GSI-Preprint-97-70
Dezember 1997

**SWELLING OF SiO_2 QUARTZ INDUCED BY
ENERGETIC HEAVY IONS**

C. Trautmann, J.M. Costantini, A. Meftah, K. Schwartz, J.P. Stoquert, M. Toulemonde

(accepted for publication in Atomistic Mechanisms in Beam Synthesis & Irrad of Matls.
MRS Proceedings, Boston 1997)

SCAN-9801067

CERN LIBRARIES, GENEVA

Swg 803

Gesellschaft für Schwerionenforschung mbH
Planckstraße 1 • D-64291 Darmstadt • Germany
Postfach 11 05 52 • D-64220 Darmstadt • Germany

SWELLING OF SiO₂ QUARTZ INDUCED BY ENERGETIC HEAVY IONS

C. TRAUTMANN¹, J.M. COSTANTINI², A. MEFTAH³, K. SCHWARTZ¹
J. P. STOQUERT⁴, AND M. TOULEMONDE⁵

¹ Gesellschaft für Schwerionenforschung, Planckstr. 1, 64291 Darmstadt, Germany,
C.Trautmann@gsi.de

² DPTA/PMC, BP 12, 91680 Bruyères-Le-Châtel, France

³ ENSET, BP 26 Merj-eddib, 21000 Skikda, Algeria

⁴ Laboratoire PHASE, 67037 Strasbourg - cedex 2, France

⁵ CIRIL, Laboratoire commun CEA/CNRS, BP 5133, 14070 Caen-cedex 5, France

ABSTRACT

A pronounced swelling effect occurs when irradiating SiO₂ quartz with heavy ions (F, S, Cu, Kr, Xe, Ta, and Pb) in the electronic energy loss regime. Using a profilometer, the out-of-plane swelling was measured by scanning over the border line between an irradiated and a virgin area of the sample surface. The step height varied between 20 and 300 nm depending on the fluence, the electronic energy loss and the total range of the ions. From complementary Rutherford backscattering experiments under channelling condition (RBS-C), the damage fraction and corresponding track radii were extracted. Normalising the step height per incoming ion and by the projected range, a critical energy loss of 1.8 ± 0.5 keV/nm was found which is in good agreement with the threshold observed by RBS-C. Swelling can be explained by the amorphisation induced along the ion trajectories. The experimental results in quartz are compared to swelling data obtained under similar irradiation conditions in LiNbO₃.

INTRODUCTION

Radiation induced volume expansion is a general effect which has been discovered in various solids in the late fifties. The swelling under irradiation can result from point defects, but also from defect aggregates or from phase transitions. In the case of point defects, the swelling mechanism is well understood [1,2], while for more complex defects, i.e. under irradiation at higher doses, it is described only phenomenologically. In this regime, the relative volume changes are larger and, depending on the material, can reach several percent (e.g. 15% for quartz) [3]. Swelling occurs in a wide range of irradiation conditions (e.g. temperature, dose, and dose rate) and under various particle beams such as electrons, neutrons or ions [4-8]. More recently, swelling has been observed when irradiating Al₂O₃ [9] and LiNbO₃ [10-12] with energetic heavy ions. The macroscopic volume increase of the bulk material was clearly attributed to the damage produced by electronic excitations. The goal of our study was to extend the swelling tests to SiO₂ crystals. It should be mentioned that in quartz, the damage under heavy ion irradiation has been studied by various techniques [7,13-15]. Evidence was given that along the ion trajectory a cylindrical zone of amorphous silica is formed having a diameter of a few nanometers. The experimental data are

in good agreement with the thermal spike model which describes the track as a cylindrical zone resulting from rapid quenching of a liquefied phase along the ion path [15].

In order to perform systematic measurements of the out-of-plane swelling in SiO_2 , we irradiated quartz with various ion species in the energy regime between 15 and 830 MeV. The swelling tests were complemented by RBS-C analysis from which the damage fraction at different ion fluences was deduced. By combining the two techniques, we followed the data analysis as presented by Canut et al in ref. [10]. Extending this analysis, it was possible to extract an energy loss threshold for swelling. Finally, we will compare ion induced swelling and damage effects in quartz and in LiNbO_3 .

EXPERIMENTAL CONDITIONS AND PHYSICAL CHARACTERISATIONS.

Irradiation

We used single crystals of synthetic quartz of a thickness of about 1.5 mm. The polished surface (optical quality) of the samples was covered with a 50 nm thin carbon layer in order to avoid electrostatic charging during irradiation or analysis. The irradiations were performed using lighter ions (^{19}F , ^{32}S , and ^{63}Cu) at the 7 MV tandem Van de Graaff in Bruyères-le-Châtel and heavier ions (^{84}Kr , ^{129}Xe , ^{181}Ta , and ^{208}Pb) at the medium energy line of the GANIL accelerator in Caen. All irradiations were performed at room temperature under normal incidence. In some cases, thin aluminium foils were placed in front of the samples in order to vary the energy and energy loss of the ions when impinging on the sample surface. By limiting the maximum energy of the ion beam to 4 MeV/u, significant velocity effects were avoided [16]. A complete list of the irradiation parameters is given in Table I, where the values for the energy loss dE/dx and the ion range were calculated with the TRIM 91 code [17]. The flux of the ion beam was of the order of $10^9 \text{ ions s}^{-1}\text{cm}^{-2}$ at the tandem Van de Graaff accelerator and $3 \times 10^8 \text{ ions s}^{-1}\text{cm}^{-2}$ at the GANIL accelerator. The maximum applied ion fluence ϕ depended on the ion species and was, e.g., 4×10^{11} and $2 \times 10^{14} \text{ ions/cm}^2$ for Pb and F ions, respectively. During the irradiation, all crystals were partially masked in order to analyse the damage of an irradiated area in direct comparison with a virgin area of the same sample.

Table I. Parameters of ion irradiation, the damage cross section A_d and track radius R

ion	energy (MeV/u)	dE/dx (keV/nm)	range (μm)	$A_d = \pi R^2$ (10^{-13} cm^2)	radius R (nm)	reference
F	0.79	2.4	7.1	0.11 ± 0.03	0.6 ± 0.1	[14]
S	1.56	4.7	11.7	1.2 ± 0.3	2.0 ± 0.3	[14]
Cu	0.79	9.1	8.7	2.6 ± 0.5	2.9 ± 0.03	[14]
Kr	3.3	12.0	27.7	3.3 ± 1.0	3.2 ± 0.5	[14]
Xe	1.5	17.0	14.7	5.0 ± 1.0	4.0 ± 0.4	[14]
Ta	0.8	17.6	13.2	11.2 ± 1.5	6.0 ± 0.8	present work
	1.5	21.1	19.6	8.9 ± 1.0	5.3 ± 0.6	
	4.6	24.5	48.0	8.5 ± 1.0	5.2 ± 0.6	
Pb	1.2	21.9	15.7	11.2 ± 1.5	5.5 ± 0.5	present work
	4.0	27.6	38.8	8.9 ± 1.0	5.2 ± 0.5	

Step height measurements:

The swelling effect was studied using a profilometer (Dektak 8000) where a high precision stage moves the sample beneath a diamond-tipped stylus. The out-of-plane swelling l was measured by scanning over the border line between an irradiated and a virgin area of the sample surface (Fig. 1). Depending on the ion fluence, the electronic energy loss and the total range of the ions, l varied between 20 and 300 nm. The surface roughness of the crystals was in the order of 5 nm. For each sample, a mean step height was extracted from several measurements.

The evolution of the step height as a function of the ion fluence is presented in Figure 2. After an initial linear increase, the swelling saturates at high ion fluences where the ion tracks begin to overlap. This saturation effect was observed only when a sufficiently high fluence was obtained such as in the case of Ta ions ($2 \times 10^{12} \text{ cm}^{-2}$) and F ions ($1 \times 10^{14} \text{ cm}^{-2}$). For all other ion species, the swelling effect was restricted to the linear regime.

Fig. 1. Profilometer scan from the irradiated ($4.6 \times 10^{13} \text{ F-ions/cm}^2$) (left) to the virgin (right) area of the crystal.

Fig. 2. Step height as a function of the fluence of the Ta ions (0.8 MeV/u).

Damage analysis by Channelling Rutherford Backscattering

The radiation damage of the irradiated crystals was analysed by means of Rutherford backscattering under channelling condition (RBS-C). The experiments were performed at the 4 MV Van de Graaff accelerator (Strasbourg) using 2 MeV He^+ ions and a backscattering angle of 170° . Figure 3 shows a typical RBS-C spectrum of a non-irradiated (curve a) and an irradiated area (curve b) of a SiO_2 quartz sample in channelling condition along the (0001) direction. Due to the damage induced by the ions, the backscattering yield increases, but is still below the yield of a randomly oriented crystal (curve c).

Using the surface approximation, the backscattering yield χ was measured by extrapolating the energy evolution of the yield over the first 500 nm up to the mean energy of the random edge. The damage fraction F_d of the material is given by

$$F_d = (\chi_i - \chi_v) / (\chi_r - \chi_v), \quad (1)$$

where χ_i and χ_v are the backscattering yield under channelling condition of the irradiated and of the virgin sample, respectively, and χ_r corresponds to the yield of the randomly-oriented crystal.

Fig. 3. RBS spectra of backscattered He ions on SiO₂ quartz in channelling conditions (0001): (a) virgin sample (b) sample irradiated with Pb ions ($2.3 \cdot 10^{11} \text{ cm}^{-2}$ at 1.2 MeV/u) (c) virgin sample in random orientation.

Fig. 4. Swelling versus damage fraction for Cu, Xe, and Kr ions with a total range of 8.7, 14.7 and 27.7 μm , respectively.

Assuming that at higher ion fluences ϕ , the overlapping of tracks leads to a damage distribution which can be described by a Poisson law

$$F_d = 1 - \exp(-A_d \times \phi) \quad (2)$$

we can deduce the mean cross section A_d of the damage. Since the damage zone along each ion trajectory has a cylindrical geometry, the track radius R can be determined from $A_d = \pi R^2$. RBS-C data analysed accordingly are listed in Table 1. The track radii of Ta and Pb ions at different energies exhibit a maximum variation of the radius of around 15% for the studied energy regime from 0.8 to 4.6 MeV/u and 1.25 to 4.0 MeV/u, respectively. This observation supports the assumption that, in our situation, the track radius can be regarded as almost constant along the full length of the ion path.

DATA ANALYSIS AND DISCUSSION:

Combining the data from the swelling and the RBS-C measurements, it becomes evident that the step height has a linear dependence on the damage fraction F_d . Figure 4 demonstrates this relation for the irradiation with Cu, Xe and Kr ions. Moreover, the slope of the curve becomes steeper for larger range of the ions. The same observation has been made in LiNbO₃ [9,10]. In order to compare quantitatively our results to the effects observed in LiNbO₃, the step height l was normalised by the damage fraction F_d and then plotted versus the total range L of the ions (Fig. 5). Although the data exhibit some scattering, in particular for the lighter ions in quartz, both materials follow a linear dependence. The line fit intercepts the range axis at $L_0 \approx 5 \mu\text{m}$ (Fig. 5) indicating that the damage responsible for swelling is not produced along the full range of the ion path. The slope of the curve has a value of about 0.04 and corresponds to the relative dimensional change l/L . Using this presentation, it is surprising to note that SiO₂ and LiNbO₃ show qualitatively and quantitatively the same dimensional change.

In our experimental set-up, the free expansion of the irradiated volume is limited by the constraint of the undamaged substrate. Therefore, the induced swelling occurs mainly normal to the sample surface and corresponds to a relative decrease of the mass density. The density

decrease can be understood on the basis of the finding that tracks in quartz consist of amorphised regions [14]. As a consequence of the transition from the crystalline to the amorphous phase, each individual track undergoes a volume expansion finally leading to a macroscopic out-of-plane swelling.

In order to test the correlation between swelling and the energy loss of the ions, we determined the relative contribution of each single ion per unit damage length. This was done by dividing the initial rate of swelling ($\Delta l / \Delta \phi$) by the projected ion range L and plotting it versus the mean energy loss. Since the ions were stopped in the crystals, we used the energy loss averaged along the ion path obtained from dividing the initial energy by the total range of the ions. If we fit the experimental data by a linear curve, a threshold for the energy loss of $(dE/dx)_c = 1.8 \pm 0.5$ keV/nm was found. The given error includes considerations that the critical energy loss is not surpassed along the full length of the ion path. In the case of the light ions (F, S, and Cu), we took this part of the trajectory into account as possibly not contributing to the swelling. It should be noted that the threshold of swelling is in good agreement with the value determined from the RBS-C analysis of the damage induced with low-velocity ions [14].

Fig. 5. Step height normalised by the damage fraction F_d as a function of the ion range for SiO₂ in quartz and LiNbO₃ [11].

Fig. 6. The initial swelling $(\Delta l / \Delta \phi)$ normalised by the ion range L versus the mean energy loss dE/dx in SiO₂ quartz.

CONCLUSIONS

Swelling effects have been found when irradiating SiO₂ quartz with various heavy ions in the electronic energy loss regime. For high fluences when track overlapping becomes significant, the step heights show saturation effects. The out-of-plane swelling depends both on the induced damage fraction and on the range of the ions. From a detailed analysis of the swelling data, a critical energy loss of 1.8 ± 0.5 keV/nm was extracted. Below this value, the damage along the ion path does not contribute to the expansion of the sample dimension. The observed macroscopic swelling can be interpreted in terms of a decrease of the mass density of around 4%. This is supported by the finding that energetic ions induce amorphisation along their trajectories [14]. The quantitative analysis of swelling and damage creation gives evidence that both oxides, SiO₂ quartz and LiNbO₃ undergo similar structural modifications under heavy ion irradiation.

REFERENCES :

1. R. Balzer, H. Peisl and W. Waidelich, Phys. Stat. Sol. **15**, p. 495 (1966).
2. F. Agullo-Lopez, C.A.R. Catlow and P. D. Townsend, in Point defects in Materials, Academic Press , pp.149 (1988).
3. L. Douillard and J. P. Duraud, J. Phys. III France **6**, p. 1677 (1996).
4. S.L. Chan, L.F. Gladden and S.R. Elliott, in The Physics and Technology of Amorphous SiO₂, edited by R.A.B. Devine, Plenum Press, pp. 83 (1987).
5. F.W. Clinard (Guest Editor) MRS Bulletin **22**, N°4 (1997).
6. D.S. Bilington and J.H. Crawford, in Radiation Damage in Solids, Princeton University Press, Princeton (1961).
7. L. Douillard, F. Jollet, J.P. Duraud, R.A.B. Devine and E. Dooryhee, Rad. Eff. Def. Sol. **124**, p. 351 (1992).
8. W. Primak, Phys. Rev. **B 14**, p.4679 (1976).
9. R.Brenier, B. Canut, S.M.M.Ramos and P. Thévenard, Nucl. Instr. Meth. Phys. Res. **B 90**, p. 339 (1994).
10. B. Canut, R. Brenier, A. Meftah, P. Moretti, S. Ould Salem, S.M.M. Ramos, P. Thévenard and M. Toulemonde, Nucl. Instr. Meth. Phys. Res. **B 91**, p. 312 (1994)
11. B. Canut, S.M.M. Ramos, R. Brenier, P. Thévenard, J.L. Loubet and M. Toulemonde, Nucl. Instr. Meth. Phys. Res. **B 107**, p. 194 (1996).
12. S.M.M. Ramos, B. Canut, M. Ambri, C. Clement, E. Dooryhee, M. Pitival, P. Thévenard and M. Toulemonde, Nucl. Instr. Meth. Phys. Res. **B 107**, p. 254 (1996).
13. R.L. Fleischer, P.B. Price and R.M. Walker, Nuclear Tracks in Solids: Principles and Applications, University of California, Berkeley, (1975).
14. A. Meftah, F. Brisard, J.M. Costantini, E. Dooryhee, M. Hage-Ali, M. Hervieu, J.P. Stoquert, F. Studer and M. Toulemonde, Phys. Rev. **B 49**, p. 12457 (1994).
15. M. Toulemonde, J.M. Costantini, Ch. Dufour, A. Meftah, E. Paumier, and F. Studer, Nucl. Instr. Meth. Phys. Res. **B 116**, p. 37 (1996).
16. A. Meftah, F. Brisard, J.M. Costantini, M. Hage-Ali, J.P. Stoquert, F. Studer and M. Toulemonde, Phys. Rev. **B 48**, p. 920 (1993).
17. J.P. Biersack and L.G. Haggmark, Nucl. Instr. Meth. **174**, p. 257 (1980).