposed to a laser in a vacuum environment. At the same time, the high adhesion obtained due to ion cleaning of the surface before MS will reduce the surface defects and increase the resistance to the delaminations during laser exposure in the air. Note that oxide-based protective films are too brittle and posses limited crack-resistance. Other hand, non-oxide ceramics have high mechanical properties, wear- and erosion
resistance. N-doped ZrB$_2$ films with high transmittance were studied in our previous work [14]. Alloying by Si improves the oxidation resistance of films [15]. Transparent films of non-oxide refractory compounds can be used also for protection of solar cells, solar mirrors, illuminators of aircraft or space transport etc. from the erosion failure due to microparticle (sand, ice, micrometeoroids) bombardment.

The aim of this work is investigation of structure and optical properties of Zr-Si-B-N films obtained by magnetron sputtering of ZrB$_2$-50% ZrSi$_2$ target. Films deposited using this target showed hardness ~20 GPa, elastic modulus ~270 GPa, elastic recovery of 57%, and oxidation resistance >1200°C [16].

1. Experimental part

The ZrB$_2$-50% ZrSi$_2$ target was synthesized from exothermal powder mixture using self-propagating high temperature synthesis. The typical scheme of vacuum chamber of PVD apparatus is presented in [17]. The targets were subjected to DC magnetron sputtering (current 2 A, voltage 500 V) in pure nitrogen (99.999%). The total pressure was maintained at 0.1-0.2 Pa. The diameter of targets was 12 cm and the target to substrate distance was 8 cm. Deposition time was kept constant at 30 min. Plates of fused quartz, 3x3 cm in size, were used as a substrate material. The substrates were cleaned ultrasonically in isopropyl alcohol for 5 min, after which they were etched for 5 min in a vacuum chamber by Ar$^+$ ion with average energy of 2 keV.

The film compositions were determined from the elemental depth profiles obtained by glow discharge optical emission spectroscopy (GDOES) using a PROFILER 2 instrument (Horiba Jobin Yvon). The microstructure of films was examined by S-3400N Hitachi scanning electron microscope (SEM) equipped with a Noran 7 Thermo energy dispersive X-ray spectrometer (EDS). X-ray diffraction (XRD) patterns were recorded on D8 Bruker X-ray diffractometer using Cu-radiation. Mechanical properties were measured using Nanohardness tester (NHT) from CSM Instruments at load of 4 mN.

Cary 5000 spectrophotometer manufactured by Agilent Technologies with an automatic universal measurement accessory UMA (Universal Measurement Accessory), was used for optical study. The transmission (T) and reflection (R) spectra of the fused quartz substrate and Zr-Si-B-N film on quartz were measured in the wavelength range 200-2500 nm at angles of incidence (0-50 ° for transmission) and (10-50 ° for reflection) in 10 ° increments in unpolarized light. The refractive index (N) was calculated using the Cauchy equation. The transmission and reflection measurement scheme is shown in figure 1. The ability to move the detector around the sample holder allows you to measure different parameters without changing the shooting area on the sample.

![Figure 1 - Measurement schemes for reflection (a) and transmission (b) (Images)]
2. Results and Discussion

The EDS, SEM, NHT, and XRD data are presented on Fig. 2. The chemical compositions of Zr-Si-B-N film according to the EDS data has been found like, at.%: 6.8 Zr, 6.0 Si, 6.5 B, 55.4 N, 0.7 Al, 16.1 O, 8.4 C. This method probably gives incorrect data for light elements such as boron, oxygen and carbon. Aluminum detection may be due to the fact that the signal excitation region affects not only the film, but also the holder from Al. The EDS and GDOES analysis showed that main elements (Zr, Si, B, N) were homogeneously distributed through the coating thickness (Fig. 2a) and total concentration of O+C is lower than 5 at. %. Impurities presence is explained by their traces either in the targets or in the residual gas in the vacuum chamber. The cross-sectional SEM image of the film is shown in Fig. 2a (insert). The thickness of film was found to be 1.2 µm. According to the SEM the film demonstrated dense and homogeneous structure. XRD study revealed the amorphous nature of Zr-Si-B-N (Figure 2b). The average indentation curves of penetration depth vs. load obtained by Nanohardness Tester are shown in Fig. 2c. It can be seen that at load of 4 mN, the indenter penetrates to a depth of about 123 nm. The calculation using Oliver and Pharr algorithm showed that coating demonstrated relatively high hardness of 11 GPa, elastic modulus of 135 GPa and elastic recovery of 53%.

![Figure 2](image-url)

**Figure 2** – SEM-EDS (a), XRD (b), and NHT (c) data for Zr-Si-B-N films

Figures 3-5 show the measurement data of spectrophotometry. Figure 3 shows the dependence of the transmittance on the wavelength for an uncoated quartz substrate and for quartz with a Zr-Si-B-N film at normal incidence and an angle of 20 degrees. It can be seen that in the wavelength range of 300-2500 nm, quartz substrate has a consistently high transmittance of 90-92% at different angles of inclination. The film deposited on a quartz substrate has lower T values of about 80%. Thus, the film's own T can be estimated as 90%. The angle of inclination does not significantly affect the values. We can also note a slight decrease in T at wavelengths less than 500 nm.

Figure 4 shows the data on reflection coefficient. The values are close to zero over the entire wavelength range and tilt angles for the quartz substrate. At the same time, the film is characterized by values of 12% at 400-2500 nm and ~4% at wavelength values less than 400 nm.
Figure 3 – Transmittance (%) vs. wavelength (nm) for quartz substrate and Zr-Si-B-N film on quartz

Figure 4 – Reflectance (%) vs. wavelength (nm) for quartz substrate and Zr-Si-B-N film on quartz

Figure 5 – Refractive index vs. wavelength (nm) for Zr-Si-B-N film

Interference patterns are observed on the spectral angular dependences of transmission and reflection of the film deposited on quartz at normal incidence and 20°, which allowed us to determine such parameters as refractive coefficients and their dispersion dependences. The values of the refractive
The refractive index gradually decreases from 2.64 to 2.17 as the wavelength increases from 470 to 1037 nm (Fig. 5). Thus, oxygen-free films with high optical characteristics were obtained. In the future, it is planned to increase the transmittance of films at small wavelengths due to additional doping. Also, the next step is to evaluate the erosion resistance and heat resistance of the films.

**Conclusion**

Zr-Si-B-N films with a X-ray amorphous structure and uniform distribution of elements through the coating thickness were deposited onto quartz substrates by magnetron sputtering of composite ZrB$_2$-50%ZrSi$_2$ target produced by the self-propagating high-temperature synthesis method. The films had hardness of 11 GPa, elastic modulus of 135 GPa, and elastic recovery of 53%. The Zr-Si-B-N films showed a transmittance up to 90%, a reflection coefficient of 4-12%, and a refractive index of 2.17-2.64 depending on the wavelength.

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