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Exponential scaling of sputtered negative-ion yields with transient work-function changes on Cs^+-bombarded surfaces

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The emission of negative secondary ions (C^-, Si^-, Ge^-, Au^-) from keV-Cs^+-irradiated elemental surfaces was monitored during the initial stages of Cs incorporation. Concurrently determined work-function variations $\Delta\Phi$ were found to be 2.75 eV for graphite, 2.3 eV for Si, 0.84 eV for Ge, and 0.62 eV for Au. This lowering of Φ results in an exponential increase of the sputtered ions' ionization probability P^-. Values of P^- derived from the $\Delta\Phi$ scaling are 0.19 for C^-, 0.093 for Si^-, 1.6×10^{-3} for Ge^-, and 5.7×10^{-3} for Au^-, and agree quantitatively with measured ion-yield data. [S0163-1829(96)05147-8]

The formation of sputtered negative ions is strongly enhanced in the presence of alkali metals at the ions's emission site.[1] This finding is utilized extensively to increase the detection sensitivity of electronegative elements in secondary-ion mass spectrometry (SIMS);[2] most often, this is accomplished by bombarding the sample with Cs^+ primary ions and detecting negatively charged secondary ions. This ion-yield enhancement is generally ascribed to a lowering of the specimen's work function (WF), 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 $\Phi - A$,[1] where A is the atom's electron affinity. Hence the formation probability P^- of negative secondary ions should depend on this quantity. Theoretical treatments of sputtered ion emission[3,4] predict an exponential scaling

$$P^- \propto \exp[-(\Phi - A)/\varepsilon_0], \tag{1}$$

where the parameter ε_0 is anticipated[4] to vary with the normal component of the ions's emission velocity, but to be roughly constant for (moderate) WF changes; its magnitude should fall in the range 0.5–1 eV.[4] Experimental data,[5] however, show ε_0 to be largely independent of the emission velocity, with values of 0.2–0.4 eV.

The validity of Eq. (1), in particular the WF dependence, has been verified in several static alkali-metal adsorption experiments:[1,6] the ion yields were monitored, as a function of alkali coverage and work function, in the low-fluence regime, i.e., without altering the surface state. On the other hand, SIMS analyses usually operate under *dynamic* conditions (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. Upon completion of an initial transient, this results in a stationary surface concentration of the projectile species which, in the case of Cs or other alkali metals, may cause a change of the WF and hence of the ion yields. Clearly, this situation is drastically different from the above-mentioned static adsorption studies. Most importantly, the steady-state WF variations (and the Cs concentrations) are not known, but are expected to depend on various parameters, foremost probably the substrate's sputtering yield Y [under steady state on average one Cs atom, charged or neutral, is reemitted per incoming primary ion together with Y target atoms; thus the Cs surface concentration should scale like $1/(1+Y)$].

The present investigation aims to determine, for the first time, to our knowledge, relative WF changes *in situ* during the gradual Cs buildup in the near-surface range of the solid, and to correlate them with the yields of negative secondary ions to assess the validity of Eq. (1) also for *dynamic* sputter conditions. To this end, pristine surfaces of elemental samples were exposed to a Cs^+ primary ion beam (impact energy 14.5 eV) while, at specific fluence increments, (partial) energy distribution of negative secondary ions were recorded. Their energy shifting is indicative of a variation of the contact potential (and thus of the WF) between the sample and the energy analyzer. It was recently demonstrated[7] that WF changes are detectable with an accuracy of 0.1 eV by these means (see below). This onset method of a (relative) WF determination is often employed using secondary electrons,[8,9] but has also been utilized with secondary ions.[5,10] The present work, however, appears to constitute the first application to dynamic Cs implantation conditions which are relevant for common SIMS analyses. Furthermore, the experiments provide values for ε_0 and, via Eq. (1), for the ionization probability P^- [the constant of proportionality in Eq. (1) is about unity].

The experiments were performed in a secondary-ion microscope [Cameca IMS $4f$ (Ref. 11)] equipped with a double-focusing mass spectrometer (electrostatic and magnetic sector fields in series). The Cs^+ primary ion beam was produced in a Cs surface-ionization source. A focused (a few μm) 14.5-keV Cs^+ ion beam of 1-nA beam current was used here which was raster scanned, at an incidence angle of 26° relative to normal, across sample areas ranging from $(125)^2$ to $(300)^2$ μm^2, which resulted in flux densities between 6.9×10^{12} and 4×10^{13} ions/cm^2 s. 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 distribution of secondary ions are measured by ramping the target

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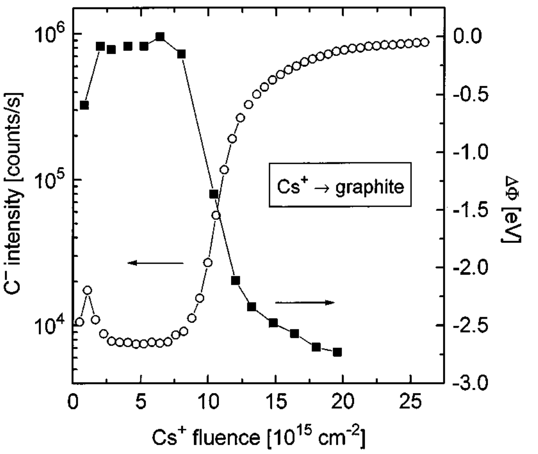

FIG. 1. C$^-$ intensity (open circles, left-hand scale) and WF variations $\Delta\Phi$ (closed squares, right-hand scale) as a function of fluence for 14.5-keV Cs$^+$ bombardment of graphite.

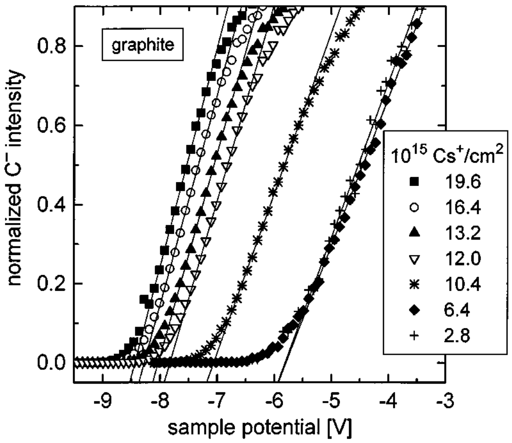

FIG. 2. The onset region of normalized C$^-$ energy spectra fitted with tangents to derive $\Delta\Phi$, with the Cs$^+$ fluence as a parameter. The sample potential is given relative to the value of -4500 V, and the ion's emission energy increases from left to right.

potential, in steps of 0.09 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. 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.

Four different elemental samples were utilized in this work: C$^-$ was sputtered from highly oriented pyrolytic graphite, Si$^-$ and Ge$^-$ from the respective n-type (100) single-crystal wafers [which, however, are amorphized at bombarding fluences of $\sim 2\times 10^{14}$ cm^{-2} (Ref. 12)], and Au$^-$ from a polycrystalline thin film ($\sim$800 nm on a Si substrate). These elements were chosen to cover a wide range of sputtering yields, as the Cs surface concentration and thus $\Delta\Phi$ were expected to scale inversely with Y [for the present bombarding conditions $Y_{\mathrm{C}}\sim 1.5$ atoms/ion, $Y_{\mathrm{Si}}\sim 2.3$ atoms/ion, $Y_{\mathrm{Ge}}\sim 4.6$ atoms/ion, and $Y_{\mathrm{Au}}\sim 12$ atoms/ion (Ref. 13)]. The samples were rinsed in isopropanol and distilled water before being inserted into the instrument's UHV chamber (operating pressure $\sim 1\times 10^{-9}$ mbar).

Figure 1 exemplifies the gradual Cs incorporation for graphite bombarded with 14.5-keV Cs$^+$. The intensity of C$^-$ is plotted (open circles, left-hand scale) 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 ions irrespective of their emission energy. 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 surface, and saturate at a fluence of $\sim 2\times 10^{16}$ Cs$^+$/cm^2, indicative of equilibrium conditions (the yield enhancement at the surface might be due to the presence of impurity species like H, O, or others). The signal evolution of Cs$^-$ (not shown) is identical to that of C$^-$, but the intensity is lower by a factor of 10^4. In order to determine WF changes, the energy slit was closed to obtain a narrow bandpass ($\sim$2–3 eV), and partial energy spectra were recorded at different bombardment fluences as described above. These data are depicted in Fig. 2 in normalized form to ease comparison. A distinct shift of the onset of the spectra towards *lower* energies (higher sample potentials) with increasing fluence is observed. The low-energy portions were fitted with tangents, and intercepts of the latter with the potential axis were used, as done in electron spectroscopies,[8,9] to determine the relative changes of the work function $\Delta\Phi$ induced by the Cs buildup. Here, the value in the low-fluence range [$\sim(4\pm 2)\times 10^{15}$ Cs$^+$/cm^2] was assumed to represent the pristine surface and was set as $\Delta\Phi=0$. The variation of $\Delta\Phi$ with fluence is shown in Fig. 1 (closed squares, right-hand scale). It can be seen that the work function of Cs-loaded graphite is *lowered* by 2.75 eV upon reaching steady-state sputtering. This value of $\Delta\Phi$ is only slightly smaller than those obtained typically in Cs adsorption experiments [$\sim$3 eV (Refs. 1,6)], but still effects a considerable yield enhancement (cf. Fig. 1). In fact, a clear (anti)correlation between the C$^-$ intensity and $\Delta\Phi$ is observed by comparing the two data sets in Fig. 1: the yield

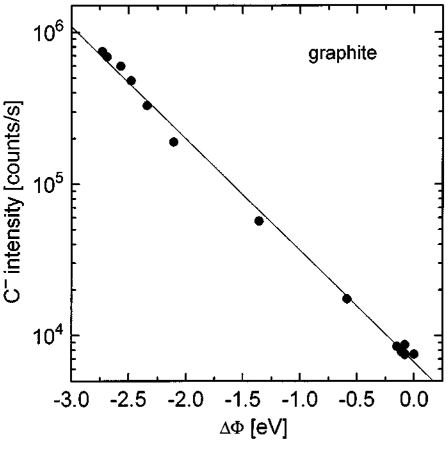

FIG. 3. Intensity vs WF change $\Delta\Phi$ for C$^-$ ions sputtered from graphite.

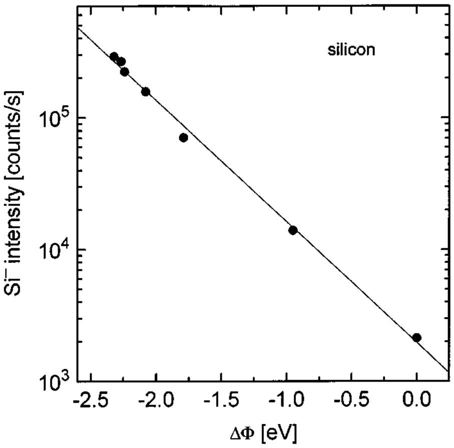

FIG. 4. As in Fig. 3, but for Si^- ions sputtered from silicon.

TABLE I. The maximum WF change $\Delta\Phi$, the value of ε_0 derived from ion-yield-vs-$\Delta\Phi$ plots, the steady-state ionization probability evaluated from Eq. (1), P^-_{th}, and from the experimental ion yield data, P^-_{exp}.

	$-\Delta\Phi$ (eV)	ε_0 (eV)	P^-_{th}	P^-_{exp}
C	2.75	0.59	0.19	0.17
Si	2.3	0.49	0.093	0.088
Ge	0.84	0.46	1.6×10^{-3}	2.2×10^{-3}
Au	0.62	0.42	5.7×10^{-3}	5.3×10^{-3}

starts to rise, at a fluence of $\sim8\times10^{15}$ Cs^+/cm^2, concurrently with the lowering of the WF, saturation is again reached at about the same fluence.

A correlation between the measured ion yields of C^- (which, apart from a transmission factor, represent the ionization probability P^-) and the $\Delta\Phi$ values is depicted in Fig. 3. A scaling in agreement with Eq. (1), i.e., an exponential dependence of P^- on the work function, is observed. From the slope a value of $\varepsilon_0=0.59$ is derived which is compatible with the theoretical predictions.[1,4] Employing the electron affinity of C, $A_C=1.27$ eV,[14] the work function of the pristine surface $\Phi_C=5.0$ eV,[15] and the stationary WF change due to Cs loading, $\Delta\Phi=2.75$ eV, the ionization probability for *equilibrium* conditions derived from Eq. (1) amounts to $P^-_{\mathrm{th}}=0.19$, assuming the constant of proportionality to be unity (that value will be compared below with estimates obtained from experimental yield data).

Measurements essentially identical to those for C have also been carried out for Si, Ge, and Au. Although the general features are comparable, there exist clear element-specific differences. In all cases the ionization probability is enhanced upon Cs buildup, and saturates for steady-state sputtering; these equilibrium fluences decrease from Si (2×10^{16} Cs^+/cm^2) through Ge (1.5×10^{16} Cs^+/cm^2) to Au (3×10^{15} Cs^+/cm^2). Also, the magnitude of the enhancement of P^- is distinctly different: a factor of ~150 for Si^- but only about 9 for Ge^- and ~ 5.8 for Au^-. These differences scale with the maximum WF shifts observed between the virgin and steady-state surfaces $\Delta\Phi=2.3$ eV for Si, $\Delta\Phi=0.84$ eV for Ge, and $\Delta\Phi=0.62$ eV for Au. Using corresponding $\Delta\Phi$ values and yield data obtained during the gradual incorporation of Cs, correlations between P^- and $\Delta\Phi$ could be established for all three elements. Figure 4 shows such a relation for sputtered Si^-. Again a scaling in accordance with the theoretical predictions [cf. Eq. (1)] is found. From these data and the respective ones for Ge and Au, values of ε_0 were derived and are compiled in Table I. Utilizing the electron affinities [$A_{Si}=1.39$ eV, $A_{Ge}=1.2$ eV, and $A_{Au}=2.31$ eV, (Ref. 14) and the work functions $\Phi_{Si}=4.85$ eV, $\Phi_{Ge}=5.0$, and $\Phi_{Au}=5.1$ eV (Ref. 15)], together with the maximum $\Delta\Phi$ shifts derived experimentally (cf. Table I), the ionization probabilities P^-_{th} for steady-state Cs implantation conditions were evaluated from Eq. (1) and are listed in Table I. It is seen that P^-_{th} is rather high for C^- (19%) and Si^- (9.3%), but distinctly lower for Au^- and Ge^-. Obviously, this finding can be ascribed to the much smaller $\Delta\Phi$ values for the two latter elements, since $(\Phi-A)$ for the pristine surfaces investigated here is almost identical. By means of the measured ion intensities, the primary ion current, and the above-cited sputtering yields, the number of *detected* secondary ions per sputtered atom can be determined. This quantity constitutes the product of P^- and the instrumental transmission factor η. Employing $\eta\sim0.20$,[11] experimental data of P^-_{exp} for the *steady state* have been determined; they are listed in Table I and are in excellent agreement with theoretical values derived via Eq. (1).

In summary, the present study demonstrates the validity of an exponential scaling of the ionization probability of sputtered negative ions with the work function for dynamic Cs^+ irradiation conditions. This result was achieved by monitoring $\Delta\Phi$ shifts *in situ* during the gradual Cs incorporation in the initial transients of sputtering toward equilibrium bombardment conditions. Steady-state ion yields are decisively influenced by the magnitude of the $\Delta\Phi$ variations; apparently the latter are governed by the stationary Cs-surface concentration which, in turn, indicates an inverse dependence on the sputtering yields.

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