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GOLD AND CALCIUM ION BEAMS FOR MATERIALS RESEARCH BY THE ATOMKI ECR ION SOURCE

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Abstract

Surface modification by highly charged heavy ions plays an increasingly important role since functionalization of surfaces and layers at micro- and nano scale can be biologically useful for the titanium and for other implants solid samples. In the Electron Cyclotron Resonance (ECR) Ion Source Laboratory of the Institute of Nuclear Research (ATOMKI) new techniques and methods were developed to produce highly charged ion beams from solid materials. In this work Calcium and Gold ion beams obtained at μA current range will be presented. The plasma and beam production is based on the sputtering technique having long term stability and providing good quality of highly charged Ca and Au ion beams which is extremely important for long and dense irradiation processes.

I. Motivation and introduction

Surfaces functionalized by different type of ion beams have much potential in medical care and nanotechnology. Hard oxide glasses, metal oxides like TiO_2 can be related to these investigations and further developed towards biosensing,

investigations of biocompatible surfaces, for example, in dental implants. Nanoscale modification of titanium implant surfaces, which are always covered by oxide, can alter cellular and tissue responses that may benefit osseointegration and dental implant therapy. The biological usefulness of the titanium implants can be improved either if their surfaces are modified or if they are coated. Calcium-hydroxylapathite cover layers on Ti surfaces are the most investigated from this point of view, including our investigations on plasma spray deposition [1]. Simple nanostructuring at different scales seems to be very important too, as well as implantation of different atoms, like C, Au, Ca, C_{60} if they modify the surface structure and creates bioactive complexes at the same time.

Furthermore chalcogenide materials can be used as versatile model for the development of technologies (including ion-beam and plasma treatments), for direct applications in nanophotonics, plasmonics and sensing. Structural modification of these layers at micro- and nanoscale creates metal nanoparticle-glass composites. The recent interest in these systems comes from the remarkable effects that may arise from the critical size reduction as well as from the composition and even bondings at the surface and shape of nanoelements. Interesting novel properties (mechanical, catalytic, optical, electronic and biological) occur as we reduce the dimensions from a bulk, solid crystal or glass to a system composed of a relatively small number of atoms.

Investigations of the optical response of subwave-length structure arrays milled into thin metal films have revealed surprising phenomena, including reports of unexpectedly high transmission of light, optical coupling to the surface in terms of the resonant excitation of surface plasmon polaritons (SPPs). The functionalization of surfaces by nanostructuring is extremely important for enhancement of chemical reactions, catalysis [2], and in the creation of biocompatible surfaces [3].

The first step of these investigations is to produce appropriate ion beams from special and in many cases from exotic ions as Calcium and Gold. In most cases special metal ion sources or, more recently ECR ion sources are used for these challenging tasks because of their favorable and unique features.

There exist several methods to produce plasmas and ion beams from solid materials: oven technique, MIVOC method, sputtering technique, laser evaporation, etc [4]. The most commonly used oven technique means the evaporation of the material from an external furnace [5]. This method is one of the most effective ones but the high evaporation temperature of some metals

means serious technical difficulty. The MIVOC method can be used when the metal has gaseous or volatile compounds (for example Ferrocene) [6]. The main advantage is the fast set up time and easy of use but the essential drawback come from the high amount of impurities. In case of the sputtering technique [7, 8] the sample is mostly mounted close to the plasma and is negatively biased respect to the plasma. The positive ions of the plasma sputter the sample and the particle (mainly neutral metal atoms) diffuse into the ECR plasma where they are ionized. It is a convenient technique to produce low intensity metal ion beams, but is limited by the decoupling between the source tuning and the evaporation process.

Since our aim was to produce metal ion beams (especially from Gold and Calcium) with good stability and without any major modification of the source (for example mounting high temperature oven to the source) the sputtering technique was chosen.

In the next chapters some technical details of the experimental setup and the beam spectra of the Gold will be presented.

II. Experimental setup

In Figure 1. the basic configuration of the ATOMKI-ECRIS is shown. The magnetic trap consists of two identical room-temperature solenoid coils and of a permanent magnet hexapole. The coils generated axial magnetic field peak values are 0.95 T at extraction side and can be increased up to 1.2 T by two removable soft iron plugs at injection side. The radial pole field of the hexapole structure permanent magnet at the plasma chamber inner wall is 1.2 T. The ECR plasma can be heated by microwave provided by Klystron amplifier up to 1 kW power. Further technical details and some applications of the ECR ion source of ATOMKI are shown in Refs. [9, 10, 11]

In the basic configuration a movable, biased, disk-shape electrode is used to tune the plasma [12]. During the metal ion beam production instead of the biased disc a movable sample holder was mounted on the axis of the plasma chamber. This sample holder designed by the ATOMKI ECR group is equipped with a thermocouple, allowing to measure the temperature of the sample during operation (Figure 2.). The sample was negatively biased with respect to the plasma up to 500 V. The optimal distance between the samples

and injection plate was 81 mm for Gold and 35 mm for Calcium. The source voltage for all recorded spectra was 10 kV. Beam current was measured by a Faraday-cup with a suppressor electrode. The size of the ion beam (10 × 30 mm) was defined by the slits in front of the Faraday cup.

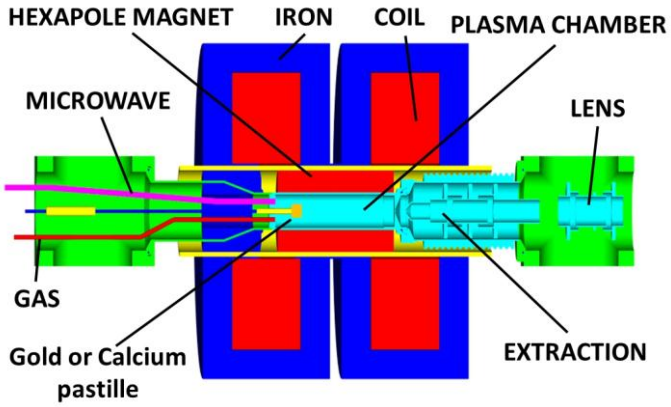

Figure 1. Layout of the ATOMKI ECRIS

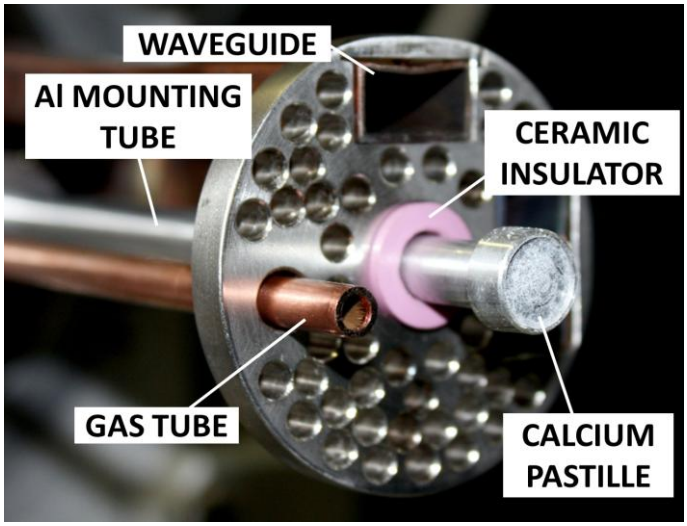

Figure 2. The movable special sample holder was mounted axially instead of biased disc. The thermometer (not visible) is placed inside the mounting tube.

III. Results

Oxygen plasma was generated and the ions of the plasma were used to sputter the metal pastilles. The samples were negatively biased up to 500 V and around 2 mA current was measured on it. It was easy to optimize the plasma parameters for the highest peak, but the charge state distribution could not be shifted significantly. In case of the Gold beam the highest peak was Au^{17+} (1.25 eμA) but we could reach 0.86 eμA from Au^{23+}. The highest charge state for Gold was 26+ which is one of the highest in the history of the ATOMKI-ECRIS. Low charge states for example Au^{9+} could not be increased above 100 nA with this technique. In case of the Calcium the highest peak was Ca^{8+} (2 eμA) and the other peaks of the Calcium were less than 0.2 eμA. Typical ECR parameters of the optimization can be seen in table 1.

Highest peak	FCC	P_{wave}	Gas	P_{inj}	Condition of the sputtering
Au^{17+}	1.25 eμA	300 W	O_2	$1.6*10^{-6}$	485 V/1.93 mA
Ca^{8+}	2 eμA	350 W	O_2	$2.1*10^{-6}$	500 V/1.98 mA

Table 1. Faraday-cup current (FCC) values of the highest peak, microwave power (klystron), injected gas, pressure measured in the injection stage, voltage and current of the pastille.

In order to choose the appropriate irradiation condition, to choose the most expedient charge state, it is necessary to calculate the particle currents instead of electric currents. As it is shown by table 2, in case of the Gold beam it is clear the highest particle current can be reached from Au^{17+}, Au^{18+}, Au^{19+}. On the other hand we must take into account Au^{17+} peak has a large neighbor (Carbon) peak which may makes the optimization and irradiation process insecure. Therefore Au^{18+} or Au^{19+} beams are the most effective ones for irradiation.

Au	9+	10+	12+	17+	18+	19+	20+	21+	22+	23+	26+
FCC (eμA)	0.095	0.134	0.2	1.25	1.13	1.04	0.82	0.66	0.52	0.26	0.58
FCC (pnA)	11	13	17	74	63	55	41	31	24	11	2

Table 2. Faraday-cup currents in terms of electric micro Ampere (eμA) and in terms of particle nano Ampere as function of the different charge states. Au^{11+}, Au^{13+}-Au^{16+}, Au^{24+} and Au^{25+} always overlapped by peaks of the support gas or by peaks of the impurities.

Typical gold mass spectrum extracted from ATOMKI ECRIS can be seen in Figure 3.

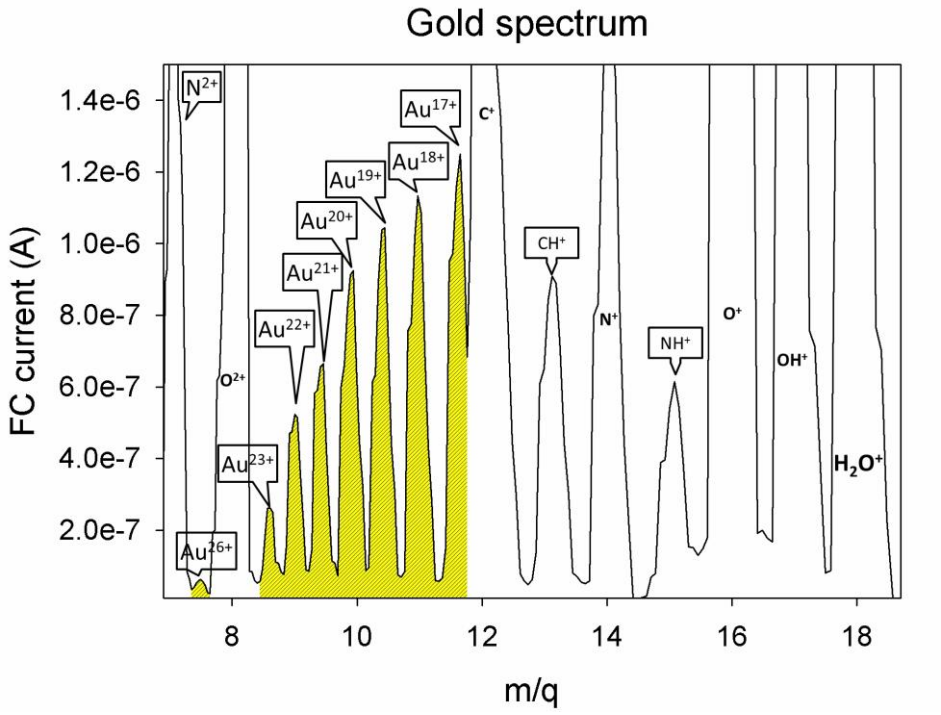

Figure 3. This figure shows a typical Gold spectrum (Faraday-cup current as function of m/q) extracted from ATOMKI ECRIS. The highest Au^{17+} peak can be found close to the single ionized Carbon atom.

In Figure 4. the photo of the extraction plate with the extraction hole from inside of the plasma chamber is seen. Lost (non-extracted) gold ions following the magnetic field lines form a gold triangle on this plate.

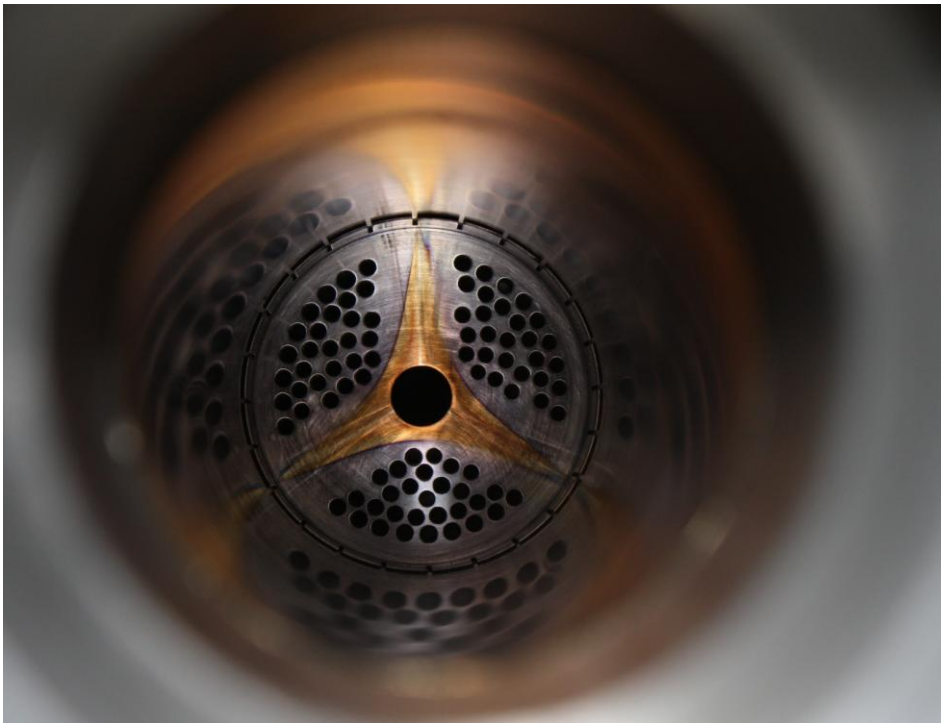

Figure 4. The yellow triangle on the extraction electrode shows the lost gold particles.

The applied oxygen gas has complex role during the sputtering process. It provides adequate plasma density which is required to ignite and maintain the plasma and to sputter the samples. On the other hand it behaves as light support gas. As a result of collisions between the oxygen ions and the heavier

ions the heavier ions are cooled down and their confinement time increases, consequently the charge state distribution is shifting to higher charge states.

Generally all the recorded spectra show similar structure and view. Remarkable parts of the mass spectra come from the support gas and from impurities. This points to the fact the limitation of the sputtering technique. As mentioned in case of this technique the ECR plasma decouples from the evaporation process, giving narrow way for extensive optimization.

Nevertheless, it was proved that ion beams based on sputtering technique have long term stability (more than 20 hours long irradiation was established) providing good quality of highly charged Ca and Au ion beams in case of an extremely long irradiation process as well. The irradiations of real samples (chalcogenides, titaniums etc) with gold and/or calcium beams are planned to be performed in the near future.

IV. Acknowledgement

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References

[1] S. Kökényesi, I. Popovich, M. Sichka, A. Kikineshi, L. Daroczi, D. Beke, J. Sharkany, Cs. Hegedus, Journal of Optoelectronics and Advanced Materials **9** (2007) 2063-2067.
[2] V. Matolin, E. Gillet, Experimental evidence Surface Science Letters **166** (1996) 115-118
[3] G. Mendonca, D. Mendonca, L. Simones, et.al., Biomaterials, **30** (2009) 4053-4062.
[4] Brown, I. G., (ed.),The physics and technology of ion sources. WILEY-VCH Verlag GmbH. 2004
[5] D. J. Clark and C. M. Lynes, J. Phys. **50** (1989) C1-759
[6] H. Koivisto, J. Arje, and M. Nurmia, Rev. Sci. Instrum. **69** (1998) 785.

[7] R. C. Vondrasek, R. Scott and R. C. Pardo, Rev. Sci. Instrum. **75** (2004) 1532
[8] D. P. May, Rev. Sci. Instrum. **69** (1998) 688.
[9] S. Biri, R. Rácz and J. Pálinkás, Rev. Sci. Instrum. **83** (2012) 02A341.
[10] S. Biri, I. Iván, Z. Juhász, B. Sulik, Cs. Hegedűs, A. Ifj. Jenei, S. Kökényesi, J. Pálinkás, Proc. 18th Int. Workshop on ECRIS, Chicago, Ill. USA, 15-18 Sept., 2008, pp. 41-47 (http://accelconf.web.cern.ch/AccelConf/ecris08/papers/moco-c04.pdf)
[11] The homepage of the ATOMKI ECRIS Laboratory. www.atomki.hu/ECR
[12] G. Melin et al, Proc. 10th Int. Workshop on ECRIS, Knoxville, TN, USA, 1-2 Nov., 1990, pp. 1-15.