Diagnostics of argon cluster ion beam for materials treatment

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Abstract. The important parameters for materials surface processing by a gas cluster ions are the mass composition, total energy and energy per atom in the cluster, which depends on the ion beam charge state. The purpose of this work is an experimental characterization of argon cluster ion beam, based on an original time-of-flight technique. The mean sizes of the cluster ions obtained from the measured mass spectra are compared with the mean sizes of the primary neutral clusters. By analyzing the mass spectra at different electron ionization current, the average charge state of cluster ion beam is evaluated.

1. Introduction
Recently, it was shown that a promising method for modifying the various materials properties is the treatment of their surfaces by gas accelerated cluster ion beams [1, 2]. Intensive cluster beams are generated from the supersonic jets of condensed gases by optimizing the gas source parameters and beam formation scheme [3, 4]. To increase the kinetic energy of the neutral clusters, they are ionized, by electron impact, and then formed cluster ions are accelerated to the high energy. The interaction of the cluster ions with the solid is determined by their total kinetic energy and cluster size (i.e. energy per atom in the cluster).

The beam of the neutral clusters formed from a supersonic gas jet has a broad size distribution, which is usually characterized by the mean cluster size. The mean cluster size value can be estimated using the empirical relationships [5, 6]. The cluster ionization involves a number of different stochastic processes. Since the energy of the ionizing electrons is much higher than the cluster particles binding energy (van-der-Waals clusters binding energy is less than 1 eV), the different channels of cluster decay are possible: fragmentation, evaporation, Coulomb explosion, etc. [7-9]. As a result, the mass spectrum of the cluster ion beam differs significantly from the primary neutral cluster beam [10].

In order to increase the cluster ion beam current, the ionizing electron current is usually grown. This leads to an increase in the probability of not only single-cluster ionization but also sequential multiple ionization. Consequently, the cluster fragmentation can be enhanced and multiply charged cluster ions can be formed [11, 12]. With the same acceleration potential, the multiply charged cluster ions acquire greater kinetic energy and they have another effect on the treatment surface. The cluster ion beam parameters depend on particular ionization and beam formation conditions. Therefore, the controlling of the cluster ion beam parameters is necessary for material processing.

2. Experimental results and discussion
The experiments were carried out using the experimental setup CLIUS of the Novosibirsk State University, the description of which is given in [13]. In order to measure the mass composition of
cluster ion beam, the time-of-flight technique (ToF) is commonly used. Since the cluster ion beam modulation was performed after its formation typically, the measurements were carried out at low ion energies [14, 15]. In this work the original TOF technique is used based on ion beam modulation at the stage of its formation. This allows one to measure the mass composition of the cluster ion beam at the technological energy level (up to 25 keV) without the use of additional devices (separator, deflecting electrodes, etc.) [16].

The mass spectra of argon cluster ions beam for various $P_0$ measured in the absence of a magnetic separator shown in figure 1. As expected, at low stagnation pressures ($P_0<0.8$ bar) monomer ions were detected mainly. When the stagnation pressure has been increased up to 0.8 bar, this led to an increase in the number of collisions between atoms in gas flow, and, as a consequence, the large clusters have formed in the beam. In results, the bimodal mass distribution was recorded. It can be seen that the cluster peak shift toward larger clusters and broaden with increasing the stagnation pressure. At high stagnation pressure the intensity of monomer ions peak very small in comparison with the cluster ions intensity. There are several reasons for this. First, at high stagnation pressures, a significant part of the monomers is condensed, forming clusters, the largest clusters are concentrated on the beam axis, displacing monomer and small clusters to the gas jet periphery. Therefore, the concentration of the monomer component in the axial region is decreased. Secondly, the larger clusters have a larger ionization cross section, so the concentration of ionized large clusters is much higher than of the ion-oligomers concentration.

![Figure 1. Mass-spectra of Ar cluster ion beam at different stagnation pressures.](image)

The mean cluster ion sizes $N_i$ calculated from the ToF mass spectra are present in figure 2. In order to determine the mean size of neutral clusters, $N_0$, the original experimental method based on the measure the cross-section of the cluster beam total intensity was used [17]. The mean sizes of primary neutral cluster $N_0$ for the same conditions measured experimentally and evaluated by empirical relations [5] are also present in figure 2. As can be seen, the measured mean cluster size good agreement with evaluation by empirical relations [5].

The difference between the sizes of initial neutral clusters $N_0$ and cluster ions $N_i$ is present in figure 3. As can be seen, $\Delta N$ is minimal for small cluster sizes and it increases significantly for a large $N_0$, the tendency is similar to a linear dependency. The same result was obtained in [18] for large CO$_2$ and Ar clusters.
In order to study the effect of ionization conditions on the parameters of a cluster ion beam, the mass spectra measured at the different ionization electron currents are presented in figure 4. In the presented experiments, the electron energy was fixed and amounted to 300 eV. It can be seen that an increase in the ionization electron current leads to significantly shift of the mass distribution function to the small clusters sizes. This can be interpreted by two reasons. Firstly, this can be explained the increase in the average charge state of the cluster ion beam caused by the multiple ionization and its correspondent higher acceleration. Secondly, this can be the result of the cluster destruction intensification upon their ionization. In [18] it was shown that the decrease of the mean size is accompanied by a broadening of the distribution function for the multiple ionization of Ar and CO₂ clusters. However, under our conditions, the half-width of the distribution function decreases with the electron ionization current increase (see figure 4). In [19] it was shown that as the electron ionization
current increases, the half-width of the distribution function is decreased but the cluster ion current, defined as the area under the distribution curve, is increased. This means an increase in the charge delivered to the detector by cluster ion beam.

Figure 4. Mass-spectra of Ar cluster ions at different electron ionization current $I_e$.

The dependencies of the mean cluster ion size and cluster ion current on the electron ionization current for our conditions are presented in the figure 5. As can be seen, the increase of electron ionization current leads to decrease the mean cluster size and cluster ion current simultaneously. It is interesting that for a large electron ionization current, the cluster ion sizes tend to constant values probably. We used relatively small clusters ($N$~1000 atoms/cluster) compared to work [19], in which the cluster sizes were about 3000 atoms/cluster. As is known, the cluster ionization cross-section $\sigma_i$ depends on their size $N$ as $\sigma_i \approx N^{2/3}$. At the same time, the large clusters are more stable upon the sequential multiple ionization [10].

Figure 5. Dependencies of the mean cluster ion size and cluster ion current on the electron ionization current.

Therefore, in our conditions, the increase in the electron ionization current does not lead to an increase in the average charge state of cluster ion beam but cause to the cluster destruction intensification, as a result of the Coulomb explosion and partial evaporation. The above facts allow stating that the average charge state of the cluster ion beam is about +1.
3. Conclusion
In order to characterize the cluster ion beam, the original time-of-flight technique was applied. The comparison of the mean cluster ion sizes $N_i$ with the mean sizes of neutral cluster $N_0$ measured for the same conditions by another method has approved that difference $\Delta N=N_0-N_i$ is near linear arise with the increase the initial sizes $N_0$. The analysis of the mass spectra measured at different electron ionization currents demonstrates that the average charge state of cluster ion beam under our conditions is about +1. The certain parameters allow one to correctly determine the effect of the cluster ion beam on the surface of the material to be processed.

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