Ionization probability of sputtered negative cluster ions: Dependence on surface work function and emission velocity

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The yields of negatively charged carbon cluster ions C_n^- ($2 \leq n \leq 21$) and C_n^{2-} ($n = 8$ and 10) emitted from graphite irradiated by 14.5 keV Cs^+ ions were monitored during the initial stages of Cs incorporation in the near-surface region of the specimen. The associated work-function variations $\Delta \Phi$ were determined *in situ* from the shifts of the sputtered-ions' emission-energy spectra; the total change amounted to $\Delta \Phi \sim 2.7$ eV. The lowering of Φ induces an *exponential* increase of the ionization probability P^- of the sputtered cluster ions. For C_n^- with $n \leq 9$, these variations of P^- were monitored for several selected emission energies (from 0.5 to 15 eV), in order to investigate a possible dependence of P^- on the ion's emission velocity. For C^- and C_2^- ions, such an influence of the velocity on the ionization probability was observed, whereas for larger clusters no distinct dependence was found in the velocity range accessible ($\leq 7 \times 10^5$ cm/s). The results indicate that a resonant electron-transfer process may effect the ionization of the sputtered cluster species.

I. INTRODUCTION

The irradiation of condensed materials with energetic ions results in the ejection of particles from the topmost surface layers, a process commonly called sputtering.[1] This sputtered flux consists of a wide variety of different species. Quite often, a sizeable fraction is emitted in the form of clusters and molecules.[2,3] Apart from their relevance in surface characterization techniques employing mass spectrometry,[4] both as the detected species and, more currently, also as the bombarding species, sputtered clusters are of potential use as tools for surface modifications,[5] or for the deposition of nanosized structures.[6] In general, the processes leading to the ejection of (large) clusters from an ion irradiated surface are far from being completely understood (general overviews can be found in Refs. 2, 3 and 7). A probably even more intriguing question concerns the possible ionization of the cluster in the sputtering event. Knowledge of the ionized fraction of the emitted clusters is of great importance in all of the aforementioned applications; obtaining, therefore, information on the dependence of the cluster's ionization probability on various cluster- and specimen-related parameters (like the electron affinity or the ionization potential of the cluster or the surface work function of the sample) appears highly desirable. In previous work,[8] we studied the emission of singly and doubly negative carbon clusters in sputtering with respect to abundance distributions, energy spectra, and fragmentation processes. The distinct correlation between the abundance distributions of C_n^- and the electron affinity values of carbon clusters[9] supported strongly the notion that the abundance distribution of stable C_n^- is largely determined by the electron affinity A of the respective cluster species. Based on this finding, an exponential scaling of the clusters' ionization probability with A was suspected in Ref. 8. A verification of this anticipation is difficult, however, because of the additional influence of the stability on cluster abundances.[8]

The formation of *atomic* negative ions in sputtering has been known for many years[10,11] to be strongly enhanced in the presence of alkali metals at the ions' emission site. This finding is utilized extensively to increase the detection sensitivity of electronegative elements in secondary-ion mass spectrometry (SIMS)[4] and to enhance the ion current in sputter negative-ion sources.[12] Such an ion yield enhancement was observed also for some (small) molecular ions.[13] This effect is generally ascribed to a lowering of the specimen's work function, Φ. The minimum amount of energy required to transfer an electron from the solid to an atom at infinity to form a negative ion is $\Phi - A$.[14] Hence, the formation probability P^- of negative secondary ions should depend on this quantity. The work-function dependence has been verified in several static alkali-metal adsorption experiments[15–17] and, more recently,[18] also for the *dynamic* conditions prevailing in many SIMS analyses (e.g., for depth profiling); then the Cs^+ ions are implanted into the near-surface region of the solid, while the sample is concurrently eroded. This results in a transient incorporation of Cs into the near surface region of the irradiated solid and, finally, in a stationary surface concentration of the projectile species that is accompanied by a change of the surface work function.

Experimental data also reported a (pronounced) dependence of the ionization probability of sputtered atomic ions on the ions' emission energy[19–21] or emission velocity,[22–24] although the respective trends were not in all cases clear cut (see, e.g., Ref. 14).

Because of the apparent lack of a generally applicable concept for the ionization mechanism of sputtered *cluster* ions and the decisive influence of the surface work function and the ion velocity on the ionization of atomic ions, the present paper was devised to investigate the ionization probability of negatively charged carbon clusters C_n ($2 \leq n \leq 21$) sputtered from graphite as a function both of the work function (WF) of the (bombarded) surface and of the emission velocity of the sputtered clusters.

For the emission of sputtered *atomic* ions, several distinct ionization schemes have been proposed[14,25,26] that differ in

the assumptions they are based on. Generally, they all tend to describe satisfactorily only a rather limited class of materials and experimental conditions, while failing for others. For the ion emission from clean metal and semiconductor surfaces where the valence electrons are important, the so-called electron-tunneling model was favored: here, the electronic interaction between a sputtered atom and the substrate is not localized and the ejection of an atom may involve a large number of electrons in the valence band. This model envisions the electronic transition as a resonant transfer process between a sputtered atom and the valence band. This approach is thus equivalent to the crossing of the atomic level of the sputtered atom with many electronic levels of the solid.[14]

The affinity level ε_a of an atom close to the surface is shifted down and broadened. The half-width $\Delta(z)$ of this level depends on the hopping matrix element between the atomic state and a state of the solid; commonly it is assumed to vary exponentially with the atom's distance z from the surface[27–30]

$$\Delta(z) = \Delta_0 \exp(-\gamma z), \qquad (1)$$

where γ^{-1} is a typical decay length ($\gamma^{-1} \sim 10^{-8}$ cm) and $\Delta_0 \sim 1-2$ eV. This broadening is due to the finite lifetime of the electron in the affinity level, with the lifetime being $\hbar/2\Delta(z)$. This state is filled as long as $\varepsilon_a(z)$ is below the Fermi level ε_F. If the sputtered species moves away from the surface with a constant velocity ν, at a distance $z = z_c$ from the surface the levels $\varepsilon_a(z)$ and ε_F will cross and the atomic level may start emptying. Because of the finite probability $\Delta(z_c)$ this may not happen immediately and the atom therefore has a certain chance to escape with the state filled, i.e., as a negative ion. The ionization probability P^- is then the probability that the electron can survive in the atomic state from $z = z_c$ to $z = \infty$. With the assumption of a constant normal velocity ν_n this results in[27,30,31]

$$P^- = \exp\left(-\frac{2\Delta(z_c)}{\hbar \gamma \nu_n(z_c)}\right). \qquad (2)$$

Generally, the resonance time of the atom at the equilibrium position on the surface, $\hbar/2\Delta_0$, is much shorter than the crossing time, $1/\gamma\nu_n$. Assuming, furthermore, that $\varepsilon_a(z)$ varies exponentially with z, P^- can be written[30,31]

$$P^- \propto \exp\left(-\frac{\Phi - A}{\varepsilon_0}\right), \qquad (3)$$

with

$$\varepsilon_0 = \frac{\hbar \gamma}{2\Delta_0}(\Phi - A + E_0)\nu_n. \qquad (4)$$

E_0 denotes the value of ε_a below the Fermi level at the equilibrium position of the atom ($z = 0$), i.e., $\varepsilon_a(0) = -(\Phi + E_0)$.

Equation (3) predicts an exponential dependence of P^- on the electron affinity of the sputtered species and on the work function of the surface. Tendencies for the former feature have been identified for atomic species.[25] A work-

function dependence of P^- has been reported in several static sputtering experiments[15,16] in which the surface was covered with varying amounts of alkali metals; it was also found under dynamic conditions when Cs was incorporated into the near-surface region by implantation of Cs^+ bombarding species.[18] The theoretical approach also predicts, via Eq. (4), an exponential dependence of P^- on the normal component of the emission velocity. Such a dependence has been observed experimentally in a number of cases, most convincingly at high velocities,[24] or by varying ν_n through changes of the emission angle that was monitored.[32] For low velocities, however, several data indicated that ε_0 approaches a constant value, independent of ν_n. In other experiments,[33] the variation of P^- with changes of the work function was monitored for a large range of emission energies. Although P^- scaled exponentially with $\Delta\Phi$, the slope (i.e., ε_0) was essentially independent of the emission energy, with values of $\varepsilon_0 \sim 0.2-0.4$ eV.

According to Eq. (4) ε_0 should also depend on Φ and, for different species, on A. For large values of E_0 [as would be the case, e.g., for the adsorption of oxygen atoms on the surface of a transition metal, where $E_0 \sim 6$ eV, (Ref. 30)] ε_0 would not be influenced strongly by small ($1-2$ eV) changes in Φ or A. By contrast, for the situation when the atom is sputtered off the element itself, E_0 should be rather small. It was, in fact, argued[28] that then the affinity level of the atom at the equilibrium position must be pegged at the Fermi level in order to ensure approximate charge neutrality. Under these conditions, the strict exponential dependence of P^- on ν_n may fail for (large) variations of Φ.

The experimental observation[32] of a leveling off in ε_0 for low velocities might be due to the fact that as the *measured* emission velocity approaches zero, the velocity ν_n at z_c (which is relevant for the survival of the filled state) might still be finite. Several authors[12,34] also questioned the purely exponential dependence of P^- on ν_n by noting that a variation of the numerator in the exponent of Eq. (3), i.e., Φ or A, by $2-3$ eV would produce drastic changes in the energy distributions of sputtered ions that have never been observed experimentally. Available data indicate, rather, that the energy spectra shift when, for example, the work function varies but their shapes remain largely unaltered.[35]

Based on this information for atomic ions, the present investigation correlated the yields of negatively charged sputtered *cluster* ions with the relative WF changes of the surface and the emission velocity of the cluster, thereby checking the validity of Eqs. (3) and (4) also for (moderately large) cluster ions. This was accomplished by monitoring the intensities of carbon cluster ions C_n^- ($2 \leq n \leq 21$) and C_n^{2-} ($n = 8$ and 10) sputtered from graphite by 14.5 keV Cs^+ ions. Energy spectra were recorded for anionic cluster with $n \leq 9$. The WF variation was effected by the gradual Cs buildup in the near surface range of the solid during the initial stages of ion irradiation: pristine surfaces of graphite were exposed to a Cs^+ primary ion beam while, at specific fluence increments, energy distributions of negative cluster ions were recorded. Their shifts in energy indicate a variation of the contact potential (and, thus, of the WF) between the

sample and the energy analyzer and allow thereby an *in situ* determination of these relative WF changes. It has been demonstrated recently[18] that this approach provides an accuracy of 0.1 eV (see below). This onset method of a (relative) WF determination has also been utilized in previous studies.[33,35,36]

II. EXPERIMENT

The experiments were performed in a secondary ion microscope (Cameca IMS $4f$)[37] equipped with a double focusing mass spectrometer (electrostatic and magnetic sector fields in series). A 14.5 keV Cs^+ primary ion beam of 1nA beam current was used that was raster scanned, at an incidence angle of 26° relative to normal, across a nominal sample area of either $(125\ \mu m)^2$ or $(380\ \mu m)^2$ that resulted in flux densities of 4×10^{13} or 4.3×10^{12} ions/cm^2 s, respectively. Secondary ions were accepted from a circular area centered within, but smaller than the bombarded region. An energy selecting slit located between both sector fields can be closed to the extent that an energy resolution of $\Delta E/E \sim 10^{-3}$ is obtainable. Since the secondary ions' pass energy is 4.5 keV, this resolution translates into an energy bandpass of a few eV. Energy distributions of secondary ions are measured by ramping the target potential, in steps of 0.1 or 0.2 V, around the -4500 V value, while keeping the remaining secondary beam optics unchanged. Thus, with the energy slit closed, only ions with a constant total energy (the sum of the ion's kinetic emission energy plus the acceleration energy) can pass the slit and, subsequently, the magnetic sector. The total energy range accessible under these conditions amounts to ~20 eV, which is sufficient to investigate the narrow energy spectra of cluster ions.

Changes of the surface WF are detected in this arrangement as a variation of the contact potential between the sample and the electrostatic analyzer; they result, therefore, in shifts of the secondary ion energy distribution. Most accurately, these shifts are determined from the steeply rising *low-energy* parts of the spectra. In order to determine WF changes, the energy slit was closed to obtain a narrow bandpass and energy spectra of C^- or C_n^- ($n \leqslant 9$) ions were recorded at incrementally increased bombardment fluences, as described above. The fluences required to monitor an energy spectrum were kept much smaller (typically by more than a factor of ten) than the individual fluence increments.

The transmission of the instrument depends on the ion's emission energy. This dependence results from the varying acceptance angle that is detected for different energies. The maximum acceptance angle θ_m decreases with increasing emission energy. For the present experimental settings, θ_m reduces from $\sim28°$ at the lowest energy (0.5 eV) investigated in the experiments described below to $\sim5°$ at the highest energy (15 eV). With the possible exception of the 0.5 eV data, the measured energy values may, therefore, represent the normal component of the emission velocity v_n. Since, on the other hand, the transmission is independent of Φ, the measured intensities at a given energy are proportional to the ionization probability P^- of the respective cluster ion at that emission energy.
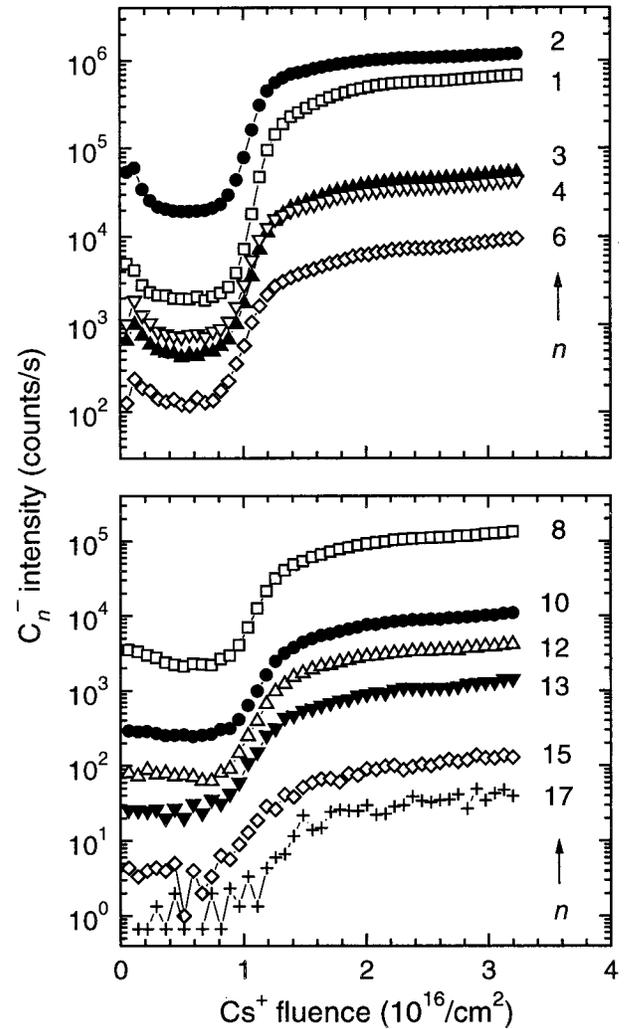
FIG. 1. C_n^- cluster-ion intensities as a function of fluence for 14.5 keV Cs^+ bombardment of graphite. The data correspond to an integration over the major part of the emission energy spectrum. To record the data shown in the upper panel, the instrument's transmission was intentionally reduced by about a factor of 100, in order to monitor all cluster species under identical detector conditions.

A highly oriented pyrolytic graphite was used as specimen in the experiments; a fresh surface was produced by removing a thin layer using adhesive tape.

III. RESULTS AND DISCUSSION

Figure 1 exemplifies the effect of the gradual Cs incorporation on the intensities of cluster ions sputtered from the graphite sample bombarded with 14.5 keV Cs^+. For several C_n^- cluster ions, the intensities are plotted as a function of the Cs^+ fluence; for this measurement the energy slit was completely open ($\Delta E \sim 120$ eV) in order to detect (almost) all emitted ions and to obtain sufficient signals for the large clusters. Upon passing through a regime of almost constant intensity (Cs atoms are implanted into the bulk with still little Cs at the surface), the ionization probability P^- and, therefore, the yield rise with increasing Cs content at the
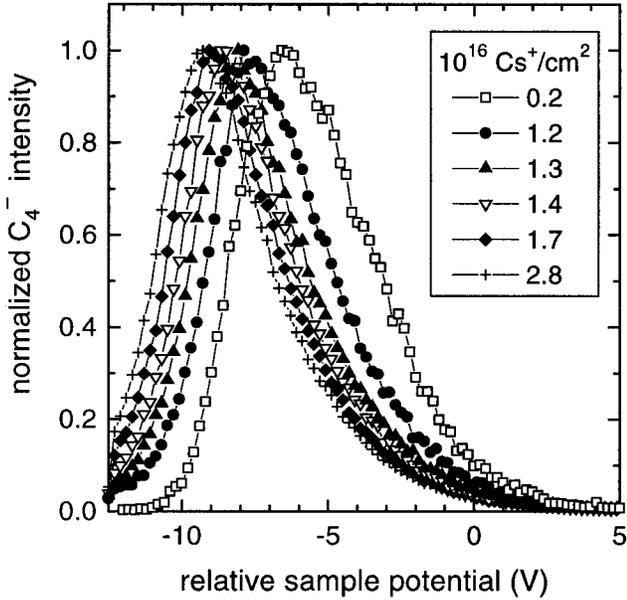
FIG. 2. Normalized energy spectra of C_4^- ions recorded at the Cs^+ fluences indicated. The sample potential is given relative to the value of -4500 V and the ion's emission energy increases from left to right. The onset regions of these spectra were fitted with tangents to derive the values of $\Delta\Phi$.

FIG. 3. The work-function variations $\Delta\Phi$ derived from the spectra shown in Fig. 2 as a function of 14.5 keV Cs^+ fluence.

surface and approach a roughly constant value at a fluence of $\sim 3 \times 10^{16} \, Cs^+/cm^2$, while saturation and, hence, equilibrium conditions are established only at a fluence of $\sim 8 \times 10^{16} \, Cs^+/cm^2$. Very similar intensity variations were observed for all C_n^- and C_n^{2-} cluster ions studied. It should be noted that for larger clusters ($n \geq 8$) the intensity is essentially constant for fluences $< 1 \times 10^{16} \, cm^{-2}$, whereas for smaller clusters the yield is enhanced in the very initial stage of ion bombardment (fluence $< 2 \times 10^{15} \, cm^{-2}$). While there is no ready explanation for these differences, it appears that the initial yield variations are more pronounced the larger the total yield enhancement (from the constant value to the final steady-state level). The latter, in fact, becomes smaller with increasing cluster size. This observation may indicate that larger clusters are more readily ionized than smaller ones, even in the absence of Cs at the surface and, hence, the enhancement upon Cs incorporation is less pronounced. We will see below that the initial decrease of the intensity for small clusters is correlated with a slight *increase* of the WF; because of their inherently higher ionization probability, large clusters are not affected by that small increase of the WF and their intensity level stays largely constant up to the point when the Cs buildup at the surface starts to *reduce* strongly the WF and enhances also the ionization probability for larger cluster species.

As mentioned above, WF changes were determined from the shifts of the emission energy distributions, with the energy slit almost closed to obtain a narrow bandpass. Figure 2 depicts such spectra for C_4^- in normalized form, with the Cs^+ fluence as parameter. A distinct shift of the onset of the spectra towards *lower* energies (more negative sample potentials) with increasing fluence is observed. The low-energy
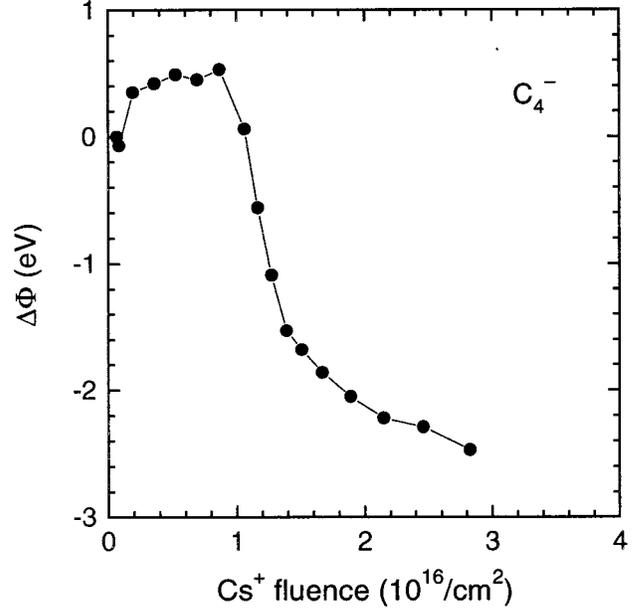
portions of these spectra (and similar ones for other ion species) were fitted with tangents and the intercepts of the latter with the potential axis were used to determine the relative changes of the work function $\Delta\Phi$ induced by the Cs buildup. Due to limitations in intensity level, complete energy spectra like the ones shown in Fig. 2 could be recorded only for C_n^- clusters with $n \leq 9$; this is a consequence of the very low flux densities employed in these measurements that were necessary to keep the WF changes during the acquisition of the spectra negligibly small. Hence, for clusters up to that size, emission energy selective intensities in dependence of the work function could be derived from these measurements. For larger clusters, only energy-integrated yields were available (see Fig. 1) and these were correlated with the WF values derived, at given Cs^+ fluences, from the energy spectra of C^-.

The values of $\Delta\Phi$ derived from the shifts of the energy spectra of C_4^- are depicted in Fig. 3 as a function of the Cs^+ fluence. As the present experimental approach cannot determine an absolute value of the work function, in those data and corresponding ones for other ion species, $\Delta\Phi = 0$ was set for the WF value derived from the energy spectrum recorded at the lowest fluence (typically between $5 \times 10^{13} \, cm^{-2}$ and $2 \times 10^{14} \, cm^{-2}$). This is different from the procedure used in our work[18] on atomic anions where the roughly constant value around a fluence of $\sim 5 \times 10^{15} \, Cs^+/cm^2$ (see Fig. 3) was set as $\Delta\Phi = 0$. We suggest that the presently employed approach might be justified by observing that the initial *increase* of the WF could be induced by the incorporation of Cs *below* the surface due to implantation (the mean range of a 14.5 keV Cs^+ ion in pristine graphite under the present impact angle amounts to about 13 nm). In these initial stages of ion bombardment the Cs concentration at the surface is very low; with increasing
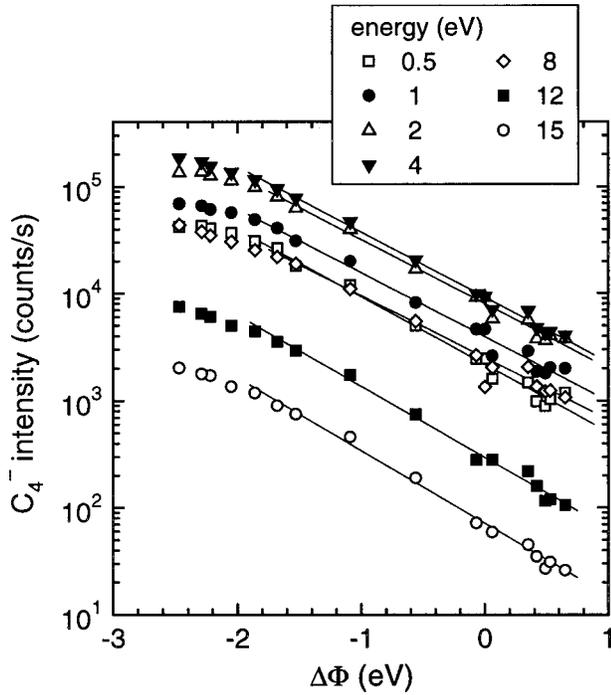
FIG. 4. Intensities of C_4^- cluster ions sputtered from graphite vs the work function change $\Delta\Phi$. The parameter is the ions' emission energy.

FIG. 5. Intensities of C_8^- cluster ions sputtered from graphite vs the work function change $\Delta\Phi$. The parameter is the ions' emission energy.

fluence, continuous irradiation and concurrent sample erosion apparently lead to a situation when Cs ions reside in or on top of the outermost surface layer, effecting a *lowering* of the work function. Figure 3 indicates that this reduction sets in at a fluence of $\sim 1\times10^{16}\,\mathrm{Cs^+/cm^2}$. In accordance with our previous results,[18] the *total* variation of the work function upon reaching steady-state sputtering amounts to about 2.7 eV.

As noted already in Fig. 1, the pronounced change of the work function effects a considerable yield enhancement. In fact, a clear anticorrelation between the cluster intensities and $\Delta\Phi$ is observed by comparing the data sets in Figs. 1 and 3: the yield starts to rise, at a fluence of $\sim 1\times10^{16}\,\mathrm{Cs^+/cm^2}$, concurrently with the lowering of the WF; saturation is again reached at about the same fluence.

The correlation between the measured ion yields of C_4^- cluster ions and the corresponding $\Delta\Phi$ values is depicted in Fig. 4 for seven different emission energies. The energy scale was established by setting the WF value derived for each spectrum (i.e., the intercept of the tangent in the low-energy region with the potential axis) as zero. Over a wide range, the intensity of C_4^- ions exhibits an exponential dependence on $\Delta\Phi$ (the straight lines are fits to the data in that regime), but for low work-function values ($\Delta\Phi < -2$ eV) a tendency to level off. The latter feature was also observed for C_2^- and C^- (for which it is most distinct) but it was not found for larger cluster ions. This is exemplified in Fig. 5, which shows the C_8^- intensity as a function of $\Delta\Phi$ for several different emission energies: For all energies, the yield increases exponentially with $\Delta\Phi$. Another important observation with respect to Figs. 4 and 5 is related to the absence of a (pro-

nounced) emission-energy dependence of P^-: the slopes of the exponential scaling that correspond to ε_0 in Eq. (3), exhibit little (if any significant) variation with the emission velocity for C_n^- cluster ions with $n \geq 8$. As mentioned above, for clusters with $n > 9$, only energy-integrated data could be recorded as a function of $\Delta\Phi$. These data are depicted in Fig. 6. Again, an exponential scaling of the intensity with $\Delta\Phi$ is found but, in agreement with the results for C_8^- (Fig. 5) and C_9^-, no indication of a saturation towards low work-function values.
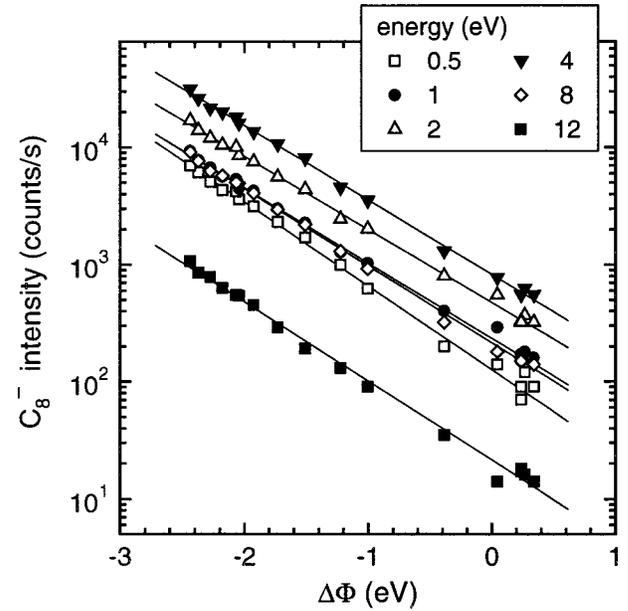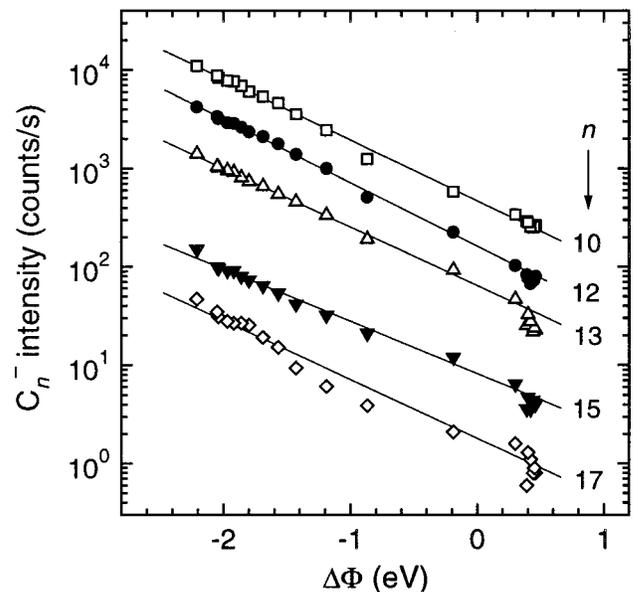
FIG. 6. Emission energy integrated intensities of several C_n^- cluster ions sputtered from graphite vs the work function change $\Delta\Phi$.
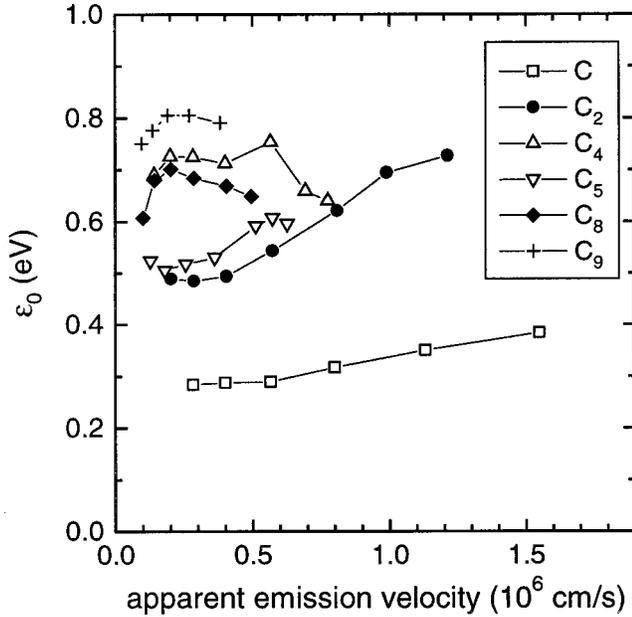
FIG. 7. Values of ε_0 [see Eq. (3)] derived from the linear least-squares fits in Figs. 4 and 5 (and corresponding data for other cluster species) vs the emission velocity of the respective cluster.

The exponential dependence of the ionization probability on Φ (see Figs. 4–6) provides the possibility to determine the parameter ε_0 [cf. Eq. (3)] for negative C_n^- cluster ions produced in sputtering. It appears that for clusters for which only energy-integrated yield data were recorded ($n > 9$), ε_0 falls roughly in the range from 0.7 to 0.9. Whereas ε_0 could not be derived with sufficient accuracy for the doubly charged C_8^{2-} ion because of the low intensity, the value for C_{10}^{2-} is identical to that (0.71 eV) of the singly charged C_{10}^- ion. For those clusters for which energy-selective yields were determined, the values of ε_0 derived from the respective exponential fits (see Figs. 4 and 5) at different energies can be depicted as a function of the cluster's emission velocity. These results are compiled in Fig. 7. The velocity values were computed from the measured emission energies and cluster masses; as mentioned in Sec. I and in the work of other authors,[30,32] these *apparent* velocities might be different from the ones the clusters have close to the surface (i.e., at $z = z_c$) and which are relevant for the ionization process. Figure 7 indicates that only for C_2^- and C^- is a distinct dependence of ε_0 on the velocity found; for the larger cluster ions, the values of ε_0 appear to be roughly constant and they exhibit no clear trends with respect to the velocity. It is noted, however, that the range of emission velocities is very small, which is due to the low emission energies of large clusters: higher energies would lead invariably to rapid fragmentation of the cluster. These essentially constant values of ε_0 are reminiscent of corresponding data[32] that also reported a leveling off for ε_0 at low velocities.

While this limited velocity range restricts severely the possibility to test the validity of Eq. (4), the dependence of ε_0 on Φ may also mask the influence of ν_n. For C_2^- and C^- a more extended range of velocities is accessible experimentally. For these anions the dependence of C_2^- and C^- on ν
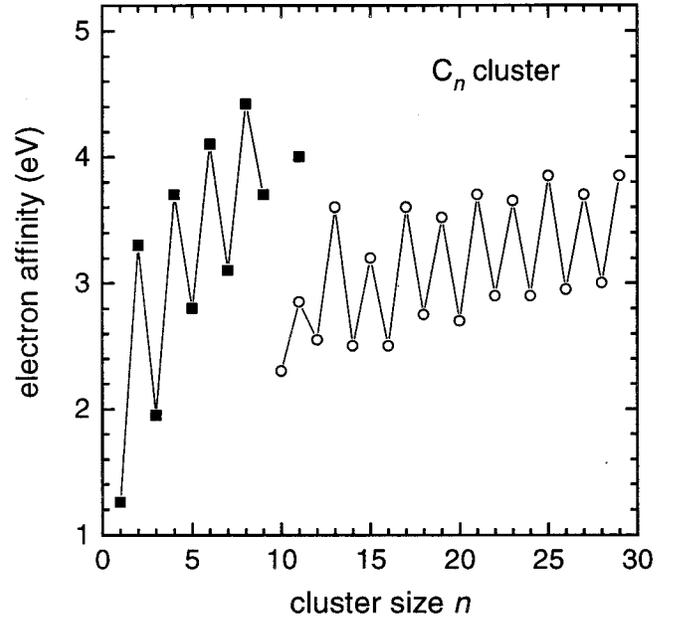
FIG. 8. The electron affinity A of C_n cluster as a function of cluster size n. These data were derived from experiments using photoelectron spectroscopy (Ref. 9). The results indicate that small clusters ($n \leqslant 9$) form predominantly chains, whereas for larger clusters, rings are the dominant structure.

appears to follow the general form $\varepsilon_0 = a + b \nu_n$, an expression proposed in previous work[34] to explain the absence of strong changes in measured energy spectra due to WF changes (see Sec. I). A definite conclusion as to the validity of such a correlation would require, however, a determination of ε_0 for still higher velocities.

Finally, it may be worthwhile to consider the behavior of P^- for large changes of Φ. It was seen in Fig. 4 (and from related data for C_2^- and C^-) that for a reduction of the WF by less than about 2 eV, the yields deviate from the exponential variation with $\Delta\Phi$ and exhibit a tendency to saturate. In fact, for a given value of A, the ionization probability P^- is then expected to approach a constant value for $\Phi \sim A$. Hence, for a given cluster, a constant value of P^- should occur for $\Phi < A$. As the WF of pristine graphite is $\Phi \sim 5$ eV,[38] and the steady-state value in the experiment amounts to $\Phi_{ss} \sim 2.5$ eV, the latter condition should be fulfilled for cluster species with $A \geqslant \sim 2.5$ eV. Whereas the electron affinity of carbon atoms is 1.262 eV,[39] the A values of carbon clusters are much higher. Figure 8 compiles corresponding data obtained experimentally by means of photoelectron spectroscopy.[9] Apparently, most of the cluster species investigated here (with the exception of C_3 and C_{10}) have an electron affinity distinctly greater than the above given limit. On the other hand, the higher the electron affinity of a cluster, the stronger the influence a variation of Φ has on the magnitude of ε_0, see Eq. (4). In this case, the change of Φ in the numerator of the exponent in Eq. (3) might be balanced in part by a related change of the denominator. Inspection of

Fig. 8 indicates that such an effect could be important for most C_n clusters up to $n=9$.

The validity of Eq. (2), and as a consequence of Eq. (3), refers generally to the case that the affinity level of the departing species, ε_a, varies rapidly with z and crosses ε_F at the crossing distance z_c with a large slope. Typically, this would be the case for species with a small electron affinity A; in the present paper, this would apply to C atoms, with $A=1.26$ eV. By contrast, for small values of ν_n and a constant (or almost constant) ε_a, the ionization probability can be written as[14,27,40]

$$P^- \simeq \begin{cases} 0 \\ 1 \end{cases} \pm \frac{2}{\pi} \exp\left(-\frac{\pi|\varepsilon_F-\varepsilon_a|}{\hbar\gamma\nu_n}\right) \quad \text{for} \quad \begin{cases} \varepsilon_F<\varepsilon_a \\ \varepsilon_F>\varepsilon_a \end{cases}. \quad (5)$$

With $\varepsilon_F=\Phi$ and $\varepsilon_a=A$, the upper part of Eq. (5) is, apart from the constants in the exponent, equivalent to Eq. (3) and produces the exponential variation of P^- with the work function. The lower part, on the other hand, causes P^- to approach (gradually) a constant value. This transition is more rapid the larger the magnitude of the constant in the exponent. Differences in the value of ε_0 (see Fig. 7) may therefore result in differences in that transition for various cluster ions. It might be necessary to access a wider range of WF changes to clarify this question.

IV. CONCLUSION

In summary, the present study demonstrates an exponential scaling of the ionization probability P^- of sputtered negative C_n cluster ions with the work function of the surface. The $\Delta\Phi$ shifts were monitored *in situ* during the gradual Cs incorporation in the initial transients of sputtering towards equilibrium bombardment conditions. These data provide, therefore, evidence that the same ionization mechanism (i.e., a resonant electron-transfer process as envisaged in the electron-tunneling model) is operative both for *atomic* and for *cluster* ions: close to the surface, the affinity level of the nascent cluster is below the highest occupied state of the sample and is filled; with the cluster departing from the surface, at a given distance these levels cross and the cluster's affinity level would start emptying. Due to the finite transfer probability, this may not happen immediately and, if the velocity is high enough, the cluster may escape with the filled level as a negative ion. A distinct dependence of P^- on the emission velocity as predicted by such models was observed only for the smallest species (C_2^- and C^-). At least, in part, this might be due to the very low apparent emission velocities of the larger cluster ions and the rather limited range of velocities accessible. For small cluster ions P^- tends to approach saturation for the lowest work-function values, in agreement with the general predictions of resonant charge-transfer processes.

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