APPLICATIONS OF HIGH-ENERGY IONS IN MATERIALS SCIENCE*

A. Denker#, W. Bohne, H. Homeyer, J. Opitz-Coutureau, J. Röhrich, E. Strub,
Ionenstrahllabor ISL, HMI, Berlin, Germany

Abstract

High energy ion beams are increasingly employed in modern science and technology. The high quality of ion beams from a cyclotron allows challenging new applications and the elaboration of existing techniques: High-tech filter production by heavy ion irradiation as well as eye tumour therapy profit from the high beam stability, whereas materials analysis benefits from the good beam emittance and time structure. The possibility of cocktail beams allows a fast switching between different ion species, making effective radiation hardness tests possible. Different applications, ranging from high current irradiations (like self-organisation of materials) to single ion track applications, will be presented. Examples from materials science using heavy ions for ERDA (Elastic Recoil Detection Analysis) of complex layered structures as well as the non-destructive analysis of art objects by high energy PIXE (Proton Induced X-ray Emission) will be shown.

INTRODUCTION

Today, more than 8000 dedicated small accelerators [1] have been installed world-wide for ion implantation, Rutherford Back Scattering analysis (RBS), Proton Induced X-ray Emission (PIXE), or Accelerator Mass Spectrometry (AMS) among other themes, thus leaving their original nuclear physics assignment. Most of these accelerators, installed not only in research institutions, but also in industry, hospitals, and even in the Louvre, use low and medium energies. Yet, there is an increasing demand from solid state and medical physics as well as from materials science for high energy ions with energies above 1 MeV/u for heavy ions. Cyclotrons are perfectly suited to fulfil the demands arising from those fields, due to their large variability in ion species, ion energies, beam intensities, and their good beam stability over time.

MATERIALS MODIFICATION

Heavy ions with high energies - above 1 MeV/u - deposit locally more energy in a shorter time in materials than the most powerful lasers currently available. The enormously high energy deposition along the flight path of an ion can destroy the chemical bonds, leading to permanent materials modifications. These tracks may be conducting tracks in an insulating matrix or may have different optical properties than the surrounding material.

The etching rate in polymer foils along such tracks is up to three orders of magnitude higher than in the surrounding material, which enables the formation of pores [2]. The number of pores per cm^2 is defined by the number of ions, whereas the size and the shape of the pores can be tuned exactly by the etching time, solution, and temperature. The use of fast heavy ions from an accelerator provides good control of allocation, direction, and length of the ion paths. This is an advantage over the irradiation using nuclear fission products.

Many laboratories perform materials modifications mostly for research purposes [3-6]. However, the irradiation of polymer foils in order to produce filters is already realized on a regular industrial base. Table 1 lists examples of present-day employments of ion track filters [7-9]. The pore sizes vary between 0.05 and 15.0 µm, whereas the pore density ranges from single tracks up to 10^9 pores per cm^2. The variety of irradiated plastic material is steadily increasing: Black ion track membranes provide less fluorescence background in microscopy, other membranes are used for fuel cells [10,11]. At the moment, industrial companies use accelerators in research laboratories, however, a dedicated cyclotron is under construction for filter production in Dubna [12,13].

Table 1: Examples of applications of ion track filters in various fields.

field	**examples**
filtration	removal of dust, micro-particles and bacteria, high performance liquid chromatography (HPLC) sample preparation and solution filtration
biology	counting of micro-organisms, cytology, marine biology (plankton), cell culture, DNA fragment fractionation
blood filtration	red blood-cell deformability and filtration, plasmaphoresis, leukocytes removal, chemotaxis
air monitoring	collecting of aerosols, dust, pollens
analysis	absorbable organic halides and dissolved phosphates, nitrates, and ammonia analysis
delivery	controlled diffusion of biological reagents, controlled drug dispensing, pressure exchange elements

Ion track membranes can also be used as templates for nano-structured materials, the creation of metallic needles or nano-tubes. E.g., a gold nano-tube array has been used to immobilise glucose oxidase as enzyme biosensor [14], and cobalt nano-wires have been tested for field emission [15]. Furthermore, it is possible to create devices for microwaves filtering application by filling these tubes with magnetic material [16].

If the irradiated material is thicker than the range of the ions, the etching of the tracks provides a controlled keying of the surface. Thus plastic foils can be metallised

*Revised by

#denker@hmi.de

without any adhesives. This technique is used for flexible circuit boards, having increased bond strength and temperature resistance [17-19].

The requests for industrial production are far more challenging than for experimental purposes: First of all, strictly keeping to the beam schedule becomes an essential issue. Secondly, the beam stability is of crucial importance, as it determines e.g. the homogeneity of the pore density of the foils. Going from irradiation of some 100 cm^2 for research purposes to real production involves the irradiation of many square metres, meaning a change of several orders of magnitude in irradiated area. To be time-, manpower-, and cost-effective, the pore density of the foils has to be constant over these huge areas, demanding excellent long and short term beam stability for fast, heavy ions. In addition, the beam intensity has to be high, to keep the irradiation times reasonable as needed fluences range from 10^6 to $10^8/cm^2$. Cyclotrons are perfectly suited to fulfil all these demands, but beam tuning has to be done very carefully. At ISL, many efforts have been made to achieve high beam stability on short as well as on long terms.

The interaction of fast ions with solids is one of the main research topics at ISL, ranging from the study of ultra-fast dynamics over examinations of the applicability of non-equilibrium thermodynamics to the study of materials transport in thin-film packages induced by irradiation with high-energy ions: Self-organisation phenomena in swift-heavy-ion-irradiated NiO layers have been observed [20]. After irradiation with high fluences, the NiO layers were reorganised in 100 nm wide and 1 µm high NiO lamellae. This effect is attributed to transient melting of the material surrounding the ion trajectory. Furthermore, practical applications like the irradiation of polymer foils on an industrial level, are performed.

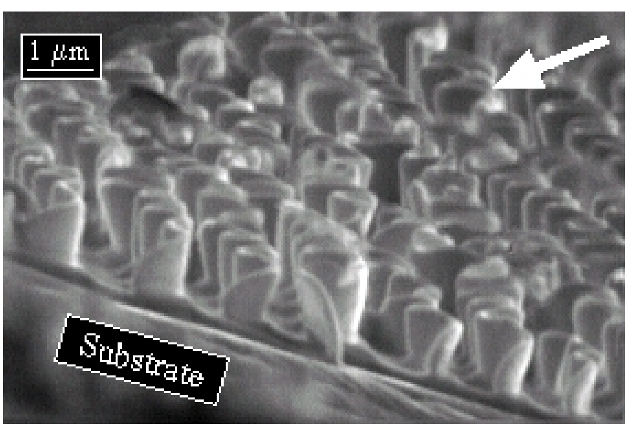

Figure 1: Creation of lamellae on a $NiO/SiO_2/Si$-Wafer [20]. The 260 MeV Kr beam had an incidence angle of 70° with respect to the target normal.

RADIATION EFFECTS

The ionisation along the ion track in an electronic device can switch its status or even destroy the device. The measurable effect on an electronic device produced by the impinging ion is called Single Event Effect (SEE). Beside low energy protons, high-energy ions contribute to the cosmic radiation, solar wind, and radiation belts of the earth. Especially electronics in aircrafts and satellites is exposed to this radiation [21]. Electronic devices operated on ground level may also suffer from these effects due to cosmic showers [22]. The harsh operation conditions can be simulated by ion irradiation, and thus, the radiation hardness can be tested by applying the same dose as they would collect during their operation lifetime. These experiments allow to determine if the device will endure the irradiation or provide information on the degradations to be expected. Moreover, the biological effects of high levels of radiation which astronauts experience was investigated [23]. The interaction of fast ions with living cells or tissues can be studied under controlled conditions, giving an interdisciplinary link to medical applications.

The increasing number of satellites and the modern miniaturised electronics, being much more sensitive, result in growing requests of radiation-hardness tests. For instance, the website of the European Space Components Coordination (ESCC) provides information on qualified electronic devices [24] and the NASA has created the Electronic Radiation Characterization (ERC) project with the goal of "supporting NASA's current and future needs in providing reliable electronic systems in the natural space and terrestrial radiation environments" [25].

Facilities for radiation hardness are installed at many accelerators, among others at the IUCF [26], UC Davis [27], NSCL [28], PSI [29], Texas A&M [30], LBNL [31], BNL [32], UCL [33], JYFL [34,35], GANIL [36], JAERI [37], and HMI [38]. The test facilities have either large vacuum chambers or target stations in air, the latter ones are used mostly for protons. With a cyclotron as accelerator the use of so-called cocktail beams is possible: These beams are mixtures of different ions with the same mass to charge ratio. After acceleration, they have the same velocity, thus, approximately the same range in material. However, the stopping power differs tremendously (see table 2). The different ion species are separated in the cyclotron due to the mass defect. No changes in the beam line settings are needed, only small frequency adjustments of the cyclotron are necessary. This allows switching between different beams within minutes, improving the effectiveness of the tests.

Table 2: Example of a cocktail beam. This 3.5 MeV/u beam is available at the Ionenstrahllabor of the Hahn-Meitner-Institut. The linear energy transfer (LET) and the range have been calculated using SRIM 2003 [39].

Ion	Energy (MeV)	LET in Si ($MeV/(mg/cm^2)$)	Range in Si (µm)
$^{12}C^{2+}$	42	2.7	50
$^{18}O^{3+}$	63	4.4	49
$^{36}Ar^{6+}$	126	16	33
$^{84}Kr^{14+}$	294	41	38
$^{132}Xe^{22+}$	463	69	39

At the moment, ISL operates two high-energy target stations in normal atmosphere where satellite components or electronic devices can be tested for their radiation hardness. Among others, the electronic components of the ROKVISS (RObot Komponent Verification on ISS) [40] were irradiated, yielding the information on the latch-up protection. Detectors used for manned space flight like the Dosimetry Telescopes (DOSTEL) [41] were calibrated. Single electronic devices like high-power diodes [42] were tested with the aim of performance improvement. A challenge of these experiments is the required low beam intensity of about 100 particles per second with precise on-line dosimetry. Several low transmission grids in front of the cyclotron attenuate the beam, already reduced to 10^9 particles/s by slits, to the desired values.

For materials modification as well as for radiation hardness tests, a large multi purpose irradiation chamber has been constructed: BIBER (Berlin Ion Beam Exposure and Research facility). The BIBER chamber is a horizontal laying tank with its axis perpendicular to the beam. This allows easy opening of the tank by moving the two doors on a railroad system. BIBER is installed at the so-called dual beam-line, enabling simultaneous irradiation of the samples with low- and high-energy ion beams. Although the volume of the chamber is 900 litres, BIBER is operational after only 20 minutes of pumping.

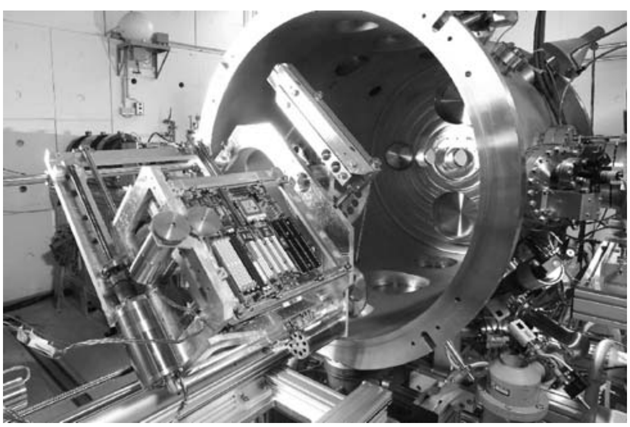

Figure 2: The BIBER chamber for materials modification and radiation hardness tests. The high-energy beam arrives from the right, the low-energy beam from the left.

With the sample holder of the BIBER chamber a maximum sample size of 300 x 300 mm^2 and 4 kg weight is feasible. The strokes of the manipulator are ± 150 mm for x and y, ± 50 mm for z to correct for varying thickness of the samples, and 360° of rotation. A contact-free dosimetry using Micro Channel Plates (MCPs) allows on-line monitoring of the beam intensity during the irradiation using residual gas ionisation. The calibration with a Faraday cup allows a linear measurement of the beam current over nearly 6 orders of magnitude.

The flexibility of the chamber is reflected in the wide spread of performed experiments: Irradiation of foils and SiO_2 films for research and industrial purposes have been carried out as well as the determination of the single event upset rate of flash memories.

MATERIALS ANALYSIS

ERDA – Elastic Recoil Detection Analysis

The knowledge of the elemental composition and structure of solids is of utmost importance for materials science. A well suited tool to determine this is the Elastic Recoil Detection Analysis (ERDA): The samples are irradiated with high energetic heavy ions at grazing incidence, the mass and the energy as well as the number of the out-scattered atoms (recoils) of the sample components are measured at a fixed angle relative to the beam direction. ERDA [43] is a standard-free absolute method as the scattering probability is given by the Rutherford cross section and all the experimental parameters are known. The computable element specific energy loss in material allows the calculation of the concentration depth profiles from the measured energy spectra, simultaneously for all components of the sample. The detection sensitivity is almost the same for all elements. For hydrogen the sensitivity is even enhanced by a factor of four. No restrictions of the detectable mass exist when using heavy projectiles.

ERDA is performed at numerous accelerator laboratories (e.g Tandem-Labs in Munich, Canberra and Rossendorf). Two different techniques are applied for the identification of the recoils: i) the energy loss and the energy of the recoils are measured with two different detectors. ii) the energy and the time-of-flight (TOF) of each recoil on a fixed flight path is determined. The latter technique profits in particular from the time structure of pulsed ion beams from cyclotrons.

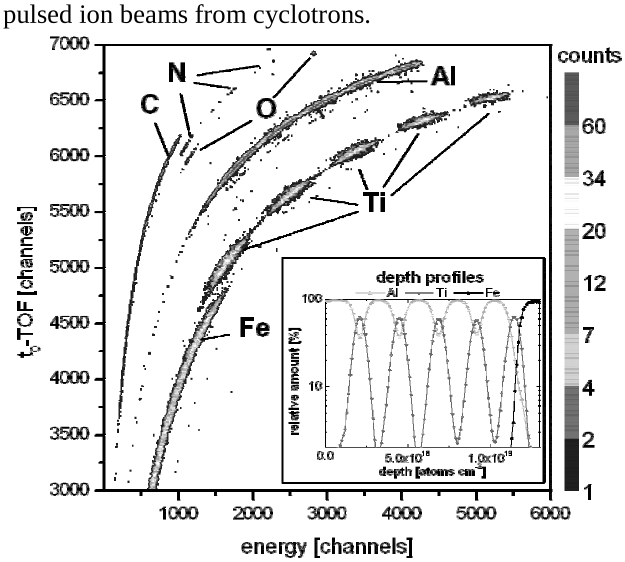

Figure 3: ERDA data ("scatterplot") from the measurement of a Ti/Al multilayer on steel. Each of the layers (5 double layers of 150 nm Al and 100 nm Ti) can be separated well from each other.

At ISL the element respectively mass identification is done by means of the TOF method, i.e. the coincident measurement of energy and flight time for each recoil [44]. Since the detection efficiency for the used channel-plate detectors is less than 100% for protons and alpha particles, also the RF signal from the cyclotron is used for the TOF measurement. With a pulse width of about 0.5 ns it is possible to resolve light elements. The detection efficiency is 100% even for hydrogen. The detection limit is in the order of 0.001 at.% for all elements. The applied energy of the heavy projectiles of about 1.5 MeV/u enables depth profiling up to a maximum layer thickness of several micrometers with a resolution of less than 20 nm at the surface. More than 2000 samples from various fields, like semiconductors, metals, and in a few cases polymers and teeth have been analysed routinely since 1998. The main focus is on photovoltaic materials, mostly produced at the photovoltaic department of the HMI.

PIXE – Proton Induced X-ray Emission

Proton Induced X-ray Emission (PIXE) [45] uses the interaction of protons with the electrons of the sample atoms. The irradiation of any material with a proton beam induces the emission of characteristic X-rays, that identify the elements in the material, independent of their chemical bonding. PIXE also stands for Particle Induced X-ray Emission, however, mostly proton beams are used. For analytical purposes, only X-rays above about 2 keV, i.e. from elements heavier than phosphorous, can be used due to the absorption of the X-rays in the sample itself, in the entrance window of the detector, and in the air between sample and detector, if the measurements are performed in normal atmosphere. Many places world-wide employ protons with energies of about 3 MeV for PIXE analysis. The use of higher proton energies, however, increases the analytical depth due to the larger range of protons and larger cross sections for hard, penetrating X-rays. High-energy PIXE in vacuum for heavy element analysis was used in South Africa [46] and Canada [47], with high energy protons from cyclotrons.

At the ISL, a 68 MeV proton beam in air is used [48] for the PIXE measurements. The range of these protons in the irradiated object is up to a few centimetres, offering the fairly unique possibility of a non-destructive analysis to this depth. For the heaviest elements, 68 MeV protons also induce emission of K X-rays with large cross sections. These high energy X-rays are weakly absorbed and, therefore, can be also detected if they are produced deep inside the sample. The sensitivity limit of the concentration is 0.1 % down to a few ppm, depending on the element and sample composition. Due to the high cross sections, only low beam intensity is needed, so that the analysis is non-destructive, an important feature when analysing art or archaeological objects.

Analysed items range from Egyptian coffin masks, over Chinese porcelain to medieval silver coins. One of the last projects was the analysis of Italian Renaissance sculptures from the Skulpturensammlung Berlin (see fig. 4). 81 sculptures were transferred from the Bodemuseum to the high-energy PIXE set-up and analysed. The material science term “bronze” cannot be applied to those objects, as only for a few objects pure Cu/Sn alloys were employed. A vast palette of alloys has been used with Cu contents from 60 to 99% [49] and Zn, Pb, Sn as major ingredients.

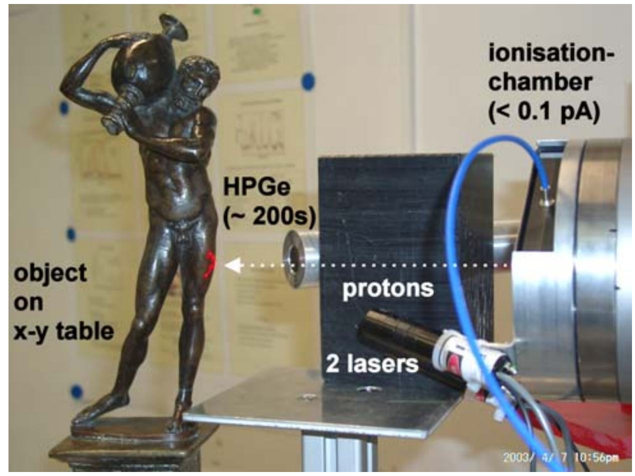

Figure 4: High-energy PIXE set-up at ISL. The lasers mark the analysed spot. (Amphora porter, Inv. no. 313 from the Skulpturensammlung Berlin).

CONCLUSIONS

Starting new applications offers challenging and interesting fields for the use of cyclotrons. The user community becomes more and more manifold, ranging from art historians over physicists and semiconductor specialists to physicians. Dedicated ion accelerators have been operated for radioisotope production and radiation therapy now for at least 10 years. To simplify the operation and to minimize the necessary manpower, they have been tailored to their specific tasks. Many of the practical applications request usually only part of the beam time of a large accelerator, and they face the fact, that different users requesting different ion species and different energies share one accelerator. New fields can be developed and fostered until they have grown enough to build an accelerator facility of their own.

The various experiments require a dedicated beam preparation covering strong variations concerning ion type, ion energy, and beam intensity. The beam currents vary over a vast range of intensities: filter production needs intense heavy ion beams, radiation hardness tests require extremely low beam intensities of about 100 particles per second with precise on-line dosimetry. In addition to the adaptation of the beam intensity to the request of the users, the beam spot size should be tailored precisely to their specific requests. Hence, a close collaboration between the accelerator staff and the users is needed in order to fulfil exactly the demands of the users. Industrial collaborations and tumour therapy have high demands on the reliability and stability of the machine, whereas the other applications and experiments using the accelerator will profit from the efforts undertaken to improve beam stability and intensity.

Besides the proposals for dedicated proton accelerators for cancer therapy there exists already a proposal of a specific accelerator only for filter production, demonstrating the increasing importance of this field. Ion beam applications are becoming more and more important for manufacturing and technology of every day products.

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