Modifications induced by swift heavy ions

C TRAUTMANN

Gesellschaft für Schwerionenforschung, Planckstr. 1, 64291 Darmstadt, Germany

Abstract. On their way through matter, energetic heavy ions induce a continuous trail of ionization and excitation. A narrow path of irreversible physical, chemical and structural changes, the latent track, is formed. In this report, some of the most important techniques (transmission electron and atomic force microscopy, small-angle X-ray scattering, chemical etching) to study and to characterize ion induced modifications will be presented. Furthermore, selected examples for application oriented projects will be given.

Keywords. Ion tracks; transmission electron microscopy; scanning force microscopy; small-angle X-ray scattering; track etching.

1. Introduction

Tracks of energetic particles in solids have been investigated for more than three decades. In particular, the availability of accelerators for heavy ions and nowadays even for cluster beams promoted a wide variety of systematic track studies using well defined irradiation conditions. The field has continuously developed both in basic understanding and in technological applications (Fleischer *et al* 1975; Spohr 1990; Fleischer 1998). This paper gives a short review of several techniques presently used to gain a better knowledge of the mechanisms of track formation and of track properties. Recent studies by means of transmission electron and atomic force microscopy, small-angle X-ray scattering and chemical etching are presented. Finally, also some selected examples for new technological applications of etched tracks in polymers are given.

All irradiation experiments have been performed with ions of energies of several MeV per nucleon (MeV/u). In this energy regime, the stopping process in matter is dominated by inelastic interactions of the ions with the target electrons (electronic energy loss) whereas elastic collision processes with the target atoms (nuclear energy loss) can be neglected (figure 1).

During the slowing down process, the energy of the fast ions is transformed into excitation, ionization and kinetic energy of ejected target electrons. Most of the primary ionizations and excitations occur close to the ion trajectory in a cylindrical region with a radius of a few nanometers (track core). At larger distances, in the so-called track halo, the ionizations are caused by energetic δ -electrons of secondary cascade processes. The size of the halo depends on the projectile velocity and may reach up to about 1 μm (Katz *et al* 1990; Kraft and Krämer 1993; Gervais and Bouffard 1994). Defects induced in the halo are significant only in materials which are sensitive to radiolysis, such as alkali

halides, polymers, or biological objects. The damage creation in this region is similar to processes known from conventional radiation such as gammas, X-rays or electrons.

2. Imaging of ion tracks

2.1 Transmission electron microscopy

The first direct observation of damage induced by fission fragments in mica was made by Silk and Barnes (1959) using transmission electron microscopy (TEM). During longer periods of observation, however, the damaged areas disappeared due to the annealing effect of the electron beam, making it very difficult to obtain detailed information on the structure of the tracks.

In later years, a significant effort was achieved to observe tracks in various other solids mainly in insulators [ZrSiO_4 (Fleischer *et al* 1965; Bursill and Braunshausen 1990), MoO_3 (Izui and Suzuki 1963) or in semiconducting layered crystals MoS_2 (Izui and Fujita 1963; Morgan and Chadderton 1968)]. To date, improved technologies allow the observation of tracks with much higher resolution. Tracks have been imaged in all kinds of other materials [e.g., high T_c superconductors (Bourgault *et al* 1989a, b; Legris *et al* 1993; Zhu 1993; Wiesner *et al* 1996), SiO_2 quartz (Meftah *et al* 1994), yttrium-iron garnet (Fuchs *et al* 1987; Toulemonde 1988, 1993; Houpert *et al* 1989a, b; Studer 1991; Dunlop *et al* 1997), sapphire (Ramos *et al* 1998)], including even a few selected metals (Barbu *et al* 1991; Henry *et al* 1992; Dammak *et al* 1995a, b). In most non-radiolytic insulators, tracks appear as disordered cylindrical zones as demonstrated for muscovite mica in figure 2 (Vetter *et al* 1998a). The boundary between the amorphized track region and the crystalline surroundings is extremely sharp.

Another TEM image is given in figure 3 showing a single track of an uranium ion in germanium sulfide. It is interesting to note that the cross sections of the track is not circular but has an elliptical shape. Their long axes are oriented along the crystal axis with the smallest lattice constant. Obviously, the anisotropy of the GeS lattice is reflected in the resulting track geometry. In addition, the amorphized track core is surrounded by four regions of oriented strain manifested by the dark butterfly shaped contrast in the crystalline material at a distance of about 10–20 nm (Scholz *et al* 1993; Vetter *et al* 1994, 1998b; Vetter 1995).

2.2 Scanning probe microscopy

Since several years, the technique of scanning tunnelling (STM) and scanning force microscopy (SFM) is applied to investigate ion irradiated surfaces of various solids (Porte *et al* 1989, 1991; Coratger *et al* 1990; Kemmer *et al* 1992a; Yan *et al* 1994; Biró *et al* 1995, 1996).

Figure 1. Qualitative relation of nuclear and electronic energy loss as a function of the ion energy.

Figure 2. Tracks of U ions (11.4 MeV/u) in muscovite mica (Vetter *et al* 1998a).

A special feature of this technique is the characterization of ion induced modifications on a nanometer scale such as amorphization, modified friction and elasticity (Kemmer *et al* 1992b; Bouffard *et al* 1993; Hagen *et al* 1994a; Neumann *et al* 1996a). The dynamic friction coefficient of the track zones was analysed quantitatively by simultaneously recording topographical and lateral-force images. For tracks in mica, the coefficient inside the track zone was found to be about a factor of two larger than compared with the virgin material outside the track (Hagen *et al* 1994b). In order to test changes of the elastic properties, the microscope is operated in a mode where the sample position is varied periodically to the sample surface (figure 4). This results in a periodic

Figure 3. Tracks of U ions (11.4 MeV/u) in germanium sulfide irradiated normal to the crystal surface (Vetter *et al* 1998a).

Figure 4. Scheme of the SFM modulation mode. Driven by a sample modulation of constant amplitude, the cantilever is deflected as a function of the surface elasticity (Neumann *et al* 1996b).

deformation of the sample surface and in a vertical cantilever deflection. The deflection is enlarged (reduced) if the sensor probes a harder (softer) surface area (Neumann *et al* 1996b).

The force modulation image of a mica surface irradiated with gold ions is shown in figure 5. The circular dark areas indicate that the track zones have a reduced elasticity. It should be noted that the averaged diameters obtained by force-modulation and by lateral-force imaging are in good agreement.

3. Small-angle X-ray scattering

Besides the observation of individual ion tracks, it is also possible to use techniques where specific information about many tracks is obtained. Especially diffraction technique using small-angle scattering of X-rays (SAXS) and neutrons was established in the early eighties (Dartyge *et al* 1981; Albrecht *et al* 1985, 1986).

A large number of ion tracks (about 10^{10}) act as scattering objects. The change of the electronic (X-rays)

or atomic (neutron) density along the tracks results in a highly anisotropic scattering. A typical SAXS set-up is shown in figure 6. The scattering pattern of a lithium fluoride crystal irradiated with xenon ions is presented in figure 7. Here, the grey scale is a measure of the X-ray intensity recorded by means of a position-sensitive detector. The light spot in the centre originates from the catcher of the primary X-ray beam. The high contrast along the vertical axis of the detector plane originates from the electron density difference of the damage in the tracks compared to the surrounding unirradiated crystal.

For the analysis of the scattered intensity distribution, it is assumed that each track can mathematically be described by a cylinder of a Gaussian radial density variation with the z -axis of the cylinder corresponding to the ion trajectory. For such a configuration, the intensity distribution $I(k_r, k_z)$ in the reciprocal space is given by

$$I(k_r, k_z) = \Delta\rho^2 4\pi^2 a^4 \sin^2(k_z R/2)/k_z^2 \exp(-k_r^2 a^2/2),$$

Figure 5. Force-modulation image of a mica surface ($170 \text{ nm} \times 170 \text{ nm}$) irradiated with Au ions (13.4 MeV/u). The dark impact zones indicate reduced surface elasticity (Neumann *et al* 1996b).

where R is the length of the cylindrical track, k_z and k_r the length of the momentum vector, respectively parallel and perpendicular to the ion path. k_r is obtained from the relation $k_r = 4\pi/\lambda \sin \Theta$, where 2Θ denotes the scattering angle and λ the wavelength of the X-ray beam. $\Delta\rho$ is the maximum electron density difference between the damaged material of the track and the virgin crystal, and a defines the Gaussian radius of the track at which $\Delta\rho$ decreases to $1/e$.

Figure 6. Scheme of SAXS set-up.

Figure 7. Anisotropic scattering pattern of a lithium fluoride crystal irradiated with 10^{10} Xe ions/cm² (11.4 MeV/u) (Schwartz *et al* 1998).

Using a Guinier plot ($\ln(I(k_r))$ vs $(k_r)^2$), the Gaussian track radius can be determined from the slope of a straight line fitted to the data. Figure 8 represents the data of lithium fluoride crystals irradiated with gold and xenon ions. The deduced track radius is between 1 and 2 nm and corresponds to the core radius in which complex defect aggregates are formed (Schwartz *et al* 1998; Trautmann *et al* 1998a).

4. Chemical etching

Another possibility to reveal the existence of ion tracks is the technique of selective chemical etching. Using a suitable etchant, the modified or damaged material along the ion track is dissolved at a faster rate than the bulk material. Although the ion track itself is destroyed, this technique still allows us to obtain specific information such as the number of tracks per unit surface area, orientation and geometry of the etched pores, and radiation sensitivity of the solid under study (Fleischer *et al* 1975).

In order to illustrate the diversity of chemical etching, etched pores in various materials are presented in figures 9–11.

Due to the sensitivity of polymers, an extremely high etching rate along the ion trajectory leads in many cases to almost cylindrical pores with a narrow pore size distribution (figure 9) (Trautmann *et al* 1996a).

Etching of tracks in LiF crystals results in pyramidal shaped etch pits illustrating that the chemical attack depends on the crystal orientation (figure 10) (Müller *et al* 1998; Trautmann *et al* 1998b).

Up to now, etchable tracks in metals have been demonstrated only in a very special metal namely the glass-like iron boron alloy $\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$ (Trautmann

Figure 8. The logarithm of the scattered intensity as a function of the square of the scattering vector k_r for LiF crystals irradiated with Xe and Au ions (11.4 MeV/u) (Schwartz *et al* 1998).

et al 1993a, 1996b,c). In this material, the resulting etch pits have wide opening angles (figure 11).

Successful track etching is linked to a critical energy loss depending on the radiation sensitivity of a given material. For the $\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$ alloy, the critical energy loss for homogeneous track etching is around $3.4 \text{ keV/\AA}$ (figure 12) (Trautmann *et al* 1993b) which is rather high compared to the threshold of $0.4 \text{ keV/\AA}$ for tracks in polyimide (Trautmann *et al* 1996d).

5. Applications

Ion-induced material modifications, have been exploited and applied in many scientific and industrial applications

(Fleischer *et al* 1975, Spohr 1990). Big accelerators such as the UNILAC at the GSI in Darmstadt offer favourable conditions for the controlled generation of precise microstructures. In the following section, two selected examples are presented.

5.1 Thermo-responsive membranes

There has been a long tradition of using etched tracks in polymers as high precision membranes. More recently, the ion-track etch technique was combined with the field of hydrogels (Yoshida *et al* 1993). For this purpose, a thermo-responsive gel (N-isopropylacrylamide) was grafted onto the surface of an ion track filter (poly-

Figure 9. Cylindrical pores in polyimide (Trautmann *et al* 1996a).

Figure 11. Conical surface pores of etched tracks in amorphous metal ($\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$) (Trautmann *et al* 1993a).

Figure 10. Pyramidal shaped etch pits in LiF (Trautmann *et al* 1998).

Figure 12. Curves of the energy loss as a function of the energy for various ion species (Ziegler *et al* 1985). Only in the case of filled symbols track etching in the amorphous metal is possible (Trautmann *et al* 1993b).

Figure 13. Transmission electron micrograph of pores in the swollen (left) and in the shrunken state (right) (Yoshida *et al* 1993).

Figure 14. Continuous cycling of the temperature controlled opening and closing of a single responsive pore measured in a conductivity cell (Reber 1998).

ethylene-terephthalate). In an aqueous solution, such a membrane closes its pores below 31°C when the hydrogel swells significantly by taking up a large amount of water (figure 13). The flow of particles through the pores can be controlled by varying the temperature or pH-value of the environment (Reber *et al* 1995; Tamada *et al* 1995; Yoshida *et al* 1996; Omichi *et al* 1997a, b; Yoshida *et al* 1997a, b; Hiroki *et al* 1998). Figure 14 shows the continuous cycling of the effective pore size as a function of the applied temperature, monitored by the flow of an electrolyte through the membrane (Reber *et al* 1998).

A variety of novel applications are expected from these responsive membranes including chemical valves, sensors or controlled drug delivery systems.

5.2 Microstructures by replica technique

Etched pores in polymers can also be used as templates for microgalvanic replication (Vetter and Spohr 1993).

Figure 15. Replica technique to produce metallic needles.

The principle of this technique is shown in figure 15a–c. In a galvanic process, the pores are filled with metallic material. In a subsequent step, the plastic material is removed in an organic solvent. Microstructures with an extremely large aspect ratio can be produced. Using suitable galvanic conditions, it is possible to obtain parallel or funnel shaped columns, hollow tubes, or tips from different metals. The deposition process can also be controlled in such a way that material is deposited as a single crystal (Vetter 1994; Dobrev 1998).

In combination with an ion microprobe (Fischer 1991), it was demonstrated that not only stochastically distributed

Figure 16. Microneedles replicated from a polycarbonate membrane with a regular ion track pattern.

but also ordered structures can be created (figure 16) (Vetter *et al* 1999).

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