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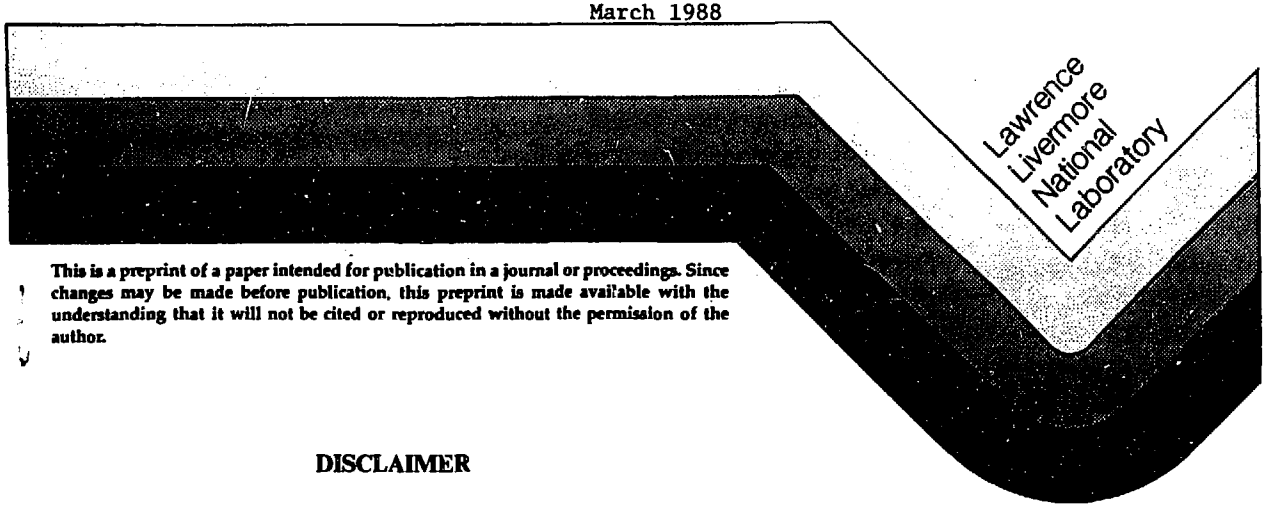

IMPROVED ADHESION FOR SiO_2 PARTICLES ON SILICA SUBSTRATES USING HELIUM-ION IRRADIATION

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ABSTRACT

We have examined the effects of irradiation with 200 keV helium ions on the adhesion and optical transmission properties of 220 nm thick antireflective, optical coatings that consisted of layers of spherical, 20 nm diameter silica particles. In the as-deposited state these sol-gel coatings have very low adhesion to the fused silica subtrates. Results for adhesion and optical transmission have been obtained for doses of 10^{13}-10^{17} He/cm^2. Significant improvement in adhesion was found for doses exceeding about $2X10^{14}$ He/cm^2. Optical transmission measurements for wavelengths of 200-1200 nm showed increasing absorption with dose. We have evidence that the helium ions decompose various contaminants in the coating into two types of degradation products. One is volatile and the other remains in the coating as optically absorbing species. UV/oxidative-gas treatment effectively removes the absorbing species.

INTRODUCTION

The antireflective (AR) optical coatings of interest here are designed for use in high-power laser systems operating at 1064 nm. They are prepared from colloidal suspensions of spherically uniform, oxide particles and consist of layers of uniform, discreet particles, which have low resistance to abrasion. These coatings are easily damaged during cleaning by standard drag-wiping procedures. Although this low resistance to abrasion is not a critical problem in our present application, it could be detrimental in the future. Thus, we have attempted to improve the resistance to abrasion by increasing the particle/particle and particle/substrate adhesion using ionizing radiation. In addition, a more adherent coating may tolerate higher laser power densities before exhibiting damage.

We have previously shown that the adhesion of antireflective, porous SiO_2 coatings on fused silica substrates can be dramatically enhanced by irradiation with 200 keV helium ions to doses of 10^{14}-10^{17} He/cm^2 [1]. The term "stitching" has been used to describe such enhancement phenomena when the dominant energy deposition process at an interface is electronic excitation [2]. The term "mixing" is generally applied to situations where atomic displacements dominate and significant atomic exchange occurs across the interface. Since the coatings of interest consist of layers of spherical, 20-nm-diam silica particles, adhesion enhancement is required at both particle/particle and particle/substrate interfaces. We selected 200 keV helium ions as the ionizing radiation because (a) the implanted helium should readily diffuse out of the quartz substrate, (b) essentially all the energy deposited throughout the layer and at the layer/substrate interface was calculated by TRIM-86 calculations [3] to result in electronic excitation, and, hopefully, (c) the residual displacement damage in the silica near the end of range at the minimum dose required for acceptable adhesion would not significantly modify the optical transmission properties of the specimens.

In our earlier study, enhanced adhesion was observed for all the applied doses, and extrapolation of the dose-dependence of the optical transmission data suggested that doses below about $3X10^{13}$ He/cm^2 would not affect the transmission properties of the specimens over the entire wavelength range of 200-1200 nm. Thus, we have extended the dose range down to 10^{13} He/cm^2 in search of threshold doses for enhanced adhesion and for measurable levels

of optical absorption. In addition, we have performed studies designed to elucidate the nature of the increasing optical absorption with dose and the molecular species adsorbed on the particles of the high surface area coatings.

EXPERIMENTAL CONSIDERATIONS

Simple porous silica AR coatings on fused silica subtrates (5 cm diameter X 1 cm thick) were prepared by the application of a colloidal suspension of 20 nm, spherical silica particles in ethanol to one side of a substrate spinning at 1500 rpm at room temperature. Details of the fabrication of the silica particles have been published [4]. After evaporation of the ethanol, the coating was about 220 nm thick with a refractive index of 1.22 which corresponds to a porosity of about 50 percent because the refractive index of silica is 1.46. Half-coated specimens were prepared by simply rubbing the coating off one half.

For the irradiations, one specimen was mounted on each of four separate faces of a water-cooled, stainless-steel holder using three screws with washers; a thin layer of indium was inserted as a cushion between each specimen and the holder. The temperature rise in the surface region during the helium bombardment at current densities just below 1 $\mu A/cm^2$ (i.e. < 0.2 W/cm^2) did not exceed 85 C (the lowest temperature measureable by an infrared pyrometer) for doses up to $1X10^{16}$ He/cm^2. Our implanter was configured for uniform irradiation over a diameter of 7.62 cm. The uniformity of implantation was assessed by comparing the dose received in each of four Faraday cups at the corners of the raster. The maximum deviation in any one cup from the average dose in the four cups during any of implantations was <2 percent. After evacuation to less than $5X10^{-7}$ Torr, the irradiations were performed at a pressure of less than $2X10^{-6}$ Torr. In some cases we used a tantalum shutter to limit the irradiation to only one half of a specimen.

A quadrupole residual gas analyzer (RGA) was attached, via a 45 degree curved tube, to the implantation chamber to monitor the gases released during the irradiation. A sequence of spectra was recorded with a computerized data acquisition system. The net signal at any time (i.e. dose) for each detected species was determined by subtracting the signal existing just prior to the irradiation from that during the irradiation.

The adhesion of the coating to the quartz substrate was evaluated qualitatively using adhesive tape (i.e. Tuck Tape [5]). The tape was laid across each irradiated specimen, rubbed with a finger in a plastic glove to ensure good contact with the coating, and then slowly pulled away from the specimen with the tape being pulled back at about 45 degrees to the surface. The coating was considered "adherent" when the adhesive part of the tape remained on the coating, indicating that the bonds between the particles and the substrate and between particles were stronger than that between the backing of the tape and its adhesive. Apparently the porous nature of the coating and the flow characteristics of the adhesive resulted in a large area of contact and, effectively, good bonding between the particles of the coating and the adhesive. For cases not leading to separation of the adhesive from the backing of the tape, visual observation of interference colors was used to verify the presence of the coating.

After transmission measurements on the irradiated specimens, we exposed them to oxidative gases in the presence of ultra-violet (UV) light. Such exposures are known to remove organic contamination from surfaces [6]. In particular, we placed specimens on a hot plate at about 100 C for six hours in an environment of UV light from a low-pressure mercury vapor lamp and oxidative gases resulting from the bubbling of oxygen through aqueous hydrogen peroxide.

RESULTS AND DISCUSSION

Adhesion Measurements:

During tape tests of both the irradiated and non-irradiated halves of coated specimens exposed to doses of 0.1, 0.3, and $1.0X10^{14}$ He/cm^2, noticeably more force was required to remove the coating from the irradiated region than from the non-irradiated region. Adherence in the sense described above was not observed for the two lowest doses; however, regions of specimens irradiated to 10^{14} He/cm^2 were adherent. Combining these results with our previous higher dose results [1], which showed clear evidence of adherence for doses of $3X10^{14}$ He/cm^2 and above, we conclude that the threshold dose for adhesion must be about $2X10^{14}$ He/cm^2.

A measure of the persistance of the adherence was obtained from tape tests of a coated specimen after irradiation to $3.3X10^{15}$ He/cm^2. After 13 and 28 days exposure to laboratory air, the initially adherent coating was no longer adherent; however, the force required to remove the coating remained greater than that for non-irradiated coatings. Following irradiation to $1X10^{16}$ He/cm^2 and UV/gas treatment, tape tests on a half-coated specimen showed that the coating was still adherent after five days.

Gas Release Measurements:

Figure 1 shows the gases released during the initial part of the irradiation of a coated specimen. Since acquisition of a spectrum took about 20 seconds, each peak was measured at a different dose; thus, the first mass/charge (M/Q) = 2 peak and the M/Q = 44 peak occurred at doses of 0.06 and $1.07X10^{14}$ He/cm^2, respectively. The M/Q = 4 peak represents the helium background level. Our preliminary assignment of the major components of the other significant peaks to molecular species are (M/Q:molecule or fragment): 2:H_2, 12:C, 13:CH, 14:CH_2, 15:CH_3, 16:CH_4 (methane), 17:OH, 18:H_2O, 25:C_2H, 26:C_2H_2 (acetylene), 27:C_2H_3, 28:C_2H_4 (ethene) + CO, 29:C_2H_5 + COH, and 44:C_2H_4O (ethylene oxide) + CO_2. For reference, ethanol (C_2H_5OH or C_2H_6O) has a molecular weight of 46.

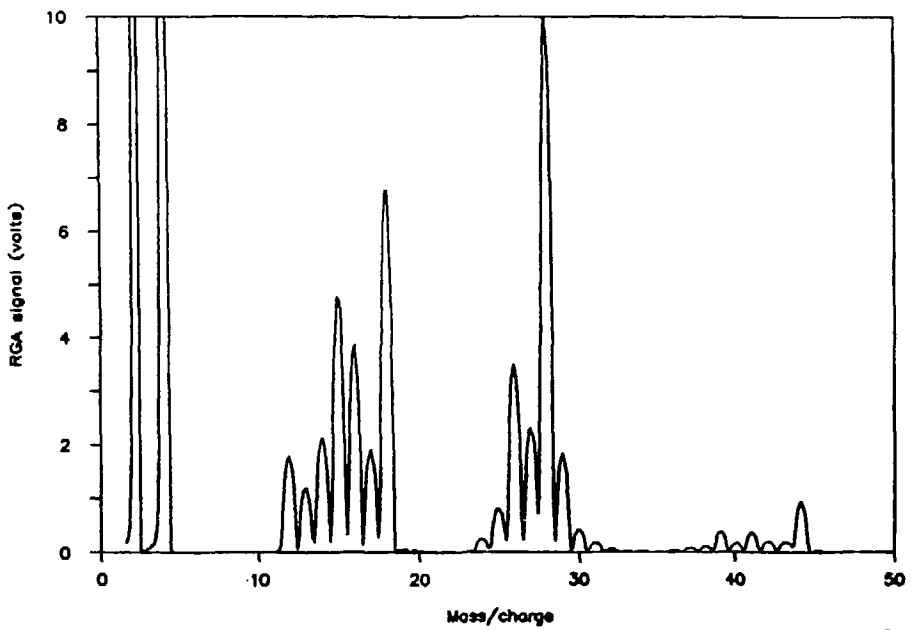

Fig. 1 Initial spectrum of gas released during irradition of 220 nm coating of SiO_2 particles on fused silica by 200 keV He^+.

Figure 2 provides the dose dependence of the net RGA signal for the key gases. Extrapolation of the data suggests that essentially all the gas release would be completed at a dose less than $4X10^{15}$ He/cm^2. For comparison, spectra taken during irradiation of a non-coated fused silica blank had a maximum net RGA peak (i.e. H_2) less than 0.8 volts. Although these data provide information on the gases released, the nature and amount of the molecular species and fragments remaining in the coating (i.e. on the particles) is unknown. However, the dose dependence of the gas release suggests that the residue would not change after a dose of about $4X10^{15}$ He/cm^2.

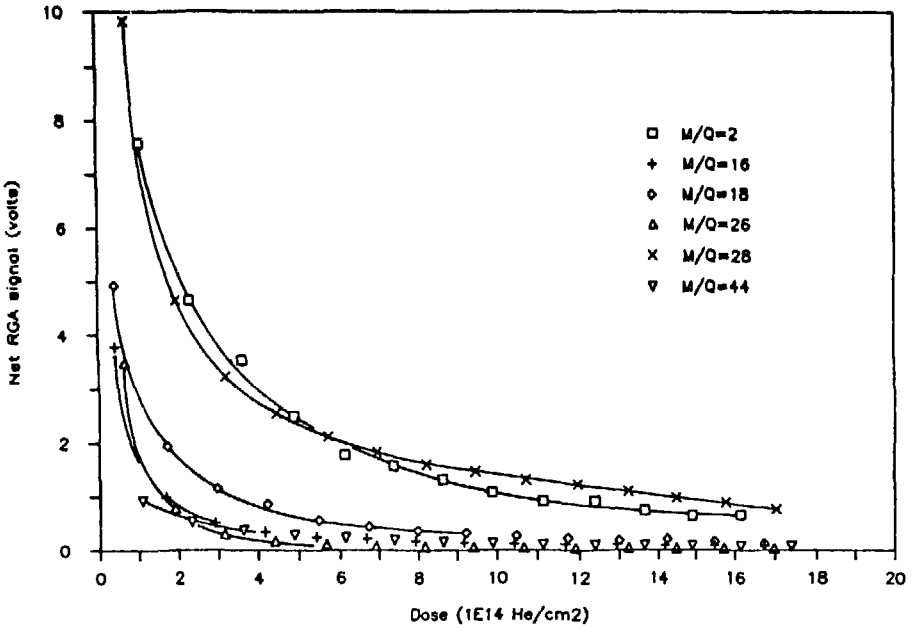

Fig. 2 Dose dependence of gas release during irradiation of 220 nm coating of SiO_2 particles on fused silica by 200 keV He^+.

Optical Transmission Measurements:

In our previous study we detailed the optical transmission for wavelengths of 200-1200 nm using a Perkin-Elmer model 330 spectrophotometer [1]; however, the most significant absorption was observed for the 200-800 nm range. Thus, we have now concentrated our attention to this latter range. Significant absorption was observed even for specimens irradiated to only low doses (i.e. 0.1, 0.3, $1.0X10^{14}$ He/cm^2); however, the UV/gas treatment resulted in essentially full recovery of transmission for wavelengths above 300 nm. Note that interpretation of low absorption for these high-surface area coatings at wavelengths below 300 nm can be clouded by atmospheric contamination. Following irradiation of a half-coated specimen to $1X10^{14}$ He/cm^2, the coated side exhibited considerable absorption below about 300 nm, whereas the uncoated side displayed only slight absorption below 300 nm. Above 300 nm the transmission through the uncoated side was not affected measurably by the irradiation.

Transmission results for a half-coated specimen irradiated to $1X10^{16}$ He/cm^2 are shown in Fig.3. For the uncoated side, the absorption resulting from irradiation is essentially recovered by the UV/gas exposure, indicating minimal effects from residual radiation damage in the fused silica substrate. The strong absorption found after irradiation of the coated side was greatly reduced by the UV/gas treatment (Fig.3b). However, compared to the as-

deposited coating, the treated coating displayed (a) shifts in the transmission maxima and minima that are indicative of a reduction in the coating thickness and (b) slightly reduced maxima and minima values that would be consistent with a change in the refractive index. Both changes could be explained by the previously noted increased coating density with dose [1]. In fact, some indication of this shifting and reduction of the maxima and minima can be seen in the transmission curves for doses of $0.1\text{-}1X10^{15}$ He/cm^2 in that previous study.

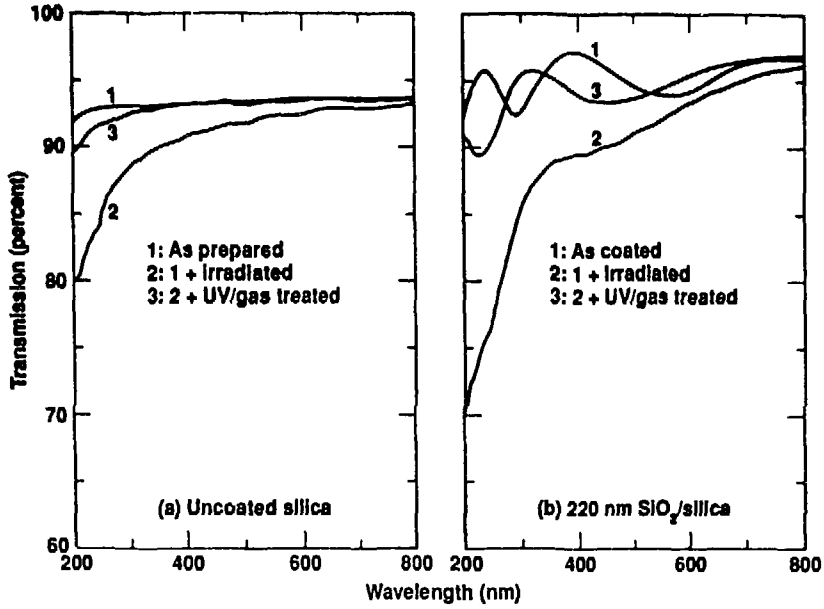

Fig. 3 Spectral transmission for half-coated fused silica specimen irradiated with 200 keV He^+ to $1x10^{16}$ He/cm^2. (a) uncoated side and (b) side coated with 220 nm coating of SiO_2 particles.

Processes Leading to Enhanced Adhesion:

Considering our present and previous [1] results, the observed enhancement of adhesion following helium-ion irradiation appears much more complicated than previously thought [1]. The complications can be attributed presence of the organic contamination products from the silica suspension used in the deposition of the coatings. Irradiation apparently both releases gases and leaves residues. Above a dose of about $4X10^{15}$ He/cm^2, very little additional gas was released and the as-irradiated transmission properties did not change appreciably. Both of these observations would be consistent with unchanged residue.

The major loss in optical transmission can be recovered by removal of the residue by the UV/gas treatment. However, after the treatment recovered most of the transmission, evidence of irradiation-stimulated compaction of the coatings was observed. Although adherence was not found following UV/gas treatment of as-deposited coatings, the treatment does not reduce the adherence of an irradiated coating.

As we discussed in our previous paper [1], a definitive understanding of the fundamental processes involved in stitching has evaded researchers, but two basically different mechanisms have been proposed to explain enhanced adhesion: (a) bond breaking and reconstruction across the interface [2,7-11] and (b) atomic intermixing caused by Coulombic ejections in dielectric materials like silica [10,12-14]. Both mechanisms may be operating during

helium-ion irradiation of our coating/substrate system; however, the process would be complicated by the presence of the contaminating species.

During the initial stages of the irradiation, some contamination was released and an optically asorbing residue was left, presumably on the surfaces of the particles and substrate. Thus, the as-irradiated adherence may have occurred across residue/residue, residue/SiO_2, and/or SiO_2/SiO_2 interfaces; however, the strength of the bonding and its survival during the UV/gas treatment suggests that the SiO_2/SiO_2 interfaces dominate. The 24 eV/A of electronic excitation deposited in silica by each 200 keV helium ion produces energetic electrons that can lead to increased surface reactivity [9]. Such enhanced surface reactivity could explain (a) the retention of residue on silica surfaces not in contact with other silica surfaces, and (b) the increased adhesion with dose, which may be a consequence of irradiation-induced removal of residue from the interface between particles or between particles and the substrate, allowing bonding at the SiO_2/SiO_2 interfaces.

CONCLUDING REMARKS

For 200 keV helium-ion doses greater than $2X10^{14}$ He/cm^2, the adhesion of SiO_2 particles on silica substrates is significantly improved. Since the presence of organic contamination from the silica suspension greatly complicates the interpretation of the data, the fundamental processes leading to the enhanced adhesion cannot be specified. Future irradiation studies should concentrate on pre-cleaned coatings (i.e. after the UV/gas treatment). Then determination of the electronic bonding states near the interfaces may be possible. Finally, investigations using protons have been initiated.

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