APPLICATION OF THE ATOMKI-ECRIS FOR MATERIALS RESEARCH AND PROSPECTS OF THE MEDICAL UTILIZATION*

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Abstract

In the ATOMKI ECRIS Laboratory long-term projects were initiated to use heavy ion beams and plasmas for materials research and to explore the possibility of industrial or medical applications of such ions. In the paper four applications are shown. (1) A new ECR-device was developed in collaboration with Japanese institutes to produce endohedral fullerenes, namely caged Fe in C_{60}. (2) Titanium bio-implants are covered with fullerene ions to form an intermediate layer between the metal and the organic tissues in order to shorten the time of the cell growth and to improve the properties of the connection. (3) Laser and electron irradiations showed that the structure and properties (volume, refractive index) of certain amorphous thin films can be effectively modified. We extend these investigations using heavy ion beams, focusing on the effect of the ion charge. (4) Highly charged slow ions were found to be efficiently guided by insulating nano-capillaries even at large tilt angles. This phenomenon is investigated for different kinds of capillary arrays and materials.

INTRODUCTION

In the history of the ECRIS workshops majority of the talks, posters and papers dealt with the technical features of ECR ion sources. During their operation lifetime most sources undergone several minor or major modifications or upgrades. The main goal is usually to increase the beam intensity and/or the charge of the extracted ions. Another large volume of the papers discussed the physics of the ion sources, both experimentally and theoretically. In these fields excellent results were achieved and presented in the ECR workshops and in ion source conferences.

Nowadays a continuously increasing demand is detected for the application of heavy ion beams in industry and medicine. The application of plasmas and ion beams produced by ECR ion sources is normally published in other conferences or in independent papers. These contributions usually do not show the details of the ion sources or the "beam-making" itself. However, a specific application of a heavy ion beam frequently requires the modification of the ion source itself or, at least, unusual plasma formation or ion extraction.

In this paper we show a few possible, promising applications of heavy ion beams. Each of these projects just started at the ATOMKI ECRIS Laboratory, some of them in collaboration with other institutes. The first results already appeared, but the major achievements are expected within the next 1-5 years.

NEW MATERIALS IN ECR DISCHARGE

Fullerene plasmas and beams have been produced in ECR ion sources for various scientific and practical reasons and purposes [1]. High intensity singly and multiply charged beams are needed for collision experiments. The endo- and exohedral fullerenes are getting more and more important for materials research and, in some cases, for medical applications. Endohedral means that an alien atom or molecule is encapsulated inside the carbon cage. The most known endohedral fullerene is the N@C_{60} molecule (here the @ sign means that the atom at left locates inside the molecule at right). It has been investigated to develop a sensitive indicator to measure molecular distortions, molecular motions etc. and in conjunction with quantum computing [2].

At the ATOMKI-ECRIS fullerene plasmas have been produced since 2000 by using filament ovens to evaporate fullerene. One of our goals has been the production of high intensity singly and multiply charged fullerene ion beams. Another research topic is the investigation of mixture plasmas (C_{60} + X, where X is N, O, Fe or other atoms). In C_{60}+N mixture plasmas endohedral N@C_{60} was observed in the beam spectra and in macroscopic quantity in the soot deposited on the wall of the plasma chamber [2].

The fullerene encapsulated iron would be another promising new material if one could produce it first in a beam then in bulk quantity. In the past years we made some efforts in this direction. The composition of C_{60}+Fe mixture plasmas was studied by extracting ions from it. The iron component of the plasma was obtained from ferrocene powder or using high-temperature filament ovens to melt pure iron rods [3,4]. These and other results and demands led us to a major modification of the ATOMKI-ECRIS. Since 2006 it has been operating in two modes ("A" and "B") [5]. In "B"-mode the ion source is equipped with a large plasma chamber and a weak hexapole around it. This mode is specialized for the production of large-sized, low-ionized plasmas and provided the fullerene beams for a number of experiments.

The ATOMKI-ECRIS-B source was selected as a prototype for an other new ECRIS just built in Toyo

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University, Kawagoe, Japan [6]. The new ion source was designed to produce iron encapsulating fullerene ions in beam and in deposited layer form. The details of the technical solutions and the latest beam results are presented in a separated paper at this workshop [7]. Here we list only the basic features of the source.

- Geometry: plasma chamber diameter is 14 cm, length is 35 cm.
- Microwave: 8-10 GHz and optionally 2.45 GHz, as second frequency.
- Mirror field: two identical room-temperature coils, peak fields max. 0.64 Tesla.
- Hexapole: NdFeB, modified AECR-U design, field at poles is 0.72 Tesla. The magnet borders at radial positions were calculated to form parallel slits for a future easier radial approach to the plasma (see Figure 1.).
- Fullerene gas: using simple filament oven or evaporation boat.
- Iron gas: by induction oven (under development).
- Extraction: grounded, movable puller, einzel triplet.
- Beamline: bending magnet to transport upto 5 KV beams with M=800.
- Other: an optional processing chamber is under construction to be connected at the extraction side. It will be equipped with biased meshes and cooled electrodes to help the iron-fullerene synthesis.
- Name: because the ion source is being built at the Bio-Nano Electronics Research Center of the Toyo University and it is aimed to produce new materials useful for physical, biological and medical research and application, it is called Bio-Nano-ECRIS.

The Bio-Nano-ECRIS delivered the first gaseous and fullerene plasmas and beams in 2008. Further details and results are in [7].

BONE CELL GROWTH ON TITANIUM COATED WITH FULLERENE

Current clinical implant therapy includes microscopic modification of bone formation on machined titanium implants. This concept is called “osseointegration” and now is widely accepted in clinical dentistry and surgery. Efforts have been and still are being made to accelerate and increase bone formation around dental and orthopedic implants and to improve lifetime and mechanical stability. Nanotechnology offers physicists, engineers and biologists new ways of interacting with relevant biological processes. Nanoscale modification of titanium implant surfaces 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.

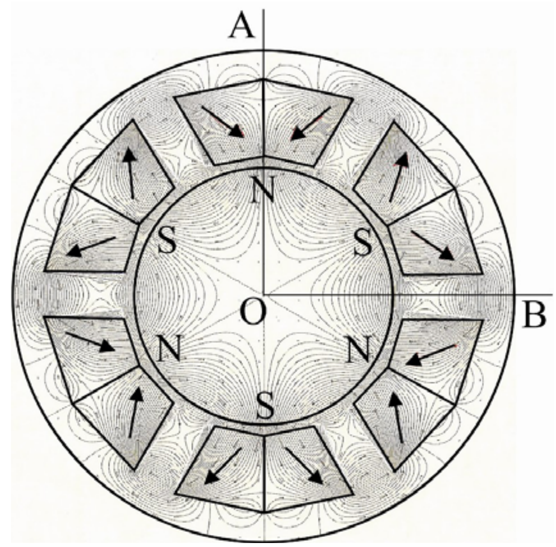

Figure 1. The structure of the hexapole of the Bio-Nano-ECRIS. Nd-Fe-B magnet material: NMX-S45SH. Note the parallel slits at gap positions.

To our knowledge fullerene (C_{60}) coating has never been tried yet as an intermediate layer between the metal and the organic tissue in order to increase the cells growth speed and to improve the properties of the cells connection. C_{60} molecules, if ionized, can be shot to the metal surface with any required velocity. Depending on this velocity, the carbon balls may remain intact or may be partly or fully damaged by hitting the metal surface. The strength of the connection is obviously depends on the projectile velocity which is needed to be explored experimentally. On the other side, fullerene molecules can be very reactive, hydroxyl and other group of atoms and molecules are connected to them likely and easily. Such derivatised fullerenes can be medically useful [8]. Therefore, in collaboration with the Faculty of Dentistry of the Debrecen University, we have started a research program in order to coat titanium surfaces by fullerenes with various velocity and thickness. Then biological tests will be carried out on the covered samples by growing bone cells on them.

For an ion source point of view the task was to irradiate simultaneously 10 pieces of identical Ti samples (size is approx. 10x10 mm, thickness is 0.5 mm) with as homogenous fullerene beam, as possible. An irradiation facility was built in the primary (zero degree) beamline. The Ti samples located approx. 50 cm distance from the plasma electrode. The analyzed (90 degrees) beamline was used only to check the composition of the beam, before and after the irradiation. The ATOMKI-ECRIS-B source [5] can produce “pure enough” fullerene beam in two point of views: around 90% of the beam is single-charged, and more than 80% of the extracted beam is fullerene. The rest less than 20% is mostly H_2O and N_2/CO. The necessary energy (extraction voltage) of the fullerene beam was chosen with the help of published data [9]. The structure of carbon films, deposited from ionized fullerenes accelerated to different energies, depends on the deposition energy. Below 300 eV fullerenes are deposited preserving the molecular identity while above 800 eV the deposited material can be considered already almost as amorphous carbon [9]. In our experiments we aimed to make half of the samples covered with "intact" fullerenes and the other half with "partly-broken" fullerenes. Therefore U=250 V and U=500 V acceleration energies were chosen to get 250 eV and 500 eV beam energy, respectively. Composition of a typical analyzed beam: H_2O+: 10 nA, (N_2/CO)+: 10 nA, C_{60}^{3+}: 3 nA, C_{60}^{2+}: 30 nA, C_{60}^{+}: 100 nA. These currents were measured in the Faraday-cup after the bending magnet, the extraction voltage was U=250 V. At U=500 V all these currents were higher about 2-3 times. A vertical sample holder together with a 5-segments beam profile monitor was designed and constructed. This device enabled us to set a 50 mm diameter fullerene beam (see Fig. 2). Due to the radial multipole magnets ECR-beams always have a specific, well-known structure. Nevertheless, we could always set a beam where the 5 current values on the 5 segments differed from each other by less than 10%. The beam current impacted the samples was about 300 and 800 enA at U=250 V and U=500 V, respectively. The rate was calculated to produce the Ti-surfaces to be covered with 1 C_{60} molecular layer and others with 5 layers.

After building the ATOMKI-ECRIS-B mode we tested both our 14.3 GHz klystron and 12.2 GHz TWTA, as microwave sources – without any remarkable difference in this experiment. The applied microwave power was varied between 4 and 20 W. The solenoid field was much lower, than normally, the two magnetic peaks just surpassed the resonance values. No mixing gas was used. The fullerene source was the simple filament oven we used earlier many times [3]. We placed 10 Ti-samples to the copper holder and altogether 4 irradiations were done during 4 days. The Table 1 summarizes the main characteristics of the irradiations (columns 2-5).

The irradiation of the titanium with fullerenes was followed by biological experiment. Human embryonic bone cells (type: palatal mesenchymal pre-osteoblast, HEPM 1486, ATCC) were cultured onto the Ti substrates for 48 hours, followed by a fixing in formaldehyde for 10 minutes. Then the cells were dual labeled with special markers (FITC-falloidin) for 45 minutes at 4º C to make the actine and vinculine parts more visible. The confocal imaging was performed on a laser scanning microscope (LSM 510, Carl Zeiss). The morphology of the cells is different compared to the control substrate (pure glass), but remarkable differences between the four series could not be observed so far. The control cells on glass are quite spread showing an interconnected morphology. The cells grown on the Ti substrates are more spindle-like shape showing denser actine and vinculine structure. In Figure 3. confocal images of the bone cells grew on glass and titanium substrates (latter covered with C_{60}), are shown.

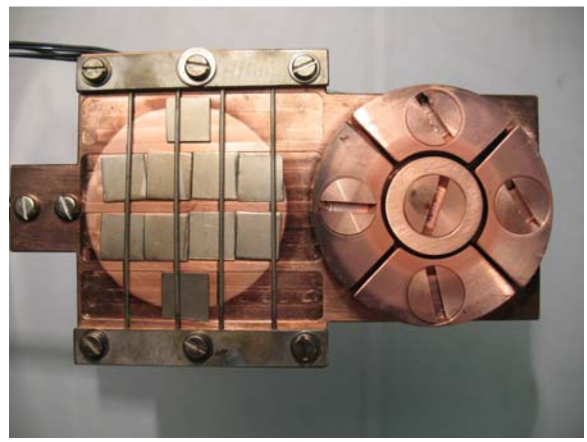

Fig. 2. The 5-segments copper beam profile monitor (right) and the sample holder with 10 Ti samples (left). This device is mounted on a vacuum feedthrough with 100 mm longitudinal run.

The last column of Table 1 shows the number of the grown bone cells (result of averaged microscope counting) on the fullerene layer. While these numbers show some tendency, it is too early to draw conclusions from them for the optimal beam energy or ion dose.

Table 1. Titanium irradiation with fullerenes. One series contained 10 Ti-samples.

Ti sample series	C_{60} fraction in beam (%)	Beam energy (eV)	Number of C_{60} layers on Ti	Time of irradiation (min)	Number of bone cells (10^5/ml)
1	80	500	4.3	90	8.0
2	93	500	1.2	23	3.4
3	74	250	4.9	87	6.6
4	84	250	1.1	32	8.9

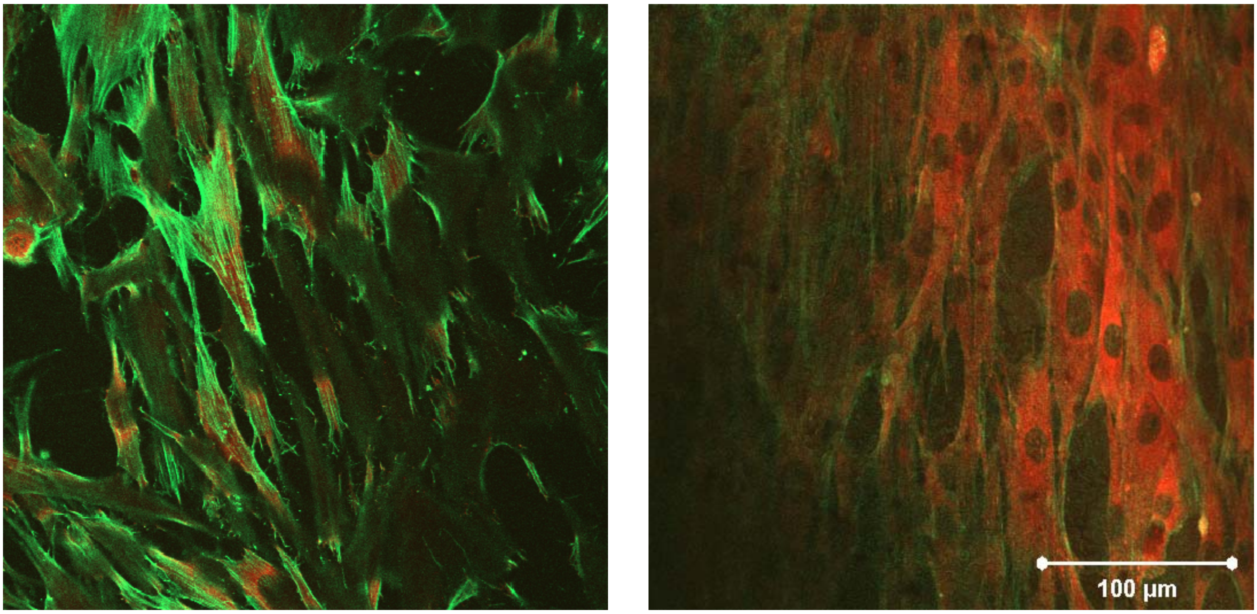

Fig. 3. Confocal laser scanning microscope images of bone cells grown on glass (left) and on Ti surface covered with 250 eV C_{60} layer (right).

This first experiment obviously ended with success in the sense that it was clearly proved the C_{60} coating does not prevent bone cells grows. Further experiments however are necessary to explore the optimal beam properties (energy, dose, density, composition) to improve both the physical (Ti-C_{60} connection) and biological (C_{60}-cells) properties of the connections.

OPTICAL CHANGES IN THIN FILMS

Ion bombardment and ion implantation are versatile tools for modification of properties of thin near-surface layers of solid materials. In case of singly charged ions and a large variety of materials this effect is rather well understood and widely used in different branches of the modern industry. The effect of the bombardment of multiply and highly charged ions has been studied only in a few materials, such as HOPG (highly oriented pirolytic graphite), mica, Al_2O_3, SiO_2 and Se [10-13]. These studies concentrated on the nanohillock and crater formation caused by impact of single ions depending on the ion charge state and on the materials properties. There have not been studies on the effects caused by ions while traveling through and stopping inside the solid, since the charge state dependence was thought to be too small to detect experimentally [14,15].

However, we have observed significant charge state dependence in darkening of amorphous AsSe thin films bombarded with Ne^{q+} (q=4..8) ions. Previous ion irradiation experiments with 80-180 keV protons and deuterons have shown [16,17] that the ion bombardment causes structural rearrangements in AsSe and in similar amorphous chalcogenide thin films, which in turn result in optical band gap decrease (i.e. decrease of optical transmission at certain wavelengths). The relative transmission change during bombardment with Ne^{q+} (q=4..8) ions (measured at 600 and 640 nm) versus ion fluence plots are shown in Fig. 4. The total kinetic energy of all ions was set to 120 keV, therefore the ion source extraction voltage was from 15 to 30 KV. The thickness of the AsSe films was 800 nm which is about three times as large as the expected thickness of the modified layer (SRIM [18] calculations gave 196 nm range and 116 nm longitudinal straggling). In Fig 4 one can see the optical transmission decreasing with the ion fluence while reaching saturation value at about ~$3\cdot10^{14}$ ion/cm^2 in this particular case. The saturation value of the relative transmission depends on the thickness of the modified layer (see l in the equation) and on the depth distribution of the induced absorbance $\Delta\alpha(z)$:

$$\left(\frac{T}{T_0}\right)_{sat} \propto \exp\left(-\int_0^l \Delta\alpha dz\right).$$

Our experiment shows that the $(T/T_0)_{sat}$ is larger for the sample irradiated with Ne^{8+} ions than for the one irradiated with Ne^{4+} ions. Since the $\Delta\alpha(z)$ is proportional to the total energy/volume deposited in the material by the ions (i.e. the higher the deposited energy the larger the $\Delta\alpha$) [16, 17] and the ions with higher charge are expected to have higher specific energy loss [15], the observed difference in the $(T/T_0)_{sat}$ values by necessity means that thickness of the modified layer is smaller for the Ne^{8+} ions than for Ne^{4+} ions by 25%. As the modified layer thickness is in strong correlation with the stopping range of the ions, the above stated relation is true also for the range of the ions.

This result has impact on our knowledge of charge equilibration processes of ions traveling in solids and also on a number of basic scientific and technical problems, which along with the details of the experiment will be discussed in detail in a forthcoming paper [19].

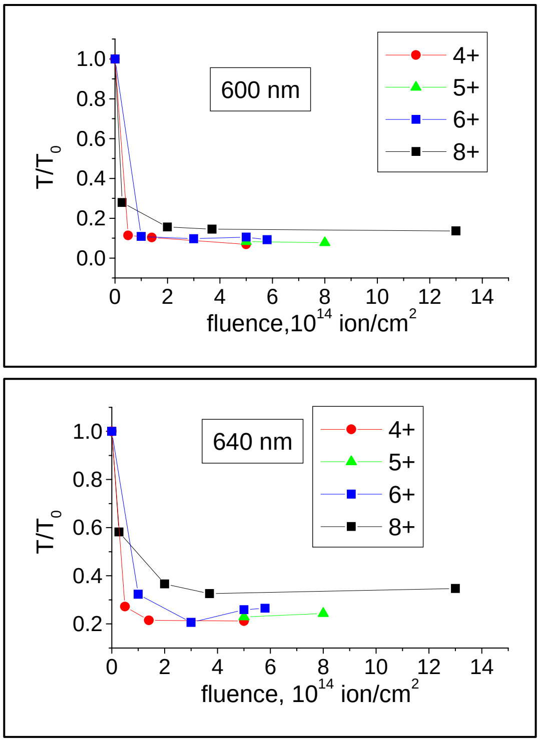

Fig 4. The change of optical transmission (T) of a 800 nm thick AsSe film measured at 600 and 640 nm relative to its initial value (T_0) during bombardment with Ne^{q+} (q=4..8) ions versus the ion fluence.

CAPILLARY GUIDING

Charging up of insulating surfaces during irradiation by ion beams involves mesoscopic or long range interaction of the ions and the charged surfaces. Insulating nanocapillaries have attracted considerable attention since the discovery of capillary guiding caused by the self-organizing charging up of the inner capillary walls [20]. Ions with a few keV kinetic energy are efficiently transmitted through the capillaries of thin insulating foils mostly in their initial charge state, and the transmitted ions are directed along the capillaries with a narrow angular distribution. There is significant transmission even if the capillaries are tilted by large angles, i.e., when there is no geometrical transparency for straight line trajectories. Due to these properties, insulating nanocapillary arrays might find numerous applications, e.g., in guiding, directing and focusing slow ion beams in nanoscale devices. They might be used for irradiating single cells and writing on charge sensitive surfaces.

In order to collect more data with different kinds of capillaries that is useful for the full understanding of this self-organizing phenomenon, experiments were carried out on the 90 degree beamline of the ATOMKI-ECRIS-A source. Neon (6+, 7+) and argon (8+, 9+) beams were transported into the capillaries. The extraction voltage was usually 500 V and a collimator set of two 1 mm diaphragms at a distance of 205 mm restricted the beam divergence to ±0.3 degrees from axis at the end of the beamline. The beam intensity on the targets fall in the pA or nA range. The typical beam current for 3 keV Ne^{6+} was about 300 pA. For 6 keV Ne^{6+}, it was 500 pA.

The sample holder with the capillaries was mounted in the middle of a vacuum chamber with three axial and one rotational freedom. Separately, a spectrometer was mounted on a rotating table to measure the charge and currents of the transmitted ions at different observation angles. The incidence angle of the ions was changed by tilting the target samples. Two dimensional angular distributions were recorded by the multi-channel-plate (MCP) detector placed behind the target samples. The ion spectrometer and the MCP were used alternatively.

Most of the target samples were prepared of membranes of nanochanneled Al_2O_3. The thickness of the samples was about 15 µm and the capillaries were ordered in a honeycomb structure. The average inner capillary diameters of the different samples used in the experiments were about 140 and 260 nm. In order to prevent macroscopic charging up of the samples, niobium layer of about 20 nm thickness was deposited on both sides of the membranes by dc-sputtering. Macroscopic sized single capillaries were also investigated. Those capillaries were made of glass and had an inner diameter of a few tenth of mm.

The angular and charge state distribution of Ne^{6+} and other ions transmitted through Al_2O_3 capillary samples were measured by different methods. The major outcome of these experiment was that the ions have been efficiently guided by the capillaries up to a few degrees tilt angle, similarly to the earlier investigated polyethylene terephthalate [20] and SiO_2 [22] capillary samples. Most of the transmitted ions preserved their initial charge as it can be seen in Fig. 5. The results obtained by the ion spectrometer were compared with those studied by the MCP array. The details of the experiment and some of the results have been published in other papers [21,22], others are to be published. Preliminary experiments have shown that under certain conditions macroscopic glass capillaries can guide slow ions as well.

COMPARISON

The Table 2 gives a simple overview of the four different applications of heavy ions detailed in the preceding chapters. The tasks and beam requirements are very different, but the ECR source proved to be versatile enough to fulfill all these requirements and serves as a real multi-purpose facility.

Table 2. Summary and comparison of the projects require heavy ion beams from the ion source point of view.

Project short name	Endohedral fullerenes	Ti implants coating	Thin layer modification	Capillary guiding
Ion source	ATOMKI-ECRIS-B and Bio-Nano-ECRIS	ATOMKI-ECRIS-B	ATOMKI-ECRIS-A	ATOMKI-ECRIS-A
Plasma/beam	Fe^+, C_{60}^+	C_{60}^+	$Ne^{4+...8+}$	$Ne^{6+,7+}$, $Ar^{8+,9+}$
Beam diameter (mm)	10-20	50	4	1
Extraction voltage (V)	500-5000	250-500	15000-30000	500-1000
Microwave frequency (GHz)	8-12	12-14	14.3	14.3
Microwave power (W)	1-50	4-20	200-400	200-600
Specification	Synthesis in plasma or on surface	Irradiation in the zero-degree beamline	Beams with same total energy	Puller on high negative voltage

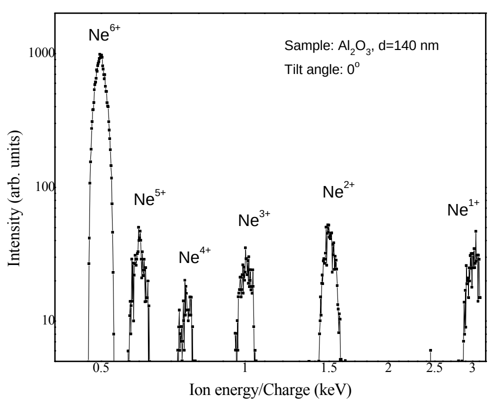

Fig. 5. Charge state distribution of the ions transmitted through 140 nm long capillaries at 0° tilt angle. The incident beam was of 3 keV Ne^{6+} ions.

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