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Surface modification of sapphire for enhanced infrared window performance

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Two ion implantation conditions were evaluated for improving the mechanical performance of sapphire IR window material. Both increased the average strength as measured by 4-point bend tests and were effective in preventing the propagation of surface flaws. Ion implantation that produced a damaged crystalline surface improved the reliability at lower stresses more than the implantation that produced an amorphous surface. Neither process significantly affected the IR transmission.

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. Ceramic components often 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 may 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.

Some implantation conditions produce a damaged crystalline surface in sapphire where other conditions produce an amorphous surface layer¹. Implantation that leaves the surface crystalline causes an increase in hardness (15 to 40%) and corresponding increases in apparent fracture toughness. The amorphous layer has a lower hardness and modulus than the crystalline form. Reference 2 is

a review of the changes in mechanical properties of ceramics introduced by implantation.

The process also introduces "radiation damage" in the form of point defect clusters, generally as interstitial clusters surrounded by dislocation loops. These point defects introduce large residual compressive stresses.

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

2. EXPERIMENTAL DETAILS

High-purity low dislocation density single crystals were obtained from Crystal Systems, Inc. (Salem, MA). 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 polish on all faces. Specimens with either the c-axis or the a-axis normal to the implantation surface were used. Unless otherwise noted, the specimens were annealed for 5 days at 1400 to 1500° C in flowing oxygen to remove any residual polishing damage and surface impurities.

Several cation species were implanted with a Varian 200 kV implanter in order to determine 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.

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Flexure bars were implanted with 1×10^{17} Cr/cm² (180 keV) or 1×10^{17} Si/cm² (100 keV).

The damage profile was characterized by Rutherford backscattering-ion channeling (RBS-C). 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.

The IR transmittance was measured with a Perkin-Elmer 983G IR Spectrometer. Scattering was obtained from the bi-directional transmittance distribution function (BTDF) determined 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 plastic depth of the indent. The procedure is particularly useful for determining the properties of the thin (100 to 200 nm thick) implanted layers.

Fracture strength was determined from 4-point bend tests on 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.

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 estimate 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. The average surface stress can be calculated from a comparison of the length of cracks made during Vickers hardness indentations in stressed and unstressed samples. The depth of the stressed layer due to implantation was taken as the extent of visible damage observed in transmission electron microscopy.

3. DISCUSSION OF RESULTS

3.1. Ion beam analysis of residual damage

The mechanical polishing of the as-received crystals and Cr-implantation both introduced sub-surface damage but with different spatial distributions, as shown by the ion channeling spectra. Figure 1 is a plot of χ (disorder) in the Al-sublattice vs. depth for a c-axis normal crystal as-received, and after annealing and being 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 studies¹ have shown that the implantation damage consists of interstitial point defect clusters surrounded by partial-dislocation loops.

The values of χ for samples annealed for 5 days at 1400-1500° C were very low (0.025-0.30) approaching the theoretical lower limit for the technique. The crystallographic perfection of these specimens was high. The aligned spectra of the samples implanted with Si were coincident with the random spectra to a depth of about 150 nm, indicating an amorphous surface layer.

Fig. 1. 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

Average residual stresses in the implanted layer were determined for both c-axis and a-axis orientations after implantation to 1×10^{17} Cr/cm² (180 keV). 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 diffraction⁴ on one of the same c-axis crystals yielded a value of 1.4 ± 0.4 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 orientation⁵.

3.3. Optical properties

The effect of ion implantation on IR transmittance ($\lambda = 1-6 \mu\text{m}$) depended upon the specific ion species implanted. Figure 2 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

Fig. 2. Transmittance for annealed and ion implanted crystals.

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 $1-10 \times 10^{16}$ ions/cm² in the case of Fe and Cr. The amorphous layer had no effect.

There was essentially no effect of ion implantation on the scattered light measurements at 0.6328 and $3.39 \mu\text{m}$.

3.4. Mechanical properties

Measurements of hardness, elastic modulus, and flexure strength were made for annealed and Cr-implanted specimens of both orientations. Flexure strength was determined only for the Si-implanted c-axis orientation.

There was an increase in hardness of about 35% for the c-axis crystals at 1×10^{17} Cr/cm². There was no effect on the elastic modulus. Both the hardness and elastic modulus amorphous layers decreased (~70 and 40%, resp.). Crystals with the a-axis normal to the surface showed similar results for Cr-implantation, with a maximum hardness increase of 25%.

The most important property change caused by the surface treatments was in flexure strength. Figure 3 contains Weibull plots of the maximum stress at fracture for both orientations.

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, implanted-amorphous, and implanted-crystalline. Each post-polish treatment improved the fracture strength: much improvement was found for low cumulative failures and 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 amorphous group and to 1300 MPa for the implanted-crystalline samples.

Similar trends were obtained for specimens having the a-axis normal to TS and the c-axis parallel to TA. The increase 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 orientation⁶.

Fig. 3. Cumulative failure vs. applied stress in 4-point bending for sapphire crystals.

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.

Improvements in fracture stress for annealed and amorphous implantation are postulated to be due to removal of residual mechanical polishing damage. The improvement due to implantation-crystalline is mainly caused by the high residual 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. SUMMARY

Surface modification techniques that increase the resistance to fracture of sapphire have been demonstrated. Neither ion implantation condition significantly affects the IR transmittance at wave lengths above $1.5 \mu\text{m}$. Both techniques reduce the

frequency of failures at lower applied stresses. The amorphization removes surface flaws and residual polishing damage, whereas, implantation (crystalline) introduces a large residual compressive stress in the near-surface region.

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