A moisture-resistant antireflective coating by sol-gel process for neodymium-doped phosphate laser glass

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Using methyl triethoxysilicane as precursor, a moisture-resistant coating for neodymium-doped laser glass was developed by the sol-gel process. Colloidal silica was added in coating solution as modifier. The refractive index of this coating varied from 1.31 to 1.42. A porous antireflective (AR) silica coating with the index of 1.27 was coated on the moisture-resistant coating surface. The two-layer coating possessed transmission up to 99.1% at wavelength of 966 nm, surface root-mean-square (RMS) roughness of 1.245 nm, and roughness of average (RA) of 0.961 nm. In the case of laser of 1053-nm laser wavelength and 1-ns pulse duration, the damage threshold of the two-layer coatings was more than 15 J/cm^2.

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As a mature technique in inertial confinement fusion (ICF) field, the sol-gel coatings have been widely applied on the optical elements, such as neodymium-doped phosphate laser glass amplifier. In order to improve the quality and stability of laser beam of the amplifier, coatings with both moisture-resistant and antireflective (AR) functions should be coated on the surfaces of the phosphate glass amplifier because phosphate glass is hydrophilic.

As a pioneer, Thomas[1,2] in LLNL (Lawrence Livermore National Laboratory) researched and developed the AR and moisture-resistant (MR) coatings by the sol-el process over twenty years. Belleville[3] improved laser properties of the AR coating. Tang[4], and Jia[5] *et al.* also studied single-layer and two-layer AR coatings on optical glasses, respectively.

The moisture-resistant coating based on methyl triethoxysilicane applied in "Shenguang-II" system, the ICF laser in China in the past, had high laser damage threshold and good MR property, but the thermal expansion of the coating much differed from the matched substrate so that the inner stress between the coating and the substrate was easy to be induced, leading to worse abrasion-resistant performance and brittle fracture. At the same time, the transmission of this coating was not high enough and its damage threshold value became deteriorated gradually during the long period of use.

Selecting methyl triethoxysilicane as precursor in present paper, polysiloxane solution added by base catalyzed silica colloidal as modifier was developed. Using this sol-colloidal inorganic-organic composite, modified MR coating was made on the surfaces of the neodymium-doped phosphate glass. Brittle fracture property the coating was eradicated, together with improvement of abrasion-resistant performance. A layer of AR coating was coated on the formed MR coating, for the sake of higher transmission and longer service life.

Silica colloidal (3 wt.-%) was prepared from hydrolysis and condensation of tetra-ethyl-silicate (TEOS) in water and ethanol catalyzed by ammonium hydroxide in the molar ratio of 1:2:34:0.6 under ambient conditions. The mixture was stirred 6 h and then aged in a closed glass container at 50 °C for several days. The colloidal suspension was refluxed for 24 h to remove ammonia. It was finally filtered through a 0.2 μm membrane filter prior to use.

Poly organic silicate sol was synthesized from hydrolysis and condensation of Methyl tri-ethyl-silicate in water and ethanol catalyszed by hydrochloric acid in the molar ratio of 1:6:2:0.01. The water in mixture was removed by distillation. The pre-polymer sol of organic silicate was diluted in anhydrous ethanol for suitable coating thickness. The diluted sol was filtered through a 0.2 μm membrane prior to use.

Poly organic silicate sol and silica colloidal suspension were mixed and stirred in a closed glass container, in proportion to give 90%, 80%, 70%, 60%, 50%, 40%, and 30% in the total, leaving 10%, 20%, 30%, 40%, 50%, 60%, and 70%, respectively.

The MR coating was carried out by sol-colloidal mixture on the surfaces of different substrates, size of $\Phi 35\times 4$ (mm), using spin or dip coater in a clean room. After coating, the samples were dried at 60 °C for 30 min. The AR coating was carried by colloidal silica suspension on the formed MR coating. Coating thickness was varied either by changing the spin speed or by changing the concentration of the coating solution. All samples were heated briefly to 150 °C over a period of 2 h.

Moisture-resistant coatings prepared from the sol-colloidal mixture with the ratio of 50%:50%, were dip-coated on single-crystal silicon wafer of Φ30 mm. The structures of coatings after heat treatment are investigated by Fourier transform infrared spectroscopy (FTIR) spectra, as shown in Fig. 1.

In this the following assignment[6−8] was proposed for the $Si(OC_2H_5)_4/CH_3Si(OC_2H_5)_3/H_2O/C_2H_5OH$ system: 3400 cm^{-1} (−OH stretching), 2987/2948/2896 cm^{-1} (C−H stretching), 1268 cm^{-1} (Si−C stretching), 1080 cm^{-1} (Si−O−Si and Si−O stretching).

It is observed that a majority of hydrogen-bonded OH groups[6] exists coating after heat treatment at 150 °C for 2 h. With the cure temperature increasing, −OH and

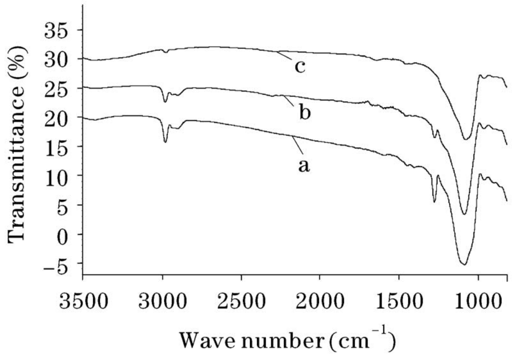

Fig. 1. FTIR transmission spectra of coatings. (a) From poly organic silicate sol, heated 150 °C for 2 h; (b) and (c) from sol-colloidal mixture with the ratio of 50%:50%, heated at 150 and 400 °C for 2 h, respectively.

O−H groups interact, and dehydration occurs. This reinforced Si−O−Si network structure. The infrared (IR) spectra also reveal that −OH groups decreased with increasing the cure temperature, whereas it still shows small residual feature after cure at 400 °C. The CH and Si−C groups exist after 150 °C treatment and disappear after 400 °C. The Si−O−Si network structure is strengthened and coatings are condensed as the heat treatment temperature increasing.

The neodymium-doped phosphate glass has strong absorption in visible light band while K9 glass does not have, and K9 glass has approximate the same refractive index to the former (1.51—1.52), so it is taken as substitution substrate when we measure transmission. The poly organic silicate sol and silica colloidal suspension were mixed in given proportion. The single layer MR coating was dip-coated on K9 glass substrate. Reflective index of the coating heated at 150 °C for 2 h was measured. The index was calculated from the following standard formula, where n_c was the coating refractive index, n_1 was the substrate index (1.52), n_2 was the index of air (1.00), and $R = \left[\frac{n_c^2 - n_1 n_2}{n_c^2 + n_1 n_2}\right]^2$ was the maximum reflection from one surface[2].

As shown in Fig. 2, refractive index of coatings decreased with the increasing of colloidal silica percentage, varying from 1.31 to 1.42. The maximum transmission also reduced, however, it was higher than 92% of the transmission of bare K9 glass. In order to obtain two-layer coatings with matching refractive index, we can select certain percentage mixture solution according to requiring refractive index in the range of 1.31—1.41.

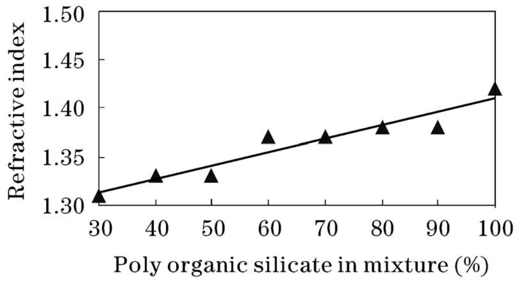

Fig. 2. Refractive index of coating plotted versus poly organic silicate percentage.

Some clouding was observed on coating when poly organic silicate sol percentage was less than 30%. It might be because that organic silicate could not compose adequate network when silica colloidal was predominant. Under this condition, organic silicate structural residue stacks on colloidal silica particles after cure.

A controlled experiment was carried out in order to test deliquescent-proof performance of single layer MR coating. Half of phosphate glass substrate area was coated by sol-colloidal mixture, 50% to 50%, while the other half was bare. After cure, this sample was hanged in a closed container, constant temperature at 80 °C and relative humidity of 95%. 7 days later, there were some visible deliquescent speckles on the uncoated half of substrate, while none on the coated half. 14 days later, speckles on the coated half of substrate, shown in Fig. 3(a), were smaller than these on uncoated half, shown in Fig. 3(b). 28 days later, speckles on coated half increased in average size, shown in Fig. 3(c), while the uncoated half was full of speckle in large size, shown in Fig. 3(d). The microscope magnification was 50×.

Single layer MR coatings were coated on K9 class substrate by sol-colloidal mixture, 50% to 50%. After cure at 150 °C, it was left in a closed container at temperature of 20 °C, relative humidity of 97%. Engage angle and transmission were measured every seven days. The results are shown as Fig. 4. It indicates that the transmission

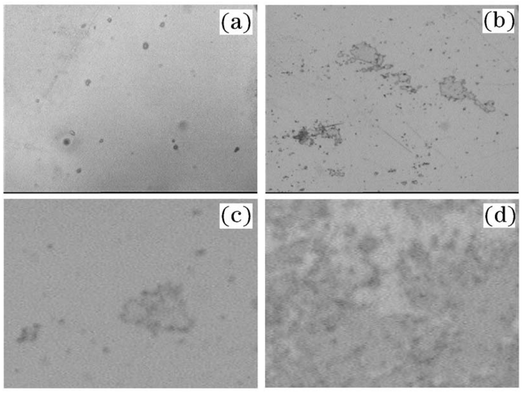

Fig. 3. Deliquescence speckles on substrate.

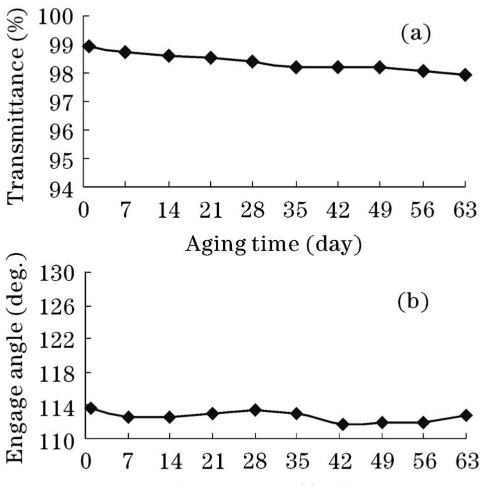

Fig. 4. Transmission and engage angle of coatings.

reduces but changes a little, about 1%, while engage angle is approximately unchanged during more than 60 days. There is no deliquescence speckle and clouding observed on coating.

Transmission spectra of two-layer coating on K9 glass and bare neodymium-doped phosphate glass substrate were shown in Fig. 5. In wide band from 600 to 1100 nm, the transmission of two-layer coating was high, the maximum up to 99.1% at wavelength of 966 nm.

Good surface roughness of coating benefited laser beam quality. The surface roughness of two-layer coating was shown in Fig. 6. The substrate was neodymium-doped phosphate glass. Figure 6(a) was surface morphology, and Fig. 6(b) was one cross section. The root-mean-square (RMS) roughness of coating surface was 1.245 nm and the roughness of average (RA) was 0.961 nm. They indicated that coating had excellent smooth surface.

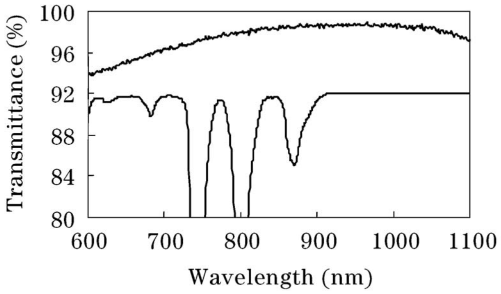

Fig. 5. Transmission spectra of coatings.

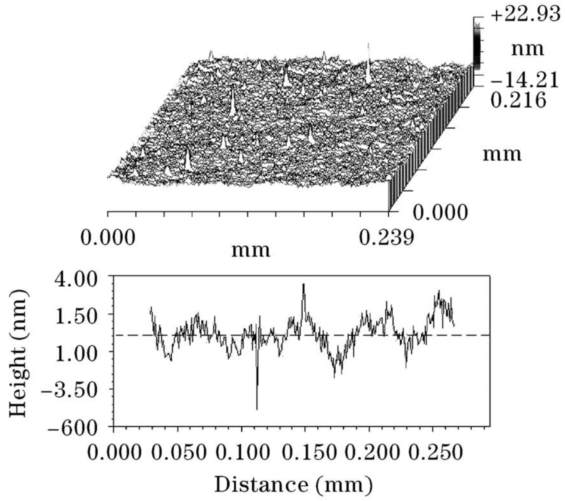

Fig. 6. Morphology of coating: surface and cross section.

The damage threshold of optical coating must be high enough in ICF laser system. If the damage threshold was low, coating would be damaged when high capacity laser passed. The laser damage threshold of two-layer coating on the surface of neodymium-doped phosphate glass was tested by a special laser facility. Measurements were carried out at 1053-nm laser and 1-ns pulse duration, the damage threshold was more than 15 J/cm^2.

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