

Size distribution of atomic clusters formed by energetic-heavy-ion sputtering

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A cesium sputter ion source is used to produce cluster beams of various materials. The size distributions of these clusters have been studied. The dependence of the cluster yields on the structure of the substrate used has also been studied for carbon.

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Emission of atoms and simple molecules from solid surfaces by energetic-heavy-ion sputtering is well known. It has recently been established that even more complex structures such as fullerene C_{60} [1–4] or biological molecules [5] can be sputtered out by heavy-ion bombardment. The mechanism of emission of such complex molecules has been the subject of several recent studies because of their significance in diverse areas [6]. We report here the size distributions of atomic clusters formed by cesium ion bombardment on several substrates in an effort to understand the mechanism of their emission.

The present investigations were carried out in the Ion Beam Laboratory of the Institute of Physics, Bhubaneswar. The laboratory is centered around a 3 MV Pelletron accelerator equipped with a rf source for helium and hydrogen and a SNICS (source of negative ions by cesium sputtering) source for solid targets [7]. The SNICS source is known to be a prolific source of composite clusters [8]. In this source a cold cathode of a substrate is bombarded with Cs^+ ions of a few keV energy to produce a negative ion beam of the cathode material (provided the material can form negative ions). In general the negative ion beam currents depend on the cathode composition, the cathode potential, the cesium ion flux, and the cathode temperature. The ion source output contains, in addition to the monomers, an appreciable amount of atomic aggregates of various sizes generally referred to as clusters. Irrespective of the cathode material used, ions of atoms and molecules containing hydrogen, oxygen, copper, etc. are also observed. In order to mass analyze the clusters of different sizes and species we first accelerate the clusters to about 15 keV and perform a momentum analysis with the help of the injector magnet of our system [7]. Because of the maximum bending power of the magnet, there is obviously an upper limit on the size of the cluster which can be analyzed; this limiting mass value in our case is ~ 1400 amu. The yield of specific species is measured with the help of a Faraday cup which monitors the current of a particular mass selected species. Our sensitivity is limited to negative ion currents more than 0.1 nA in the Faraday cup. The materials used in the present investi-

gations are carbon, silicon, gold, and zinc, covering the range of insulators, semiconductors, and metals.

The measured size distribution of atomic clusters for various substrates are shown in Figs. 1–4. The following points are evident from the figures.

(i) Clusters of various sizes ranging from dimers to ones containing several atoms are produced.

(ii) The cluster yields follow an exponential decay trend as a function of cluster size.

(iii) For carbon clusters obtained with a graphite cathode, the cluster yield shows two distinct components. For $n < 10$ the clusters having an even number of carbon atoms are produced more abundantly compared to the neighbors containing an odd number of carbon atoms. This trend gets reversed for $n > 10$ where the yields of clusters consisting of an odd number of carbon atoms are comparatively larger than the one having an even number of carbon atoms.

Besides the elemental clusters, several composite clusters containing hydrogen, oxygen, copper, etc. were also detected in the beam but are not shown in Figs. 1–4.

We start with a discussion of the carbon cluster yield measurements. There have been several measurements of cluster size distribution studies for carbon clusters [9–11] using both heavy-ion sputtering and other tech-

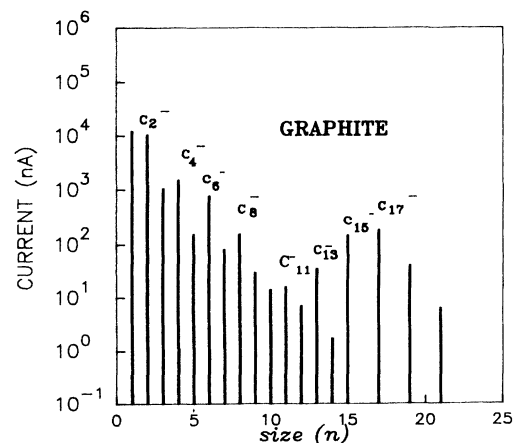


FIG. 1. Measured cluster yields as a function of the size for graphite substrate.

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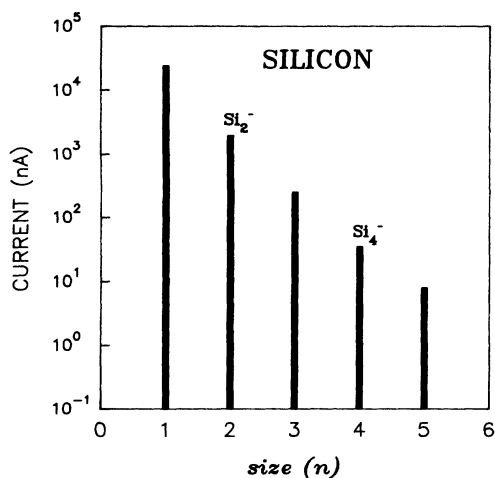


FIG. 2. Same as Fig. 1 for silicon substrate.

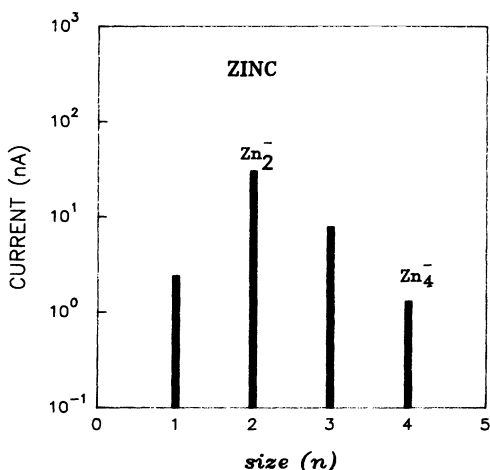


FIG. 3. Same as Fig. 1 for zinc substrate.

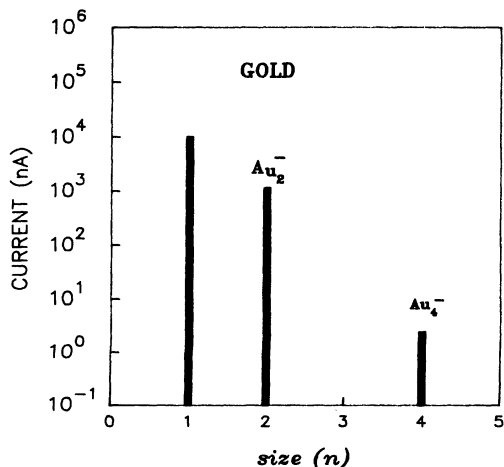


FIG. 4. Same as Fig. 1 for gold substrate.

niques such as laser ablation, etc. Based on careful mass analysis, Middleton [12] has pointed out that in studies based on a SNICS source, the peak at C_{11}^- is essentially due to Cs^- and subsequent peaks are basically due to CsC_2^- , CsC_4^- , CsC_6^- , CsC_8^- etc. Due to a limitation of our mass resolution we are unable to differentiate between C_{11}^- and Cs^- and also the other higher carbon clusters since the corresponding difference in mass due to the possibility of carbon getting attached to Cs is just one. We have, however, found that the C_{11}^- beam contains substantial quantities of Cs^- as follows.

We accelerated C_{11}^- and allowed it to pass through the stripper gas in the high voltage section. After stripping, momentum analysis was performed using a 90° analyzing magnet. It was found that an appreciable amount of Cs^+ is present, which leads us to the conclusion that it is indeed getting injected along with C_{11}^- . But this does not rule out the possible presence of C_{11}^- in the beam. Hintenberger *et al.* [13] have seen a change of periodicity around $n=10$ by generating carbon clusters with a graphite spark source with no cesium. The change in periodicity has been interpreted [11,14,15] to indicate the change in the structure of the cluster from linear to a monocyclic ring structure around $n=10$. More careful experiments with a better mass resolution will be required to eliminate composite structures containing Cs^- from pure carbon clusters in the mass region exceeding 132 amu. However, there seems to be adequate experimental data to indicate the presence of carbon clusters with $n > 10$ also. If indeed the cluster yields beyond $n=10$ correspond to a different structure and follow a different systematics as compared to the clusters with $n < 10$, it would be interesting to see whether these clusters originate as substructures in the cathode material and are knocked out as a result of collision process or are formed due to nucleation of the monomers after the sputtering process. To verify this conjecture, we have also measured the size distribution of the clusters using soot (prepared by burning kerosene) and fullerite (C_{60}) as cathode substrates. Graphite and fullerite are crystalline in nature whereas soot is an amorphous material. Graphite has a planar structure and the lattice planes perpendicular to the c axis have the honeycomb arrangement. Fullerite has a fullerene structure consisting of 60 carbon atoms, whereas soot has no substructures.

The size distribution curve for soot and fullerite are shown in Figs. 5 and 6. As in the case of graphite substrate, the cluster yields fall exponentially for $n < 10$. However, the second component beyond $n=10$ is missing in the case of soot and much less pronounced in the case of fullerite. This distinct difference in the cluster size distribution for the three cathode materials, viz., soot, fullerite, and graphite, may be due to the difference in the structure of the cathode material.

With fullerite as the cathode material, 20 nA of C_{60}^- is also observed which is not seen for other substrate materials. The mode of formation of a fullerene C_{60}^- cluster may be due to a direct momentum transfer from projectile Cs ion resulting in direct knock on the fullerene. The presence of a C_{60} cluster as the sole representative in the neighboring cluster size domain asserts the ultra-

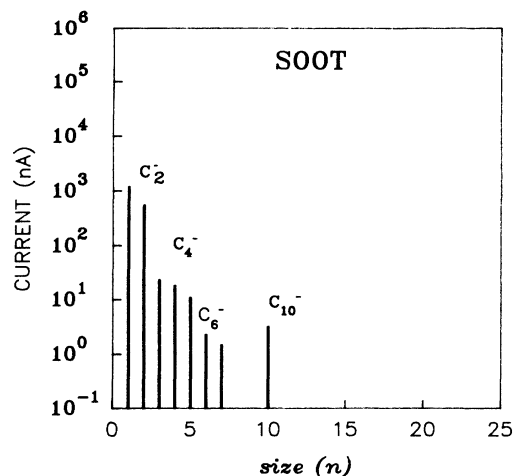


FIG. 5. Same as Fig. 1 for soot substrate.

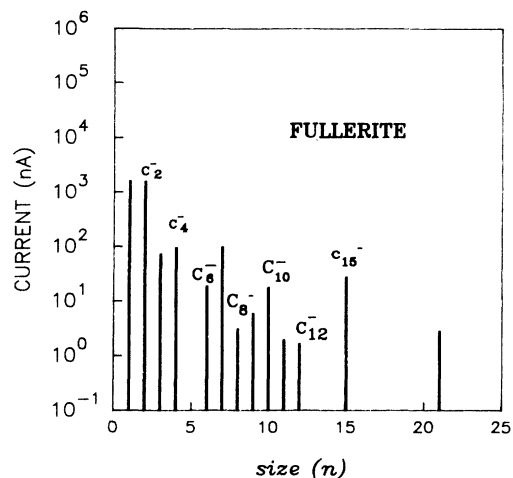


FIG. 6. Same as Fig. 1 for fullerite substrate.

stable nature of the fullerenes. The presence of clusters of size > 10 in the case of graphite may be due to a shock induced flaking of graphite, where ring structures are ejected. This points to the conclusion that the structural difference of the substrate might result in differences in the size distribution of clusters of a particular element. Thus one could envisage a direct knock on the atoms, shock induced flaking of the substructures if they are present in the cathode material, and nucleations of the monomer after sputtering.

We now discuss the possible mechanism of cluster formation in the different materials with an exponentially falling cluster size distribution for $n < 10$. Experiments and models based on binary collisions predict more than one sputter ion per incident ion. These are essentially produced by primary and secondary knock-on processes. There is in general a very low probability for cluster production by direct knock-on processes. However, since the ions originate at close proximity around the primary ion track and have low velocities, there is a finite probability of more than one ion coming within the range of nucleation and with low relative velocities. These can arrange themselves as a cluster. Molecular-dynamics simulation indicates such a mechanism for cluster production. With low ion densities and small confinement times, only small cluster sizes and an exponentially falling yield distribution can be expected. The present measurements indeed

exhibit such a trend and can be described in the form $y \sim e^{-bn}$, where n is the cluster size and b reflects the nucleation conditions such as density, temperature, and confinement time of the plasma of sputtered monomers. The value of the parameter b fitted from the cluster yield data and the TRIM (transport of ion in matter) [16] calculation results for all the substrates mentioned above are given in Table I. The Monte Carlo computer program, a sputtering version of TRIM, was used to determine sputtering yields and the energy of sputtered particles in physical (collisional) sputtering processes. Basically the incident ions and the recoil atoms are followed throughout their slowing-down process until their energy falls below a predetermined energy; usually 5 eV is used for the incident ion, and the surface binding energy is used for the knock-on atoms. The energy value of the incident Cs ion is also given. The value of b is minimum for fullerite and maximum for gold substrate. In the case of carbon clusters obtained from fullerite and graphite the value of the slope, i.e., b , is comparable but is drastically different when the substrate material is soot. The physical implication of these differences in b for various substrate materials is not known.

We therefore conclude that there is a strong need to carry out further investigations in order to understand the various subtle physical phenomena leading to the formation of the clusters by heavy ion sputtering. While

TABLE I. Table of cathode characteristics. The parameter b is fitted to cluster yield data.

Substrate	Energy of Cs ⁺ (keV)	Density of the substrate (gm/cm ³)	b	TRIM output	
				No. of ejected atoms per ion	Energy (eV/atom)
Graphite	4.1	3.516	0.67	0.055	0.9
Soot	5.4	2.266	1.13	0.08	1.7
Fullerite	4.0	1.7	0.59	0.058	1.3
Silicon	4.2	2.321	2.01	0.18	3.9
Zinc	3.8	7.105	1.57	12.23	58.2
Gold	4.1	19.31	2.81	8.56	371.1

there is direct evidence for direct knock on, flaking and nucleation mechanisms for cluster formation in the above studies, theoretical models to describe the above processes are yet to be developed.

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