STATUS OF ION BEAM MODIFICATION AND ANALYSIS OF MATERIALS AT STU MTF

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Abstract

The new Ion Beam Centre (IBC) equipped with 6 MV tandem ion accelerator and 500 kV ion implanter systems was built at the Slovak University of Technology, Faculty of Materials Science and Technology (STU MTF). The facility provides Ion Beam Modification of Materials (IBMM) and Ion Beam Analysis (IBA), which includes Rutherford Backscattering Spectrometry (RBS), Particle Induced X-ray Analysis (PIXE), Elastic Recoil Spectrometry (ERDA) and Nuclear Reaction Analysis (NRA). Presented are selected experimental procedures carried out in the IBC during the first year of operation. They present examples of a typical IBA performed, such as thin film characterisation in nm to tens of μm range, elemental depth profiles and sensitivity to the light elements enhancement by non-Rutherford cross-section regime application along with the crystalline sample channelling spectra and boron content measurement.

Key words

Ion Beam Modification, Ion Beam Analysis, ion implantation, RBS, PIXE, NRA, ERDA, channeling

INTRODUCTION

Selecting the most appropriate ion beam parameters (type of ion, energy, ion flux, fluence (dose), beam size, etc.), the ion–solid interaction can be adjusted, from weak or slightly perturbative (ideal for the nondestructive analysis (1)), to strong (able to substantially modify the material structure, composition and properties).

Particle accelerators have proven to be competitive devices in the condensed matter scientific and technological field, and have allowed evolving the applied branches such as Ion

Beam Analysis and Ion Beam Modification of Material. Even at STU, efforts have been made to engage in this global process since the beginning of this process development (2). However, the result of this effort corresponded to the real material and other conditions for research at the University at that time. Thanks to the new IBC at STU MTF within the Advanced Technology Research Institute (ATRI) as part of the CAMBO Trnava Scientific Park, it is now possible to continue to use IBA and IBMM in material research at STU at the latest technological level.

The summary of IBC Trnava first-year of operation, including examples of the IBA and IBMM experiments performed, is presented.

EXPERIMENTAL

The 6 MV Tandetron tandem ion accelerator and the 500 kV ion implanter have been in operation since the beginning of the year 2016. The facility provides ion beams in a wide range of energies - from 40 kV to tens MeV, beam currents – from sub nA to mA; virtually all elements from hydrogen to bismuth can be accelerated. Accelerator systems with the 90° mass separating magnets in the injection section provides isotopically pure beams. The maximum achievable energies are: 12 MeV for proton, 18 MeV for He^{2+} and e.g. 54 MeV for Au^{8+} beams, depending on the extracted ion charge state. Long-term stable and energy-narrow (10^{-3} - 10^{-4}) ion beams have been achieved.

Pure and carbon-free vacuum in all the vacuum parts of both accelerator systems ensure oil-free pumping systems, based on the scroll and turbo-molecular vacuum pumps. Secure, reliable and efficient operation of accelerators as well of analytical and implantation end stations are covered by their central computer control systems. Since operating parameters, settings and accelerator states are recorded in the computer's memory, the repetition of the accelerator setups starting from the ion source, through already used beam parameters is considerable simplified.

The implantation end stations are available for the synthesis and modification of materials at both accelerators. Samples of a diameter up to 4 inches at the Tandetron and up to 8 inches at the implanter can be treated at the room temperature, at the controlled elevated temperature up to 800 °C, or cooled down to LN2 temperature (4).

The following analytical methods are available for material analysis (5):

- RBS – typical application is depth profiling of heavy elements at light substrate, depth resolution few nm
- RBS/C - RBS in channelling or blocking mode – provides information about crystalline material, e.g. the amount and depth distribution of lattice disorder; location of the impurity atoms at the lattice site, the damage/defects of the crystal, etc. (6)
- ERDA - based on the detection of energy and velocity/mass of atoms that are knocked out from the sample by incoming heavy ions. The currently installed ERDA system is an extension of the RBS measurement system and is limited to the light element depth profiling
- PIXE - the accelerated particles knock electrons out of the occupied energy levels, what leads to the production and emission of characteristic X-rays. Specific energy peaks identify the sample elements at the sensitivity of ppm, as the K, L, and M X-rays are a fingerprint of each element (3).
- NRA - products of the ion beam induced nuclear reactions are detected. The light isotope concentration depth profiles (typically of elements: H, D, Li, B, C, O, and F) in complex matrices can be measured at a sensitivity of 10 ppm.
- PIGE - Particle Induced Gamma ray Emission – is a special case of the NRA when prompt gamma rays are detected, which are emitted from the nuclei's that are excited after the nuclear reaction induced by the charged particle.

Overview of IBA techniques and their typical applications and detection capabilities is summarized in Table 1.

Table 1: Synopsis of the IBA techniques, their detection capability and main applications (1)			
Main Application		Relevant Techniques	Detection Capability
Materials Science	Ion Beam Analysis - IBA	Rutherford Backscattering Spectrometry (RBS)	$Z > 1$
Archeometry and Cultural Heritages		Elastic Recoil Detection Analysis (ERDA)	$Z < 17$ (typically including H)
Earth and Environmental Science		Particle Induced X-ray Emission (PIXE)	$Z > 11$
Biological Sciences		Nuclear Reaction Analyses (NRA)	$Z < 17$ (often for C, N, O and isotopes)
Nuclear Safety and Radioprotection		Particle Induced Gamma ray Emission (PIGE)	$Z < 17$ (Li, B, F, Na, Mg, Al, Si)
Fundamental Nuclear and Atomic Physics		Scanning Transmission Ion Microscopy (STIM)	sample density
Forensic Science		Ionoluminescence (IL)	defects and sample structure

The Ion Beam Center was presented in more detail elsewhere [4]. A brief overview of the first year facility operation, in particular with respect to the major achievements of the device parameters regarding modification and analysis, is given below. Not all the values are listed chronologically, but rather only extreme ones are given.

Ion Beam Modification of Materials

The summary of the first year of IBMM running at the ATRI facilities is as follows:

500 kV implanter: elements H, B, N, P, Ne, Ar, Cu, Ga, Fe, Co, W, including ^{57}Fe isotope were accelerated from natural elemental abundance sources in the energy range from 30 keV to 400 keV. The efficiency of the beam transport from the ion source to the sample depends on the ion optics of the system, which is dependent on the ion beam energy. The maximum beam current from the ion source on the high-voltage terminal was 4 mA (Ar, N), while a beam current of 0.5 mA (Co) and at least 1.6 μA (W, Fe) were achieved in the implantation chamber. Applied implantation doses varied from 1×10^{16} at/cm² to the maximum of 8×10^{17} at/cm² (Co).

6 MV Tandetron: elements H, He, B, C, Si, Cu, Ni, W and Au have been accelerated in the energy range from 480 keV (H) to 54 MeV (Au). The maximum beam current of 10 μA (H, Si) or 13 μA (Cu) was at the implantation end-station. During 25 MeV Cu implantation, a 325 Watt beam power was reached. Applied implantation fluences varied from very low 1×10^7 at/cm² (54 MeV Au) to 3×10^{16} at/cm². Implantation of 30 MeV Cu was performed at an elevated temperature of 700 °C.

Ion Beam Analysis

RBS: Most of the RBS analyses were carried out in a standard RBS mode, i.e. using a He beam in the energy range from 600 keV to 2 MeV, while up to 10 MeV beam was used to characterize the thick layers. Thin films of an equivalent thickness less than 1 nm to the thickness of 12 μm were characterized.

Examples of the Au and Cu thin layers thickness on the Si substrate RBS measurements are given in Fig. 1 and Fig. 2. RBS was used to calibrate the thin layer deposition device because it gives the absolute value of thickness in units of at/cm^2 .

Fig. 1 RBS spectra of various Au layer thicknesses on Si substrate in nm range were performed by the 600 keV He beam. For thickness calibration, a 60° sample tilt and 170° backscattering angle were used

Fig. 2 RBS spectra of different Cu layer thicknesses on Si substrate in the hundreds nm range were measured using the 1700 keV He beam. For thickness calibration, a normal ion beam incident (no sample tilt) and 170° RBS angle was used

Application of 2 MeV H increased the depth of the RBS analysis. Fig. 3 documents the RBS spectra of 12 μm thick TiN layer, which enables sample stoichiometry determination.

Fig. 3 RBS spectra of a 12 μm TiN layer on a Si substrate measurement. A normal 2 MeV H beam incident and 170° RBS angle was used. Stoichiometry of $\text{Ti}(0.55)\text{N}(0.45)$ was revealed

The non-Rutherford back scattering regime was used to enhance the C, N and O signal during measurement. Compared to the standard RBS, improved sensitivity for light elements by one to two orders of magnitude can be reached, as can be seen in Fig 4.

Fig. 4 The use of non-Rutherford cross section for carbon and oxygen signal enhancement at elevated beam energies. Carbon signal enhancement relative to the standard 1.7 MeV He RBS (a) is one order of magnitude using 3 MeV H beam (b), 1.5 orders of magnitude for 6.35 MeV He beam (c) and two orders of magnitude using 9.5 MeV He beams (d)

Examples of the MoS₂ and TiNC films interdiffusion on Al₂O₃ and Si substrates are shown in Fig. 5 and Fig. 6.

RBS/C: The crystal sample alignment with the specific crystallographic axes and the channeling spectra measurement is a demanding task. This requires typically to measure hundreds of RBS spectra. The first step was to preform automation of the measurement process. Automation of the basic evaluation of the channeling spectra measurements will follow in the near future. An example of the Si crystalline channeling spectra was presented in (7).

Fig. 5 Interdiffusion of a MoS_2 film on a Al_2O_3 substrate. A 600 keV He RBS spectrum (a) and acquired sample element concentration depth profiles (b)

Fig. 6 Interdiffusion of a TiNC film on a Si substrate. A 3.5 MeV He RBS spectrum (a), normal beam incident, RBS angle 170° and acquired sample element concentration depth profiles (b)

PIXE: PIXE measurements of solid samples are done routinely [7]. There are ongoing activities to improve the quantitative evaluation of PIXE measurements, without the use of special reference samples. Since it is a complex problem, a detailed and comprehensive PIXE X-ray detection system characterization is required. Recently, the PIXE setup was adapted to measure aerosol filters.

NRA: Depending on the nuclear reaction product, for NRA analysis either a/ γ rays are detected by LaBr scintillation or alternatively by HPGe detectors, or b/ protons or alpha particles are detected by silicon charged particle detector. For the $^{31}\text{P}(\alpha, p)^{34}\text{S}$, $^{10}\text{B}(\alpha, p)^{13}\text{C}$, $^{11}\text{B}(p, \alpha)^8\text{Be}$ nuclear reactions, the standard RBS/ERDA experimental setup was used. As an example, the alpha particle spectra from $^{11}\text{B}(p, \alpha)^8\text{Be}$ reaction taken by 750 H^+ beam from samples with various boron content is given in Fig. 7. Energy of the emitted α particles was 3.7 MeV.

Fig. 7 Measurement of boron content in carbon samples. A 750 keV proton beam, incident angle 0° and detection angle 160° was used. After filtering out the backscattered protons by 6 μm thick kapton foil, the energy spectra of alpha particles – of $^{11}\text{B}(p,\alpha)^8\text{Be}$ nuclear reaction product were recorded. Each color represents an individual spectrum taken from a sample with a specific boron concentration.

In order to achieve the (p, γ) or (α , γ) nuclear reaction analysis, an extension of the IBA experimental setup was needed (7). A small single-sample electrically isolated chamber was added to the IBA chamber. The experimental assembly allows the ion beam energy sweeping by applying high voltage on the sample holder. So far, the $^{19}\text{F}(p,\alpha\gamma)^{16}\text{O}$, $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$, $^{22}\text{Ne}(p,\gamma)^{23}\text{Na}$ and $^{20}\text{Ne}(p,\gamma)^{21}\text{Na}$ resonance nuclear reactions have been used.

ERDA: The hydrogen depth profiles were measured by ERDA. An example of the hydrogen depth concentration profiles was given in (7).

The SIMNRA simulation program [8] was used for the RBS and ERDA spectra evaluation.

CONCLUSION

After mastering the new IBC experimental devices, including implantation and analytical systems, a number of initial preparatory and verification experiments were carried out. On the basis of the presented illustration of the experimental work performed during the first year after commissioning the Ion Beam Centre facility, we can state that the operation of complex experimental facility was fully mastered. In addition to the energy calibration of ion accelerators and related systems, modification of materials, ion implantation and the whole range of the available ion beam based analytical methods was brought to life and began to be regularly used for research purposes.

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References:

1. A. ZUCCHIATTI, A. REDONDO-CUBERO. 2014. *Nucl. Instr. Meth. B* 331 48.
2. P. KOVÁČ, P., M. PAVLOVIČ and J. DOBROVODSKÝ. 1994. A 0.9-MV Accelerator for Materials Research at the STU Bratislava. *Nucl. Instr. Meth. Phys. Res. B* **85** 749.
3. INSTRUMENTATION FOR PIXE AND RBS IAEA, IAEA-TECDOC-1190, VIENNA, 2000.
4. P. NOGA, J. DOBROVODSKÝ, D. VAŇA, M. BEŇO, A. ZÁVACKÁ, M. MUŠKA, R. HALGAŠ, S. MINÁRIK, R. RIEDLMAJER. 2017. *Nucl. Instr. Meth. Phys. Res. B* 409, 264, <https://doi.org/10.1016/j.nimb.2017.04.051>
5. M. NASTASI, J.W. MAYER, Y. WANG. 2014. *Ion Beam Analysis – Fundamental and Applications*, CRC Press.
6. A. VANTOMME. 2016. “50 years of ion channeling in materials science”. *Nucl. Instr. Meth. B* 371, pp. 12-26.
7. J. DOBROVODSKÝ, M. BEŇO, D. VAŇA, P. BEZÁK, P. NOGA. 2018. The first year operation experience with Ion Beam Analysis at the new STU. *Nucl. Instr. Meth. Phys. Res. B*. <https://doi.org/10.1016/j.nimb.2018.10.006>
8. SIMNRA home page, <http://home.mpcdf.mpg.de/~mam/>.