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Formation of nitrogen-substituted carbon cluster anions by gas-feed Cs-sputtering from different forms of carbon

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Abstract. We have investigated the mechanism of formation of C_n^- and C_nN^- cluster anions during Cs^+-ion sputtering from surfaces of different crystallographic forms of carbon (polycrystalline graphite, amorphous C and C_{60}), in the presence of high purity N_2 or NO_2 gas. The normalised yields of sputter-ejected C_nN^- ($n \leq 10$) cluster anions display an oscillatory dependence on n: the odd n clusters being more abundant than the even n ones. Significantly, C_nN^- clusters produced from the three different forms of C, show similar oscillatory variations with n. Moreover, the C_nN^- yields follow a single power law decline as a function of cluster size for all three surfaces sputtered, and over a wide range of operating conditions. This strongly indicates that the intrinsic structure of the ion-induced surface does not play a significant role in the formation of sputtered cluster anions. The observed abundance patterns of C_n^- and C_nN^- clusters also suggest that mono-nitrogen substitution of the carbon clusters does not allow the chain to ring transformation to occur up to $n = 10$.

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1 Introduction

The formation and characterisation of atomic clusters are of great interest [1–6] to both experimentalists and theorists. This is due to the interdisciplinary nature of the field, and its possible application in developing novel materials. Techniques for producing clusters of many chemical elements and compounds are now available. Mass spectrometric techniques have been used to study the gas-phase distributions of neutral and charged clusters produced using high temperature ovens [7], laser vaporization [8,9], ion bombardment [10,11], and laser vaporization coupled with molecular beam expansion [12,13].

The irradiation of a solid surface with energetic particles results in the ejection (sputtering) of a variety of neutral or ionised molecules and clusters [14,15]. Experimental studies of cluster emission by sputtering originally focused on the mass distribution of ionised clusters [14,16–18]. Neutral clusters became accessible more recently using post-ionisation techniques [19] such as laser photo-ionisation [20–22], particularly for larger clusters. A disadvantage of sputtering is that the resulting species are often internally excited and show a strong tendency to fragment [15,23].

Several attempts have been made to understand the formation of sputtered clusters. The collision cascade model successfully describes the emission of mono-atomic secondary ions in the interaction of singly charged keV ions with surfaces [24]. Collision cascades initiated by ion irradiation result in the ejection of surface and near-surface atoms. The yield of the sputtered species increases with the nuclear stopping power of the ions impinging on a target. However, the linear cascade theory cannot explain the yield of singly charged ion-induced clusters [25,26]. The statistical cluster formation model [27] assumes that clusters form at the surface after the constituent atoms have received kinetic energy in independent, random collisions from the same collision cascade. Clusters can form if the internal energy within the center-of mass system of an ensemble of n sputtered atoms is less than the bond strength of the n-atom cluster. This combinatorial model predicts an exponential decay of the yield with increasing cluster size [25]. The models that predict a power-law cluster intensity distribution are either of a thermodynamical nature [28] or treat cluster emission as a shock wave initiated process [29]. Both descriptions result in a power law exponent of $\delta \approx 2$, which is not expected to vary with

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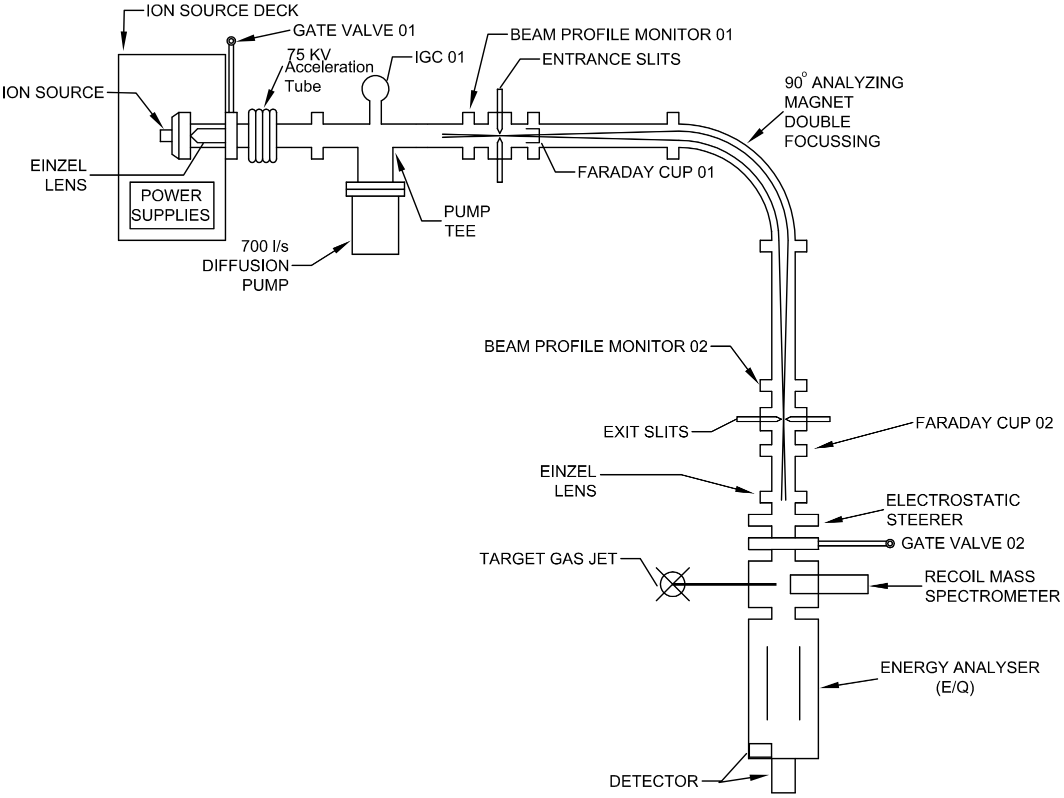

Fig. 1. Schematic layout of the ion source test bench set-up used for the production of carbon cluster anions.

changes in the sputtering conditions. At present, the most satisfactory method for reproducing the observed yields, internal energies and life times of clusters is molecular dynamics (MD) computer simulations [30–34].

Though small carbon clusters have been studied rather extensively [35–38], an understanding of all their properties is far from complete. For example, the isomers with linear chain and planar ring configurations appear to coexist under normal experimental conditions [36,39]. A simple method of studying the isomeric structure of the sputter-ejected nascent clusters is to add a hetero-atom to it very soon after it is born at the impacted surface. However, adding a N atom may perturb the intrinsic structure due to the strong bonding between N and C, and one of our objectives is to study the effect of adding a N atom to the intrinsic structure of nascent C clusters ejected from different types of surfaces. Carbon cluster ions are also ideal for exploring the relation between structure and chemistry of clusters. Multiple isomers are especially probable in systems where the activation barriers to isomerisation are high. Carbon with its strong, directional bonding is one such candidate.

Here, we describe the production of mono nitrogen-terminated carbon cluster anions from different crystallographic forms of carbon using the well-established gas-feed cesium sputter technique, described later. This is the first attempt at using this technique for the production of gas spray induced mixed cluster anions such as C_nN^-, though such cluster anions have earlier been investigated using surface ionisation of organic compounds [40] and laser ablation [41]. The yield of C_nN^- clusters as a function of cluster size will be discussed in the context of known models and MD computer simulations. We also show that a study of the nitrogenation of carbon clusters reveals certain important aspects about their nature and formation.

2 Experimental

2.1 Description of the set-up

The experiments were conducted using an extended ion source test bench [42], depicted schematically in Figure 1. The set-up consists of a GF-SNICS source (Gas feed Source of Negative Ions by Cs Sputtering) developed in our laboratory following Middleton [43,44], an electrostatic cylindrical Einzel lens, a 75 kV general purpose accelerating tube, and a double focusing 90° analyzing magnet with a mass-energy product of about 10 amu MeV. The GF-SNICS source is shown schematically in Figure 2a. The set-up includes beam diagnostic elements such as beam profile monitors, horizontally adjustable slits and movable Faraday cups. The ion source, the Einzel lens and their power supplies were kept at a negative dc potential of 20 kV. The anion species from the source were accelerated to ground potential from the negatively biased deck and thus gain an energy of 20 keV. The slits were adjusted so that neighbouring masses up to 300 amu could be well resolved. The anion yields were measured in a Faraday

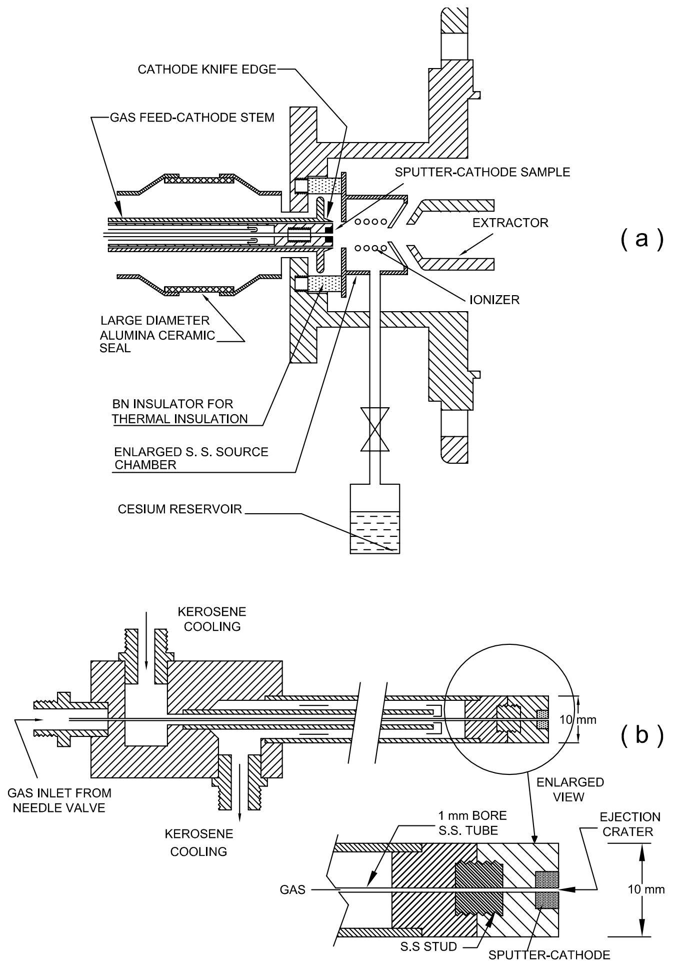

Fig. 2. (a) Schematic drawing of the gas feed-source of negative ions by cesium sputtering (GF-SNICS), used in our experiments. (b) A sectional drawing of the close loop-kerosene cooled-gas feed cathode stem. The inset shows an enlarged view of the typical sputter-cathode sample geometry employed in the gas spraying experiments.

cup (FC-02) located near the image slits of the analyzing magnet with the help of a Keithley 485 picoammeter. The rest of the set-up was not used during the present measurements.

The sputter cathode sample and the sample mounting arrangement of the SNICS were modified to accommodate the gas spray system (Fig. 2b). The gas to be sprayed was introduced into the source through a 1-mm bore stainless steel (SS) tube passing through the center of a 10-mm diameter SS tube used for closed-loop kerosene cooling and mounting of the cathode sample. A 1-mm diameter hole was drilled through the center of the SS stud and the sample (see inset in Fig. 2b). The flow of gas into the source was controlled by a needle valve. The sample holder was made of oxide free high conductivity (OFHC) copper. The sputter sample was a cylindrical solid rod or pressed pellet of 4-mm diameter and 4-mm length. It was push fitted into the copper holder so as to maintain good thermal contact and ensure sufficient cooling, and hence adequate Cs-coverage of the sample.

2.2 Gas feed cesium sputter technique

Cs^+-sputtering offers an efficient and convenient technique for producing a variety of atomic, molecular and cluster anions directly from solid surfaces. The presence of less than a monolayer of an alkali metal, such as Cs on the sputtered surface dramatically improves the formation probability of anions. Since, its discovery by Krohn [45], this phenomenon has been utilized extensively in the development of negative ion sources. An established method for generating molecular anions, employed in most of the Tandem Accelerator facilities, is to spray an appropriate gas onto the cathode during sputtering. Middleton showed that gases can be sprayed in high intensity Cs sputter source not only to widen the range of anion species, but in certain cases, to enhance the yield of anion beams available from intrinsic solid surfaces. He measured the C^- yield by spraying CO_2 gas on a variety of gas feed-sputter cathodes under similar ion source operating conditions. That the largest C^- yield was obtained with Ti, a particularly good getter material, and the lowest from the least chemically active Au, strongly suggest a surface origin of negative ion ejection [44].

3 Results

3.1 Formation mechanism of C_nN^- clusters

That the gas spray induced negative ions originate at the sputtered surface is also suggested by the following observations with the gas feed Cs sputter source. (1) During NO_2 gas spray Cs-sputtering, the formation of NO_2^- molecular anions is observed from the three crystallographic forms of carbon. It is unlikely that NO_2^- anions would form in abundance *above* the surface. (2) The yield of sputter-ejected C_nN^- anions increases several times when the sprayed gas is changed from N_2 to NO_2, keeping all other ion source parameters fixed. This may be ascribed to the relatively higher gettering efficiency of NO_2 on the ion-induced surfaces, and indicates a surface origin. (3) N_2 gas spray on polycrystalline carbon (graphite) shows a non-linear growth of C_nN^- species as a function of gas pressure, while a linear growth is expected for gas phase reactions under single-collision conditions. This indicates that nitrogen-attachment to sputtered carbon clusters occurs predominantly at the surface, rather than above the surface in the gas phase.

Figure 3 shows the typical growth of some of the mono-nitrogen-substituted carbon cluster species (C_nN^-) as a function of N_2 pressure. The N_2 gas was introduced through the graphite sample ejection-crater by a needle valve and the corresponding C_nN^- yield was measured in the pressure range of 1.0×10^{-7} torr to 2.0×10^{-5} torr using an ion gauge controller near the ion source. The C_nN^- yield initially rises almost linearly with N_2 pressure for all n, then saturates before showing a steep fall at higher pressure due to detachment and dissociation losses of sputter-ejected anions inside the ion source under bad vacuum conditions. To minimize the loss of sputter-ejected

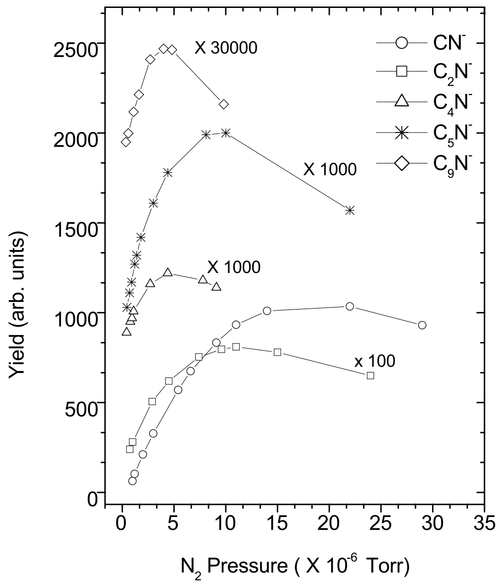

Fig. 3. Typical growth of C_nN^- cluster anions sputter-generated by 5 keV Cs^+ ion bombardment of high purity polycrystalline carbon as a function of the nitrogen gas pressure. The growth curves for certain (representative) species only are presented.

anions inside the gas feed-ion source, we collected the data at an operating pressure of 1.0×10^{-6} torr N_2, but the corresponding nitrogenated anion yields were only slightly above the background, particularly at higher n.

Since NO_2 gas spray produced considerably higher yield of C_nN^- under similar operating parameters, the data were recorded at a reduced pressure of NO_2 (7×10^{-7} torr). Replacing N_2 by NO_2 not only helps in significantly improving the signal to noise ratio for the nitrogenated cluster anions, but also reduces the destruction losses by achieving higher yields at lower NO_2 gas pressures. Sputtering was done with 5 keV Cs^+ ions impinging at 70° to the surface normal. The typical intensities of the C_nN^- clusters from graphite was in the range of 0.1–70 nA (while it was ~1.5 μA for CN^-) under the usual operating parameters of GF-SNICS source, but can be increased at higher values of the running parameters.

At a low concentration of sprayed gas, pure carbon cluster formation is expected to precede nitrogenation of sputtered clusters, since the sprayed gas does not alter the original abundance distribution of the intrinsic C_n^- clusters. A part of the N-substituted carbon clusters emerge as anions as they decouple from the Cs-covered surface undergoing sputtering. We propose that the C_nN^- is formed by the reaction between neutral C_n emerging from the surface and N (formed by dissociative adsorption of NO_2 preferentially at defect sites produced by Cs^+ bombardment) residing on the surface, which has a relatively low work function due to partial Cs coverage. The reaction is of the form:

$$C_n + (N + \text{surface}) \rightarrow C_nN^- + \text{surface}. \quad (1)$$

The surface acts as the third body that takes care of the conservation of momentum and energy in the reaction.

3.2 Sputtering of polycrystalline graphite

The abundance distribution of the normalised intrinsic (no gas spray) carbon cluster anions C_n^- ($n \le 10$) generated by 5 keV Cs^+ ion bombardment of high purity polycrystalline graphite is shown in Figure 4a. The cathode current, which is an approximate measure of the Cs ion current at the bombarded surface, was maintained at 1.0 (±0.1) mA, by controlling the Cs reservoir temperature. The graphite rod sample was sputter-cleaned inside the ion source for about 30 min before recording the data. The base vacuum was 8.0×10^{-8} torr. Though the C_n^- yield shows an overall decline with increasing cluster size (n), the yield exhibits odd-even oscillations, well known from singly charged ion-induced sputtering [46]. The relative stability of odd or even numbered clusters reflects variations in the electron affinity of the clusters, which is in turn sensitive to these different cluster geometries. UV photoelectron spectroscopy and other studies [46–48] show that carbon clusters with $n < 10$ have linear chain-like structures, while the larger ones form monocyclic rings.

Figure 5a shows the normalised and background-subtracted yield distribution of the C_nN^- clusters Cs^+-sputtered from the same sample, but in the presence of NO_2 gas at 7.0×10^{-7} torr. The yield of nitrogenated-carbon cluster anions also declines with the cluster number n. Both odd as well as even n members are observed. This is in contrast to the C_nN^- clusters generated from laser ablation of nitrogen bearing compounds, in which only odd n members are observed and the even n counterparts are largely undetectable [41]. This may be explained by the fact that the laser ablated C_nN^- clusters have to endure a relatively long waiting period while the plume expands and undergoes fairly complex chemical reactions, which may result in a poor survival probability for the relatively fragile even n clusters in the highly collisional plasma plume.

The normalised yield of C_nN^- clusters exhibits an oscillatory pattern with the odd n species being relatively more abundant. Such an oscillation can be qualitatively ascribed to the oscillatory values of the vertical electron detachment energy (VEDE) of C_nN^- clusters anions. *Ab initio* calculations performed on the ground state geometries of the C_nN^- [41] predict not only that the VEDE of the odd-n species are much larger than those with even n, but also that the odd-n cluster anions are relatively more stable. The strong correlation between C_nN^- yield and the computed electron affinity clearly indicates that the abundance distribution of stable C_nN^- is largely determined by their electron affinity. This is probably due to the fact that the ionisation probability of sputtered negative ions scales exponentially with the electron affinity [49], moreover in present case C_nN^- clusters with odd n are also relatively more stable [50].

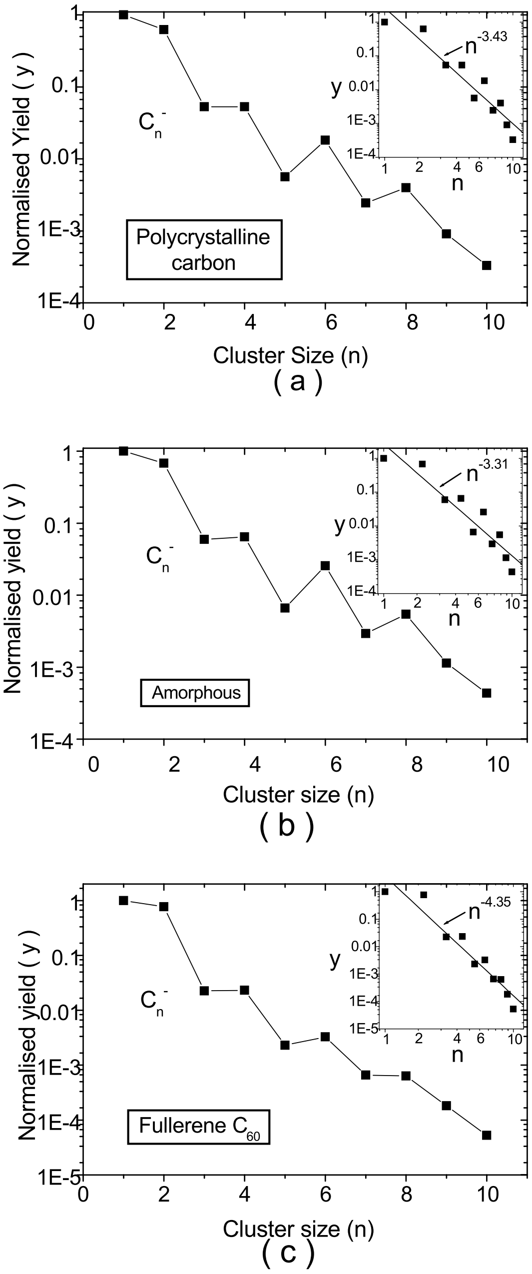

Fig. 4. Normalised yields of the cluster anions C_n^- *vs.* the cluster size n ($n \leq 10$). The cluster anions were sputter-generated by 5 keV Cs^+ ion bombardment from the surfaces of (a) polycrystalline carbon, (b) amorphous carbon, and (c) fullerene. Insets show log-log plots of the C_n^- yield *vs.* n for the corresponding target material.

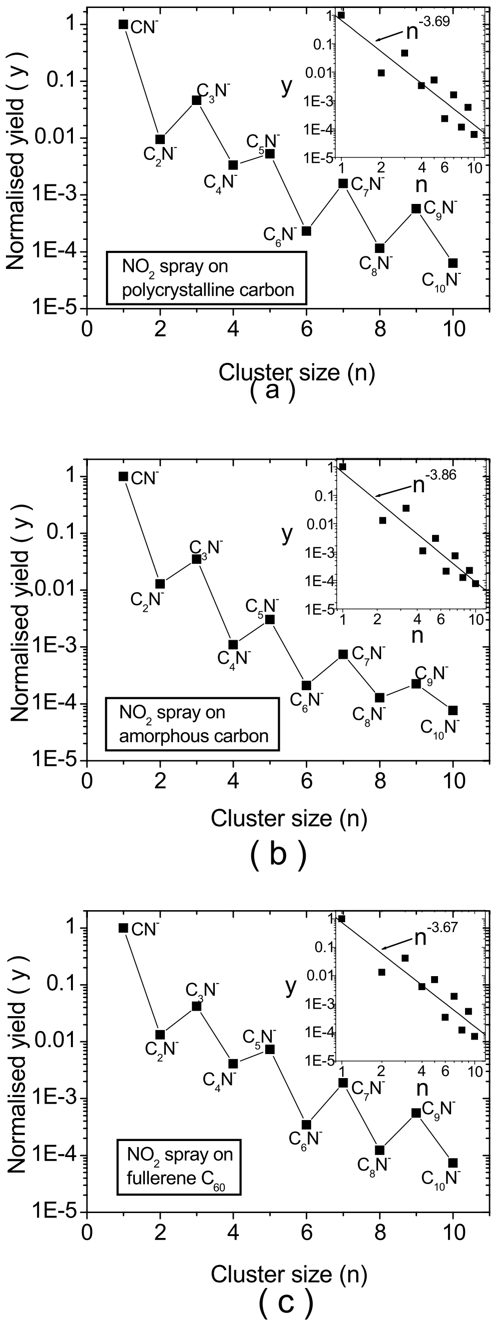

Fig. 5. Normalised and background subtracted yields of the cluster anions C_nN^- *vs.* the cluster size n ($n \leq 10$). The cluster anions were sputter-generated by 5 keV Cs^+ ion bombardment in the presence of NO_2 gas from the surfaces of (a) polycrystalline carbon, (b) amorphous carbon, and (c) fullerene. Insets show log-log plots of the C_nN^- yield *vs.* n for the corresponding target material.

3.3 Sputtering of amorphous carbon

Figure 4b shows the normalised abundance distribution of the intrinsic carbon cluster anions (C_n^-) sputtered from a high purity amorphous carbon rod. The predominantly amorphous nature of the sample was confirmed by X-ray diffraction. The cathode current was maintained at 1.2 (±0.1) mA. The sample was sputter-cleaned *in situ* for 30 min. The size dependence of the yield is quite similar to that for crystalline graphite, with an odd-even pattern being superimposed on a general decline in the yield with increasing n.

Figure 5b shows the yield distribution of C_nN^- sputtered from the same amorphous C sample, in the presence of NO_2 gas introduced through the sputter-crater. The NO_2 gas pressure was again maintained at 7.0×10^{-7} torr. The cluster-size dependence of the yield of the nitrogenated carbon cluster anions from amorphous C is qualitatively quite similar to that for crystalline graphite.

3.4 Sputtering of fullerene (C_{60})

One of the several unusual and interesting properties of the carbon allotrope C_{60} is that it has a rather high formation energy, which prevents retrograde reactions. Once a C_{60} molecule is destroyed it does not exhibit any defect annealing that often occurs in metals, semiconductors and even polymers. The irreversibility of fullerene destruction, coupled with the fact that a comparatively small change in the overall charge distribution is sufficient to destroy the C_{60} molecule, lead to several interesting phenomena [51].

The sample was prepared by pressing the C_{60} powder (Mer Corporation, 99.9%) into a pellet (at ∼100 bar) in the copper holder. No *in situ* cleaning of the fullerene sample was performed since sputtering may damage the C_{60} cages, and the fullerene surfaces are in any case fairly inert in air due to their hydrophobicity [52]. The cathode current was 1.0 (±0.1) mA. Figure 4c shows the abundance distribution of the intrinsic carbon cluster anion C_n^- produced by Cs^+-bombardment of the fullerene pellet. Under the similar operating conditions, the size-dependence of the yield is qualitatively similar to the behavior exhibited by crystalline graphite and amorphous carbon. The nitrogenated C_nN^- clusters were again produced by sputtering the fullerene surface in the presence of NO_2 at a pressure of 7.0×10^{-7} torr. The C_nN^- clusters from fullerene show the same decline in yield with n, coupled with the odd-even oscillation (Fig. 5c) arising from the oscillatory nature of the VEDE of the C_nN^- cluster anions.

4 Discussion

4.1 Oscillations in the cluster yield

Secondary-ion emission is a complex phenomenon involving strong electronic perturbations of the outgoing atom and the surrounding solid. A complete understanding of the negative ion formation mechanism is lacking, though there has been some progress [53–56]. Ion emission phenomena from metal, alloy and compound surfaces have been reviewed by Blaise and Nourtier [57], Williams [58] and Wittmaack [11]. The physics of cluster ions is controlled by the interplay of stability effects and the cluster-size dependence of ionisation probability and electron affinity. Microscopic models that describe the formation probability (P^-) of secondary negative ions usually lead to an expression of the type:

$$P^- \propto \exp[-(\Phi - E_{\mathrm{A}})/\varepsilon_0] \tag{2}$$

where Φ is the work function of the surface, E_{A} is the electron affinity of the sputtered species, and ε_0 is a model-dependent parameter. In the excitation model, $\varepsilon_0 = kT_{\mathrm{e}}$ where T_{e} is the electron temperature due to a collective excitation of surface conduction electrons [59]. According to the electron-tunneling model, ε_0 depends on $v_\perp$, the component of the velocity of the sputtered particle along the surface normal. While the velocity dependence of the secondary ion yield is exponential at high velocities ($v_\perp \geq 10^6$ cm s^{-1}), it is nearly independent of $v_\perp$ at lower velocities [49,60]. Since the average velocity of sputtered atoms is generally lower than 10^6 cm s^{-1} and that of sputtered clusters is even lower, we assume ε_0 to be constant. Then we can use equation (2) to explain the relative ionisation probabilities in terms of only the work function and the electron affinity. Thus, the secondary negative ions with higher electron affinity must get ejected with higher probability. This is in qualitative agreement with the observed yields from the surfaces of the different forms of C, under a wide range of operating conditions.

4.2 Power-law decline of the cluster yield

The insets in Figures 4a–4c show the relative yield distributions of C_n^- cluster anions sputtered from crystalline graphite, amorphous C (am-C) and C_{60} surfaces respectively, by 5 keV Cs^+ ions. Insets in Figures 5a–5c show the yields of C_nN^- cluster anions sputtered from the same three surfaces in the presence of NO_2 gas under otherwise similar conditions. The cluster size dependence of the relative yields measured far from the sample surface can be approximated by a power law:

$$Y(n) \propto n^{-\delta}. \tag{3}$$

The least-square-fit values of the exponent δ are indicated in the insets in Figures 4 and 5. The values of δ for C_n^- cluster anions sputter-ejected from graphite and am-C are similar (Fig. 4). The values of δ for C_nN^- cluster anions obtained from graphite and am-C are also close to each other (Fig. 5). To explain this close similarity in $Y(n)$ and δ for graphite and am-C surfaces, we need to consider the ion-bombardment-induced structural evolution of the surface and sub-surface atomic layers during the formation of sputtered clusters.

We now point out two important aspects in which the fullerene-sputtered clusters differ from those of graphite and am-C and attempt to explain these in terms of densification effects as well as differences in the interaction of NO_2 with the different crystallographic surfaces. Firstly, the value of δ for the pure C_n^- clusters sputtered from the C_{60} surface is significantly lower than graphite and am-C (Fig. 4), while the δ for C_nN^- clusters sputtered from the C_{60} surface is quite similar to those from the polycrystalline and amorphous counterparts (Fig. 5), under similar operating conditions. Ion irradiation of C_{60} is reported to lead to a highly densified material, with a density up to 2.1 g cm^{-3} [61]. Under Cs^+ irradiation, the sputtered surface may undergo structural changes associated with densification. This may result in a higher probability of dissociative-adsorption of NO_2 at the sputtered surface and lead to a greater yield of sputtered C_nN^- cluster anions than from graphite and am-C. This is in complete

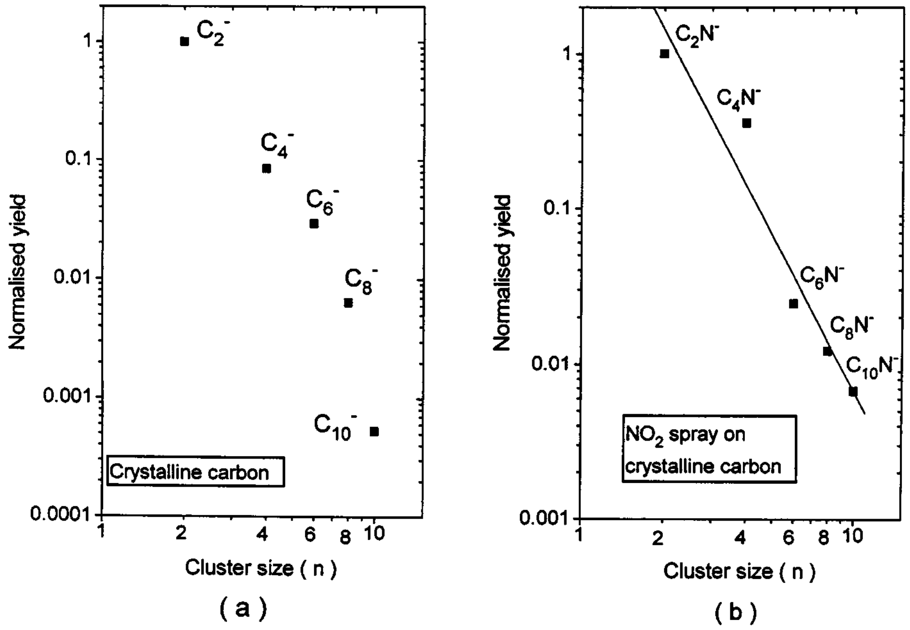

Fig. 6. Normalised yields of (a) C_n^- and (b) C_nN^- *vs.* the cluster size n (even n only). Both the plots are from the crystalline carbon sample data.

agreement with our observation that C_{60}-sputtered clusters have a considerably higher (several orders of magnitude) C_nN^-/C_n^- ratio as compared to graphite and am-C surfaces. Since, the enhancement in the cluster anion yield increases with n, the power law exponent (δ) turns out to be quite close to those for graphite and am-C.

Secondly, we also observe an unexpected increase in the yield of pure C_n^- cluster anions from C_{60} when NO_2 is sprayed, while no such enhancement is noticed with graphite and am-C. This may be ascribed to the chemisorption of NO_2 on the sputtered fullerene surface, leading either to a decrease in the work function (see Eq. (2)), or to a destruction of the C_{60} molecules. The destruction of the sputtered C_{60} may proceed *via* a chemical reaction that results in cleavage of double bonds and formation of carbonyl groups with subsequent opening of the fullerene cages [62]. The energy thereby released could also enhance the ejection of all anions including C_n^-.

We emphasize that in spite of the two above observations relating to fullerene sputtering, most features of the clusters emanating from the three different polymorphs of carbon are similar. Most importantly, the yield distribution of the C_nN^- clusters shows a similar oscillatory behavior and follows a *single* power law decline. This indicates that the cluster formation does not depend significantly on the crystalline structure of the surface. MD simulations of cluster formation in sputtering [31,32,34] show that larger clusters are formed predominantly during the late stage of a collision cascade. The nascent clusters are ejected from the surface due to correlated atomic collisions from beneath the energized surface. As a result, the pristine structure of the surface is largely destroyed by the time that the sputtered clusters are born.

Interestingly, the exponent δ, for intrinsic carbon cluster anions (C_n^-) sputtered from graphite or am-C surfaces increases with the total anion yield from the ion source. The total anion yield from the ion source can be increased by introducing higher amounts of Cs inside the source, while keeping the Cs ion bombardment energy constant at 5 keV. This type of ion flux dependence of the power law behavior of sputtered clusters is not predicted by the models described in Section 1 [24,27–29].

4.3 Chain to ring transformation

Most experimental and theoretical work pertaining to small carbon clusters indicate that linear chains should be formed up to $n = 9$, though their structures have not been assigned unambiguously [36]. For neutral clusters smaller than C_{10}, the even-numbered clusters are predicted to be open shell species with ${}^3\Sigma_g^-$ ground state and high electron affinity, while the odd clusters are predicted to have a closed shell ${}^1\Sigma_g^+$ ground state and markedly lower electron affinity [63]. The role of the charge carried by cluster ions has also been addressed. Linear structures are normally believed be relatively favorable to anions. Reaction studies performed with reagents mixed in the He carrier gas prior to laser generation of the carbon plasma clearly demonstrate that long linear carbon chains ($n \geq 10$) can indeed be produced in this way, but only when the ends are terminated by such groups as –H or –CN [64].

The abundance distribution of pure C_n^- clusters exhibits the expected odd-even oscillations with a sudden departure from its oscillatory pattern at $n = 10$ (Fig. 4), which may be attributed to a chain-to-ring transformation [46–48]. However, we do not observe a similar departure from even-odd oscillatory pattern at $n = 10$ in the case of sputtered C_nN^- cluster anions, (see Fig. 5). Moreover, in the log-log plots of *even* members of C_n^- (Fig. 6a) and C_nN^- (Fig. 6b) sputter-generated from graphite, we observe a sudden drop in the C_n^- yield at $n = 10$, whereas no such drop is observed for $C_{10}N^-$. Rather, a power law can be fitted to the even n family of C_nN^- cluster for all three C surfaces (though the data from only graphite is displayed). This implies that the chain to ring structural transition probably does not occur up to $n = 10$ for sputtered nitrogen-terminated carbon cluster anions. However, the same could not be verified for C_nN^- cluster anions with $n > 10$, since, these are not distinctly observable above the background level due to strong interference arising out of neighbouring CsC_n^- cluster anions. It is interesting to note that Wang *et al.* [41] also consider the ground state structure of $C_{10}N^-$ to be chain-like in their *ab initio* calculations.

5 Conclusions

We have produced single nitrogen-substituted carbon cluster anions C_nN^- ($n \leq 10$) by the gas feed Cs-sputter technique. By spraying a gas with a relatively high "gettering efficiency" on the ion induced surface, this technique could easily be extended to different hetero-atom substituted cluster anions which were sputter-ejected intrinsically with prolific yields. Both odd and even-n C_nN^- clusters were observed to grow with an increase in the NO_2 gas pressure, while clusters with even n were hardly detectable in the case of laser ablation. The normalised yield of sputter-ejected C_nN^- clusters oscillates as a function of n: clusters with odd n being more abundant than those with even n. This is attributed to the oscillatory electron affinities of these cluster anions. We have shown that the oscillatory behavior of the C_nN^- clusters is not affected by the crystallographic nature of the carbon surface being sputtered. The cluster yield as a function of n can be fitted to a single power law for all three surfaces sputtered, over a wide range of operating conditions of the ion source. We thus infer that the intrinsic structure of the ion-induced surface does not play a significant role in the formation of sputtered cluster anions. The abundance pattern of sputter-ejected C_nN^- cluster anions and the power law behavior exhibited by the even n sub-family for all three forms of C – which shows no deviation at $n = 10$ – indicates that mono-nitrogen-substituted sputter-ejected carbon clusters anions are chain-like. Pure carbon clusters are known to exhibit a chain to ring transformation at $n = 10$.

Studies of C_nH^- and C_nO^- clusters are in progress and would be reported separately.

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