Surface modification of sapphire for IR window application

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ABSTRACT

Two surface modification techniques, a "super polish" (SP), and ion implantation, were evaluated for improving the mechanical performance of sapphire IR window material. Both techniques increased the average strength as measured by 4-point bend tests and were effective in preventing the propagation of surface flaws. Ion implantation improved the reliability at lower stresses more than the SP. Neither process significantly affected the IR transmission. The SP produced a smoother surface as shown by optical scatter measurements.

1. INTRODUCTION

Single crystal Al_2O_3 (sapphire) has high strength, good thermal shock resistance, low optical scatter, and excellent transmission at wave lengths between 0.5 and 5 μm . This combination of properties makes sapphire the material of choice for IR windows in many applications involving aggressive environments. Typical of most ceramics, however, the full realization of the high strength is limited by the relatively low fracture toughness. Many ceramic components fail by the propagation of surface flaws under applied tensile stresses.

Reliability and design stresses may be increased by eliminating surface flaws and avoidance of tensile stresses. The former might be accomplished by improved surface finishing techniques. A residual compressive stress in the surface may also be effective in healing or closing small surface flaws and also may counteract an applied tensile stress. A "super polishing" technique developed by Laser Power Optics (San Diego, CA) was evaluated as an example of the first approach. Ion implantation was used to introduce a residual surface compressive stress and to harden the surface of sapphire.

The use of energetic ion beams to modify the near-surface region of materials has been investigated extensively in recent years. It is an accepted industrial procedure for doping semiconducting materials and for improving the wear, erosion, and oxidation resistance of metallic alloys. The process consists of bombarding the surface of a material in a vacuum chamber with a beam of electrostatically accelerated ions. Because of the kinetic energy, the ions become embedded to a depth controlled by the incident ion energy for a given ion-target material combination. The range is generally less than a micrometer. The ion comes to rest by dissipating its kinetic energy in elastic collisions that may displace target atoms (ions) from normal lattice sites and by inelastic processes that may ionize target atoms. Large numbers of point defects are produced and the bombarding ion remains as an impurity (or alloying addition). Large compressive stresses are introduced by these point defects and foreign ions.

It has been previously shown that ion implantation may cause increases in hardness of 15 to 40% and corresponding increases in apparent fracture toughness in many ceramics. Reference 1 is a review of the changes in mechanical properties introduced by implantation. The process also introduces "radiation damage" in the form of point defect clusters, generally as interstitial clusters surrounded by dislocation loops. This damage has been characterized for sapphire and other materials of interest for optical applications².

This paper summarizes the changes in optical and mechanical properties introduced into sapphire by the two processes, SP and implantation.

2. EXPERIMENTAL DETAILS

Most of the studies were conducted on single crystal sapphire obtained from Crystal Systems, Inc. (Salem, MA). The material was the Hemlite grade: total impurities <100 ppm, low dislocation content. Single crystal discs (2.54 cm diam x 1 mm thick) and bend bars (3.8 cm x 0.508 cm x 0.254 cm) were supplied with a 80-50 (scratch-dig) polish on all faces. Specimens with either the c-axis or the a-axis normal to the implantation surface were examined in this study (Fig. 1).

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Fig. 1. Orientation of sapphire crystals

Unless otherwise noted, the specimens were annealed for 5 days in the temperature range of 1400 to 1500° C in flowing oxygen to remove any residual polishing damage and surface impurities.

The super polish was produced on selected specimens by Laser Power Optics using a proprietary process sometimes called Noncontact Polishing (NCP). Surface roughness (RMS) was 1.1 nm .

The Surface Modification and Characterization Facility at Oak Ridge National Laboratory was used for the ion implantations and ion beam analyses. Several cations were implanted in a Varian 200 kV implanter in order to survey the effects on IR transmittance. Implantation conditions were: 1×10^{17} Si/cm² (100 keV); 4×10^{16} Fe/cm² (160 keV); 1×10^{17} Cr/cm² (180 keV); 7×10^{16} Ga/cm² (160 keV); 1.5×10^{16} W/cm² (250 keV). The samples were implanted at room temperature. All flexure bars were implanted with 1×10^{17} Cr/cm² (180 keV).

The subsurface damage profiles for as-polished, implanted, annealed, and SP specimens were determined from Rutherford backscattering-ion channeling (RBS-C) spectra. A beam of 2 MeV He ions from a Van de Graaff accelerator was scattered from crystals with a crystallographic direction (c-axis or a-axis) aligned with the incident ion beam and with "random" orientations. Since the energy of the backscattered ions is a function of the mass of the scattering site, a separate spectrum is obtained for each chemical species in the sample. The ratio of the number of backscattered He ions from the aligned to the random orientation (χ) is a measure of the number of target ions that are not on lattice sites. A value of unity indicates a random (or amorphous or fine polycrystals) and a value near zero indicates a perfect crystal. The theoretical lower value of χ is about 0.025 (for a perfect crystal)..

Optical properties were determined in the Optical Component Characterization Laboratory. The IR transmittance was measured with a Perkin-Elmer 983G IR Spectrometer. Scattering was obtained from the bi-directional transmittance distribution function (BTDF) determined with the Complete Angle Scatterometer. Scattering measurements were made at 0.6328 and 3.39 μ m.

The hardness and elastic modulus were measured with a load-depth sensing instrument, Nanoindenter. This instrument gives a continuous recording of the load and displacement of the indenter during both the loading and the unloading cycles. The elastic modulus is given directly from the initial slope of the unloading curve and the hardness is calculated from the depth of the plastic indent. The procedure is particularly useful for determining the properties of the thin (100 to 200 nm thick) implanted layers.

The flexure or fracture strength was determined from 4-point bend tests on the 38 x 5.08 x 2.54 mm specimens with the loads separated by 6.35 mm and the supports separated by 19 mm on the 38 x 5.08 mm faces. The maximum tensile stress at failure was calculated from simple beam theory. For the specimen size and test geometry used in this study, the maximum tensile stress (σ_m) is given as:

$$\sigma_m = \frac{0.75P}{wt^2} \quad (1)$$

where P is the load at fracture, t is the thickness and w is the width of the specimen.

Two crystallographic orientations were examined: load applied along the c-axis with the tensile axis parallel to the a-axis, and load applied along the a-axis with the tensile axis parallel to the c-axis. The data were analyzed using Weibull statistics.

The residual surface stresses were estimated from the indentation method of Lawn and Fuller³. This technique is based on the observation that a surface stress affects the length of a radial crack as the crack approaches the surface. By measuring the

length of cracks made during Vickers hardness indentations in stressed and unstressed samples, the average surface stress can be calculated from

$$\sigma = \frac{K_c \{1 - (c_0 / c)^{1.5}\}}{2 \psi d^{0.5}} \quad (2)$$

where K_c is the fracture toughness of an unstressed specimen, c is the crack length in the presence of a stress, c_0 is the crack length in the unstressed surface, d is the thickness of the stressed layer, and ψ is a geometric term of value about unity. The depth of the stressed layer due to implantation was taken as the extent of visible damage observed in transmission electron microscopy. The residual surface compressive stresses determined in this manner^{4,5} agree well with those determined by glancing angle x-ray diffraction for sapphire implanted with Cr in a companion study⁶.

3. DISCUSSION OF RESULTS

3.1 Ion beam analysis of residual damage

Analysis of the RBS-C spectra for the Al-sublattice indicates the number of Al ions that are not on normal lattice sites and is thus a measure of "damage" in the crystal. It does not, however, give information on the specific nature of the damage. The mechanical polishing of the as-received crystals and Cr-implantation both introduced sub-surface damage. Figure 2 is a plot of (disorder) in the Al-sublattice vs. depth for a c-axis normal crystal (a) as-received, and (b) implanted to 1×10^{17} Cr/cm² (180 keV). The disorder is a maximum at the surface of the polished crystal and extends to a depth of ~200 nm. The nature of this disorder was not determined. The value of χ is low at the surface of the implanted crystal, reaches a maximum at ~200 nm, and extends to about 350 nm. Other studies² have shown that this damage consists of interstitial point defect clusters surrounded by partial-dislocation loops. The implanted Cr has an approximate Gaussian distribution centered at ~150 nm from the surface.

The values of χ for samples annealed for 5 days at 1400-1500° C and for those given the SP were very low (0.025-0.30) approaching the theoretical lower limit for the technique. The crystallographic perfection of these specimens was high.

Fig. 2. Disorder (χ) in the Al-sublattice at various depths from the surface for as-polished and Cr-implanted crystals. (c-axis orientation)

3.2. Residual stress

Residual stresses were determined by the indentation technique for both c-axis and a-axis orientations after implantation to $1 \times 10^{17} \text{ Cr/cm}^2$ (180 keV)^{4,5}. The residual stresses were compressive for both orientations but were almost a factor of 2 higher for the c-axis crystals (1.313 vs. 0.752 GPa). Measurements by x-ray diffraction on one of the same c-axis crystals yielded a value of $1.4 \pm 0.4 \text{ GPa}$. The higher values are in the same range as the fracture stress for highly perfect single crystals tested in tension. The higher residual stress in the c-axis crystals for a given implantation condition is consistent with observations that disorder (damage) for this orientation increases with ion fluence at a greater rate than for the a-axis orientation⁷.

3.3 Optical properties

No difference could be detected in the IR transmittance ($\lambda = 1\text{--}6 \mu\text{m}$) among the as-polished, annealed, and the SP samples. The effect of ion implantation depended upon the specific ion species implanted. Figure 3 contains the spectra for 1-mm-thick, c-axis crystals in the annealed conditions and implanted with Fe, Cr, and Ga. Spectra for crystals implanted with W or Si were similar to that for Cr at wave lengths greater than $2 \mu\text{m}$. With the exception of Ga, the decrease in transmittance at $3 \mu\text{m}$ was 1.5 to 2% for each ion species. The decrease for Ga ranged from about 13% at $4 \mu\text{m}$ to 23% at $2 \mu\text{m}$. The change in transmittance with ion fluence was slight for the range of $1\text{--}10 \times 10^{16} \text{ ions/cm}^2$ in the case of Fe and Cr.

Fig. 3. Transmittance for annealed and ion implanted crystals

There was essentially no effect of ion implantation on the scattered light measurements made at 0.6328 and $3.39 \mu\text{m}$. The BTDF curves of Fig. 4 reveal that light scattered by the SP samples at $3.39 \mu\text{m}$ was as much as 4 times lower near the specular laser beam (0.1 to 2°) and 2 to 5 times lower in the range of $2\text{--}25^\circ$. The SP treatment had little effect on scatter at $0.6328 \mu\text{m}$.

3.4 Mechanical properties

Measurements of hardness, elastic modulus, and flexure strength were made for annealed, SP, and ion implantation for both orientations. Flexure strength was also determined for as-received (as-polished) specimens.

As noted in Section 3.1, the annealed and SP crystals had a high degree of crystallographic perfection. Some samples contained so few defects that attempts to produce plastic indentations for the hardness measurements required application of stresses that approach the theoretical shear strength in order to "punch out" enough dislocations to cause plastic flow⁸. It is obvious that such specimens can not be hardened or strengthened. Implanted sapphire exhibits no such yield point, presumably due to the high density of point defects and dislocation loops produced by the implantation.

Figure 5 shows the relative hardness and elastic modulus as a function of Cr-fluence for sample with the c-axis normal to the surface. The hardness of the implanted sample in this case is referenced to annealed crystals that did not exhibit the yield point effect. There is an increase in hardness of about 35% for a fluence of 1×10^{17} Cr/cm². There is no effect on the elastic modulus. Crystals with the a-axis normal to the surface showed similar results, with a hardness increase of 25%.

The most important property change caused by the surface treatments was in flexure strength determined from 4-point bend tests. Figure 6 contains Weibull plots of the maximum stress at fracture for both orientations. The Weibull parameters η (average life or stress) and β (shape parameter) can be used to describe the effects of the surface treatments used in this study, and are summarized in Table 1.

Specimens having the c-axis normal to the tensile surface (TS) and the a-axis parallel to the tensile axis (TA) were tested as-received mechanical polish, annealed, SP, and Cr--implanted. Each post-polish treatment improved the fracture strength: much improvement was found for low cumulative failures and a slight improvements at the highest applied stresses. The Weibull average stress at failure increased from 900 MPa for the as-polished specimens to 950 MPa for the annealed specimens to 1100 MPa for the SP group and to 1300 MPa for the implanted samples. To the extent that these results from a relatively small sample size can be extrapolated to give a stress at which 1% failures should be expected, values of 45, 90, 170, and 500 MPa were obtained for the four conditions.

Table 1. Summary of Fracture Studies

Condition	No. Samples	β	η	1% Failures
c-axis $\perp$ TS; a-axis $\parallel$ TA				
as-polished	10	0.7	900 MPa	45 MPa
annealed	21	0.9	950	90
SP	10	1.2	1100	170
implanted	15	2.2	1300	500
a-axis $\perp$ TS; c-axis $\parallel$ TA				
annealed	5	1.8	900	300
SP	10	2.6	1150	425
implanted	10	3.8	1400	800

Similar trends were obtained for specimens having the a-axis normal to TS and the c-axis parallel to TA. Ion implantation produced a larger increase than SP which was higher than the annealed state. No as-polished samples of this orientation were tested. The effect at low cumulative failure was not as pronounced for this orientation but all curves were steeper. These observations are consistent with the inherently greater resistance to failure for this orientation⁹. The extrapolation to 1% failure rate gives values of 300, 425, and 800 MPa for the annealed, SP, and implanted samples, respectively.

Fig. 4. Light scattering from conventional and SP 1-mm thick sapphire crystals (c-axis) orientation.

Fig. 5. Relative hardness and elastic modulus for sapphire as a function of Cr-fluence.

Failures at stresses lower than about the Weibull average generally could be traced to some point on the tensile surface. At higher stresses, the samples shattered into a coarse powder upon fracture as a consequence of the very high stored elastic strain energy.

It is proposed that the improvements in fracture stress for the annealing and SP treatments are caused by the removal of residual mechanical polishing damage. The improvement due to implantation is mainly caused by the very high residual

Fig. 6. Cumulative failure vs. applied stress in 4-point bending for sapphire crystals having orientations designed in Fig. 1.

compressive stresses that nullify the applied tensile stress until very high loads are reached. This compressive stress may also cause some flaw (crack) closure.

4. SCALE-UP

Annealing for 5 days at 1400 to 1500° C removes much of the residual polishing damage and increases the resistance to fracture at low applied stresses. However, large samples must be heated and cooled at very slow rates in order to prevent

cracking. These slow rates and the scarcity of furnaces with large volumes that operate in this temperature range suggests that the surface modification techniques may be more practical for large specimens.

The SP technique has been demonstrated on a sapphire infrared window blank that was machined from a boule produced by Union Carbide. Laser Power Optics then used the SP technique to produce the final window that had dimensions in excess of 10 x 23 cm. This window met or exceeded all specifications of the HEDS program.

Although ion implantation was not demonstrated for sapphire discs greater than 2.54 cm diam in this study, there are commercial facilities that can routinely implant cations in specimens with dimensions greater than those used in the SP demonstration.

5. SUMMARY

Surface modification techniques that increase the resistance to fracture of sapphire have been demonstrated. Neither the super polish technique or ion implantation significantly affects the IR transmittance at wave lengths above 1.5 μ m. The SP reduces light scatter and removes subsurface polishing damage. Both techniques reduce the frequency of failures at lower applied stresses. The SP removes surface flaws, whereas, implantation introduces a large residual compressive stress in the near-surface region.

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