Some interesting aspects of swift heavy ions in materials science

D. K. Avasthi

Irradiation of materials, by high energy, heavy ions (referred to as swift heavy ions or SHI), results in highly excited lattice atoms with negligible contribution from elastic collisions. Atomic displacements and structural modifications of such a lattice, brings out interesting changes in the materials. Silicide formation at the interface in Ti/Si and Fe/Si has been observed due to electronic excitation-induced ion beam mixing. SHI irradiation of organic crystals shows significant changes in dielectric constant providing a possibility of making buried optical waveguide structures. The irradiated polymers after etching give micro-filters, which can be used in different ways. Ion track diameters have been estimated from the monitoring of hydrogen release, using Elastic Recoil Detection, during ion irradiation of polymers. Possibilities of having an insight to varying damage zones inside a track are demonstrated.

ENERGETIC ion beams play a vital role in the field of research in materials science[1-3]. Ion beam effect on the materials depends on the ion energy, fluence and ion species. Low energy ions up to a few hundred keV available from ion implanters have been in use in semiconductors, modification of surface and interface, etc. The interaction of the ion with material is the deciding factor in the ion beam-induced material modification. The ions lose energy during their passage through the material, which is either spent in displacing atoms (of the sample) by elastic collisions (referred to as nuclear stopping) or exciting the atoms by inelastic collisions (referred to as electronic stopping). The nuclear stopping is dominant at low energies and the energy lost in this process is called nuclear energy loss. The other mode of energy loss is by exciting or ionizing the atoms by inelastic collisions and the energy spent in this process is called as electronic energy loss. Electronic stopping is dominant at high energies, where the displacement of atoms due to elastic collisions is insignificant. Heavy ions with energies so high that the electronic energy loss process dominates, are referred to as swift heavy ions. It is expected that the lattice atoms are not displaced in the case of electronic excitation generated by SHI. However, it has been known that displacement of lattice atoms occurs in insulating materials in a cylindrical core along the ion path. The passage of the ion through an insulator produces a positively charged cylinder, which explodes radially due to Coulomb force, causing coherent radial atomic movements until the ions are screened by the conduction of electrons. Due to the resulting cylindrical shock wave, which is known as Coulomb explosion[4], columnar defects are formed. The other competing process, which can lead to the formation of the columns, is thermal spike[5]. According to this model, during the passage of SHI the kinetic energy of the ejected electrons is transmitted to the lattice by electron–phonon interaction, resulting in the increase of local lattice temperature above the melting point of the material. The temperature increase is followed by a rapid quenching, which results in an amorphous columnar structure when the melt solidifies. Beyond a certain threshold of electronic energy deposition, such ion track formation has also been observed in some metals[6-8].

The basic difference of materials modification by low energy ion (a few tens of keV to a few MeV) implantation and swift heavy ion irradiation (typically a few tens of MeV and higher) is that the low energy ions get embedded in the material and cause modification by their presence and due to the collision cascade produced by the impinging ions. Whereas in SHI irradiation, the modification of thin films or the near-surface region of the bulk samples is due to the electronic excitation. In this case, the impinging ions do not get embedded in the film due to their large range (typically a few tens of μm or larger). It is, for this reason, advisable to use thin film samples for SHI irradiation for a better understanding of interaction of swift heavy ion with matter. In such a situation, the elastic collision effects causing collision cascade can be safely neglected and the effect of the embedded ion does not come into picture.

Swift heavy ions from Pelletron[9] at the Nuclear Science Center (NSC)[10], are being used to probe into exotic effects of large electronic excitations in different type of materials[3], e.g. metals, semiconductors, superconductors,

D. K. Avasthi is in the Nuclear Science Centre, Aruna Asaf Ali Marg, Post Box 10502, New Delhi 110 067, India.

polymers, organic crystals, etc. The salient features have been ion beam mixing in the metal/Si interface, defect production and annealing of defects in semiconductors, flux pinning in high T_c superconductors, desorption of H in polymers, micro filters by chemical etching of ion irradiated polymers, optical waveguide formation, etc. On-line monitoring of light elements by elastic recoil detection analysis (ERDA)[11,12] is performed, which provides information on the effective zone of ion-induced damage in the polymers. The present paper gives a brief account of some of these basic as well as application-oriented studies at NSC or elsewhere in heavy ion accelerator laboratories.

Modifications at the interface

Electronic excitation-induced mixing at interface

When a thin film deposited on a substrate is subjected to ion irradiation, intermixing of the atoms in the film with that of in the substrate takes place. Such atomic mixing at the interface forced by the energetic ion beam is referred to as ion beam mixing as shown in Figure 1. It finds applications in the generation of new phases, novel materials and enhancing the adhesion of the film to substrate. The ion beam mixing is widely used for meeting these objec-

tives with the help of low energy ion beams. The ion energy and species in low energy ion beam mixing are chosen in such a way that they impart a large amount of energy to the atoms at the interface of the thin film and the substrate by the process of elastic collisions. Normally, the fluence required for ion beam mixing with low energy ions is 10^{16} ions/cm^2. It has been observed[13] in recent years that the electronic energy deposition beyond a certain threshold can cause the movements of atoms even in metals, which can lead to mixing. Ion beam mixing in Ti/Si (ref. 14) and Fe/Si (ref. 15) systems have been observed at the electronic energy deposition above 1 keV/A obtained by the irradiation of 200 MeV Ag ions. The amount of mixing is found[15] to be dependent on the electronic energy loss. It was studied in the case of Fe/Si as shown in Figure 2. The figure gives the characterization of the irradiated natural Fe (10 nm)/^{57}Fe (10 nm) on Si substrate. The presence of silicide phase is characterized by the presence of two peaks, having quite low intensity in the pristine sample at the location shown by the arrows in the figure. The presence of weak peaks of silicide in the pristine sample is due to a small amount of interface mixing, which is inherently present. All the irradiations were performed at fluence of about 2×10^{14} ions/cm^2. Irradiation by 243 MeV Au and 210 MeV I produces more of silicide phase compared to
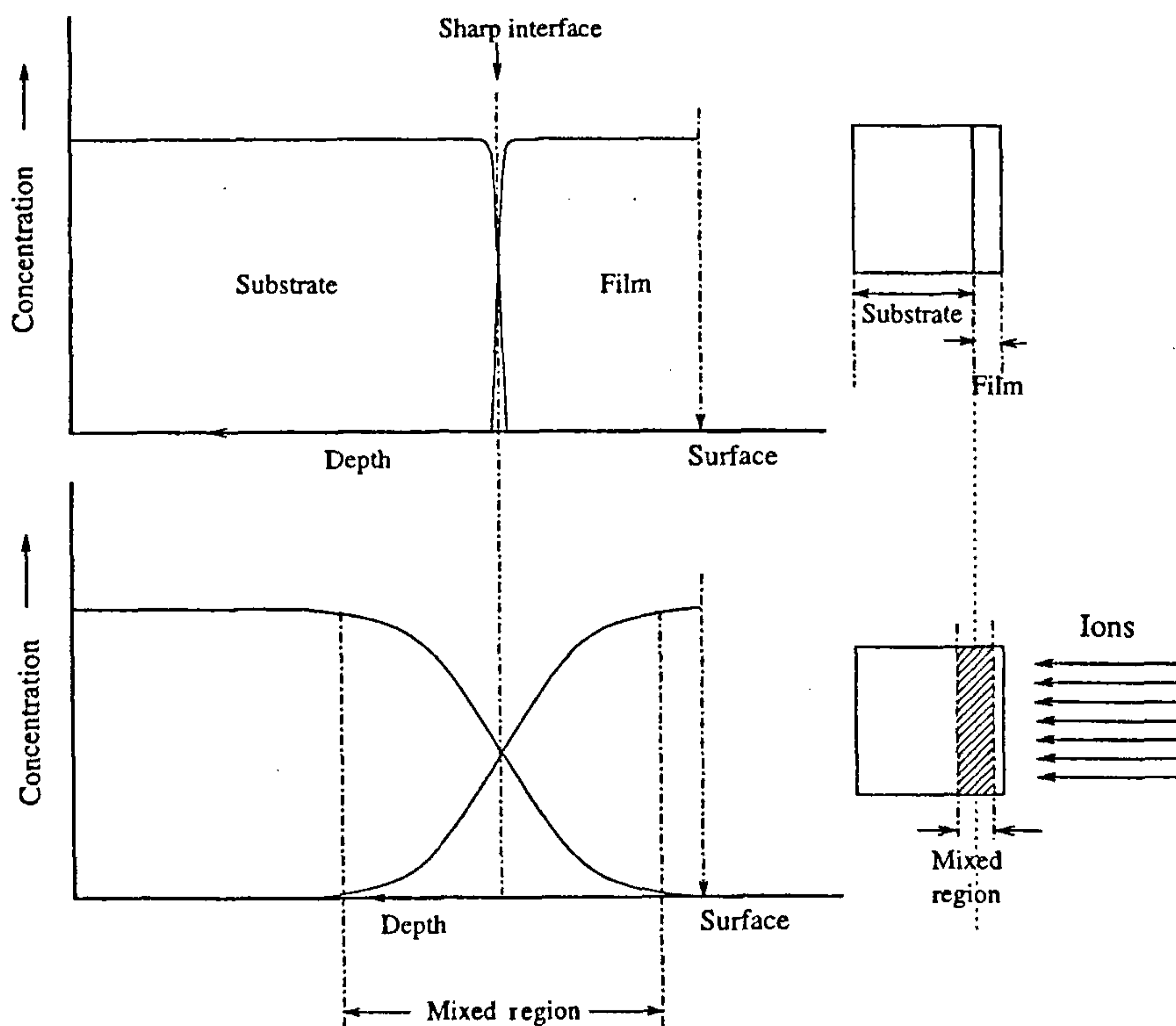

Figure 1. Schematic of ion beam mixing.

the irradiation by 160 MeV Ag ions. This is evident from a comparison of the intensity of silicide phase peaks in the Mossbäuer spectrum. The values of electronic energy loss for 243 MeV Au, 210 MeV I and 160 MeV Ag ions in Fe are 47, 36, and 32 keV/nm, respectively. It shows that the amount of mixing is proportional to the electronic energy loss. In the irradiation of a diamond-like carbon (DLC) film deposited on Si substrate by 50 MeV Si ions, the formation of SiC (ref. 16) at the interface has been observed. Mixing at the interface has been observed in several multilayer systems[17–20] by swift heavy ion irradiation. Interestingly, the interface roughness can be changed by large electronic excitation, which is important to study the effect of interface roughness on the giant magneto resistance (GMR) properties of the multilayer. It is however not easy to control the interface roughness during the deposition of multilayer. SHI offers a unique possibility of engineering the interface. There are a number of evidences[13–20] of ion beam mixing mediated by the swift heavy ions passing through the material. A first report[13] was made earlier in 1993. The cause of mixing is the displacement of atoms by the electronic excitation and not by the elastic collisions because of the fact that the electronic energy loss is about two orders of magnitude larger than the energy loss due to the nuclear stopping. The fluence required for mixing with SHI is about 10^{13} ions/cm², which is two to three orders of magnitude smaller compared to the low energy ion beam mixing. Unlike ion beam mixing by low energy ions, SHI-induced mixing does not have the impinging ions in or near the mixed

phase region. Due to high energy, the SHI gets embedded far deep in the substrate, quite away from the mixed region. A notable observation in these experiments has been that the electronic excitation threshold for atomic motions in metallic thin films is lower than that of the bulk metal.

Optical waveguide formation in organic crystals

An optical waveguide is a layer of material, whose refractive index is significantly different from that of its surrounding so that light rays remain confined to this region during their transmission. The possibility of the formation of such waveguides in some organic crystals was demonstrated by the irradiation of crystals by energetic ions[21]; the waveguide is formed deep inside as per the range of the ion as shown in Figure 3. It has been shown at NSC that irradiation of organic crystals by 100 MeV Ag ions can produce a waveguide structure near the surface. The depth of the waveguide, in principle, can be varied as desired by proper selection of ion mass and energy. Significant changes in the refractive index (from 1.521 in the pristine organic crystal to 1.564 in the case of irradiated organic crystal) in the irradiated region have been observed[22]. The dielectric constant of the irradiated region also has been found to increase by about an order of magnitude. The on-line hydrogen measurement by ERDA technique indicated[22] that these changes are correlated with the loss of hydrogen in the irradiated region.

SHI in polymers

Swift heavy ions produce cylindrical damage zones in polymers, which have various applications. The damaged zone can be etched by suitable chemicals to get through holes with diameter ranging from a few tens of nm to a few μm. Diameter of the etched holes can be varied by etch time and other conditions, depending on the requirement of the application. The pore density can be changed by the ion fluence, which is controlled either
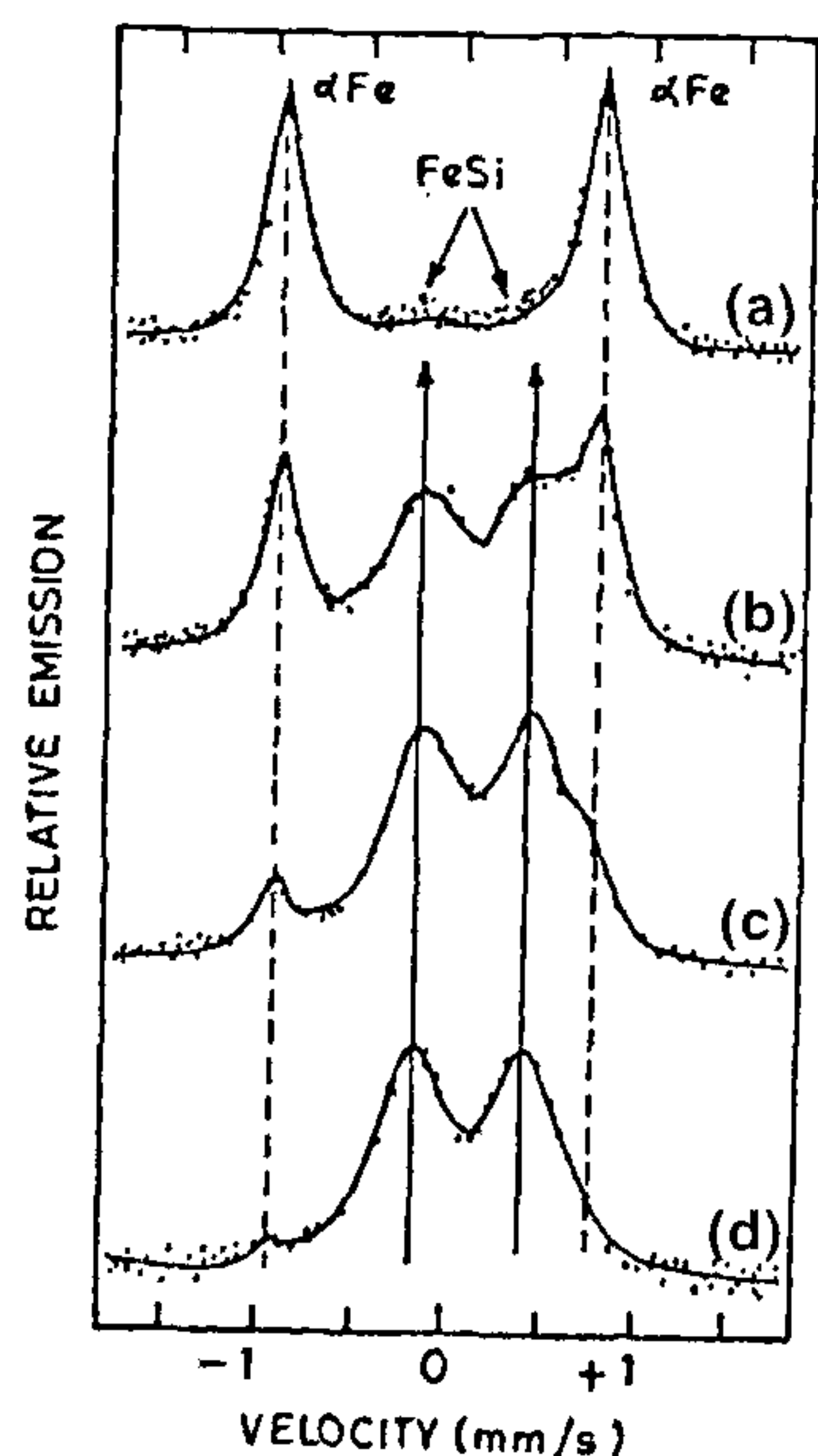

Figure 2. CEM spectra of the (a), pristine; (b), 160 MeV Ag ions irradiated; (c), 210 MeV I ions irradiated; and (d), 243 MeV Au ions irradiated natural Fe/⁵⁷Fe/Si sample.
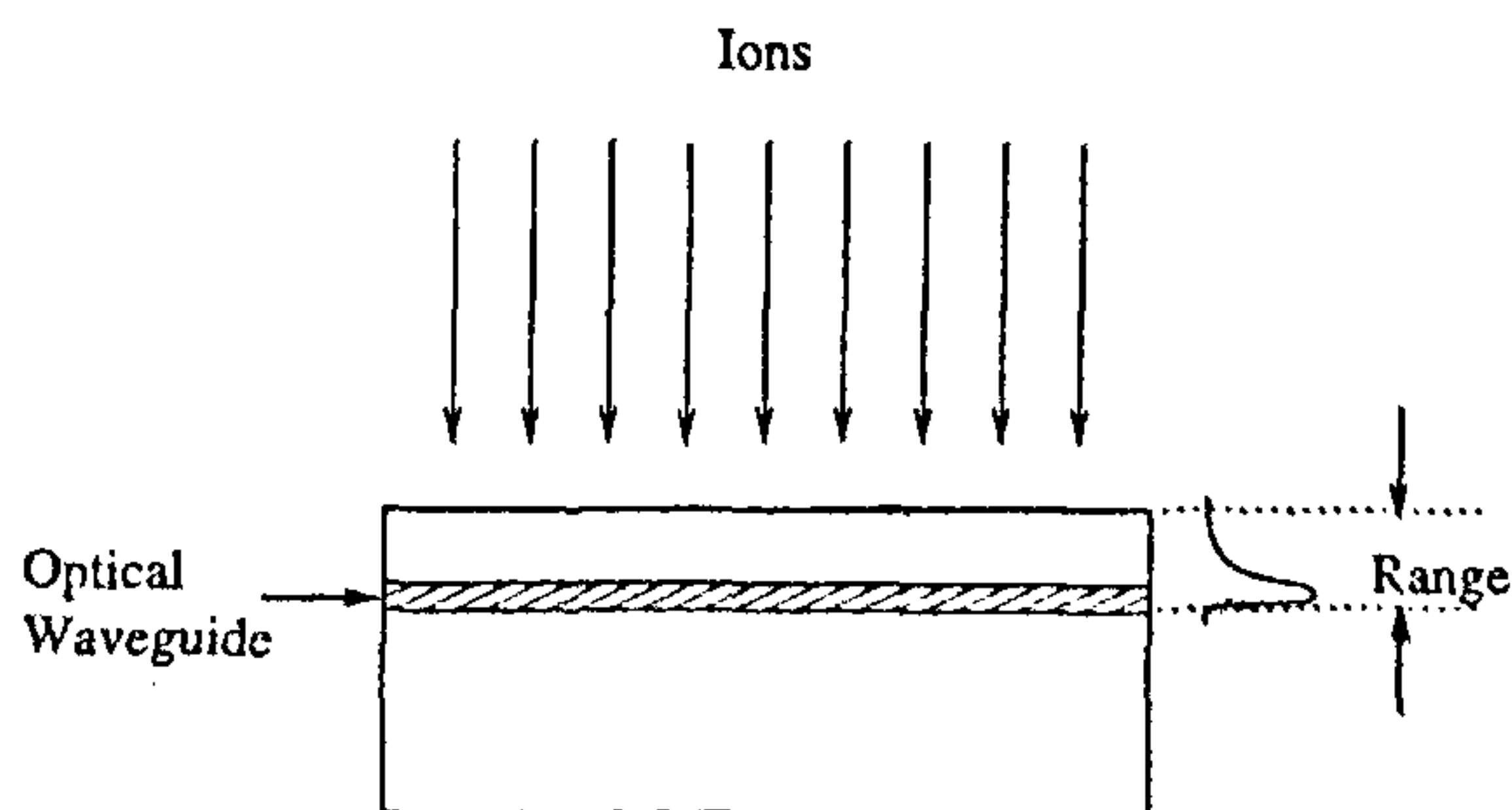

Figure 3. Generation of a waveguide in an optical crystal under energetic ion impingement.

by ion current or irradiation time or both. The pore density can be varied from one per cm^2 to 10^6 per cm^2 for micro pores and up to 10^{11} per cm^2 for nano pores. Thus ion beams provide a way to produce randomly placed pores (holes) in a polymer with a desired density and desired diameter from 0.05 μm to several μm. Typical lowest ion current available from the Pelletron accelerator corresponds to the ion fluence of the order of 10^8 ions/cm^2. The accelerator operation becomes unstable at very low ion currents. Therefore the irradiation of the polymer at lower fluence $(10^6$ ions/cm^2 and lower) requires an alternative arrangement (as shown in Figure 4), which is achieved by scattering the ion beam from a thin Au foil (not shown in the figure) and using the scattered ions at an angle of 20° (with respect to the beam direction). This set-up installed in an experimental chamber is shown in Figure 4. The polymers for irradiation at low fluence are mounted on the ladder.

The etched pores can be easily viewed down to 0.5 μm in an optical microscope. The holes with diameter in sub-micron region require electron microscope or atomic force microscope for their characterization. There is growing interest in nano pores and micro pores in polymers generated by swift heavy ions due to a variety of applications. Generation of pores in the polymers by

chemical etching of the irradiated polymer and possible applications are shown in Figure 5. Materials of interest can be filled in these micro pores by the template technique[23,24]. There are possibilities of making diode arrays by electro-deposition of suitable materials in the micro-structure[25]. Micro channel plates can be made by the deposition of suitable material at the inner side of the holes of the microfilter. The micro channel plates are used as timing detectors in time of flight experiments and are among the important parts in many equipments, like secondary ion mass spectrometer (SIMS), residual gas analyser (RGA), etc. The micro filter can be used for slow drug delivery at suitable places for medical treatment. Normally, a drug or medicine is applied to a wound or infected area at a regular interval, say once a day. Controlled release of the drug or medicine through the microfilter of optimum size offers the possibility of providing the drug or medicine continuously through its pores at the infected region. These microfilters also find applications in the biomedical field in filtering the bacteria of specific dimensions. Normally, in filter application, the micro holes get clogged. The clogging can be removed by expansion of these micro holes to use them again. Such a possibility has been demonstrated by Reber et al.[26], where hydrogel was coated in the inner walls of the micro holes.
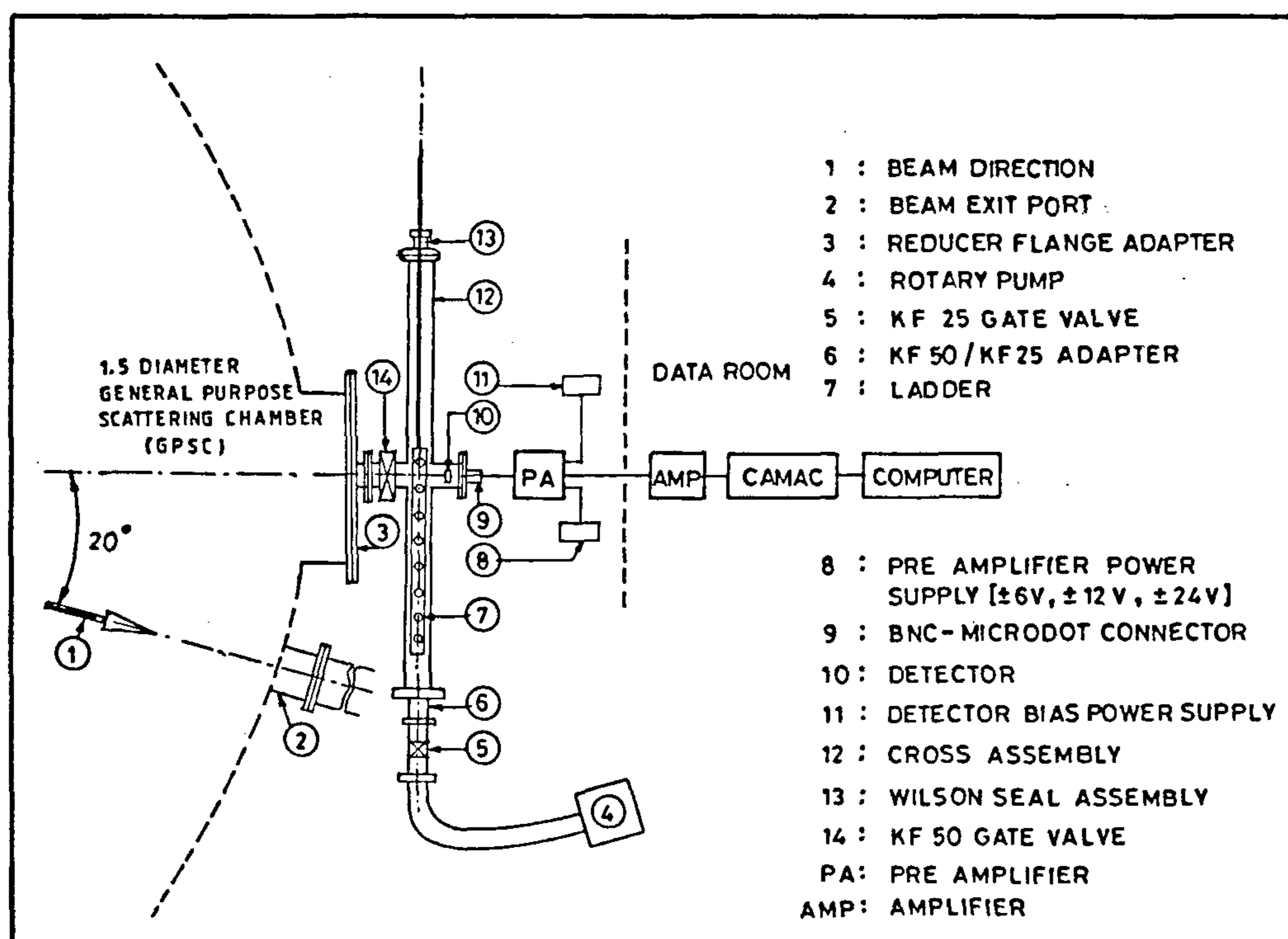

Figure 4. Schematic of experimental set-up of low flux irradiation. Ion beam impinges on a Au thin foil and the polymer for low flux irradiation is kept at an angle of 20° with respect to the beam direction. Centre of the chamber where Au foil is kept is not shown. The arrow shows the incident ion beam direction. Scattered ions (from Au foil) are incident on ladder, which has polymer foils on it.

The hydrogel expands at elevated temperature of 80°C, which allows control on the size of micro holes. A similar possibility of variable micron size pores exists in piezo-electric polymer materials, where control on the pore size can be achieved by applying an electric field, which is yet to be demonstrated. Recently there has been a successful attempt in growing an organic crystal through micron size pores[27]. This has applications in optical devices.

Determination of the dimensions of the ion damaged zone is of interest from the application point of view and for the understanding of the ion–polymer interaction. Next we have carried out some experiments to look into the ion-damaged zones and within it as described in the following sections.

Ion track radius by on-line ERDA measurement

The energetic ion creates damage along its path due to its large electronic energy deposition. The track diameter is a quantity of interest for the understanding of basic ion insulator interaction. There have been a few attempts to measure the track diameters by scanning force microscopy and other state-of-the-art surface morphology probing equipments. At NSC, a novel approach has been demonstrated to determine the track diameters in polymers by on-line measurement of H loss[28] during ion irradiation by on-line elastic recoil detection analysis.

Hydrogen is liberated due to electronic excitation of constituent atoms causing the breaking of bonds associated with H. Free H atoms combine to form hydrogen molecules. These molecules, being the lightest gaseous molecules having high diffusivity, escape from the polymer causing reduction in H content due to ion irradiation. Thus the incident ion along its path releases H and it diffuses out of the polymer as hydrogen molecules. Each ion is effective over a larger area than its own size, releasing H from a cylindrical zone of damaged polymer, whose radius can be estimated by the following relation.

$$H(\phi) = H_{in} \exp(-\rho.\phi),$$

where $H(\phi)$ represents the hydrogen concentration (in atoms/cm^2) at fluence ϕ, H_{in} represents initial content of H in the sample, ρ the cross section of release for H and ϕ the ion fluence. The H concentration in the film decreases due to the loss of H from the cylindrical damage zone. Thus the concentration of H in the polymer decreases with the fluence, which is measured on-line by ERDA[28]. The ERDA technique allows the determination of light elements (H in this case) by detecting H recoils in a silicon surface barrier detector.

The variation of H content with ion dose is shown in Figure 6. The concentration of H (ref. 28) is plotted as a function of ion fluence (of 110 MeV Ni ions) in two polymers, polystyrene and polyvinyldiflouride (PVDF). The initial slope gives the cross-section of H release, which is equivalent to πr^2 where r is the track radius. The curves show that the release of H is more in the case of PVDF compared to polystyrene, indicating that each ion is effective in bigger diameter in PVDF compared to polystrene. The track radius in polystyrene and PVDF is found to be around 3 nm and 6 nm, respectively, consistent with other available reports[29] on track radius measurements using other techniques.
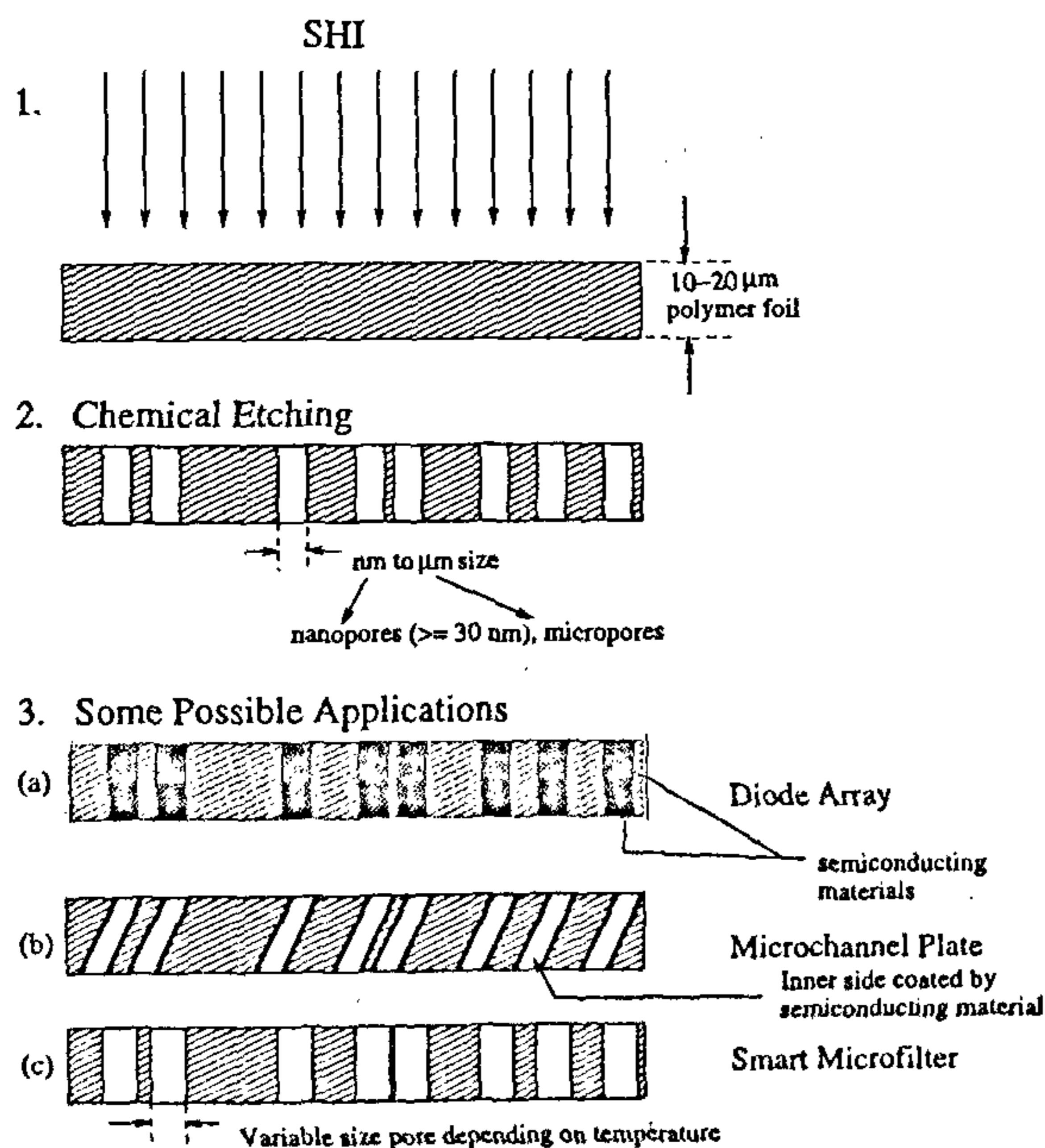
Figure 5. Schematic of producing a microfilter and some possible applications.
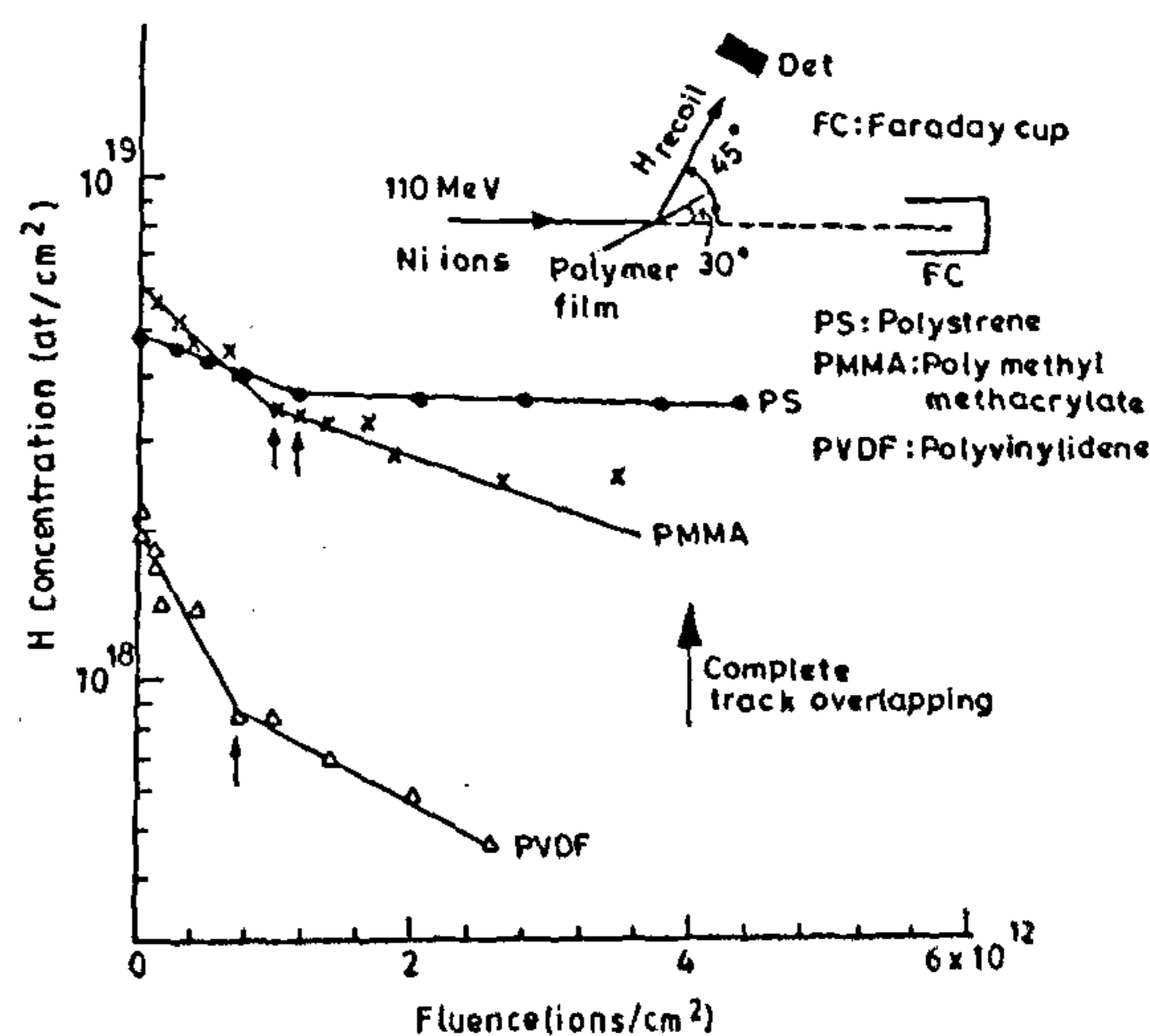
Figure 6. Variation in H content in polymer film under ion irradiation, which provided information on the track diameter.
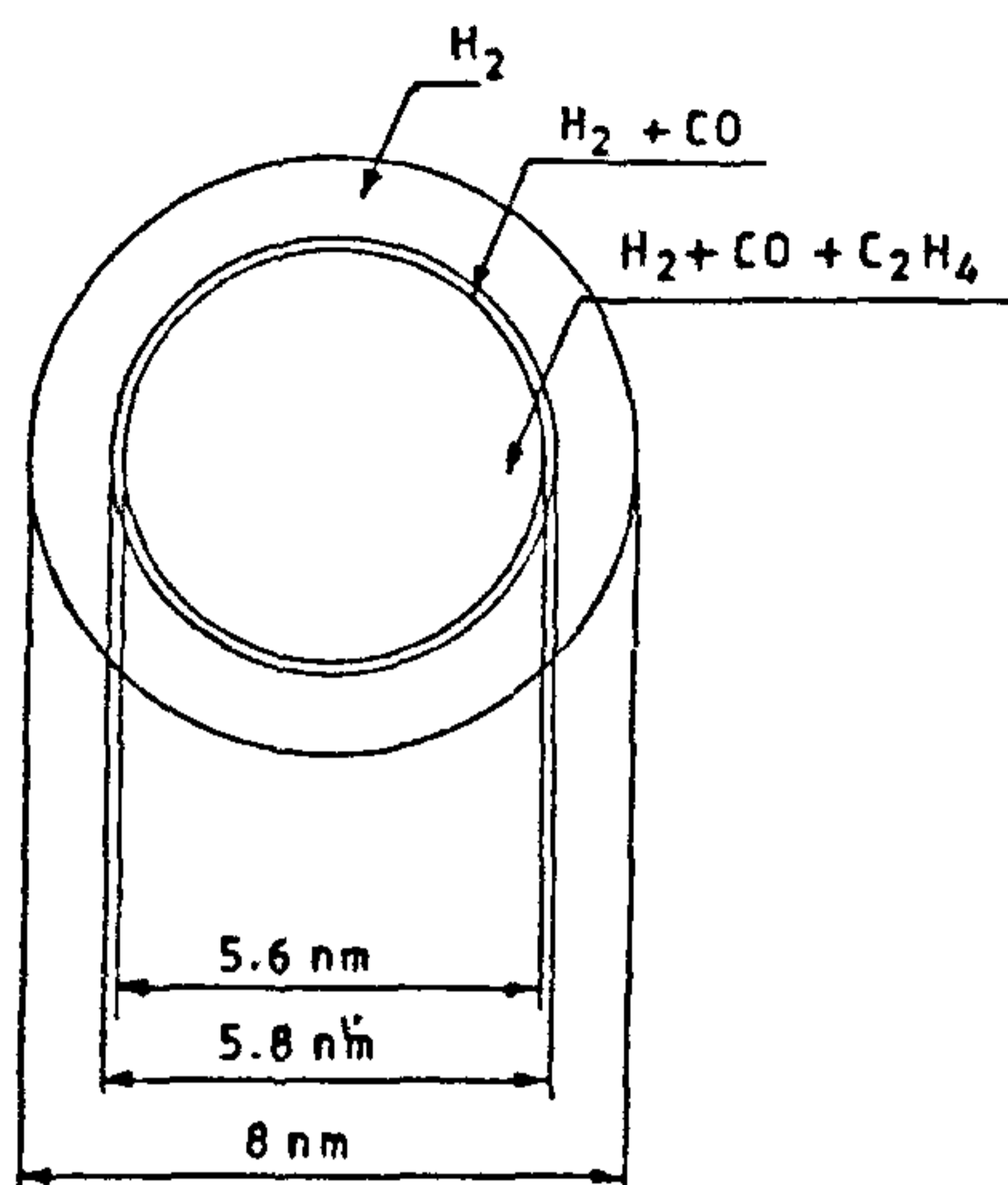
Figure 7. Damage zones in polymer, where from the evolution of various gases takes place under the impact of swift heavy ions.

Insight of varying damage zones inside ion track

Apart from the measurement of ion track dimensions as discussed earlier, it has been possible to look into varying damage zones within an ion track by on-line measurements. One such example is quoted here.

Damage zones in polymer: In an experiment in UHV chamber of materials science beam line at NSC, a thin (20 μm) polymer film was irradiated with 200 MeV Ag ions. Each ion produces damage along its path. Due to high electronic excitation (about 10 keV/nm), various gases are formed within the ion damage core. These gases diffuse out, resulting in an increase in the partial pressure of the gases, which reaches a saturation value and decreases, when the overlap of the track diameter begins. This decrease in the partial pressure is because of the fact that the amount of gas release is decreased when the ion goes into an already ion-damaged track zone. The decay of the partial pressure of the gases with the ion fluence thus gives an idea of the cylindrical zone[30] through which the gases are released. The partial pressure measurements were performed using quadrupole mass analyser. The changes in the partial pressure of gases H_2, CH_4 and CO were measured as a function of ion fluence. The estimation of damage cross-section by partial pressure measurement is similar to that done by on-line ERD. The only difference is that ERD measures the H left behind in the sample whereas in the partial pressure measurement technique, the hydrogen coming out of the sample is measured. It was observed that the release of different gases followed different curves indicating that different gases get released from the cylindrical zones of different diameters[30] as shown in Figure 7. The inner damage core produced

three different gases whereas the outer zone gave only hydrogen. This can be understood from the fact that the influence of the ion reduces with the radial distance and therefore more gases are evolved from the inner zone (of diameter 5.6 nm) having a larger damage. In this particular case, the damage by the incident ion beyond a radial distance of 5.8 nm is so small that only H is evolved in the outer zone of 5.8 nm to 8 nm. The effect of the impinging ion beyond a radial distance of 8 nm is negligible and therefore no gas is evolved beyond this distance.

Conclusions

Electronic excitation produced by SHI has vast potential in the field of modification of materials. The mixing at interface induced by SHI in metal/Si and multilayer systems is of interest. The damage generated by ion beams in organic crystals can be exploited for the formation of optical waveguides. Interesting possibilities exist in utilizing the micro and nano pores in many applications. The on-line ERD measurements of H release, provide a nice way to measure the ion track radius. As a consequence of impact of a swift heavy ion, zones of varying damage in polymers have been observed. It is clear that SHI in materials have several interesting and unique aspects with a variety of applications.

1. Proceedings of 11th International Conference on Ion Beam Modification of Materials Amsterdam (eds Vredenberg, A. M., Polman, A., Stolk, P. A., Snolesand, E. and Brongersma, L. M.), North Holland, Amsterdam, 1998.
2. Proceedings of the International Conference on Swift Heavy Ions in Matter (eds Klaumuenzer, S. and Stolterfoht, N.), North Holland, Berlin, May 1998.
3. Proceedings of the International Conference on Swift Heavy Ions in Materials Engineering and Characterization (eds Avasthi, D. K. and Kanjilal D.), New Delhi, North Holland, Amsterdam, October 1998.
4. Lesueur, D. and Dunlop, A., *Radiat. Eff. Deffects Solids*, 1993, **126**, 163.
5. Szenes, G., *Phys. Rev. B*, 1995, **51**, 8026.
6. Dunlop, A., Lesueur, D. and Dammak, H., *Nucl. Instrum. Methods B*, 1994, **90**, 330.
7. Tombrello, T. A., *Nucl. Instrum. Methods B*, 1995, **103**, 318.
8. Lesueur, D., *Radiat. Eff. Defects Solids*, 1993, **126**, 123.
9. Kanjilal, D., Chopra, S., Narayanan, M. M., Iyer, I. S., Jha, V., Joshi, R. and Datta, S. K., *Nucl. Instrum. Methods A*, 1993, **238**, 97.
10. Mehta, G. K. and Patro, A. P., *Nucl. Instrum. Methods A*, 1988, **268**, 334.
11. Ecuyer, J. L., Brassard, C., Cardinal, C. and Terrault, B., *Nucl. Instrum. Methods*, 1978, **149**, 271.
12. Avasthi, D. K., *Nucl. Istrum. Methods B*, 1998, **136**, 729.
13. Dufour, C., Bauer, Ph., Marchal, G., Grilhe, J., Jaouen, C., Pacaud, J. and Jousset, J. C., *Europhys. Lett.*, 1993, **21**, 671.
14. Avasthi, D. K. *et al.*, Proc. of DAE Symp. on Solid State Physics, 1996.
15. Assmann, W., Avasthi, D. K., Dobler, M., Kruijer, S., Mieskes, H. D. and Nolte, H., *Nucl. Instrum. Methods B*, 1998, **146**, 271.

16. Nita Dilawar, S., Sah, B. R., Mehta, V. D., Vankar, D. K., Avasthi, and Mehta, G. K., *Vacuum* 1996, **47**, 1269.

17. Dhuri, P., Ajay Gupta, S. M., Chaudhuri, D. M., Phase, and Avasthi, D. K., *Nucl. Instrum. Methods B*, 1999, **156**, 148.

18. Gupta, R., Ajay Gupta, D. K., Avasthi, G., Principee, and Tosello, C., *Nucl. Instrum. Methods B*, 1999, **156**, 153.

19. Paul, A., Ajay Gupta, Choudhari, S. M., Phase, D. M. and Avasthi, D. K., *Nucl. Instrum. Methods B*, 1999, **156**, 158.

20. Ajay Gupta, A., Paul, Ratnesh Gupta, Principee, G. and Avasthi, D. K., *J. Phys. B, Condens Matter Phys.* 1998, **10**, 9669.

21. Townsend, P. D., *Nucl. Instrum. Methods B*, 1990, **46**, 18.

22. Aithal, S., Nagaraja, H. S., Mohan Rao, P., Avasthi, D. K. and Sarma, A., *J. Appl. Phys.*, 1997, **81**, 7526.

23. Chakravarti, S. K. and Vetter, J., *Nucl. Instrum. Methods B*, 1991, **62**, 109.

24. Vetter, J. and Dobrev, D., *Nucl. Instrum. Methods B*, 1999, **156**, 177.

25. Biswas, A., Avasthi, D. K., Singh, B. K., Lotha, S., Singh, J. P., Fink, D., Yadav, B. K., Bhattacharya, B. and Bose, S. K., *Nucl. Instrum. Methods B*, 1999, **151**, 84.

26. Reber, N., Omichi, H., Spohr, R., Tamada, M., Wolf, A. and Yoshida, M., *Nucl. Instrum. Methods*, 1995, **105**, 275.

27. Vetter, J., GSI Darmstadt, Germany (private commun.).

28. Mittal, V. K., Lotha, S. and Avasthi, D. K., *Radiat. Eff. Defects Solids*, 1999, **147**, 199.

29. Trautmann, C., *Nucl. Instrum. Methods B*, 1995, **105**, 81.

30. Avasthi, D. K., Singh, J. P., Biswas, A. and Bose, S. K., *Nucl. Instrum. Methods B*, 1998, **146**, 504.

Phenotypic flexibility of plants and adaptive dynamics of specialist–generalist insects

T. N. Ananthakrishnan

Host plant flexibility resulting in intraspecific variation enables plants to assume the most adaptive phenotypes in a particular environment, significantly altering the performance and fitness of phytophagous insects. The structural diversity of plants over time has created a selection process leading to behavioural and biochemical adaptations resulting in specialist and generalist insects. With host plant populations comprising phenotypically heterogenous individuals, insects have the potential to adapt to an individual plant's chemical profile. The potential role played by plant signals in modulating and inducing the biosynthesis of many secondary metabolites has become an important aspect of insect–plant interactions which have relevance in agriculture.

INTENSIVE studies on diverse aspects of insect–plant interactions have emphasized the role of a bewildering number of secondary plant chemicals in enabling both wild and cultivated plants to cope up with insect attack. The evolution of insect–plant associations has been invariably guided by the plant chemistry which set the stage for the extensive radiation of herbivorous insects[1]. The ability of insects to identify preferred hosts is astounding, each species being endowed with unique sensory systems enabling recognition of its host plant range based on relevant cues, as well as adjusting to continually changing plant conditions. While entomocentrism involving host preferences tends to vary among individuals or populations causing them to select different diets, phytocentricism emphasizes the role of genetic variation in plants which influences the association of insect species on phenotypically flexible plants[2]. Nevertheless it cannot be denied that plants have a significant effect on insect evolutionary changes or strategies from a chemical viewpoint and play a fundamental role in insect population dynamics[3]. The chemical diversity of host plants has posed the problem of fitness and adaptation in insects calling for an equally efficient physiological adaptation in plants to overcome the barriers of feeding and oviposition.

While host choice for mating and oviposition has ecological and evolutionary implications, relevant insect adaptations are shaped by contemporary ecological forces[4]. The optimal defence and resource availability hypotheses explain the qualitative and quantitative patterns of plant defences[5-8]. The optimal defence hypothesis assumes that herbivory is the primary selective force shaping quantitative patterns of secondary metabolism, the resource availa-

T. N. Ananthakrishnan lives in Flat 6, 'DWARAKA', 22 Kamdarnagar, Chennai 600 034, India.