

# APPLICATION OF AN ECR ION SOURCE FOR IONIC FUNCTIONALIZATION OF IMPLANT MATERIALS ON THE NANOSCALE

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## Abstract

Surface modification by variously charged heavy ions plays an increasingly important role since functionalization of surfaces and/or deeper layers at micro- and nanoscopic scale can be biologically useful for materials of medical implants. The functionalized surfaces have a huge potential in the field of nanotechnology, sensor devices as well.

Our group explores the physical and biological effect of such treatments. In the recent phase of the research work the implantation of titanium and zirconium-dioxide samples by calcium, gold and silicon ions is required.

The 14.5 GHz Electron Cyclotron Resonance Ion Source (ECRIS) of Atomki - a classical room-temperature ion source - was used in this study as an ion implanter to deliver low energy particles from wide range of elements.

A new vacuum chamber and a sample holder for effective irradiation and the production of the beam itself were developed. The technical details of the irradiation and the first result of the physical investigations are described in this paper.

## INTRODUCTION

Plasma processing is a frontier technology and discipline born out of the need to control a group of parameters in materials processing unattainable by strictly chemical process. Materials treated by the plasma, or by the ions of the plasma have a huge area of the possible application field e.g. industry and biomedicine. The field is multidisciplinary involving and combining plasma physics, atomic and molecular physics, surface science and (depending on the final aim of the process) biomedical and engineering disciplines.

Plasmas and ion beams provided by an ECR ion source have some unique future which makes it one of the best candidates to carry out such surface treatment experiments. Due to the high gas efficiency, ECRISs can produce ion beams from a variety of materials, even from

solid. By changing the extraction voltage of the source and/or of the charge state distribution (CSD) of the plasma the implantation depth of the ions into the materials can be varied easily. Usually it must be around 10 nm, which is available applying standard terminal voltage. Last but not least there is another remarkable advantage: as an additional irradiation parameter the effect of the charge state of the ions can also be investigated.

The Atomki ECRIS [1,2] is highly suitable device for this task, because it is an independent ion source (there is no post acceleration) offering beam time more freely. Furthermore, the modularity of the source opens the possibility to change the configuration within reasonable time.

## MOTIVATION

Our main efforts have been and steel are being made to accelerate and increase bone formation around dental and orthopaedic implants and to improve lifetime and mechanical stability. Modification of the medical implant and material surfaces by variously charged ion beam extracted from ECR ion source are investigated. We have started three subtopics (A-B-C) aiming different goals and requiring different irradiation conditions and ion beams. In the recent phase of the research work the implantation of titanium (the surface is always oxide) and zirconium-dioxide (ceramic) samples by calcium, gold and silicon ions is required. Those attributes are listed in the table 1 and the topics are described shortly below.

Table 1: This table shows the three subtopics started in the Atomki ECR Laboratory

	A	B	C
Target material	TiO <sub>2</sub>	TiO <sub>2</sub>	ZrO <sub>2</sub>
Beam	Au	Ca	Si

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- A. The material of the target surface is titanium-dioxide ( $\text{TiO}_2$ ) having good properties e.g. corrosion resistance and also bioinertness. These properties make this material suitable for medical applications. Gold nanoparticles (GNP) in the  $\text{TiO}_2$  can be produced by forming gold atomic layers on the surface (and/or close to the surface) by applying heat treatment afterward [3]. GNPs can chemically bond many types of biomolecules which may be able to assist to reach more stable bond to bone [4]. The other favorable property of the GNPs is comes from the plasmon-effect. The energy transfer between the implants covered by GNPs and the light with appropriate wavelength may be able to destroy the bacteria molecules around the implants.
- B. The implanted Ca ions may increase and accelerate the adherence of the human tissue due to diffusion.
- C. Recently the  $\text{ZrO}_2$  (non-silica-) based restorations have become very popular in the dentistry. It can be suitable choice for fix partial dentures and for implants in esthetic area. In order to bond polymer molecules to the ceramic silicon implantation into and/or close to the surface are necessary to increase the cementation of the dental prosthesis.

## REQUIREMENTS AND DIFICULTIES

It is clearly visible in table 1 that metallic (gold, calcium and silicon) ion beams are necessary for the planned treatments. Since there is no stable gas phase of these atoms in standard conditions the production of the ion beam from solid had to be realized in case of the gold and calcium.

The implantation depth of the ions must be around 10 nm. At first we should characterize and precisely control of that. It requires physical investigation i.e. depth profile analysis of the samples made e.g. by SNMS (Secondary Neutral Mass Spectrometer) and requires theoretical calculation for realistic prediction.

After the physical investigation of the samples clinical test to investigate the effect of the treatment must be done. Such rigorously controlled actions require a series of the samples (at least 60 pieces) in order to conclude by significant statistic. The high number of the samples and their relatively big size (10 mm x 10 mm) indicate technical developments of the irradiation system (chamber, sample holder) to achieve the treatments in reasonable time.

Another difficulty is to fulfill the dose requirements: from  $10^{16}$  ion/cm<sup>2</sup> up to  $10^{18}$  ion/cm<sup>2</sup> must be produced by the ECRIS.

The implantation process in case of an insulation target (e.g.  $\text{ZrO}_2$  in subtopic C.) is not trivial. During the irradiation the sample surface can be charged up the sample which affects the incident beam, causing indefinite dose and implantation depth.

The requirements and difficulties are listed in this chapter indicated the technical and ion beam developments of the ion source.

## ION BEAM DEVELOPEMENTS

The three different kinds of ion beams were produced by three different methods. Note that the application mainly require high intensity, low charged ion beams.

For gold ion beam production the sputtering technique [5] was chosen. Instead of the biased disc a movable sputtering electrode was mounted on the axis of the plasma chamber. This holder equipped with a thermocouple [6], allowing to measure the temperature of the pastille during operation (Figure 1). Oxygen plasma was generated and the oxygen ions of it were used to sputter the metal pastilles. The pastille was negatively biased with respect to the plasma up to 2kV and about 2 mA current was measured on it. The optimal distance between the samples and injection plate was around 80 mm.

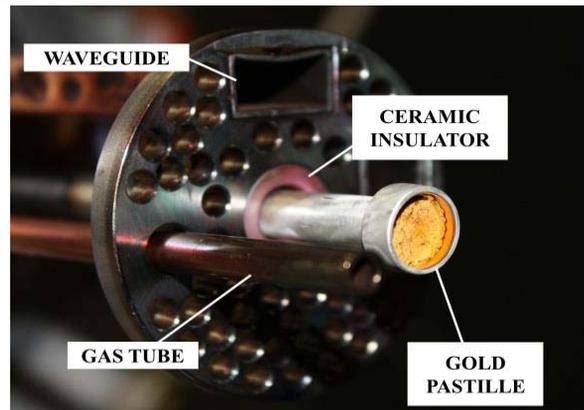


Figure 1: The movable sputtering electrode mounted axially instead of biased disc. The thermometer (not visible) is placed inside the mounting tube.

Remarkable parts of the mass spectra come from the support gas. Typical CSD of the extracted beam can be seen in the Figure 2. During the irradiation process the terminal voltage of the ion source was 2 kV (in order to reach the ~10 nm implantation depth).

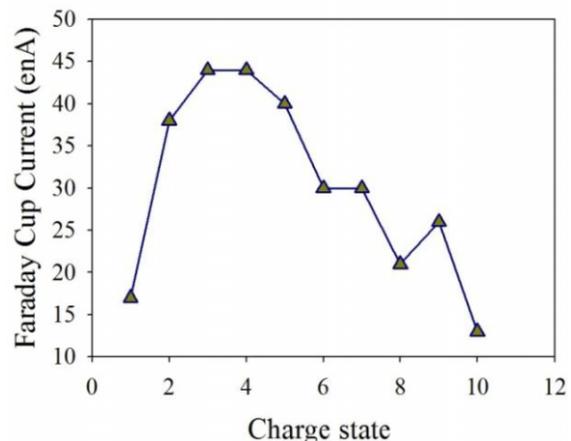


Figure 2: Typical CSD of the extracted gold ion beam used for irradiation. The plasma was tuned for  $\text{Au}^{3+}$ .

Calcium ion beam was produced by the well-known oven technique [7]. The large capacity oven developed

by the Pantechnik Company was used. It is an ohmic resistor allowing controlling the temperature from 300°C up to 1700°C. The head was placed on the axis of the plasma chamber and filled by pure calcium. Due to the vapor pressure of the calcium the optimal operation temperature was found between 500°C and 700°C. We have used helium as support gas. Just before the optimal operation point very strong getter effect was observed. This effect causes very clear calcium spectra showing almost only calcium related peaks and the peaks of the support gas (Figure 3).

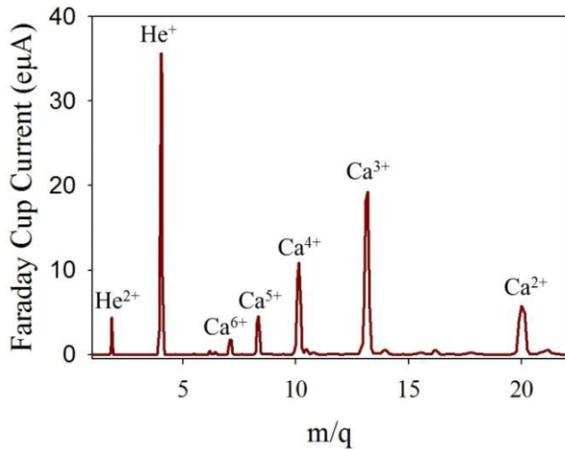


Figure 3: Calcium ion beam spectra. The extraction voltage and the temperature of the oven were 5 kV and 700°C respectively. The purity of the spectra is caused by the strong getter effect. The plasma was optimized Ca<sup>3+</sup>.

In order to obtain silicon ion beam we used SiH<sub>4</sub> (silane) gas. Special care was applied. A concentration of 1.37% is the lower flammable limit for this material in air under conditions of normal temperature and pressure. Between 1.37% and about 4.5%, mixtures can react if an ignition source is provided. Over this concentration mixture is metastable and will undergo auto ignition.

Therefore special gas handling system was designed to transfer the silane gas from high volume high pressure (2 dm<sup>3</sup> and 50 bar) gas bottle to a smaller (50 cm<sup>3</sup> and 1.5 bar) one. The small bottle was connected to the ion source through a gas dosing valve and silicon ion beam was produced. Due to the safety arrangements the risk was reduced to the normal operation level.

Typical silicon ion beam spectra can be seen in Figure 4. For low and middle charge states (Q=1-8) beam currents between 25 and 100 eµA were easily obtained (Figure 5) with good stability.

### TECHNICAL DEVELOPMENTS

Over the requirement referring the ion beam production itself, technical developments were indicated by the reasons listed above.

A new irradiation facility was developed: a vacuum chamber to change the samples easily without breaking the vacuum of the ion source and with a relatively big sample holder in it (Figure 6). The sample holder can handle 3 x 14 = 42 pieces of 10 mm x 10 mm size

samples. It is possible to irradiate 14 samples at the same time. The samples are connected to the vertical copper holder by special conductive glue.

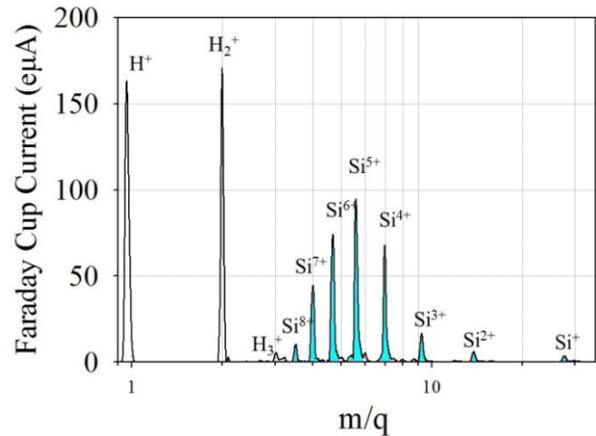


Figure 4: Typical silicon ion beam spectra (optimized for Si<sup>5+</sup>). The extraction voltage was 10 kV.

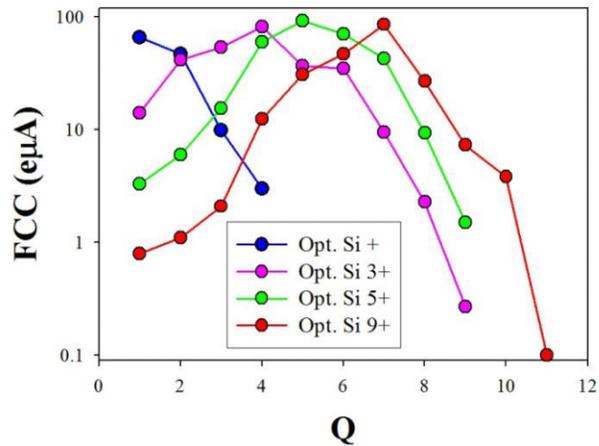


Figure 5: CSDs of the silicon ion beam spectra as a function of the optimized charge state.

To control parameters of the relatively big beam spot a simple beam diagnostic system (profile meter) was also developed. It is an improved version of the 5-segments sample holder already published in ECRIS08 workshop [2]. It was supplemented by four concentric segments to set the size and check the homogeneity of the beam.

In order to reach as high dose as possible, the irradiation facility was built in the primary (zero degree) beamline. In that case, of course all the extracted components of the plasma reach and hit the samples. Instead of the 90 degree line irradiation (with analyzed beam), this method allows to use all the charge states of the produced plasma and the losses of the beam caused by transportation are avoided. During irradiations the analyzed (90 degrees) beamline was only used to estimate the composition of the beam, before, after and several times during an irradiation.

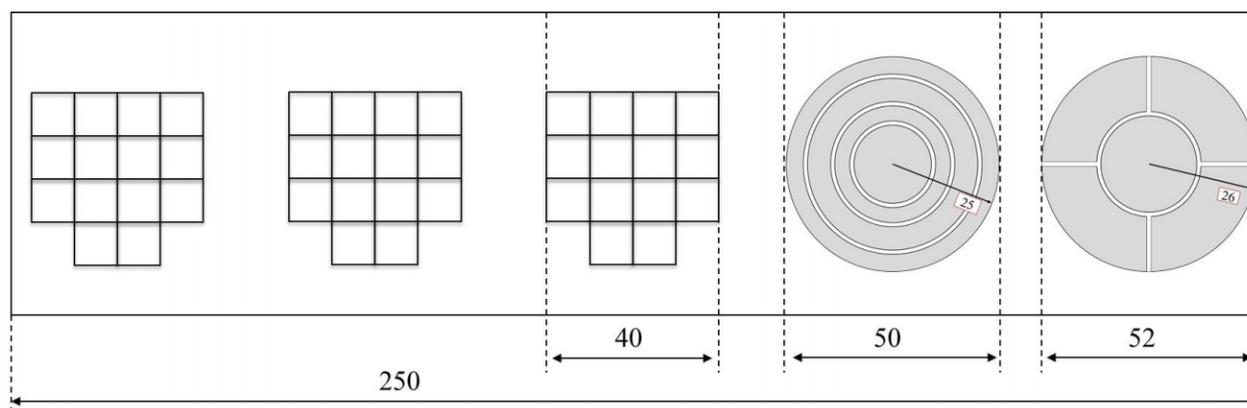


Figure 6: The drawing of the new sample holder constructed by 5 mm thick copper plate. The 5-segment profile monitor helps to set the x-y position of the beam, while the 4-segments concentric monitor helps to set the size and the homogeneity of the beam spot.

## RESULTS OF THE FIRST INVESTIGATIONS

Firstly, as the starting point of the projects (A-B-C) a small number of the samples were irradiated by the beams developed (Table 2).

Table 2: The parameters of the irradiations: name of the project, ionic piece, average charge state, irradiated dose, irradiation time.

Project	Ion	$\bar{Q}$	Dose (ion/cm <sup>3</sup> )	Time (hour)
A	Au	1.3	10 <sup>16</sup>	8
B	Au	2.2	10 <sup>17</sup>	4.5
C	Si	3.1	10 <sup>17</sup>	1.25

In order to avoid the charging up effect of the ZrO<sub>2</sub> sample, it was covered by 25 nm thick carbon layer and for comparison a sample without this layer was also irradiated.

The depth profiles of the treated samples were investigated. After such implantation the depth distribution of the irradiated materials are Gaussian like or can be handled by the superposition of Gaussian curves. The well-known SRIM (Stopping and Range of Ions in Matter) code [8] was used to make sense of the curves measured experimentally by an SNMS device (type INA-X, SPECS, Berlin).

The depth, where the density of the ions reaches the maximum (called implantation depth) was used as a representative parameter to compare the calculated and measured profiles. The data are summarized in Table 3.

In case of the titanium (oxide) target (project A and B) the implantation depth of the incident ions were well predicted by the computer code. However in case of the ZrO<sub>2</sub> sample (which is an insulation material) the sample can charge up, as we supposed, which affects the kinetic energy of the incident beam causing indefinite (lower) implantation depth. This uncertainty can be avoided by

evaporating carbon layer on the surface of the target. In this way the implantation depth becomes easy to be predicted (see last row in Table 3). The added carbon layer can be removed by heating the sample applying 800°C over 6 hours in a furnace.

Table 3: Comparison of the calculated and measured implantation depths.

Ion	Target	Depth (nm)	Calc. depth (nm)
Au	TiO <sub>2</sub>	1-10	7
Ca	TiO <sub>2</sub>	8	9
Si	ZrO <sub>2</sub>	6	25
Si	ZrO <sub>2</sub> + C layer	25	25

## SUMMARY

In the frame of a long term multidisciplinary scientific project the Atomki ECR ion source was used to produce specific heavy ion beams and plasmas for materials research and to explore the possibility of medical applications of such ions. We are focusing to the medical implants and materials since functionalization of such material's surfaces and/or deeper layers at micro- and nanoscopic scale can be biologically useful.

The requirements and difficulties of this field listed in this paper evoked technical and ion beam developments of the Atomki ECR ion source. New vacuum chamber and sample holder (new irradiation facility) for effective irradiation were designed and constructed. Calcium, gold and silicon plasmas and beams were produced by different techniques. Two different types of materials (TiO<sub>2</sub> and ZrO<sub>2</sub>) were irradiated by three kinds of ion species.

The implantation depth of the incident ions was measured and compared with the calculated one. As a result, we can control and allocate this parameter even in case of insulation target material.

As the logical continuation of this work, high number of samples will be treated by using the new irradiation facility presented in this paper. In the near future (before the clinical phase) further physical and biomedical studies of those samples are planned.

### ACKNOWLEDGEMENT

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