Conf-911202--4

COLLISIONAL ENERGY DEPOSITION THRESHOLD FOR EXTENDED DAMAGE DEPTHS IN ION-IMPLANTED SILICATES

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SAND--91-1635C

DE92 004737

ABSTRACT

Many properties of implanted fused silica (e.g., surface stress, hardness) exhibit maximum implantation-induced changes for collisional energy deposition values of ~10^{20} keV/cm^3. We have observed a second critical energy deposition threshold value of about 10^{22} keV/cm^3 in stress and hardness measurements as well as in many other experiments on silicate glasses (leaching, alkali depletion, etching rate, gaseous implant redistribution). The latter show evidence for damage depths exceeding TRIM ranges by about a factor of 2. For crystalline quartz, a similar threshold value value has been found for extended damage depths (greater than TRIM) for 250 kev ions (H-Au) as measured by RBS and interference fringes. This phenomenon at high damage deposition energy may involve the large stress gradients between damaged and undamaged regions and the much increased diffusion coefficient for defect transport.

INTRODUCTION

Implantation of materials results in surface stress induced by volumetric changes. For fused silica, after an initial expansion at low fluences, the stress is tangential due to the compaction of the implanted layer [1-3]. It has been found that the maximum stress is attained for collisional energy depositions of about 10^{20} keV/cm^3 and that other physical properties such as hardness, etch rate, and thermoluminescence (TL) also exhibit maximum implantation-induced changes near this critical value [4]. For fused silica and other simple silicate glasses, it has also been shown that while electronic energy deposition has an effect on stress and other properties, the collisional component is on the order of 100 times more effective [1,5].

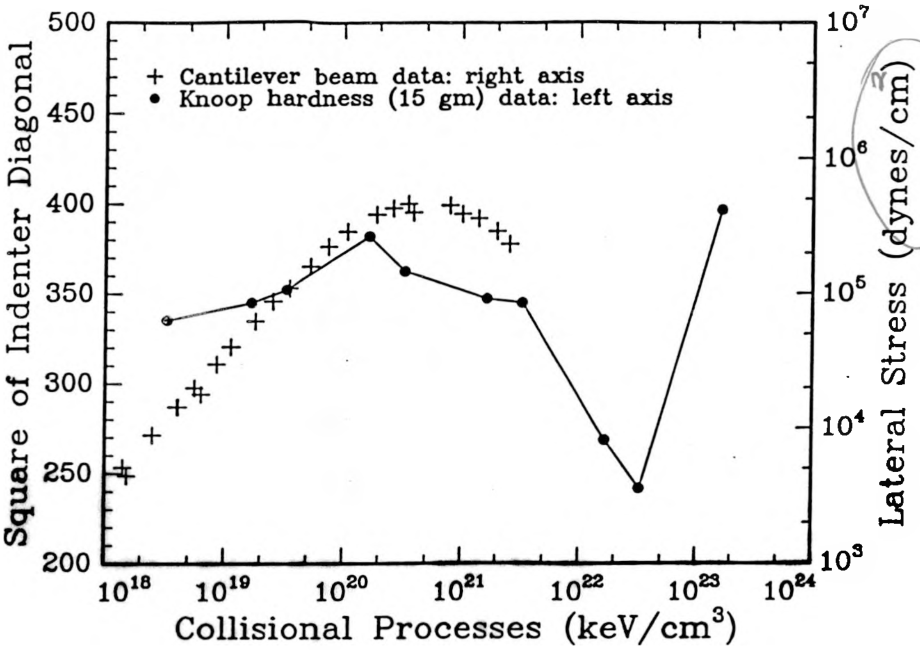
The implantation-induced damage range can be deduced, e.g., by Rutherford backscattering (RBS) measurements of the ion penetration depth. Other experiments can allow estimates of the damage range to be made. These include H penetration from aqueous solutions and--for alkali silicates--the depletion of alkali from the near-surface region of the implanted glass. A convenient review source for these types of experiments has been published [6]. For most of these experiments in which the deposition collisional energy is <10^{22} keV/cm^3, the damage range is found to be in reasonable agreement with theoretical estimates (TRIM code [7]).

This paper presents data from past work and from new experiments which indicate that for high fluence and high collisional energy deposition, there exists a threshold collisional energy at about 10^{22} keV/cm^3 above which an increased damage range is found which exceeds the TRIM ($R_p + \Delta R_p$) range by a factor of 2. A preliminary account encompassing some of the observations of this paper has been given [8].

RESULTS AND DISCUSSION

Stress and Indentation Hardness

Surface stress can be conveniently measured by cantilever beam techniques [1]. Figure 1(a) shows the lateral stress generated in fused silica by a 500 keV implant into fused silica [1]. Also shown is the square of the Knoop indenter diagonal (15 g load) for the same Ar energy [4]. As indicated in the Introduction, a maximum in stress (minimum in hardness) is seen at about a few times 10^{20} keV/cm^3. The Knoop indenter data show an increase in hardness (to a value greater than the original glass) followed by a reversal with increasing energy deposition. To augment the scanty Knoop data, new measurements of the stress that develops with higher energy deposition were made and are shown in Fig. 1(b) for 500 keV Ar. Here it is clear that there is a sharp change in stress beginning at about 10^{23} keV/cm^3. although not apparent in Fig. 1(b), the sign of the last data point at high energy has changed and thus indicates that the



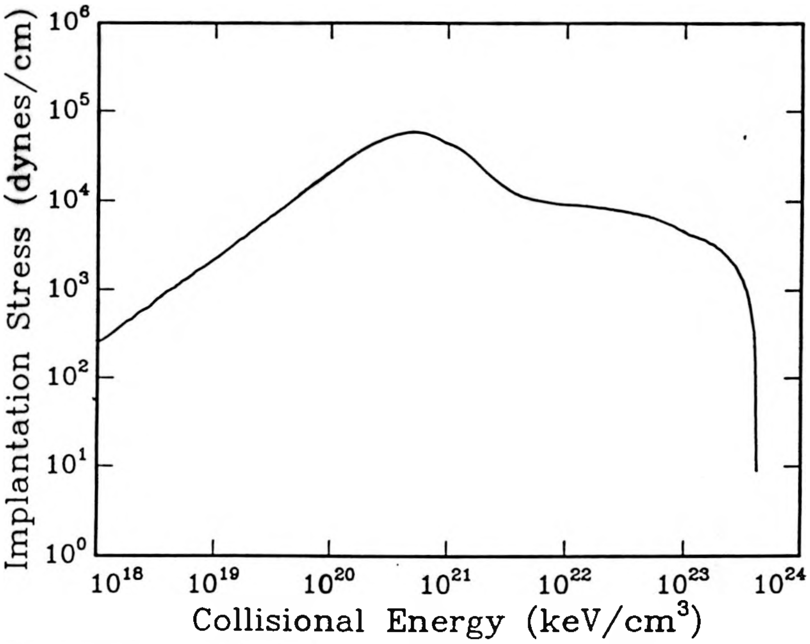
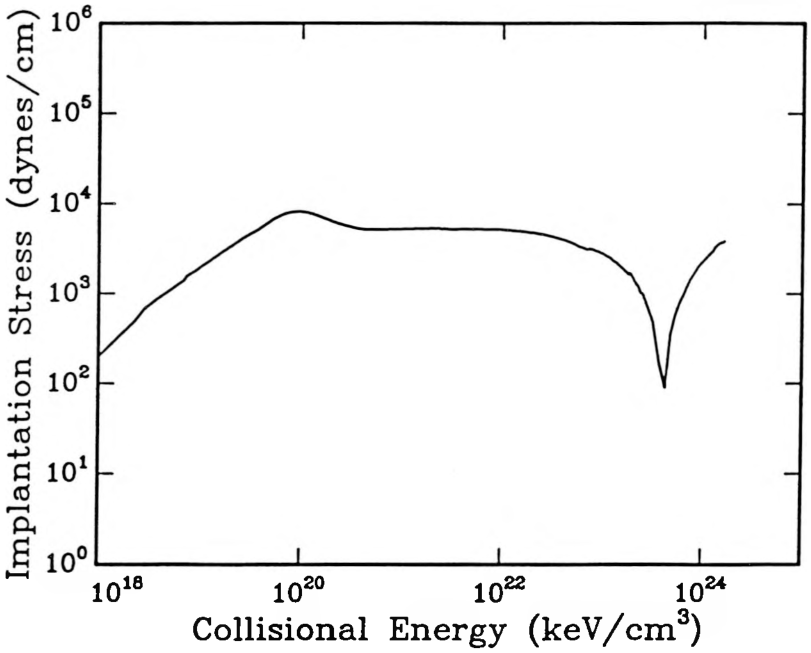


Fig. 1.

(a) Lateral stress (after Ref. 1) and square of Knoop indenter diagonal (after Ref. 4) vs. collisional energy deposition for 500 keV Ar on CFS 7940 fused silica; (b) lateral stress vs. collisional energy deposition (as in (a)) but extended to higher values; (c) lateral stress vs. collisional energy deposition for 210 keV Xe on CFS 7940 fused silica.



stress has changed from tension (compaction) to compression (expansion). The data acquisition program was limited with respect to the highest possible value of fluence and prevented further data accumulation at high fluence. The stress data change sign but the absolute values are plotted for simplification. There is a continuous change in stress as the beam goes through the null point and begins to bend in the opposite direction. The stress data is in accord with the indications of the Knoop indenter diagonal measurements although there is not complete agreement as to energy deposition values. There may be some effect on stress relief due to bubble formation; however, the data of Fig. 1(c) for 210 keV Xe indicates, as expected for this much heavier ion, that the transition in stress occurs at lower fluence levels but at about the same energy deposition value. In addition, it is clearly seen that the reversal in stress has occurred.

Etching Rate

Thermal oxides on Si were used to determine the effects of implantation on etching rate. Experiments were performed on samples of 500 nm oxide thickness. Etching was done for various times in an 0.5% HF solution and the residual thickness measured with a profilometer. Figure 2 shows the results for 40, 70, and 100 keV Ar implantations (all at 10^{17} Ar/cm^2) where the residual thickness is plotted against the etching time in seconds. The data show that the thickness of the removed material increases linearly with etching time until a depth from the surface is reached at which the etching rate assumes the value which is obtained for unimplanted oxides. the computed etching rates for the 40, 70, and 100 keV Ar implants are 4.0 Å/s, 3.5 Å/s, and 3.1 Å/s, respectively, as compared with a rate of 0.45 Å/s for unimplanted material.

Figure 3 shows the RBS (2.2 MeV He) measurements of the Ar depth profiles for the implant energies of Fig. 2. The Ar distributions are flat and the depths are in good agreement with those deduced from the etching rate data. The damaged region thicknesses are about a factor of 2 greater than the theoretical ranges (TRIM [7]; $R_p + \Delta R_p$). Figure 4 shows the influence of ion fluence/collisional deposited energy on the damage depth of 100 keV Ar implanted 5000 Å oxide. For 6×10^{14} Ar/cm^2 (~4.4×10^{21} keV/cm^3) the damage depth is about 1200 Å (TRIM: $R_p + \Delta R_p \sim 1300$ Å), i.e., the predicted and experimental depths are in substantial agreement. The data show an increased deviation from the TRIM value for 4×10^{15} Ar/cm^2 (~3×10^{22} keV/cm^3), yielding a damage depth of ~1800 Å. At a fluence level of 2×10^{16} Ar/cm^2 (~1.4×10^{23} keV/cm^3) the data are in agreement with that for the 10^{17} Ar/cm^2 implant of Fig. 2. This clear indication of an energy deposition dependent threshold for etching rate is in accord with the threshold found for the stress and hardness discussed in the previous sub-section (Fig. 1).

Leaching and Alkali Depletion

Numerous experiments on the hydration of implanted silica glasses have been performed [9-11]. These experiments also revealed a critical threshold value (>10^{22} keV/cm^3) for deep H penetration and the depths exceeded TRIM values by about a factor of 2. There was some speculation that this occurred due to a tail of beyond-range defects and/or light ion recoil implantation.

In alkali-silicates, the alkali is removed [4,12] from the implanted region and the depth of the depleted layer was found to exceed the TRIM values as energy deposition concentrations increased. The preferential removal of alkali is associated with a radiation-enhanced diffusion coefficient [4,13].

Crystalline Quartz

In an extension of the work on silicate glasses, we have examined the effects of ion implantation on crystalline quartz. Implantations of 1×10^{16} ions/cm^2 for incident ions from H to Au were made and damage depths determined from transmission interference fringes. In addition, implanted ion depth profiles were made by RBS (2.8 MeV He) for ion species from Ar through Au. The ratio of the measured ranges relative to the TRIM range are plotted in Fig. 5 as a function of collisional energy. It can be seen that there is a distinct threshold energy of about 10^{22} keV/cm^3 above which the damage depths begin to markedly exceed the theoretical values and approach a ratio of 2, as was the case for the silicate glasses.

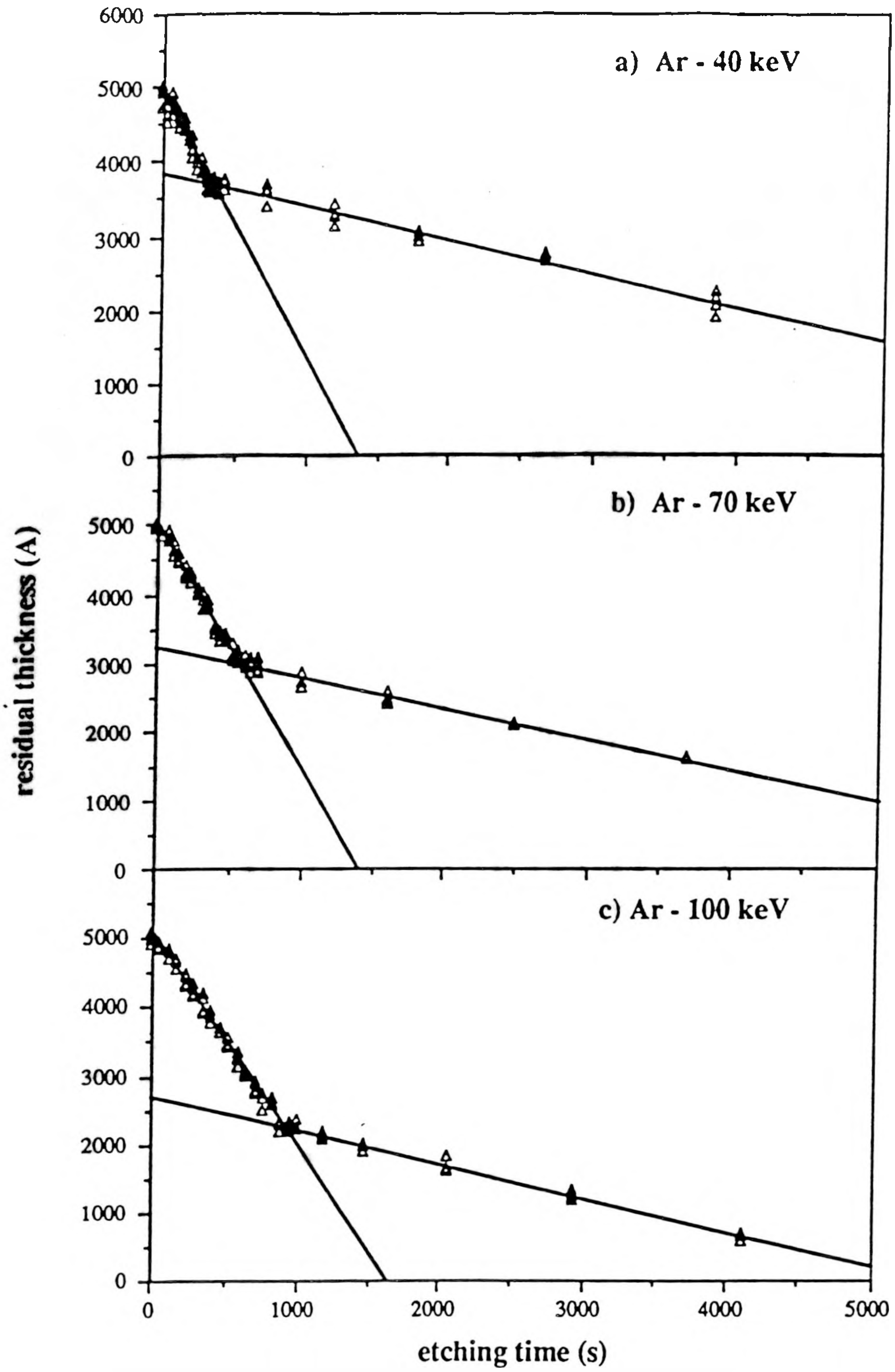


Fig. 2. Residual thickness vs. etching time for 5000 Å SiO_2 films on Si implanted with 1 x 10^{17} Ar/cm^2 at energies of: (a) 40 keV; (b) 70 keV; and (c) 100 keV.

Compilation of Experimental Results

In Figure 6 we show the results of range deviations from various experimental procedures (leaching, etching, gaseous implant redistribution, alkali depletion, and the quartz ranges) as a function of collisional energy. The variety of experiments and the solid indication of a threshold collisional energy deposition for the sudden change in physical properties to depths exceeding theoretical expectations by a factor of 2. The cantilever-beam stress data are consistent with a sudden change in effective damage layer thickness. In our earlier work [8] (which included changes in IR modes) we speculated that the sharp change could result from

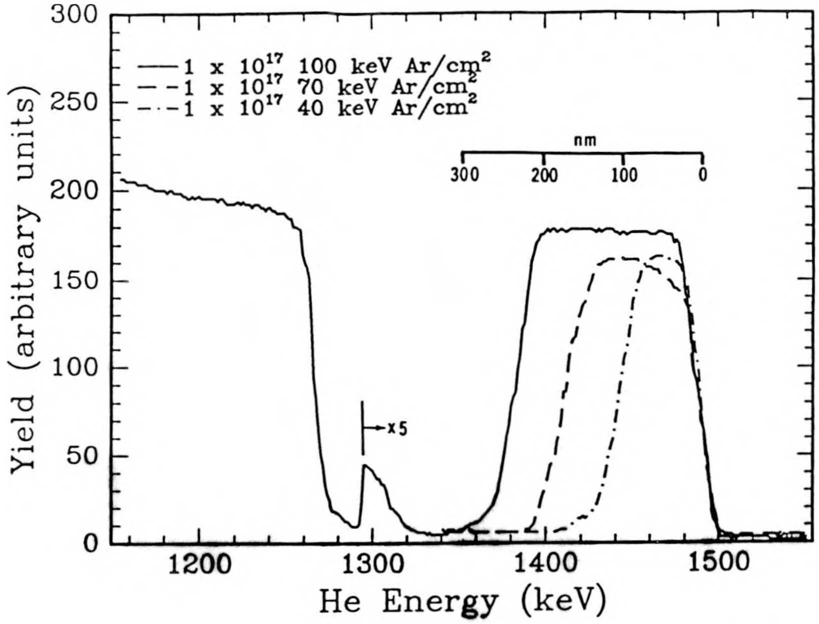


Fig. 3.

RBS yield vs. He scattering energy for 1 x 10^{17} Ar/cm^2 at 40 keV, 70 keV, and 100 keV into a 5000 Å oxide on Si. The Ar profiles are x 5 relative to the Si edge in SiO_2.

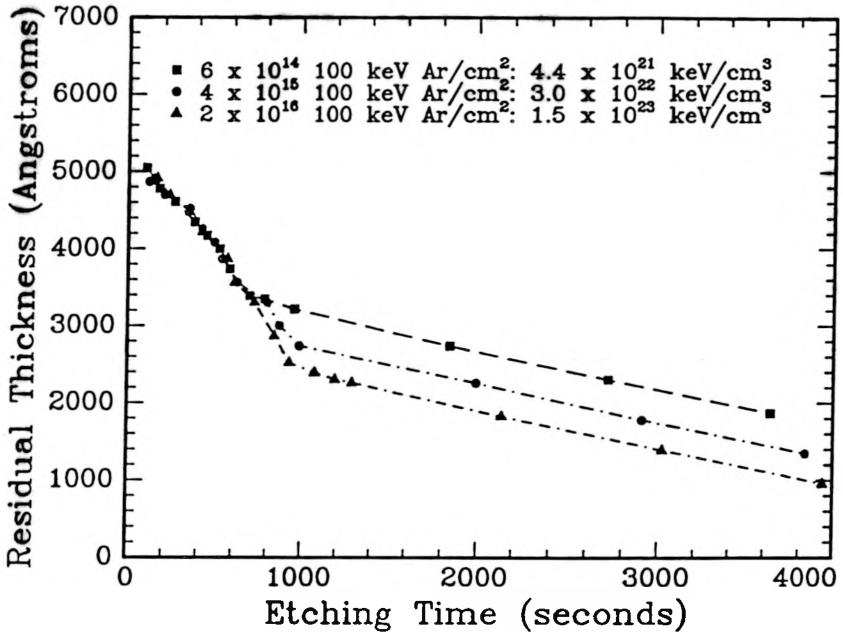


Fig. 4.

Residual thickness vs. etching time for samples of 5000 Å oxides on Si implanted with 100 keV Ar at the indicated fluences and collisional energy depositions.

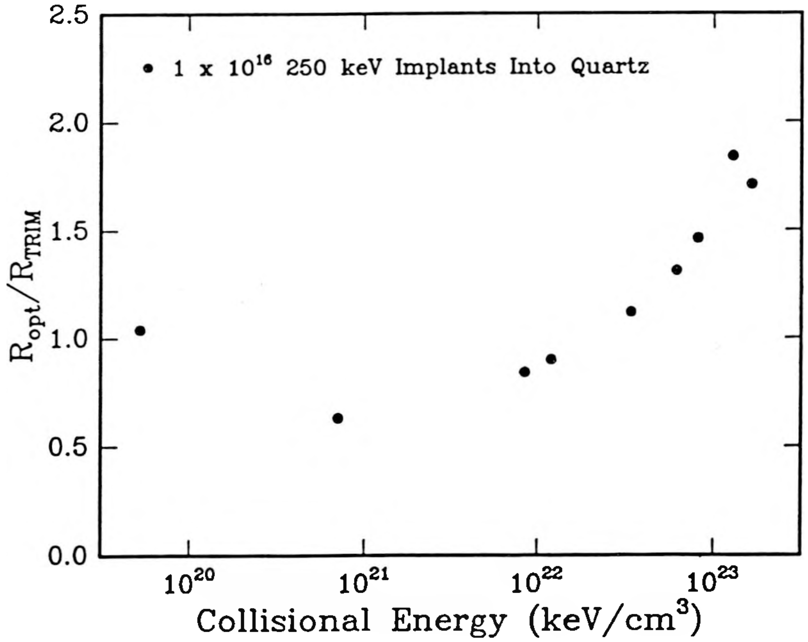


Fig. 5.

Values of R_{opt}/R_{TRIM} (from Table 1) for crystalline quartz vs. energy into collisional processes for the same 1 x 10^{16} 250 keV ions/cm^2.

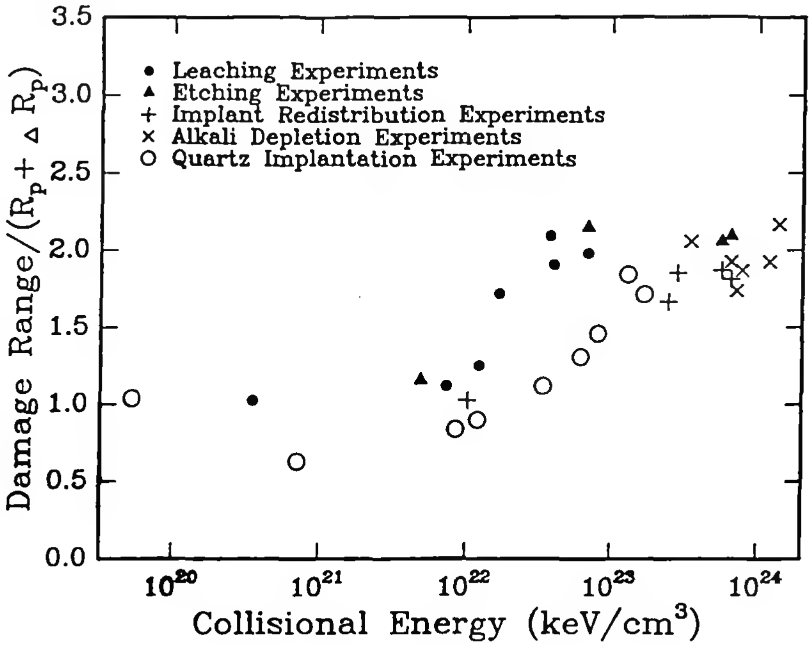


Fig. 6.

Ratio of damage ranges to TRIM range for as compiled from experiments on implanted silicate glasses involving leaching, etching, gaseous implant redistribution, alkali depletion, and for the crystalline quartz data of Table I.

the large gradients of stress between the highly damaged region (on the order of 10 dpa) and the undamaged substrate. Defect transport along these stress gradients could be expected to be significant.

ACKNOWLEDGEMENTS

The work of G. W. Arnold was supported by the U.S. Department of Energy under contract number DE-AC04-76DP00789. The work was carried out within the project "Materali Speciali per Technologie Avanzate" of C.N.R. The assistance of K. G. Minor and N. D. Wing at Sandia National Laboratories is greatly appreciated. We also thank Mr. Rampazzo of Sezione I.N.F.N.-Padova for some of the original drawings.

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