



# Multipurpose 14.5 GHz ECR ion source: Special features and application for surface modification

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## Abstract

Highly charged  $Xe^{+q}$  ions (up to  $q = 27$ ) were produced by a 14.5 GHz electron cyclotron resonance ion source and used for solid surface modification experiments. AFM investigations show that hillock-like defects are created by ions with  $q = 20$  and 24 on the surface of thin Se films as well as on the natural facets of multi-component SbSI crystals. © 2005 Published by Elsevier B.V.

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## 1. Introduction

Interactions of ions with solid surfaces result in a great variety of effects that depend on the material and the type and energy of the impinging ion. Ion implantation and surface etching are the most investigated processes that find a wide range of industrial applications. In such processes the kinetic energy of the given single or multiple-charged ion is of the primary importance. The availability of special sources of highly charged ions (HCI,

$Z^{+q}$  with high  $q$ ) opened an extending direction of research areas on the interaction of ions with high potential energy with solid surfaces [1].

The potential energy of the highly charged ions gives rise to new effects, namely potential sputtering ([2] and references therein), Coulomb explosion, and enhanced proton desorption from the surfaces. Potential sputtering occurs due to the energy transfer from a relatively slow but highly charged ion to the target atoms. Excitation of the electron system in the near to surface region of the target material seems to be an essential first stage of this process, which is followed by the rise of the kinetic energy of atoms and results in desorption, sputtering of atoms, ions or even

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clusters from the solid target. This process is in contrast to the usually analyzed crater forming sputtering effects at low ion fluences or layer-by-layer etching of the target surface during the prolonged irradiation. In cases where potential energy effects played role few nanometer high hillocks were observed by AFM on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> single crystal and mica crystal surfaces [3,4]. While the explanation of such surface modification by HCI at the nanometer scale is almost absent, it may be supposed from the known experimental data that these effects occur only in dielectrics where the above mentioned scenario can take place. The unified model of the potential sputtering, assisted with kinetic energy transfer to the target via defect formation and transformation [2] is more realistic and may be used for developing models of HCI induced structural transformations in semiconductors with high electrical resistivity and more “soft” structure in comparison with Si, GaAs.

Crystalline and amorphous Se or S-, Se- and Te-containing chalcogenides like As<sub>2</sub>S<sub>3</sub> seems to be suitable materials for these experiments, since they possess well known phase change effects (reversible crystallization–amorphization, used in optical memory devices) or light-, electron- and ion-stimulated structural transformations within their amorphous phase [5–7]. The layered-chainy structure of these materials is formed by covalent and van-der-Waals bonds which allow easy defect formation and their transformations, assisted by non-equilibrium electrons and holes that need 1–2 eV for their excitation [5,8].

We present the first experimental results on HCI induced formation of surface nanostructures on elemental amorphous Se layers and SbSJ crystals and prove the applicability of this class of materials for surface modification and nanostructure fabrication by HCI. A versatile ECR ion source of highly charged ions was used for these purposes.

## 2. The ATOMKI-ECRIS

In ATOMKI a 14.5 GHz electron cyclotron resonance ion source (ECR, ECRIS) operates as a stand-alone device to produce variously stripped

plasmas and low-energy ion beams [9,10]. So far we produced H, He, N, O, Ar, Kr, Xe ions (from gases) and C, C<sub>n</sub>, C<sub>60</sub>, Zn and Pb ions (from solids) to form plasmas and ion beams. During the last few years several improvements have been carried out on the ECRIS itself. The mirror ratio of the magnetic trap was increased by inserting additional soft iron plugs leading to longer confinement times for electrons and ions. A movable, biased electrode was installed to tune the plasma potential that affects the trapping and extraction conditions. More recently this electrode was equipped with water cooling while it is still biased and movable on the high voltage platform. This solution has dramatically decreased the outgassing of neutrals from the plasma chamber and made higher microwave powers possible. As a result, both the charge states and the intensities of the heavy ion beams increased. Before these modifications the highest analyzed Xe charge state was 21 and that went up to 27 as a result of these modifications.

## 3. Experimental setup

The surface modification experiments were performed using 20- and 24-times ionized Xe beams. The kinetic energy of the beam particles is developed by the platform potential of the ion source which was usually 10 kV. Therefore the kinetic energy of the projectiles in these experiments always exceeded the potential energy by about two orders of magnitude or more. In Fig. 1. the energy and charge ranges in the present and future planned experiments (with slow HCI and with relatively higher potential energy) are shown. In the experiments Xe<sup>20+</sup> and Xe<sup>24+</sup> ions were directed to the target surface with their total beam current in the 50–500 pA range with 0.5–30 min exposure times. This assumed to produce 1–300 impacts on a 100 × 100 nm<sup>2</sup> area of the target surface. The possible charging of the ~6 mm<sup>2</sup> open sample surface seemed to be compensated by the surface and volume conductance of the target materials (10<sup>-8</sup>–10<sup>-12</sup> Ω<sup>-1</sup>cm<sup>-1</sup>), since increasing exposure times resulted in surfaces covered with a more dense surface structures (hillocks).

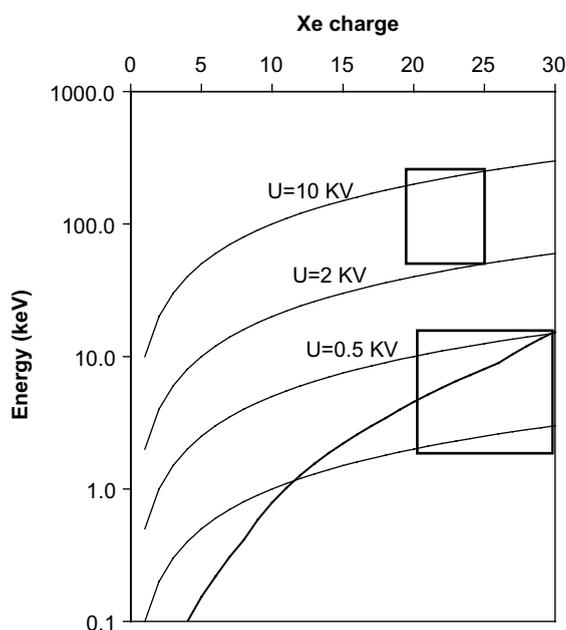


Fig. 1. The potential energy (thick line) and the kinetic energy of Xe ions. The labels on the kinetic energy curves show the ion source platform potential in keV. The upper rectangle shows the range of the present experiments. The lower rectangle is our plan.

There have been two types of targets used in these investigations. Amorphous selenium layers with total thickness of about 500 nm were deposited onto the Corning glass or mica crystalline substrata by thermal evaporation in vacuum. The samples were mounted on a special metallic sample

holder and transported in a closed dust-protected box with at atmospheric pressure to the ECR-connected collision chamber. Needle SbSJ crystals with smooth  $\sim 1.5 \times 10$  mm natural facets were grown by the previously developed gaseous transport reactions in evacuated quartz ampoule and stored in a closed dry chamber at atmospheric pressure before mounting on the same sample holder.

Irradiated samples were investigated by NT-MDT atomic force microscope (AFM) in a tapping mode also at atmospheric pressures just after the opening of the collision chamber and in repeated cycles of measurements during few days or even weeks after the irradiation.

#### 4. Results and discussion

Typical AFM images of the bombarded surfaces are demonstrated in Figs. 2 and 3. Average lateral sizes of the hillocks appearing on the surfaces are between 20 nm and 60 nm, the population distribution of the measured lateral diameters has a maximum at 30 nm for Se and 50 nm for SbSI.

The initial local roughness of the a-Se layer surface was about 0.3 nm at the scale of the measurements, but the surface on the whole consisted of 1–5 nm high and 500–800 nm wide hills which are characteristic for all thermally evaporated amorphous chalcogenide layers. It is worth to note that the shape of the few nanometer small surface

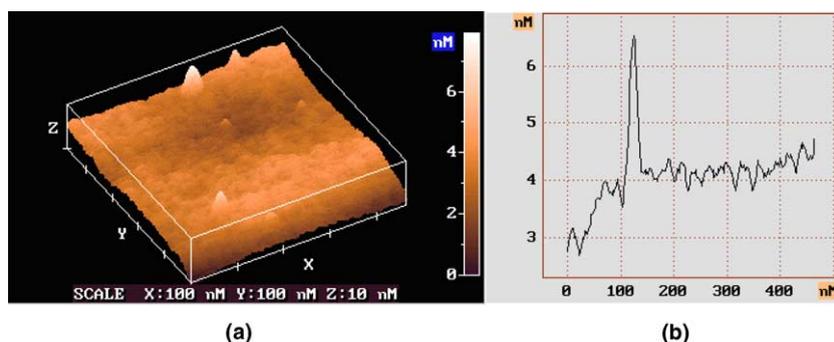


Fig. 2. AFM tapping contact mode image of a-Se surface bombarded with 200 keV  $\text{Xe}^{+20}$  ions (a) and the line profile of the surface (b).

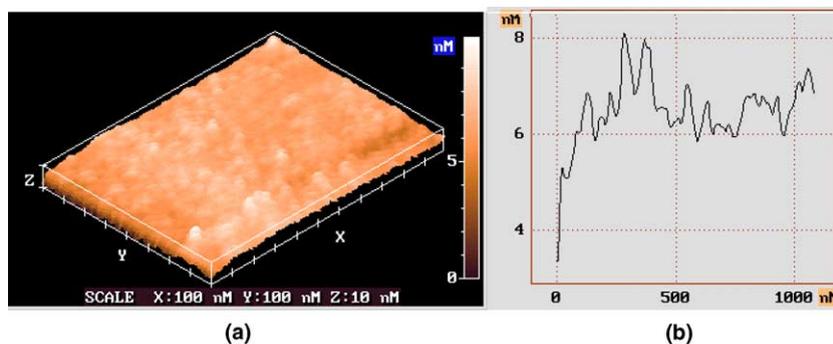


Fig. 3. AFM image of SbSJ crystal surface after the bombardment with 240 keV Xe<sup>+24</sup> ions (a) and the line profile of the irradiated surface (b).

features in AFM images and the appropriate cross sections does not necessarily correspond to real features on the surface: the sizes of the tapping needle, the resolution must be taken into account. Consequently we can only assume the conformity of observed hillocks with seeds of crystalline Se that can develop to larger crystallites of trigonal selenium with primary direction of *c*-axis vertical to the surface, similar to the process of light induced crystallization of a-Se [6,8]. The enthalpy of the crystallization process in a-Se in the vicinity of its softening temperature ( $T_g \sim 305$  K) is near 13 kJ/mol, so the energy transferred even from one projectile to the target is quite enough to create a crystallite.

The most relevant question in this situation is: how a very short, few femtosecond ion–surface interaction process [1] can develop into a crystallization process that have time constants in the microsecond to millisecond range (depending on the temperature, viscosity, volume of the transformed region, atomic mobility etc. [8])? A simple over barrier jump of the atom in a diffusion process is shorter but still it is necessary to assume a transition stage where the energy of the initially excited electron–hole system transforms to the atomic movement. The model of “defect-mediated sputtering” [2] that supposes ion induced defect creation and electron–hole trapping seems to be quite applicable for our experiments. The situation is even more simple and the efficiency of the process is higher in our material, since the original concentration of defects which form localized elec-

tron–hole states in the forbidden gap is near  $10^{18} \text{ cm}^{-3}$ – $10^{20} \text{ cm}^{-3}$ . The presence of weak van-der-Waals bonds between molecular units and chainy fragments makes the structure very flexible and promotes defect-assisted bond switching with subsequent structural transformation either to another amorphous state or to the crystalline state. In both cases 1–10% changes in the local density may occur, especially if the local composition also changes in multi-component chalcogenides [6].

In our interpretation the known spike model of the high energy ion interaction with glassy material on one side and the kinetically assisted potential sputtering on other [2] might explain our observed effects. Of course normal plasma etching of the amorphous surface with accelerated ions is also possible. In order to test this possibility we also used Ar<sup>+</sup> ions for etching, but no simple, well defined hillocks were observed in this case. It means that the potential energy of HCI and the connected processes of recharging may play essential roles also for these materials.

The ion-impact induced amorphization may be assumed for hillock formation on SbSI crystals. This process is a reverse of the above mentioned crystallization process. This includes the same stages of defect creation, electron–hole localization and the subsequent atomic movement. Since no stoichiometric SbSI glass is known, the composition probably changes in the near to surface region, first of all due to the rather easy evaporation of halogen after the ion impact. Here the process of defect diffusion from the bulk to the drains

and to the surface (I, Sb or S) is also very probable, since the mobility of interstitial atoms in the interchainy spaces (the obvious place for the defect concentration in these crystals) may enhance the enriching of the surface by atomic clusters. This is similar to the known effects of radiation induced Cd diffusion to the surface in CdS crystals.

The efficiency of the stimulated a-Se crystallization (represented by the size of the hillocks) seems to be higher in comparison with transformations on crystalline SbSI. The reversible chalcogenide optical storage media may be the best material for such experiments, with practical aim of nano-scale recording surface elements.

## 5. Conclusions

Highly charged  $\text{Xe}^{+q}$  ions (up to  $q = 27$ ) were produced by the upgraded ATOMKI-ECRIS and used for surface modification. The creation of 1–5 nm high hillocks both on the surface of Se layers and SbSI crystals irradiated with  $\text{Xe}^{+20}$  and  $\text{Xe}^{+24}$  ions was observed by AFM. To make more definite conclusions about the nature of the hillocks it seems to be necessary to observe its structure in future experiments. The study of the influence of the charge state of the bombarding ion and of

the ratio of the potential and kinetic energies on the process is our nearest task.

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