

# Effect of ion implantation on the strength of sapphire at 300–600°C

ALLEN KIRKPATRICK

*Epion Corp., 37 Manning Road, Billerica MA 01821, USA*  
E-mail: allenk@epion.com

DANIEL C. HARRIS

*Chemistry and Materials Division, Code 4T42A0D, Naval Air Warfare Center, China Lake CA 93555, USA*  
E-mail: harrisdc@navair.navy.mil

LINDA F. JOHNSON

*Physics Division, Code 4T4110D, Naval Air Warfare Center, China Lake CA 93555, USA*  
E-mail: johnsonlf@navair.navy.mil

Ion implantation with  $^{11}\text{B}^+$  or  $^{28}\text{Si}^+$  at 1000°C doubled the ring-on-ring flexure strength of *c*-plane sapphire disks tested at 300°C but had little effect on strength at 500 or 600°C. Disks were implanted on the tensile surface with  $2 \times 10^{17}$  B/cm<sup>2</sup> (half at 40 keV and half at 160 keV) or  $1 \times 10^{17}$  Si/cm<sup>2</sup> (80 keV). Sapphire implanted with  $1 \times 10^{18}$  B/cm<sup>2</sup> had only half as much flexure strength at 300° or 500°C as sapphire implanted with  $2 \times 10^{17}$  B/cm<sup>2</sup>. Implantation with B, Si, N, Fe or Cr had no effect on the *c*-axis compressive strength of sapphire at 600°C. Boron ion implantation ( $2 \times 10^{17}$  B/cm<sup>2</sup>, half at 40 keV and half at 160 keV) induced a compressive surface force per unit length of  $1.9 \times 10^2$  N/m at 20° and  $1.4 \times 10^2$  N/m at 600°C. The infrared emittance at 550–800° of B-implanted sapphire at a wavelength of 5 μm increased by 10–15% over that of unimplanted sapphire. Infrared transmittance of sapphire implanted with B, Si or N at either 1000°C or 25°C is within ~1–3% of that of unimplanted material at 3.3 μm. Implantation with Fe or Cr at 25°C decreases the transmittance by 4–8% at 3.3 μm, but implantation at 1000°C decreased transmittance by only 2–4% compared to unimplanted material. © 2001 Kluwer Academic Publishers

## 1. Introduction

Sapphire ( $\alpha\text{-Al}_2\text{O}_3$ ) is the most durable, commercially available infrared window material [1]. Although it has good thermal shock resistance, it can shatter if it is heated or cooled too rapidly. One limitation on the thermal shock resistance of sapphire is its loss of mechanical strength at elevated temperature [2–9].

McHargue *et al.* showed that ion implantation of sapphire at ambient temperature with 180 keV  $\text{Cr}^+$  ions at a fluence of  $\sim 1 \times 10^{17}/\text{cm}^2$  increased the ambient-temperature 4-point flexure strength by ~50% when tension was along the crystal *a*- or *c*-axes [10–12]. Strengthening was attributed to the compressive stress of ~1 GPa in the implanted layer on the tensile surface of the flexure bar [10–14]. Before fracture can occur, the applied tensile load must overcome the compressive stress in the surface layer. The depth of the implanted ions is only ~0.16 μm.  $\text{Cr}^+$  implantation increased the hardness of sapphire by ~35% (with a 0.5–1 N load) but had little effect on the elastic modulus. Many other studies of ion implantation into sapphire have been reported [15–21]. Hioki *et al.* [22] observed that the flexure strength of sapphire increased by 30–50% at am-

bient temperature upon implantation with nitrogen or nickel.

The thermal shock failure of glass and single-crystal MgO implanted by 70 keV  $\text{Si}^-$  ions has also been studied [23]. Material implanted with  $5 \times 10^{14}$  to  $5 \times 10^{16}$  ions/cm<sup>2</sup> broke into many more fragments than unimplanted material during thermal shock failure. The thermal shock resistance of MgO was diminished by  $\text{Si}^-$  implantation. For glass, a fluence of  $5 \times 10^{14}/\text{cm}^2$  increased the thermal shock resistance, while a fluence of  $5 \times 10^{16}/\text{cm}^2$  decreased the thermal shock resistance.

The present work explores the possibility that ion implantation could increase the flexure or compressive strength of sapphire at 600°C. A preliminary report of the results has appeared [24].

## 2. Experimental

“Hemlux” grade sapphire from Crystal Systems (Salem, Massachusetts) was fabricated into test coupons at Boston Piezo-Optics (Medway, Massachusetts). For most flexure testing, *c*-plane (0001) disks with a diameter of 38 mm and a thickness of 2 mm were used.

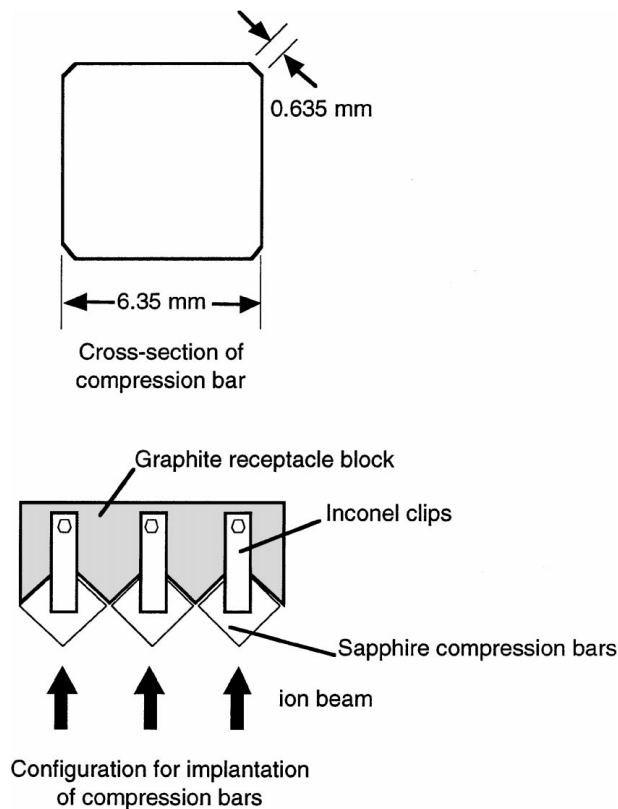


Figure 1 (a) Cross section of compression bar. (b) Configuration for ion implantation of compression bars.

Compression tests used rectangular bars with dimensions of  $6.53 \times 6.35 \times 12.7$  mm with compression along the  $c$ -axis parallel to the 12.7-mm side. The four long edges were chamfered, as shown in Fig. 1a, and all surfaces including the chamfers were optically polished. For some experiments,  $c$ -plane disks with a diameter of 38 mm and a thickness of 1 mm were fabricated at Insaco (Quakertown, Pennsylvania) and annealed at  $1200^\circ\text{C}$  in air for 24 h prior to implantation.

Ion implantation was conducted at  $\leq 1$   $\mu\text{torr}$  pressure at Epion (Billerica, Massachusetts) using a 200 keV medium current semiconductor ion implantation system which was modified to allow the material being implanted to be heated to  $\leq 1200^\circ\text{C}$  within a cylindrical tube furnace. Specimens were held at  $1000^\circ\text{C}$  for most implantations. Specimens implanted at "ambient" temperature were not deliberately heated, but probably attained a temperature of  $50$ – $100^\circ\text{C}$ . Samples for implantation were transferred through a vacuum loadlock using a graphite holder attached to a magnetically coupled vacuum transport assembly. Sapphire disks were implanted at normal incidence onto the tensile surface only. Compression bars were implanted in groups of 3 as shown in Fig. 1b. The four  $6.35 \times 12.7$ -mm surfaces were implanted in four steps with  $90^\circ$  rotations between steps. The  $6.53 \times 6.35$ -mm ends were not implanted.

Mechanical testing was conducted with an Instron machine at the University of Dayton Research Institute (Dayton, Ohio) in air with a crosshead speed of  $0.508$  mm/min. Specimens were heated at  $10^\circ\text{C}/\text{min}$  and left at the final temperature for 10 min before testing. For compression tests, the long axis of the bar was placed between ground silicon carbide transfer plates in the testing machine. A  $0.12$ -mm-thick sheet of Garlock

900 Grafoil (corrugated graphite from UCAR Carbon Co., Cleveland, Ohio.) was placed between the specimen and the silicon carbide to help make the loading more uniform. For disk flexure tests, the silicon carbide load ring had a radius of  $7.94$  mm and the silicon carbide support ring had a radius of  $15.88$  mm. Some tests were conducted with Grafoil sheets between the sapphire and the silicon carbide and other tests did not include Grafoil, as specified in the tables of results. Flexure strength was computed with the equation

Equibiaxial stress within load radius

$$= \frac{3P(1-\nu)}{4\pi d^2} \left( \frac{b^2 - a^2}{c^2} - 2 \frac{1+\nu}{1-\nu} \ln \frac{a}{b} \right) \quad (1)$$

where  $P$  is the applied load,  $\nu$  is Poisson's ratio (taken as  $0.25$ ),  $d$  is the thickness of the disk,  $a$  is the load ring radius,  $b$  is the support ring radius, and  $c$  is the disk radius.

Infrared transmission spectra were recorded with a Perkin Elmer 1615 FTIR instrument. Infrared emittance was measured at the Johns Hopkins University Applied Physics Laboratory with an emissometer described previously [25]. Sapphire was heated from the back surface by a  $\text{CO}_2$  laser at  $10.6$   $\mu\text{m}$  while emission from the front surface was measured with a Bomen DA3 interferometer. The spectrum of the ambient temperature background was subtracted from the observed spectrum. Emission from sapphire was compared to that of a blackbody at the same temperature.

Implantation-induced surface stress was calculated from the curvature of an implanted wafer. A  $c$ -plane sapphire wafer ( $25.4$  mm diameter  $\times$   $0.254$  mm thick) with one fine ground surface and one polished surface was concave on the polished side after annealing at  $1400^\circ\text{C}$ . The radius of curvature was measured by laser deflection while heating the disk between  $20$  and  $600^\circ\text{C}$ , and during cooldown. The curvature returned to its initial value upon cooling to  $20^\circ\text{C}$ . The wafer was implanted at  $1000^\circ\text{C}$  on the polished surface and then the curvature was measured again. The surface force per unit length was computed from the formula [26]

$$\text{Surface force per unit length} = \frac{1}{6} \left( \frac{E}{1-\nu} \right) \frac{t^2}{R} \quad (2)$$

where  $E$  is Young's modulus (taken as  $344$  GPa),  $\nu$  is Poisson's ratio (taken as  $0.25$ ),  $t$  is the thickness of the wafer, and  $R$  is the radius of curvature. (In this experiment, a ground surface was thought to be necessary for the laser deflection measurement. If we were to repeat the experiment, both surfaces would be polished and one surface would be coated with an opaque, low stress coating such as tungsten.)

### 3. Results and discussion

#### 3.1. Effect of implantation conditions on infrared transmittance and emittance

Preliminary experiments with  $\text{Cr}^+$  indicated that infrared transmittance is degraded when ion implantation is performed on a sapphire substrate at ambient temperature. Fig. 2 shows the effect of implanting

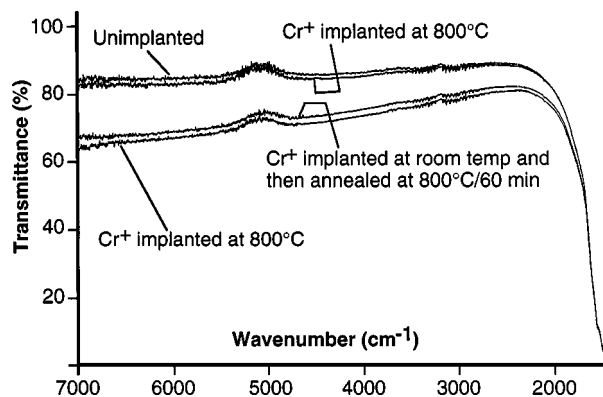


Figure 2 Infrared transmission of sapphire implanted on one side with  $1 \times 10^{17}/\text{cm}^2$   $^{52}\text{Cr}^+$  at 150 keV.

150 keV  $\text{Cr}^+$  at a fluence of  $1 \times 10^{17}/\text{cm}^2$ . If the sapphire was maintained at  $800^\circ\text{C}$  during implantation, the infrared transmittance was nearly unchanged. A significant loss in transmittance occurred if implantation was conducted at ambient temperature. Annealing the cold-implanted material at  $800^\circ\text{C}$  for 60 min (the approximate time required for implantation), did not restore the transmittance.

An implantation temperature of  $1000^\circ\text{C}$  and a fluence of  $1 \times 10^{17}/\text{cm}^2$  was chosen for samples in the present study. Fig. 3 shows the transmittance of sapphire implanted with  $^{11}\text{B}^+$ ,  $^{14}\text{N}_2^+$ ,  $^{28}\text{Si}^+$ ,  $^{52}\text{Cr}^+$ , or  $^{56}\text{Fe}^+$ . B, N and Si-implanted sapphire did not suffer very much transmittance loss when implantation was carried out at ambient temperature. Sapphire implanted with Cr or Fe at ambient temperature or elevated temperature was visibly darkened. Sapphire implanted with Si at ambi-

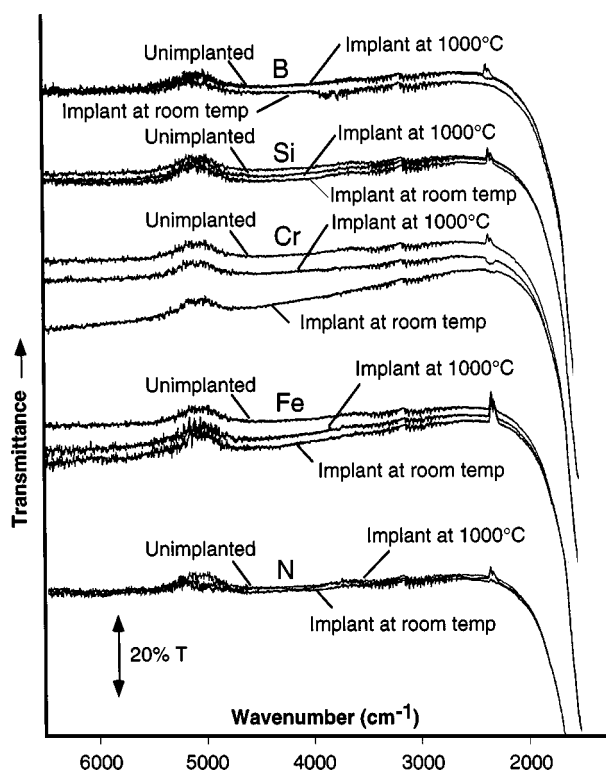


Figure 3 Infrared transmission of sapphire implanted on one side with  $1 \times 10^{17}/\text{cm}^2$   $^{11}\text{B}^+$ ,  $^{28}\text{Si}^+$ ,  $^{52}\text{Cr}^+$ ,  $^{56}\text{Fe}^+$ , or  $^{14}\text{N}_2^+$  at 150 keV. Spectra are offset for clarity. The unimplanted material serves as a baseline for each set of measurements.

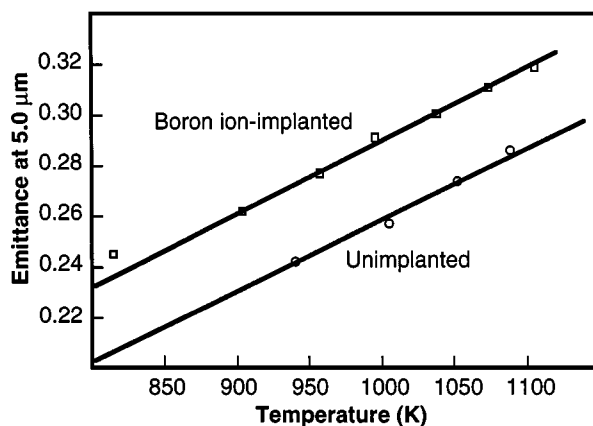


Figure 4 Emittance of 1.0-mm thick, boron ion-implanted sapphire ( $1 \times 10^{17}/\text{cm}^2$  at 150 keV on one side). Data from M. E. Thomas, M. J. Linevsky and J. W. Giles, Johns Hopkins University Applied Physics Laboratory.

ent temperature, but not at  $1000^\circ\text{C}$ , was darkened also. Implantation with B or N at either temperature gave clear, colorless material.

Because of our interest in using ion implanted sapphire as an infrared window for elevated temperature operation, it was important to see if the infrared emittance was affected by implantation. Fig. 4 shows that B-implanted sapphire ( $1 \times 10^{17}/\text{cm}^2$  at 150 keV) has approximately 10–15% greater emittance than unimplanted sapphire at  $5 \mu\text{m}$  wavelength.

### 3.2. Effect of implantation on *c*-axis compressive strength

*c*-Axis compression bars were implanted on their 4 long faces (but not on the ends) as shown in Fig. 1. Ion energies were chosen so that the mean depth of implantation would be approximately  $0.05 \mu\text{m}$ . During implantation, two faces of each sample were presented to the ion beam at  $45^\circ$  incidence. Each sample was rotated by  $90^\circ$  4 times to complete the implantation. The total fluence was chosen to be equivalent to a normal fluence of  $1 \times 10^{17}/\text{cm}^2$ . Fig. 5 shows two data points for each ion species implanted at  $1000^\circ\text{C}$  or at ambient temperature. There appear to be no significant differences in *c*-axis compressive strength among any of the implanted specimens and the unimplanted material. The near coincidence of the two measurements

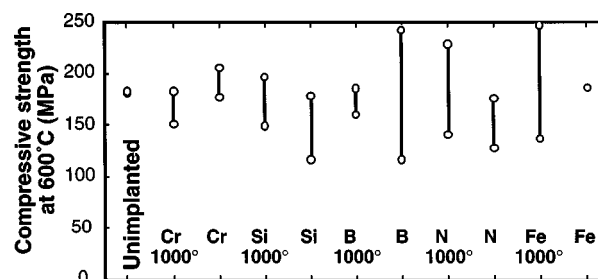


Figure 5 *c*-Axis compressive strength of sapphire bars ( $6.35 \times 6.35 \times 12.7$  mm, Fig. 1a) implanted with  $^{52}\text{Cr}^+$  (150 eV),  $^{28}\text{Si}^+$  (80 eV),  $^{11}\text{B}^+$  (30 eV),  $^{14}\text{N}_2^+$  (100 eV), or  $^{56}\text{Fe}^+$  (150 eV) at  $1000^\circ\text{C}$  or at ambient temperature. The fluence for each ion species except  $\text{N}_2^+$  was  $1.4 \times 10^{17}/\text{cm}^2$  at  $45^\circ$  incidence. For  $\text{N}_2^+$  the fluence was  $0.7 \times 10^{17}/\text{cm}^2$  so that the same number of atoms was implanted. Circles show the 2 data points for each condition except Fe at ambient temperature, which has just 1 point.

TABLE I Flexure strength of sapphire

Specimen and treatment <sup>a</sup>	Implantation temperature	Strength test temperature [Grafoil?]	Strength ± standard deviation (MPa) [number of specimens]					
			Unimplanted	B	Si	N	Fe	Cr
<i>c</i> -plane disk 38 mm $\phi$ × 2 mm thick	1000°C	300°C [no Grafoil]	322 ± 57 [6]	707 ± 59 <sup>b</sup> [6]	644 ± 167 <sup>c</sup> [6]	529 ± 118 [6]	546 ± 68 [6]	440 ± 142 [5]
<i>c</i> -plane disk 38 mm $\phi$ × 1 mm thick	1000°C	500°C [with Grafoil]	1298 ± 364 [5]	1508 ± 596 <sup>d</sup> [5]	1518 ± 463 <sup>e</sup> [5]			
<i>a</i> -plane disk 38 mm $\phi$ × 2 mm thick	1000°C	600°C [no Grafoil]	245 ± 29 [5]	252 ± 18 <sup>b</sup> [5]				
<i>a</i> -plane 4-pt flexure bar <sup>f</sup> 3 × 4 × 45 mm	1000°C	600°C [no Grafoil]	513 ± 110 [24]	690 ± 191 <sup>b</sup> [4]				

<sup>a</sup>N, Fe and Cr were implanted at energies of 50, 150, and 160 keV, respectively, all at a fluence of  $1 \times 10^{17}/\text{cm}^2$  on the tensile surface of the test specimen.

<sup>b</sup>Double implantation of B on tensile surface:  $1 \times 10^{17}/\text{cm}^2$  at 160 keV and  $1 \times 10^{17}/\text{cm}^2$  at 40 keV.

<sup>c</sup>Si implantation at 80 keV at  $1 \times 10^{17}/\text{cm}^2$  on the tensile surface.

<sup>d</sup>B implantation at 40 keV at  $2 \times 10^{17}/\text{cm}^2$  on tensile surface.

<sup>e</sup>Si implantation at 80 keV at  $2 \times 10^{17}/\text{cm}^2$  on the tensile surface.

<sup>f</sup>Tension was along the *m*-axis and the load was applied parallel to the *a*-axis. *m* was parallel to the 45-mm edge, *a* was parallel to the 3 mm edge, and *c* was parallel to the 4-mm edge.

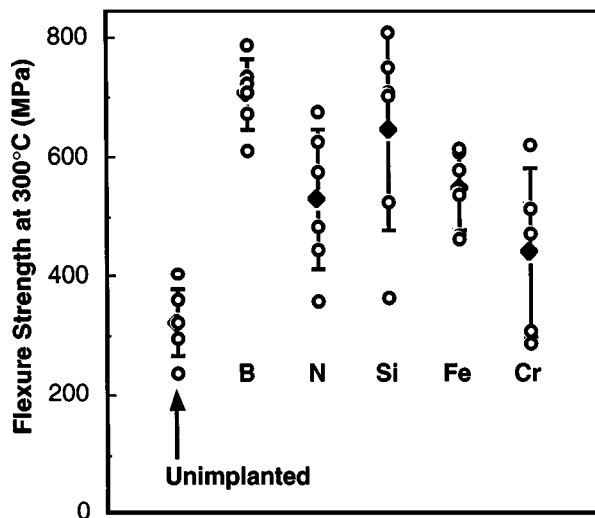


Figure 6 Ring-on-ring flexure strength of 38-mm-diameter × 2.0-mm-thick *c*-plane sapphire disks measured at 300°C. Implants were performed only on the tensile surface with a fluence of  $1 \times 10^{17}/\text{cm}^2$  at normal incidence. Implantation energies were N, 50 keV; Si, 80 keV, Fe, 160 keV and Cr, 150 keV. In the case of boron, the disks received  $1 \times 10^{17}/\text{cm}^2$  at 40 keV plus  $1 \times 10^{17}/\text{cm}^2$  at 160 keV. Circles are data points. Diamonds are mean values and error bars show ±1 standard deviation.

for unimplanted material is unusual. The scatter seen in implanted specimens is normal in our experience with sapphire.

### 3.3. Effect of implantation on flexure strength at 300°C

Results in Fig. 6 and the first row of Table I show that *c*-plane sapphire disks (2-mm-thick × 38 mm diameter) implanted with B or Si on the tensile surface had approximately twice the strength of unimplanted material when tested at 300°C without Grafoil between the disk and the load rings. N, Fe and Cr implantation also enhanced flexure strength at 300°C, but not as much as B and Si.

Double implantation of boron at 40 and 160 keV in Table I was an accidental condition. Experiments in

Table II were performed to try to simplify the boron implantation. Baseline, untreated sapphire in Set A had a strength of 322 MPa. Annealing at 1000°C for 75 min in vacuum (similar to the implantation conditions) did not significantly alter the strength in Set B. Lowering the implantation temperature from 1000°C to ambient temperature in Set C did not improve the strength compared to unimplanted sapphire. Implanting at ambient temperature and then annealing at 1000°C in Set D also gave no strengthening. Using single implantations of  $1 \times 10^{17}/\text{cm}^2$  at either 40 keV (Set F) or 160 keV (Set G) also gave no strength enhancement. Implantation (Set E) with  $1 \times 10^{17}/\text{cm}^2$  at 40 keV plus implantation with  $1 \times 10^{17}/\text{cm}^2$  at 160 keV at 1000°C doubled the strength of sapphire at 300°C, but no other treatment in Table II provided any strengthening. We expected to see strengthening in either or both of Sets F and G. The negative results might indicate that a dose of  $1 \times 10^{17}/\text{cm}^2$  at 1000°C is ineffective, while a dose of  $2 \times 10^{17}/\text{cm}^2$  at 1000°C is effective.

While the experiments in Table II were in progress, an independent investigation was initiated to try to decrease the contribution of *c*-axis contact compression in equibiaxial flexure disk experiments [27]. It was decided to decrease the disk thickness from 2 mm to 1 mm and use a thin sheet of Grafoil to cushion the contact between the load rings and test specimen. These measures increased the apparent strength of *c*-plane sapphire at 300° from 322 MPa (Table II, Set A) to 1274 MPa (Table III, Set A). Unfortunately, the standard deviation under the new conditions increased from a mean value of 17% in Table II to a mean value of 43% in Table III.

Some of the boron implantation experiments of Table II were repeated with the thinner disk and Grafoil in Table III. Compared to the strength of unimplanted material (Set A), double implantation with  $1 \times 10^{17}/\text{cm}^2$  at 40 keV plus  $1 \times 10^{17}/\text{cm}^2$  at 160 keV approximately doubled the strength (Set B). Implanting the sapphire on both surfaces (tensile and compressive) in Set C did not further increase the strength. Implanting with  $2 \times 10^{17}/\text{cm}^2$  at 40 keV (Set E) gave a higher strength

TABLE II Effect of implantation on flexure strength of sapphire at 300°C without Grafoil<sup>a</sup>

Set	Implantation	Implantation temperature	Additional annealing	Mean strength ± standard deviation	Number of specimens
A	Unimplanted	---	---	322 ± 27	6
B	Unimplanted	---	1000°C/75 min in vacuum	358 ± 96	5
C	160 keV B <sup>+</sup> 1 × 10 <sup>17</sup> /cm <sup>2</sup> and 40 keV B <sup>+</sup> 1 × 10 <sup>17</sup> /cm <sup>2</sup>	ambient	---	327 ± 33	5
D	160 keV B <sup>+</sup> 1 × 10 <sup>17</sup> /cm <sup>2</sup> and 40 keV B <sup>+</sup> 1 × 10 <sup>17</sup> /cm <sup>2</sup>	ambient	1000°C/75 min in vacuum	268 ± 48	5
E	160 keV B <sup>+</sup> 1 × 10 <sup>17</sup> /cm <sup>2</sup> and 40 keV B <sup>+</sup> 1 × 10 <sup>17</sup> /cm <sup>2</sup>	1000°C	---	707 ± 59	6
F	40 keV B <sup>+</sup> 1 × 10 <sup>17</sup> /cm <sup>2</sup>	1000°C	---	331 ± 93	5
G	160 keV B <sup>+</sup> 1 × 10 <sup>17</sup> /cm <sup>2</sup>	1000°C	---	378 ± 50	5

<sup>a</sup>38-mm-diameter × 2.0-mm-thick *c*-plane disks tested in ring-on-ring flexure without Grafoil.

TABLE III Effect of implantation on flexure strength of thin sapphire at 300°C with Grafoil<sup>a</sup>

Set	Implantation	Implantation temperature	Sides implanted	Mean strength ± standard deviation	Number of specimens
A	Unimplanted	1000°C	---	1274 ± 1233 <sup>b</sup>	5
B	160 keV B <sup>+</sup> 1 × 10 <sup>17</sup> /cm <sup>2</sup> and 40 keV B <sup>+</sup> 1 × 10 <sup>17</sup> /cm <sup>2</sup>	1000°C	one	2315 ± 608	5
C	160 keV B <sup>+</sup> 1 × 10 <sup>17</sup> /cm <sup>2</sup> and 40 keV B <sup>+</sup> 1 × 10 <sup>17</sup> /cm <sup>2</sup>	1000°C	two	1878 ± 575	5
D	160 keV B <sup>+</sup> 2 × 10 <sup>17</sup> /cm <sup>2</sup>	1000°C	one	1487 ± 605	5
E	40 keV B <sup>+</sup> 2 × 10 <sup>17</sup> /cm <sup>2</sup>	1000°C	one	2091 ± 459	5

<sup>a</sup>38-mm-diameter × 1.0-mm-thick *c*-plane disks tested in ring-on-ring flexure with Grafoil.

<sup>b</sup>Observed strength: 3399, 1180, 926, 509, 354 MPa. If the highest and lowest values were dropped as outliers, the remaining data have a mean of 872 ± 339 MPa.

than implanting with  $2 \times 10^{17}/\text{cm}^2$  at 160 keV (Set D). This last result combined with results of implantations at just 40 keV or 160 keV in Table II suggests that a dose of  $2 \times 10^{17}/\text{cm}^2$  at 40 keV provides strength enhancement while a dose of  $1 \times 10^{17}/\text{cm}^2$  at 40 keV does not. Either dose at 160 keV did not enhance the strength.

### 3.4. Effect of implantation on flexure strength at 500 and 600°C

Ring-on-ring flexure strength was measured at 500°C on 1-mm-thick disks implanted with B or Si and using Grafoil between the load rings and the sapphire. Fig. 7 and the second row of Table I show that, within the large standard deviation of the results, implanted disks are not significantly stronger than unimplanted material at 500°C. Boron implantation was also evaluated in mechanical tests at 600°C using 4-point flexure bars and *a*-plane flexure disks. Again, no significant strengthening at 600°C is noted in Fig. 7 and the last two rows of Table I.

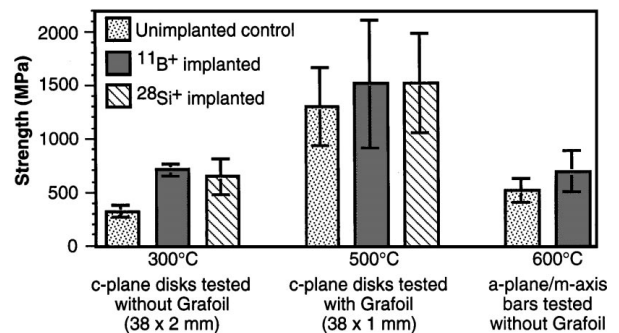


Figure 7 Comparison of flexure strengths of implanted and unimplanted materials tested at 300, 500 or 600°C. Implantation appears to give a significant strength increase at 300°C, but not at 500 or 600°C. Tests and specimens at each temperature were different, so no comparison should be made between results at different temperatures. Data come from Table I. Error bars are ±1 standard deviation.

### 3.5. Effect of B<sup>+</sup> dose on flexure strength at 300 and 500°C

Table IV lists the strength of sapphire implanted at two different fluences of <sup>11</sup>B<sup>+</sup>. At 300°C, implantation with

TABLE IV Effect of B<sup>+</sup> dose on flexure strength of thin sapphire disks tested with Grafoil<sup>a</sup>

Set	Implantation	Implantation temperature	Sides implanted	Mean strength ± standard deviation	Number of specimens
Strength measured at 300°C:					
A	Unimplanted	1000°C	---	1274 ± 1233	5
B	40 keV B <sup>+</sup> 2 × 10 <sup>17</sup> /cm <sup>2</sup>	1000°C	one	2091 ± 459	5
C	40 keV B <sup>+</sup> 1 × 10 <sup>18</sup> /cm <sup>2</sup>	1000°C	one	1260 ± 615	4
Strength measured at 500°C:					
D	Unimplanted	1000°C	---	1298 ± 364	5
E	40 keV B <sup>+</sup> 2 × 10 <sup>17</sup> /cm <sup>2</sup>	1000°C	one	1508 ± 596	5
F	40 keV B <sup>+</sup> 1 × 10 <sup>18</sup> /cm <sup>2</sup>	1000°C	one	797 ± 295	4

<sup>a</sup>38-mm-diameter × 1.0-mm-thick *c*-plane disks tested in ring-on-ring flexure with Grafoil.

$2 \times 10^{17} \text{ B}^+/\text{cm}^2$  at 40 keV approximately doubled the strength (Set B vs. Set A). Increasing the dose to  $1 \times 10^{18} \text{ B}^+/\text{cm}^2$  reduced the strength back to the level of unimplanted material (Set C vs. Set A). At 500°C, sapphire implanted with  $2 \times 10^{17} \text{ B}^+/\text{cm}^2$  is marginally stronger than unimplanted material (Set E vs. Set D). However, increasing the dose to  $1 \times 10^{18} \text{ B}^+/\text{cm}^2$  reduced the strength by a factor of 2 (Set F vs. Set E).

### 3.6. Implantation-induced surface stress

It is generally thought that ion implantation strengthens a ceramic by introducing compressive stress into the surface that must be overcome by tension during a flexure test before failure can occur. In previous work with sapphire, compressive stresses on the order of  $\sim 1 \text{ GPa}$  were observed in the implanted layer [10–14]. We attempted to evaluate the hypothesis that our samples had significant compressive stress at 300°C, but not at 500–600°C. This hypothesis would explain the observation that the flexure strength of implanted sapphire was doubled at 300°C, but was not improved at 500–600°C, compared to unimplanted sapphire.

For this purpose, a thin sapphire wafer (0.254 mm thick) with one polished surface and one ground surface was annealed at 1400°C and then implanted at 1000°C on the polished surface. Twyman observed that if a flat glass disk with two polished surfaces was ground on one surface, the polished surface became concave [26, 28, 29]. The ground surface is therefore in compression and the polished surface is in tension. Our sapphire wafer was also concave on the polished side prior to ion implantation, with a radius of curvature of  $13.9 \pm 1.2 \text{ m}$ . From Equation 2 we calculate the tensile force per unit length to be  $3.6 \times 10^2 \text{ N/m}$ . When heated to 600°C, the curvature increased, giving a tensile force per unit length of  $4.8 \times 10^2 \text{ N/m}$ . Upon cooling, the wafer returned to its initial curvature.

After implantation at 1000°C on the polished surface with  $1 \times 10^{17} \text{ B}^+/\text{cm}^2$  at 40 keV followed by  $1 \times 10^{17} \text{ B}^+/\text{cm}^2$  at 160 keV, the radius of curvature was  $29.4 \pm 2.6 \text{ m}$ , giving a tensile force per unit length of  $1.7 \times 10^2 \text{ N/m}$ . That is, *ion implantation decreased the tensile force in the polished surface*. The compressive force per unit length in the implanted surface is

$(3.6 - 1.7) = 1.9 \times 10^2 \text{ N/m}$ . If this compressive force were confined to a uniform layer with a thickness of  $0.1 \mu\text{m}$  (the approximate thickness of the implanted region), the compressive stress in the implanted layer would be  $(1.9 \times 10^2 \text{ N/m})/(0.1 \mu\text{m}) = 1.9 \text{ GPa}$ .

When the implanted wafer was warmed to 600°C, the curvature increased, giving a surface tension of  $3.4 \times 10^2 \text{ N/m}$ . Upon cooling, the initial curvature returned. The difference in tensile force per unit length between the implanted and unimplanted wafer at 600°C is  $(4.8 - 3.4) = 1.4 \times 10^2 \text{ N/m}$ . If this compressive force were confined to a uniform layer with a thickness of  $0.1 \mu\text{m}$ , the compressive stress in the implanted layer would be  $1.4 \text{ GPa}$ .

This experiment indicates that at 20°C, the implanted surface has a compressive stress on the order of  $\sim 1.9 \text{ GPa}$ . At 600°C, the apparent compressive stress is  $\sim 1.4 \text{ GPa}$ . The change between 20 and 600°C is monotonic. We are unable to conclude that this behavior can explain why ion implantation increases the flexure strength of sapphire at 300°C, but not at 600°C.

## 4. Conclusions

The purpose of this work was to see if ion implantation would increase the flexure strength of sapphire at elevated temperature. Conditions were found in which the strength of *c*-plane disks at 300°C was doubled by implantation at 1000°C on the tensile surface with  $1 \times 10^{17} \text{ B}^+ \text{ ions/cm}^2$  at 40 keV plus  $1 \times 10^{17} \text{ B}^+ \text{ ions/cm}^2$  at 160 keV. The same implantation conducted at ambient temperature was not effective. Annealing the ambient-temperature-implanted material at 1000°C failed to strengthen it. The 1000°C-implantation had no significant effect on flexure strength measured at 500° or 600°C. Increasing the dose of B<sup>+</sup> by a factor of 5 from  $2 \times 10^{17}/\text{cm}^2$  to  $1 \times 10^{18}/\text{cm}^2$  decreased the strength by a factor of 2 at 300° or 500°C. The implanted surface has significant compressive stress over the entire range from 20 to 600°C.

Implantation at 1000°C with 1 or  $2 \times 10^{17} \text{ Si}^+ \text{ ions/cm}^2$  at 80 keV also doubled the flexure strength of sapphire at 300°C, but was ineffective at 500°C. Implantation with N<sup>2+</sup>, Fe<sup>+</sup> or Cr<sup>+</sup> at 1000°C strengthened sapphire at 300°C by 36–69%. None of the ions

studied affected the *c*-axis compressive strength of sapphire measured at 600°C.

Boron implantation increased the infrared emittance of sapphire at 5  $\mu\text{m}$  wavelength by 10–15% in the temperature range 550–800°C. There was little effect on the ambient-temperature infrared transmission spectrum. Implantation with Cr<sup>+</sup> or Fe<sup>+</sup> at ambient temperature decreased the infrared transmittance of sapphire by 4–8% at 3.3  $\mu\text{m}$ , but implantation at 1000°C induced only half as much optical degradation.

### Acknowledgments

This work was supported by the Office of Naval Research. We wish to acknowledge thoughtful advice from Carl McHargue (University of Tennessee) and Jim Hirvonen (Army Research Laboratory, Aberdeen, MD), optical measurements by Michael E. Thomas, M. J. Linevsky and J. W. Giles (Johns Hopkins University Applied Physics Laboratory, Laurel, MD), and mechanical strength measurements and advice from Steve Goodrich, Dale McCullum and Bud Graves (University of Dayton Research Institute, Dayton, OH).

### References

1. D. C. HARRIS, "Materials for Infrared Windows and Domes" (SPIE Press, Bellingham, Washington, 1999).
2. F. SCHMID and D. C. HARRIS, *J. Amer. Ceram. Soc.* **81** (1998) 885.
3. R. L. GENTILMAN, E. A. MAGUIRE, H. S. STARRETT, T. M. HARTNETT and H. P. KIRCHNER, *ibid.* **64** (1981) C116.
4. P. F. BECHER, *ibid.* **59** (1976) 59.
5. S. M. WIEDERHORN, B. J. HOCKEY and D. E. ROBERTS, *Phil. Mag.* **28** (1973) 783.
6. A. H. HEUER and J. P. ROBERTS, *Proc. Brit. Ceram. Soc.* (1966) 17.
7. R. J. CHARLES and R. R. SHAW, General Electric Research Laboratory Report 62-RL-3081M (1962).
8. J. B. WACHTMAN, JR. and L. H. MAXWELL, *J. Amer. Ceram. Soc.* **42** (1959) 432.
9. E. A. JACKMAN and J. P. ROBERTS, *Phil. Mag.* **46** (1955) 809; *Trans. Brit. Ceram. Soc.* **54** (1955) 389.
10. C. J. MCHARGUE, M. E. O'HERN, C. W. WHITE and M. B. LEWIS, *Mater. Sci. Eng.* **A115** (1989) 361.
11. C. J. MCHARGUE, D. L. JOSLIN, J. M. WILLIAMS and M. E. O'HERN, *Trans. Mater. Res. Soc. Jpn.* **17** (1994) 585.
12. C. J. MCHARGUE and W. B. SNYDER, *Proc. SPIE* **2018** (1993) 135.
13. M. E. O'HERN, C. J. MCHARGUE, C. W. WHITE and G. C. FARLOW, *Nucl. Instrum. Methods Phys. Res.* **B46** (1990) 171.
14. E. D. SPECHT, C. J. SPARKS and C. J. MCHARGUE, *Appl. Phys. Lett.* **60** (1992) 2216.
15. C. W. WHITE, C. J. MCHARGUE, P. S. SKLAD, L. A. BOATNER and G. C. FARLOW, *Mater. Sci. Reports* **4** (1989) 41.
16. M. E. O'HERN, L. R. ROMANA, C. J. MCHARGUE, J. C. MCCALLUM and C. W. WHITE, *ASTM Stand. Tech. Publ.* **1125** (1992) 740.
17. S. X. REN, C. J. MCHARGUE, L. F. ALLARD, Y. CHEN, J. D. HUNN, B. N. LUCAS and R. K. WILLIAMS, *Mater. Res. Soc. Proc.* **373** (1995) 305.
18. C. J. MCHARGUE, P. S. SKLAD, C. W. WHITE and G. C. FARLOW, *J. Mater. Res.* **6** (1991) 2145.
19. C. J. MCHARGUE, S. X. REN, L. F. ALLARD, Y. CHEN, J. HUNN, R. K. WILLIAMS, A. PEREZ and G. MAREST, *Nanostructured Mater.* **6** (1995), 513.
20. C. J. MCHARGUE, G. C. FARLOW, M. B. LEWIS and J. M. WILLIAMS, *Nucl. Instrum. Methods Phys. Res.* **B19/20** (1987) 809.
21. S. NODA, H. DOI and O. KAMIGAITO, *J. Mater. Res.* **4** (1989) 671.
22. T. HIOKI, A. ITOH, S. NODA, H. DOI, J. KAWAMOTO and O. KAMIGAITO, *Nucl. Instrum. Methods Phys. Res.* **B7/8** (1985) 521.
23. V. N. GURARIE, J. S. WILLIAMS and A. J. WATT, *Mater. Sci. Eng.* **A189** (1994) 319.
24. D. C. HARRIS, *Proc. SPIE* **3705** (1999) 2.
25. M. J. LINEVSKY, R. M. SOVA, M. E. THOMAS, R. I. JOSEPH and F. F. MARK, *Johns Hopkins APL Technical Digest* **13**(3) (1992) 368.
26. E. G. NIKOLOVA *J. Mater. Sci.* **20** (1985) 1.
27. F. SCHMID, K. SCHMID, C. P. KHATTAK and D. C. HARRIS, *Proc. SPIE* **3705** (1999) 17.
28. J. C. LAMBROPOULOS, S. XU, T. FANG and D. GOLINI, *Appl. Opt.* **35** (1996) 5704.
29. M. B. SMITH, K. SCHMID, F. SCHMID, C. P. KHATTAK and J. C. LAMBROPOULOS, *Proc. SPIE* **3134** (1997) 284.

Received 8 June  
and accepted 8 November 2000