Effects of Dimethyl Formamide on Laser-induced Damage to SiO_2 Films Prepared by the Sol-gel Method

Pei-Tao GUO[a,*], Yu-Hong MAN[b], Yong-Ping ZHANG[c]

Faculty of Materials and Energy, Southwest university

[a]guopeitao@hotmail.com, [b]manyh05@swu.edu.cn, [c]zhangyyping@yahoo.com

*Corresponding author

Keywords: SiO_2 Films, Dimethyl Formamide (DMF), Laser-induced Damage Threshold (LIDT), Morphology.

Abstract. Monolayer SiO_2 films with various dimethyl formamide (DMF) concentrations were prepared on BK7 glass by the sol–gel method. The refractive index and physical thickness of the SiO_2 films were calculated using the transmission spectra of the samples. Laser-induced damage threshold (LIDT) results showed that the LIDTs of the SiO_2 films increased with increasing DMF concentration. Differences in LIDT were induced by the SiO_2 microstructure and differences in porous ratio attributed to variations in DMF concentration. Addition of DMF can improve film pore structures, produce uniform silica particles, improve the stress distribution within films, and generate porous structures that provide more space for stress relaxation during laser radiation. The damage morphology of the SiO_2 film was typically caused by defects.

Introduction

Dimethyl formamide (DMF) has a low molecular weight, high dielectric constant, electron donor properties, and the ability to form complexes. It is an organic liquid with low vapor pressure and can reduce the formation of fractures during gel drying processes to control pore size. It is also used as a template [1]. During the preparation of sol, addition of chemical additives can improve the gel pore structure, produce uniform sol–gel particles, improve the stress distribution within the gel during solvent evaporation, delay the evaporation of the fluid phase to some extent to generate a uniform film pore size distribution, and render the film difficult to crack [2]. Without additives, particles become composed of a gel network and the network gap size becomes non-uniform. Furthermore, the distribution of stress upon gel drying is uneven, which leads to the uneven distribution of film pore sizes and film cracking. Nanoporous SiO_2 films prepared by the sol–gel process are the most common optical anti-reflective coatings used in high-power laser systems. These films have high porosity, continuously adjustable refractive indices, low density, and high laser-induced damage thresholds (LIDTs) [3,4].

In this study, we prepared SiO_2 films on BK7 glass by the sol–gel method and added DMF. The optical properties and morphology were characterized by spectrophotometry and scanning electron microscopy. Laser-induced damage of the samples was tested in 1-on-1 mode according to ISO standard 11254-1, and a Nomarski microscope was used to characterize the morphology of damage sites.

Experimental

Sample Preparation

Tetraethylorthosilicate (TEOS, analytically pure) was used as the silica source, and ammonia water (28%) was used as the catalyst. A $TEOS:H_2O:C_2H_5OH:NH_4OH$ mixture with a molar ratio of 1:2:37:0.6 was used. The mixture was stirred at 60 ℃ for 5 h, mixed with various amounts of DMF (5%, 10%, 20%, and 30% in volume), stirred at 60 ℃ for 1 h, cooled to room temperature, and then aged for several days. The mixture obtained had a light blue color and was heated to reflux at 80 ℃

until the color of wet pH indicator paper above the outlet change from blue to yellow. Refluxing ejects the remaining ammonia in the mixture, thereby enhancing the stability of the silica sol.

Coatings were deposited onto clean BK7 glass substrates by the dip-coating method. The temperature ranged from 20 ℃ to 25 ℃, and the humidity was 60%. The speed used was 9 cm/min. Heat treatment was conducted for 1 h under 450-500 ℃.

Characterizations

Damage of the samples was tested in 1-on-1 mode according to the ISO standard 11254-1. A Neodymium-doped Yttrium Aluminium Garnet (ND:YAG) 1064 nm laser system in TEM_{00} mode and with 12 ns pulse width was used. The laser beam was focused on the target plane normally and adjusted by an attenuator comprising a half-wavelength plate and polarizer.

The surface and cross-sections of the films were examined using a field emission–scanning electron microscope (JSM-6700F). Optical transmission spectra were obtained at an angle of incidence of 90 ° with a UV-visible spectrophotometer (UV755B). The errors for transmittance and incident wavelength were <0.01% and 1 nm, respectively. A Nomarski microscope was used to determine whether or not the radiation sites had been damaged.

Results and Discussion

Effects of DMF Concentration on the Optical Property of SiO2 Films

The refractive index and physical thickness of the SiO_2 films were calculated from their transmittance (Fig. 1) using the method reported in [5]. The results in Table 1 show that the refractive indices of the films with added DMF, especially which with 10% DMF, are lower than those of dense SiO_2 films without DMF. SiO_2 films prepared by the sol–gel method may be ideal low-refractive index materials. The sol–gel method is a process for adjusting the refractive index of SiO_2 films [6].

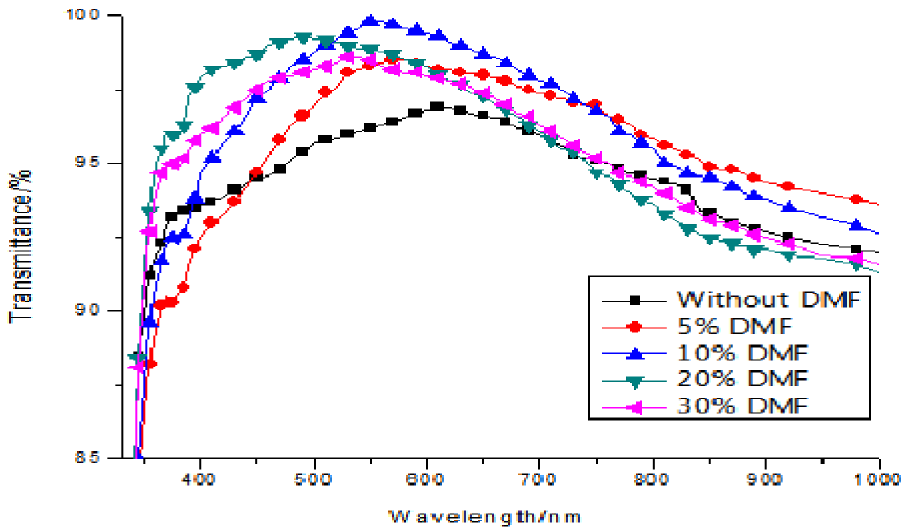
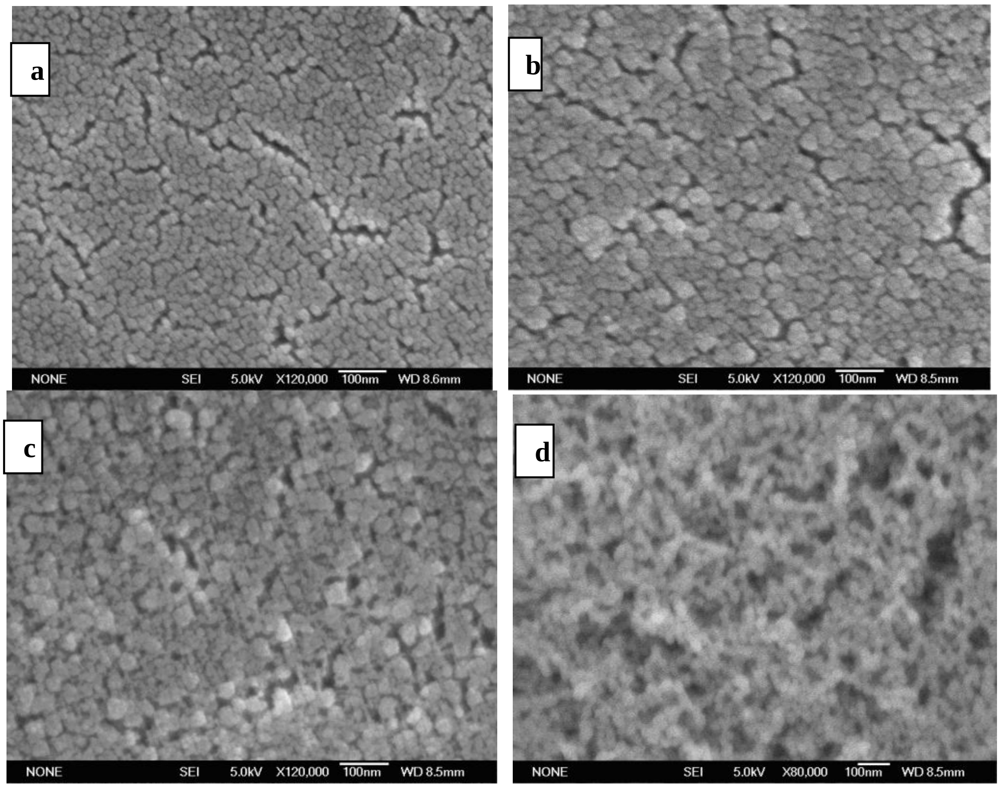


Fig.1 Effects of DMF concentration on the transmittance of SiO_2 films

Effects of Dimethyl Formamide Concentration on the Morphology of the SiO_2 Films

Fig.2 shows that the film with 5% DMF is packed with small balls and has obvious cracks on the surface. The film with 10% DMF is packed with small balls and has a few short cracks on the surface. The film with 20% DMF is packed with small balls and almost has no cracks on the surface. The film with 30% DMF is composed of clusters of small balls and has no sharp cracks on the surface. Moreover, the porous ratio of the SiO_2 films increased with increasing DMF content. The difference in morphology shown in Fig.2 is related to the DMF concentration and reactions between DMF and the SiO_2 particle surface.



a, 5%; b, 10%; c, 20%; and d, 30%

Fig.2 Effects of DMF concentration on the morphology of the SiO_2 films:

DMF has a planar configuration. Two electrons on the carbonyl group are delocalization electrons. Its C–N bond has a double-bond character; thus its two methyl C–N rotation barriers, as well as the two methyl groups, are different. DMF is a highly polar molecule because of the presence of N, O, and H and can be both a hydrogen bond donor and acceptor [7]. DMF molecules on the surface of particles in the sol exhibit hydrogen bonding with the sol particle surface and –OH group and have space-shielding effects to prevent collisions between the sol particles and further agglomeration. DMF also enhances network formation and promotes uniform distribution.

The addition of DMF also exerts dilution effects on silica colloids. The nucleophilic reaction of DMF with ethanol decreases the hydration between water and ethanol, resulting in more free water. DMF then combines with hydrolysis intermediates, which reduces the chemical activity of products (Si $(OC_2H_5)_{4-x}$, $(OH)_x$, and Si_xO_y (OH)), inhibits hydrolysis, and decreases the polycondensation rate. Increases in DMF content result in a corresponding increase in free water and decrease in sol concentration, which decreases the sol viscosity and induces uniform silica particle distribution in SiO_2 films. Sol coatings with too high or too low viscosity are not conducive to film formation. To obtain high-quality uniform films with stability, the added amount of DMF should be controlled within the viscosity range of the coating. According to the principle of gel drying, DMF renders the gel surface hydrophobic and reduces the driving force of textural damage. With increasing DMF content, the potential of colloid particles (ζ) increases and the barrier increases in the sol, leading to the increased stability of the sol. When the DMF concentration is higher than 30%, the sol viscosity is too low to form uniform films on the glass substrate.

Effects of DMF concentration on the LIDT of the SiO_2 films

Fig.3a presents a typical fitting curve showing the LIDT, which indicates the damage probability, and laser energy. The LIDTs of the SiO_2 films with different DMF concentrations are shown in Fig. 3b. Addition of DMF greatly improved the LIDTs of the SiO_2 films. The LIDT is obviously related to the microstructure and surface quality of the SiO_2 films, as confirmed by the experimental results in Section 3.2. Films packed with small balls and few cracks have high LIDTs. Films packed with small balls have low rigidity. Thus, a laser with enough energy radiating into the surface can induce thermal absorption, and the material consequently expands. Films with low density have low thermal conductivity and, thus, smaller heat-affected zones. Films with low rigidity have high collapsibility and can more easily release the stress caused by material expansion.

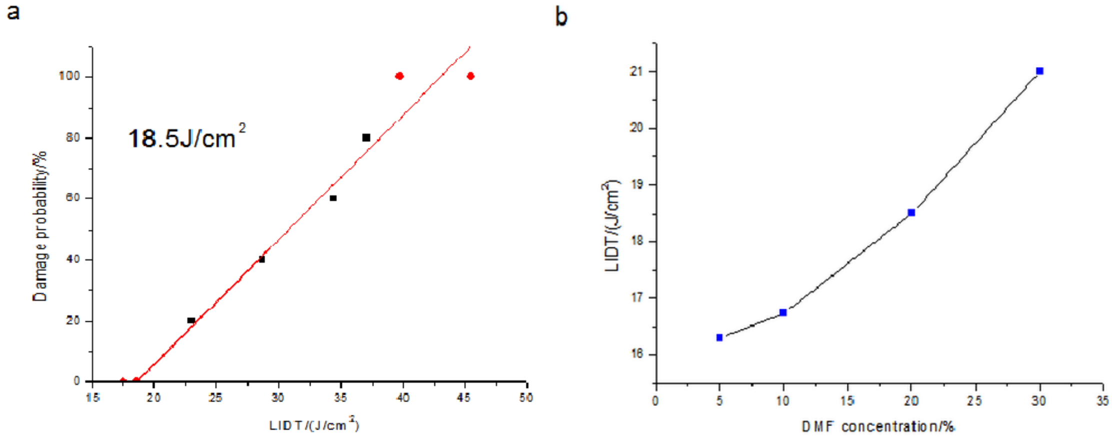


Fig. 3 Effects of DMF concentration on LIDT

Damage Morphology of the SiO_2 Films

The damage morphology of the SiO_2 films with 20% DMF is shown in Fig. 4. The damage originates from defects. The defects are surrounded by plasma scalds, which result from the presence of plasma during the damage process. No obvious ablations and cracks are observed around the defect and heat-affected zone because the uniform porous structure of the film allows the release of stress and volume expansion during the damage process. Given that the film is porous, the defect particles have some space through which pressure can be released. The pressure exerted inside the film or interface by the moving particles can dissipate, thereby reducing the probability for laser damage.

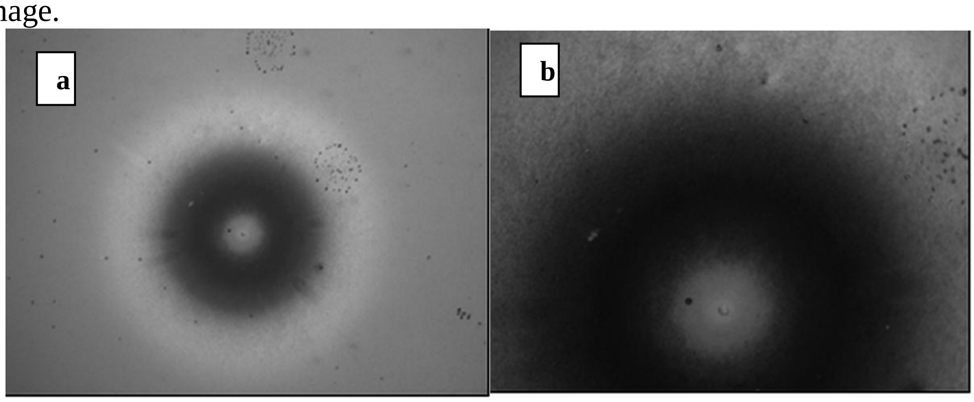


Fig.4 Damage morphology of the SiO_2 films

Conclusions

In this study, the optical properties and LIDTs of monolayer SiO_2 films were investigated. The sol–gel method with addition of DMF can be used to adjust the refractive index of SiO_2 films. As shown by the experimental results, the LIDT is related to the porous ratio of the layers and increases with increasing DMF content. The increase in LIDT is a synthetic effect of the porous ratio and microstructure of the SiO_2 films.

Acknowledgements

The author would like to express his gratitude to the Fundamental Research Funds for the Central Universities (XDJK2015C065) and Foundation of Southwest of University (SWU111055).

References

[1]Lee KH, Kim HY, Khil MS, Ra YM, Lee DR. Characterization of nano-structured poly(-caprolactone) nonwoven mats via electrospinning. Polymer 2003;44:1287-1294.

[2]Ya-YuHuang, Kan-SenChou. Studies on the spin coating process of silica films. Ceram Int 2003;29:485-493.

[3]Guo YJ, Zu XT, Jiang XD, Yuan XD, Xu SZ, Lv HB, et al. Effect of ammonia treatment on laser-induced damage of nano-porous silica film. Optik-International Journal for Light and Electron Optics 2009; 266(12):3190-3194.

[4]Guo YJ, Zu XT, Jiang XD, Yuan XD, Zheng WG, Xu SZ, et al. Laser-induced damage mechanism of the sol–gel single-layer SiO_2 acid and base thin films. Nuclear Instruments and Methods in Physics Research Section B 2008; 83(4):1426-1429.

[5]Zhang GY, Xue YY, Guo PT, Wang HH, Ma ZJ. Optical properties and microstructure of Ta_2O_5 thin films prepared by ion assisted electron beam evaporation. Journal Wuhan University of Technology, Materials Science Edition 2008;23(5):632-637.

[6]Wu G, Wang J, Shen J, Yang T, Zhang Q, Zhou B, et al. A new method to control nano-porous structure of sol-gel-derived silica films and their properties. Mater Res Bull 2001; 36(12):2127-2139.

[7]Sun G, Xu A, He Y, Yang M, Du H, Sun C. Ruthenium catalysts supported on high-surface-area zirconia for the catalytic wet oxidation of N,N-dimethyl formamide. J Hazard Mater 2008; 156:335-341.