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Size Distribution of Atomic Clusters Formed by Energetic Heavy Ion Sputtering

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A cesium sputter ion source (SNICS) 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 has also been studied for carbon.

79.20. -m, 79.20.Rf, 36.40.+d

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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 a 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 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, appreciable amount of atomic aggregates of various sizes generally referred 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 analyse 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 analysed, the limiting mass value in our case is $\sim$ 1400 amu. The yield of specific species is measured with the help of a Faraday cup which monitors the current of a particular

9/22/97

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 investigations 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 fig. 1-4. The following points are evident from the figures.

1. Clusters of various sizes ranging from dimers to ones containing several atoms are produced.

2. The cluster yields follow an exponential decay trend as a function of cluster size.

3. For carbon clusters obtained with a graphite cathode, the cluster yield shows two distinct components.For n<10 the clusters having even number of carbon atoms are produced more abundantly compared to the neighbours containing odd number of carbon atoms. This trend gets reversed for n>10 where the yields of clusters consisting of odd number of carbon atoms are comparitively larger than the one having 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 the figure 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 techniques like laser ablation etc. Based on careful mass analysis, Middleton [12] has pointed out that in studies based on 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 limitation of

our mass resolution we are unable to differentiate between C_{11}^- and Cs^-, and also the other higher carbon clusters as the corresponding difference in mass due to possibility of carbon getting attached to the 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 90° analysing magnet . It was found that appreciable amount of Cs^+ is present and leading 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 have been interpreted [11,14,15] to indicate the change in the structure of the cluster from linear to monocyclic ring structure around n=10 . 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. The size distribution curve for soot and fullerite are shown in figures 5 & 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 difference in their basic structure. Graphite and fullerite are crystalline in nature whereas soot is an amorphous material . 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. For a more quantitative comparison, a detailed mass and structural analysis of the clusters with $n > 10$ is required.

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 fullerene C_{60}^{-} cluster may be due to direct momentum transfer from projectile Cs ion resulting in direct knock on of the buckyball. The presence of C_{60} cluster as the sole representative in the neighbouring cluster size domain asserts the ultra stable nature of the fullerenes. The presence of clusters of size > 10 in the case of graphite may be due to shock induced flaking of graphite, where ring structures are ejected.

We now discuss the possible mechanism of cluster formation in the different materials with an exponentially falling cluster size distribution for $n < 10$. Both 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, b reflects the nucleation conditions such as density , temperature and confinement time of the plasma of sputtered monomers. The value of the parameter b and the TRIM calculation results for all the substrates mentioned above are given in table 1. The energy value of incident Cs ion is also given. The value of b is minimum for fullerite and maximum for gold substrate. In case of carbon clusters obtained from fullerite and graphite the value of 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.

Table 1.

Substrate	Energy of Cs^+ (KeV)	Density of the substrate gm/cm^3	b	No.of ejected atoms/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

* TRIM OUTPUT

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 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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FIGURES

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

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

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

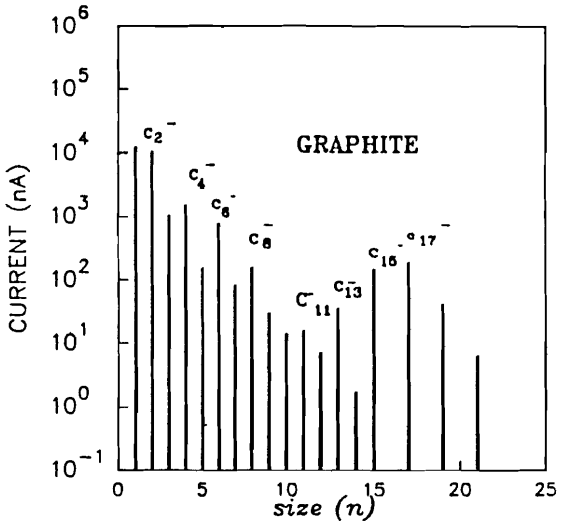
FIG. 4. Same as Fig. 1 for Gold substrate

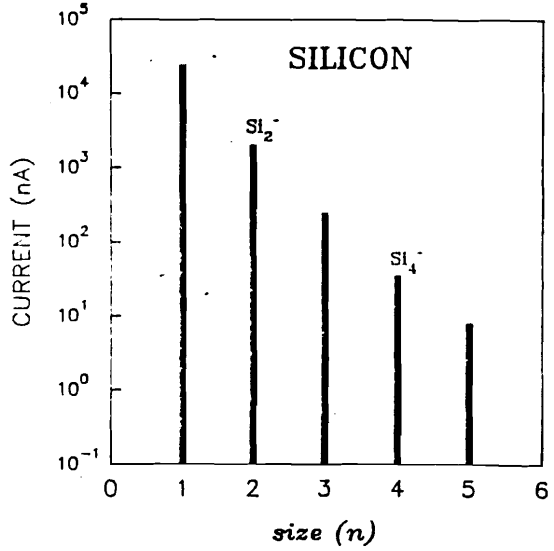
FIG. 5. Same as Fig. 1 for Soot substrate

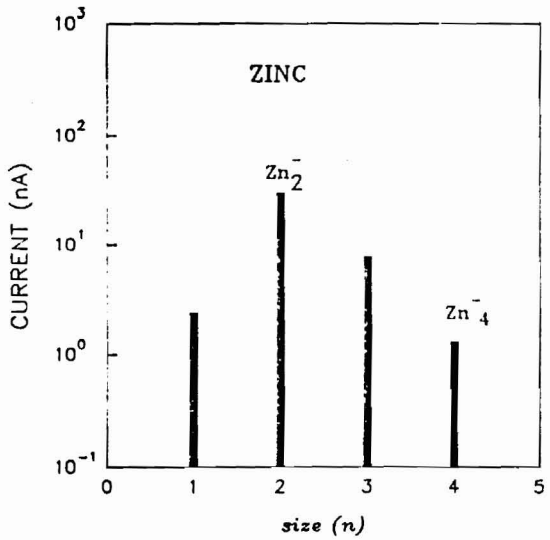
FIG. 6. Same as Fig. 1 for Fullerite substrate

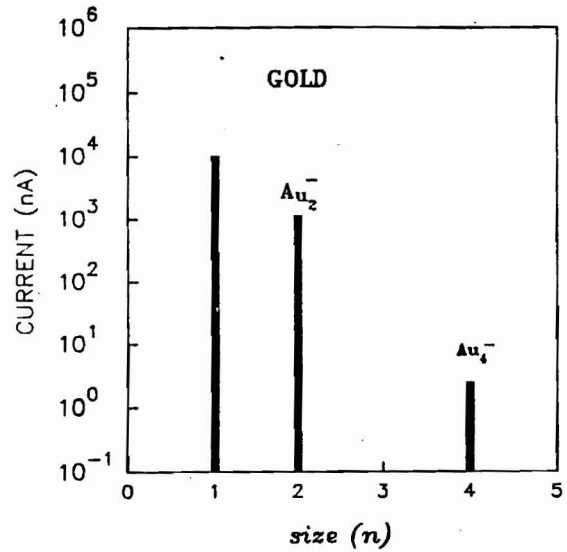
TABLES

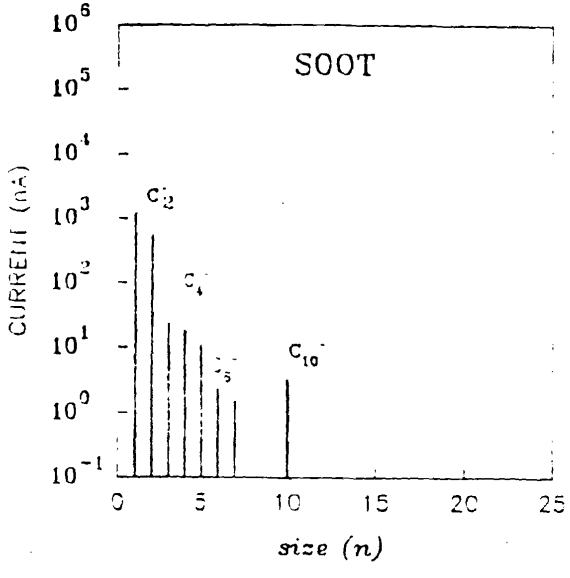
TABLE I. Table of Cathode characteristics

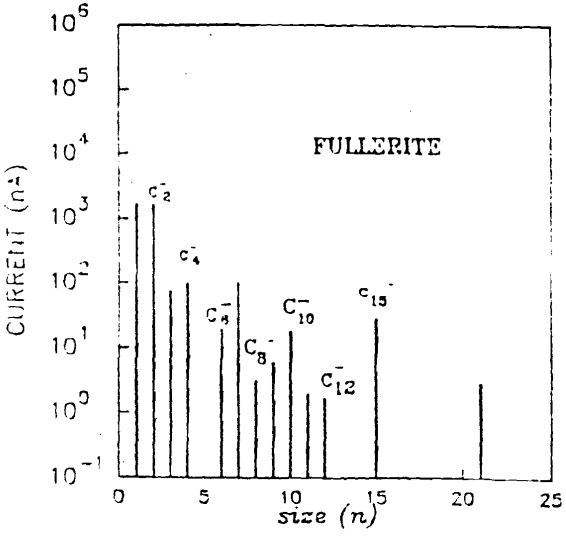

GRAPHITE
CURRENT (nA)
size (n)
C_2^-
C_4^-
C_6^-
C_8^-
C_{11}^-
C_{13}^-
C_{15}^-
C_{17}^-


SILICON
CURRENT (nA)
size (n)
Si_2^-
Si_4^-


ZINC
Zn_2^-
Zn_4^-
CURRENT (nA)
10^3
10^2
10^1
10^0
10^{-1}
0
1
2
3
4
5
size (n)


GOLD
Au_2^-
Au_4^-
CURRENT (nA)
10^6
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
0
1
2
3
4
5
size (n)


SOOT
CURRENT (nA)
size (n)
C_2^-
C_4^-
C_5^-
C_{10}^-


FULLERITE
CURRENT (nA)
size (n)
C_2^-
C_4^-
C_6^-
C_8^-
C_{10}^-
C_{12}^-
C_{15}^-