Secondary-Ion Yields from Surfaces Bombarded with keV Molecular and Cluster Ions

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(Received 2 June 1989)

We have measured negative secondary-ion yields from phenylalanine, CsI, and Au bombarded by complex ions of 5–28 keV. The primary ions were organic monomer and dimer ions and clusters of CsI. Large enhancements occur in the measured secondary-ion yields for more complex projectiles. We show that secondary-ion yields of Au^- atomic species are related to the square of the projectile momentum.

PACS numbers: 79.20.Nc, 79.20.Rf, 79.90.+b

To date, few studies have dealt with the sputtering of solids by complex (heterogeneous) keV ion bombardment. This is in marked contrast with the abundant literature on sputtering with monatomic keV ions.[1] For primary monatomic ions which are not too heavy, elastic recoil in the solid causes a cascade of target atoms to collide with other stationary target atoms. This process is well understood, and the sputter yields, defined as the number of ejected atoms per incident ion, can be accurately predicted by linear cascade theory.[2] For a molecular or cluster projectile, however, a nonlinear collision cascade can occur in which recoiling target atoms collide with other recoiling atoms (as well as with stationary atoms). This nonlinear transfer of energy causes a thermal spike and one of the consequences can be an enhanced number of ejected target atoms.[3] A yield enhancement for a simple homonuclear projectile A_n having n constituents is defined as

$$Y_{A_n}(E)/nY_A(E/n) \geq 1 ,$$

where $Y_{A_n}(E)$ is the yield of ejected atoms or ions for the cluster at energy E and $Y_A(E/n)$ is the yield for the constituent atom at equal velocity.[4] For a complex heteronuclear projectile A_mB_n, the definition is generalized to

$$Y_{A_mB_n}(V)/[mY_A(V)+nY_B(V)] \geq 1 ,$$

where V is projectile velocity.

There is experimental evidence for enhanced yields due to polyatomic projectiles; however, these data are of narrow scope. Enhanced yields have been observed with simple dimers and trimers of atomic projectiles, having energies between 4 and 500 keV.[5–8] In the realm of heteroatomic projectiles, most efforts have dealt with quite different topics.[9–13] The few studies relevant in terms of sputter yields are unclear about the role of complex projectiles. For example, Reuter[9] measured sputter yields of various metallic targets for CF_3^+ primary ions and found higher values compared to O_2^+, but the role of nonlinear effects is not mentioned. Zalm and Beckers[11] compared Si yields for CF_3^+ constituents and found that the measured yield is lower. The experimental situation is complicated by the lack of a theoretical model which predicts the behavior of sputtered particles. Better insight into the effects of complex projectiles requires a more comprehensive study of projectile-target combinations.

In this paper we report on the first systematic study of secondary-ion yields from different targets, in which the masses and types of small polyatomic ions are varied. We employed time-of-flight mass spectrometry to identify the type of negative secondary ions ejected and to measure ion yields from organic, ionic, and metallic solid surfaces. Secondary-ion (SI) yields are defined as the number of ejected ions per incident primary ion. The primary ions were ionic clusters and organic molecules of 5 to 28 keV.

A new experimental approach, described in detail elsewhere,[14] was used to simultaneously obtain SI yields for different complex primary ions. The molecules and clusters were produced by ^{252}Cf-fission-fragment–induced desorption.[15] The experiment is performed in an event-by-event mode allowing the study of sputtering phenomena in the limit of a single projectile-target interaction. Secondary-ion yields due to different primary projectiles can be extracted from one single experiment and provide ready data for comparison because the experimental conditions (target surface conditions, transmission efficiencies, detection efficiencies) are the same.

Yields have been obtained for the bombardment of phenylalanine, gold, and CsI targets with both organic and ionic projectiles. The organic ions were the molecular and dimer ions of coronene ($C_{24}H_{12}$) and phenylalanine [$C_6H_5CH_2CH(NH_2)COOH$] and the phenylalanine fragment $(M\text{-COOH})^+$. The ionic projectiles were the atomic and cluster ions of CsI (Cs^+, Cs_2I^+, and $Cs_3I_2^+$).

An example of the molecular-ion yield from the phenylalanine target due to $(CsI)_mCs^+$ projectiles is shown in Fig. 1. The yields are plotted as a function of the energy per mass unit (keV/u) so that yields with different projectiles can be compared at constant velocity. Similar plots (not shown here) have been generated for the phenyl target using coronene projectiles. In Fig. 2, the Au^--ion yield was measured with the projectiles

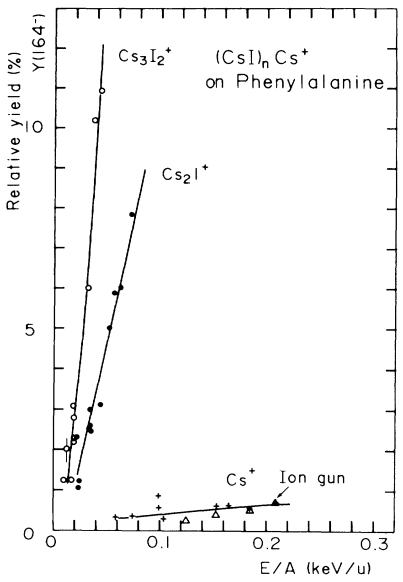

FIG. 1. Yield of $(M\text{-H})^-$ molecular ion (mass 164) from a phenylalanine target as a function of primary-ion energy per mass unit (E/A). Primary ions are $(CsI)_mCs^+$, $m=0$, 1, and 2, and Cs^+ from a pulsed Cs-ion gun.

Cs^+, Cs_2I^+, and $Cs_3I_2^+$ [Fig. 2(a)] and with the organic tal situation is complicated by the lack of a theoretical projectiles of coronene [Fig. 2(b)]. We have also measured SI yields using Cs^+ projectiles from a pulsed Cs-ion gun and the yields, as expected, are equivalent to Cs^+ projectiles produced by fission fragments.

Several trends within the experimental boundaries can be considered: (i) The SI yields increase with the mass of the projectile (independent of the velocity). For example, for Cs^+ and Cs_2I^+ projectiles at 0.074 keV/u, the yields of the phenylalanine $(M\text{-H})^-$ ion are 3×10^{-3} and 7.8×10^{-2} ion per primary impact, respectively. (2) The SI yields increase linearly with E/A, i.e., with the square of the velocity for all projectiles except Cs^+. (3) The rate of increase in SI yield with velocity becomes larger as the projectile mass is increased.

The last feature suggests that enhanced SI yields occur for complex primary ions as their velocity increases. To display yield enhancement, we have plotted in Fig. 3 the SI yields for $(CsI)_mCs^+$ projectiles bombarding Au [Fig. 3(a)], CsI [Fig. 3(b)], and phenylalanine [Fig. 3(c)], having divided by the number of atoms in the projectile. If cluster-impact processes in a solid are simply the sum of atomic-impact processes, then by dividing the SI yield for a cluster by n, one would expect to obtain the value for a single-atom primary ion, and hence the same value in each case. This assumes that the ionization efficiency for the ejected secondary is independent of primary-ion complexity. Such a result would indicate no yield enhancement. This is clearly not

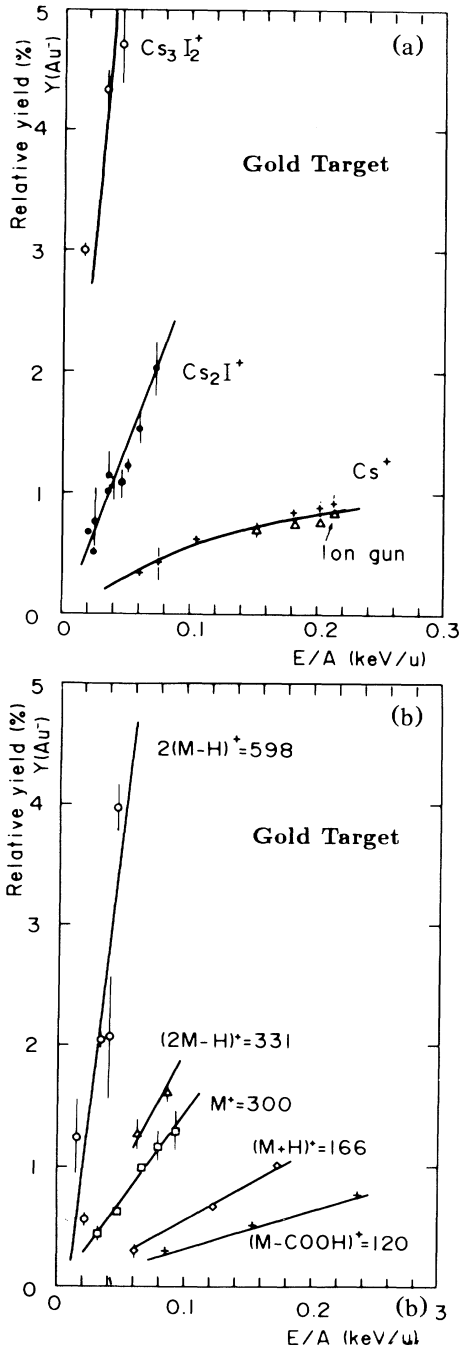

FIG. 2. Yields of Au^- ions as a function of primary-ion energy per mass unit (E/A). Primary ions are (a) Cs^+, Cs_2I^+, and $Cs_3I_2^+$ and (b) organic ions from a coronene deposit (masses specified).

the case with the first two CsI clusters, as shown in Fig. 3. This figure shows that for $Cs_3I_2^+$ cluster projectiles the SI yield of I^- and Au^- is enhanced with respect to the yields obtained with a Cs^+ primary ion. Also, the enhancement in the Au^- yield is similar to the enhance-

ment in the I^- yield. Compared to Au and CsI, much larger SI yield enhancements are observed from the phenylalanine surface.

For the gold target, Fig. 3(a), the secondary-ion yields of Au^-, for Cs^+ projectiles, follows closely the square of the nuclear stopping power, S_n^2, as a function of E/A. With CsI clusters as projectiles, the Au^- yield behavior is quite different. Let us consider the two types of projectiles: the organic molecular ions M^+ and $2(M\text{-H})^+$, and the ionic cluster ions Cs_2I^+ and $Cs_3I_2^+$ (see Fig. 2). From the experimental values we deduce the following relationship between the SI yield of Au^- and the mass of the projectiles:

$$Y(M) = kM^2 \times V^2 = kP^2,$$

where P is momentum, M is the mass of the projectile, and k is a constant depending on the type of projectile (ionic cluster, organic molecules, etc.). Consequently, for the velocity regime considered the SI yield of atomic species appears to scale quadratically with the momentum of the projectile. Thompson and Johar[6] have also seen, for Sb_2^+ and Sb_3^+ projectiles at 30 keV/constituent, a mass dependence of the total Au sputter yield, though not as pronounced as in our case of Au^- SI emission.

In Fig. 4 we show the normalized yields of the com-

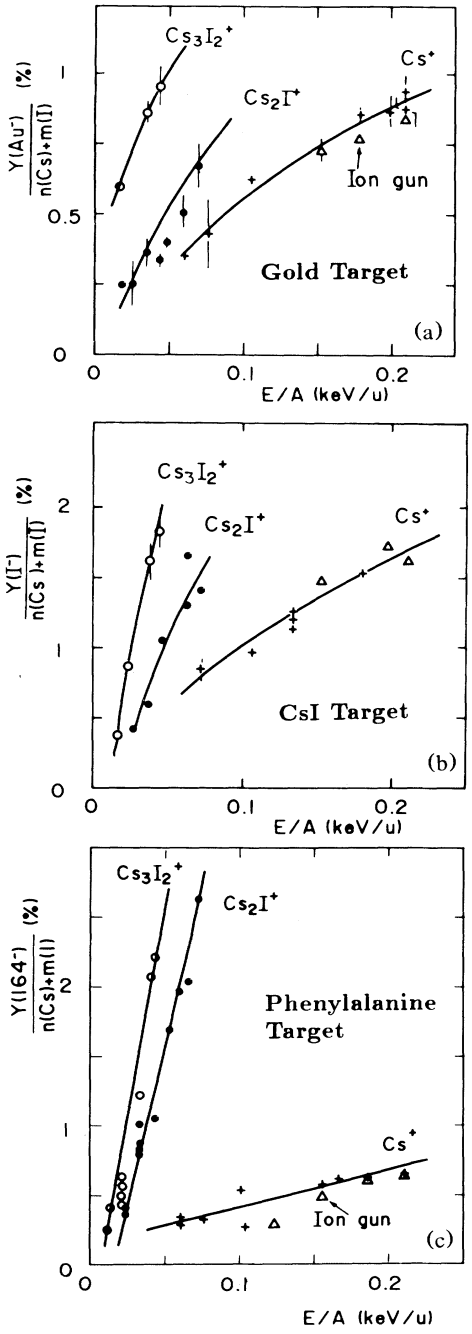

FIG. 3. Normalized secondary-ion yields as a function of primary-ion energy per mass unit. Primary ions are $(CsI)_mCs^+$, $m=0$, 1, and 2, and Cs^+ from a pulsed Cs-ion gun. Targets: (a) gold; (b) CsI; (c) phenylalanine.

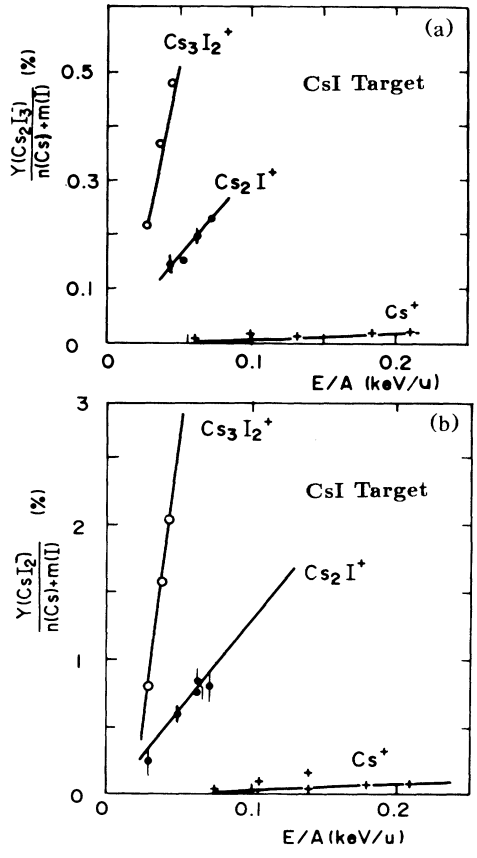

FIG. 4. Normalized yields of $(CsI)_nI^-$ clusters from a CsI target as a function of primary-ion energy per mass unit. Primary-ion source: CsI. Primary ions are $(CsI)_mCs^+$, $m=0$, 1, and 2. (a) $(CsI)_2I^-$; (b) $(CsI)I^-$.

plex secondary ions $Cs_2I_3^-$ [Fig. 4(a)] and CsI_2^- [Fig. 4(b)], using a Cs^+ projectile and the ionic cluster projectiles Cs_2I^+ and $Cs_3I_2^+$. Using the yield notation $Y\{\text{projectile, SI}\}$ we note that

$$\frac{Y\{(CsI)_m Cs^+, CsI_2^-\}}{Y\{(CsI)_m Cs^+, Cs_2I_3^-\}} = \text{const}$$

($m = 0$, 1, or 2) independent of the projectile velocity. This implies rather similar processes for the ejection of clusters whatever the projectile complexity.

A question which arises is whether the SI ionization efficiencies vary with the projectile complexity, i.e., whether, with cluster projectiles, the SI yield scales linearly with the total sputter yield. As mentioned above, enhancement effects have been observed for the emission of Au atoms by I_2^+ and by Sb_2^+ and Sb_3^+ projectiles.[6] The enhancement factor is $\simeq 1.5$ for the emission of neutrals compared to 2 for the emission of ions by Cs_2I^+ (however, the velocity regime in Ref. 6 was about half of that used in this study). A comparison of enhancement factors between neutral and SI emission by organic projectiles could not be made due to the lack of pertinent sputter-yield data for neutrals.

The data presented here demonstrate the high secondary-ion yields generated by surface bombardment with complex ions in the keV energy range. The largest yields occur from organic targets. Yield increases up to a factor of 50 have been observed when, for example, phenylalanine is bombarded with $Cs_3I_2^+$ instead of Cs^+. The results remain to be analyzed using a model applicable in the velocity regime concerned.[16,17] A discussion of any model will require a more comprehensive data set including secondary-electron yields, kinetic energy and angular distributions of the secondary ions, and information about the morphology of craters generated by cluster impact. Polyatomic clusters and molecules provide coherence in the bombardment of a surface by many atoms, and hence coherence in energy deposition: They allow the study of atomic collisions which are spatially and temporally correlated and under extreme conditions of temperature and pressure. In addition to the varied fundamental aspects which remain to be explored, we note that the high SI yields generated by complex ion bombardment could be attractive for surface characterization by secondary-ion mass spectrometry.

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