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Temperature effects in the sputtering of a molecular solid by energetic atomic and cluster projectiles

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Abstract

Temperature effects in the sputtering of an organic molecule were investigated by subjecting a well defined film of coronene to Au₁ and C₆₀ primary ions at 100 and 300 K. Strong field photoionization of the sputtered neutral flux was employed to monitor the change in flight time and kinetic energy distributions of intact and fragmented species.

Keywords

temperature effects; photoionization; C₆₀ sputtering; molecular solid; organic film

Introduction

Given all the benefits in using cluster ion beams for the analysis of various inorganic and organic molecules by means of surface mass spectrometry, some fundamental aspects involving the interaction of cluster ion beams and solid surfaces remain to be explored. For example, molecular depth profiles created using carbon cluster bombardment exhibit a strong dependence on temperature for unknown reasons.^[1] A molecular view has been provided by molecular dynamics (MD) simulations which have resulted in a valuable bank of knowledge concerning the removal of material induced by atomic and cluster ion beams. It is crucial that fundamental research concerning the desorption process of inorganic and organic material stimulated by cluster projectiles is performed to serve as an avenue in addressing such issues and to aid in optimizing the detection of intact molecules. Unfortunately, to date, not much experimental evidence exists that provides insight into the fundamentals of cluster ion beams interacting with molecular solids, in particular, for C₆₀.

In this paper, we investigate the effect of temperature on the desorption of intact organic molecules while irradiated by atomic and cluster projectiles. Temperature effects were investigated by directly comparing the flight time and kinetic energy distribution of material desorbed and photoionized from a well defined coronene (C₂₄H₁₂) film at 100 and 300 K as Au₁ and C₆₀ primary ions bombard the surface.

Experimental

The experiments were performed using a time-of-flight secondary ion mass spectrometry (ToF-SIMS) instrument equipped with a 40 keV C_{60} ion source, a 25 keV Au ion source, cryogenic cooling capabilities, and calcium fluoride windows permitting the integration of 1450 nm, 125 fs, 400 μ J, 1 kHz light generated by an optical parametric amplifier coupled to a titaniumsapphire femtosecond pump laser system, all described in detail elsewhere.^[2,3] Primary ions of Au₁ and C_{60} with kinetic energies of 20 keV were used to bombard thick organic films of coronene at an incidence angle of 45° with respect to the surface normal. The strong field photoionization of desorbed neutral species is accomplished with a focusing of 250 μ m in diameter which extends spatially 1 mm and is positioned to known height of 500 μ m above the organic film by means of an *x*, *y*, and *z* manipulator outside the vacuum. The experiments were conducted at 100 and 300 K. Liquid nitrogen was introduced into the sample stage cryogenic cooling lines and measured to reach a stable temperature of 100 K.

A thick organic film was prepared by physically vapor depositing $C_{24}H_{12}$ (Aldrich Chemical Co.) onto cold precut $5 \times 5 \times 0.5$ mm Si shards (Ted Pella Inc.) within a deposition chamber described in detail elsewhere.^[4] The film thickness was monitored by a quartz crystal microbalance and validated by atomic force microscopy (AFM; Nanopics 2100, TLA Tencor Inc.) to be in the order of 800–900 nm.

Results and Discussion

The kinetic energy distribution of desorbed neutral $C_{24}H_{12}$ molecules can be measured by varying the delay time τ between the 100 ns primary ion beam pulse and the 125 fs laser beam pulse. A flight time distribution is converted to kinetic energy distribution with the following criteria:^[5,6]

$$f(E) \propto \frac{s(\tau) \cdot \tau^2}{\Delta r + v \Delta t} \quad (1)$$

where $s(\tau)$ is the $C_{24}H_{12}$ signal intensity at delay time τ , $v r/\tau$ denotes the velocity selected by the particular choice of τ , Δr is the spatial extension of the laser beam in the direction along the surface normal, and Δt is the laser pulse width (125 fs). Note, $s(\tau)$ is determined from the integrated area of a mass peak of interest from the mass spectrum collected at a particular τ .

The resulting kinetic energy distribution of neutral $C_{24}H_{12}$ intact molecules from 20 keV Au₁ and C_{60} primary ions at 100 and 300 K are shown in Fig. 1a) and b), respectively. The distribution contains neutral intact molecules ejected from the organic film over a wide polar angle interval extending up to $\pm 30^\circ$. At 100 K, Au₁ primary ions eject $C_{24}H_{12}$ molecules with a most probable energy of 0.09 eV unlike C_{60} primary ions which eject molecules with a most probable energy of 0.51 eV. In addition, the contribution of the high energy tail (i.e. 1 to 5 eV) is enhanced when the film has been bombarded by C_{60} primary ions. The trends for the kinetic energy distribution at 100 K are consistent and well reproduced by MD simulations. For instance, simulations demonstrate benzene molecules are ejected with greater kinetic energy when C_{60} ions bombard thin overlayers of benzene onto a silver single crystal when compared to Ga ions.^[7] The difference is a reflection in the removal of benzene molecules by C_{60} ions as a process that is much more energetic. Although the simulations are for thin overlayers, this behavior has been observed experimentally in the kinetic energy distributions of molecular and fragment secondary ions.^[8] To our knowledge, this is the first experimental observation eliminating ionization effects by probing the neutral

molecules and corroborates the findings from simulations of organic systems under C₆₀ bombardment.

The kinetic energy distribution of sputtered C₂₄H₁₂ molecules at 300 K shows unexpected trends. The desorption of C₂₄H₁₂ molecules stimulated by either projectile are ejected with a most probable energy of approximately 0.08 eV and show slight differences in the high-energy component of the distribution. What is most striking is the shift to a lower most probable energy of ejection and the reduction of the high-energy component in the tail of the distribution when the film is bombarded by C₆₀ ions. The shift may be related to the increase in internal energy of the molecules as the temperature is increased altering the detection of intact molecules. For instance, at 300 K, the most probable energy can be associated to molecules that survive and reach the detector due to sufficiently low internal energy that is not conducive to fragmentation of the molecule. However, the high-energy tail of the distribution is diminished by the loss of intact molecules fragmenting from the increase of internal energy. Consequently, the shape and peak of the energy distribution is obscured.

The kinetic energy distribution of the intact molecule provides insights into the dynamics of the sputtering for both projectiles, but a more thorough understanding of the dynamics can be obtained by looking into the sputtered fragments as well. In the case of C₆₀ bombardment, flight time distributions for fragment C₆H₂ and the intact C₂₄H₁₂ molecule at 100 and 300 K are shown, respectively, in Fig. 2a) b). At 100 K, it is clear that both flight time distributions are indistinguishable from one another which might be caused by photofragmentation of the molecule. Another possibility is that the molecule and fragment have identical velocities. In contrast, at 300 K, the C₆H₂ flight time distribution is noticeably different when compared to the flight time distribution for C₂₄H₁₂. Given the sputtering dynamics should not change with temperature, the flight time distribution for the fragment at 300 K suggest it might possibly be comprised of two populations: one reflecting the sputtered fragment and the other sensitive to a temperature of 300 K. As shown in Fig. 3, a flight time distribution of temperature-sensitive C₆H₂ fragments can be approximated by taking the difference between the 300 and 100 K distributions and fitted by the time-density Maxwell-Boltzmann distribution^[9]

$$I(\tau) = C\tau^{-4} \exp\left(-md^2/2kT\tau^2\right) \quad (2)$$

where I is the signal intensity at time delay τ , m is the mass of the desorbed species, d is the distance from the surface to the laser plane, τ is the delay between the primary ion pulse and laser pulse, k is the Boltzmann constant, C is a proportionality constant, and the fitting parameter T is the translational temperature of the desorbed species. It is clear that a temperature of 493 K fits reasonably the 300 K flight time distribution for the C₆H₂ fragment. This would imply when C₆₀ ions irradiate the surface of the C₂₄H₁₂ organic film, an evaporative mechanism of low-mass fragments occurs which are released at 300 K. It is believed these fragments are created by the cracking of the intact C₂₄H₁₂ molecule within the center of the crater induced by the C₆₀ projectile. Recent MD simulations have shown the center of the crater to be a localized region of fragmentation either due to dissociation or reactions with other molecules or atoms from the C₆₀ cluster.^[10] It is quite possible that within this region there exists localized heating due to vibrational and rotational excitation of the molecules and exothermic reactions. The low thermal conductivity of the organic film could prevent dissipation of the heat, resulting in the evaporation of loosely bound fragments, such as C₆H₂, that exhibit a Maxwell-Boltzmann distribution. To our knowledge, this is the first time that such behavior has been documented for C₆₀ primary ions bombarding an organic film. This behavior has not yet been observed when using Au₁ primary ions.

Conclusion

The overall goal of this research is to bring forth experimental evidence that highlights temperature effects in the sputtering of an organic film subjected to the bombardment of atomic and cluster primary ions. It was demonstrated that the dynamics in the removal of organic molecules by C₆₀ primary ions results in the emission of molecules with the greatest translational energy at 100 K. Raising the temperature to 300 K was shown to alter the detection of intact molecules which might be associated to elevated internal energies conducive to fragmentation. Sputtered fragments induced by C₆₀ ions were identified to exhibit an evaporation-like mechanism only present at 300 K but quenched at 100 K.

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Figure 1. The kinetic energy distribution of intact neutral coronene ($C_{24}H_{12}$) molecules desorbed by 20 keV Au_1 and C_{60} primary ions at a) 100 K, and b) 300 K.

Figure 2. The flight time distribution for the C_6H_2 fragment and $C_{24}H_{12}$ desorbed by 20 keV C_{60} primary ions at a) 100 K, and b) 300 K.

Figure 3. The flight time distribution for temperature sensitive C₆H₂ fragments desorbed by 20 keV C₆₀ primary ions at 300 K fitted by the time-density Maxwell-Boltzmann distribution with a temperature of 493 K.