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Sputtering of Ag under C_{60}^+ and Ga^+ projectile bombardment

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Abstract

Cluster ion bombardment often results in large secondary ion yield enhancements relative to atomic ion bombardment. The yields of neutral particles and secondary ions sputtered from a silver surface were investigated through experiments and molecular dynamics (MD) computer simulations. The results show that the neutral Ag yield produced by 15 keV C_{60}^+ bombardment is 5.6-fold higher than that found for 15 keV Ga^+ bombardment, which is in agreement with simulations. The enhancement effect is observed to be about the same for both neutral species and their corresponding secondary ions. Experimental results also indicate that the Ag neutral species produced by C_{60}^+ bombardment have emission velocity distributions that maximize at much lower values than those observed by Ga^+ bombardment, suggesting the presence of non-linear collision cascades.

Keywords: Cluster beam; C_{60}; Postionization; Sputter yield; Kinetic energy distribution

1. Introduction

Recent SIMS studies with a novel buckminsterfullerene (C_{60}) cluster beam source suggest molecular ion intensities can be increased by several orders of magnitude when compared to atomic bombardment experiments [1], and that desorption of organic molecules induced by this source is often more efficient than the more traditional cluster sources such as SF_5 [2]. Here we present a preliminary investigation into the mechanism behind this enhancement using Ag as a model system. Predictions from molecular dynamics (MD) computer simulations are utilized to establish the efficacy of the theoretical model for this projectile, and to provide atomic level insight into the important desorption mechanisms. Results show that the yield of both neutral and ionic Ag, Ag_2 and Ag_3 are enhanced by about the same amount when comparing 15 keV C_{60}^+ ion bombardment to 15 keV Ga^+ ion bombardment. The measured relative yields of all the neutral species are in reasonable agreement with calculation. Moreover, the kinetic energy distribution of Ag atoms is observed and calculated to peak at an anomalously low value, indicating the presence of non-linear collision cascades [3,4]. In general, we suggest that the MD approach will be valuable in understanding how these types of large clusters produce SIMS spectra with vastly improved information content.

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2. Experimental

The TOF-SIMS spectrometer is similar to that described previously [5], except it has been modified to accommodate both a Ga^+ ion source and a C_{60}^+ ion source. The C_{60}^+ ions are produced by vaporizing the C_{60} powder and ionising by electron impact [2]. The source can produce singly and multiply charged C_{60} ions and the ratio of C_{60}^+ to C_{60}^{++} can be varied by changing the electron impact energy. For all experiments reported here, an impact energy of 30 eV was employed which is appropriate for the production of only C_{60}^+ ions.

Postionization of neutral species is accomplished using a previously described Ti:sapphire femtosecond laser system [6]. Briefly, an Ar^+ ion laser is used to pump the Ti:sapphire oscillator and produce 800 nm laser pulses with 50 fs pulse width and 300 nJ per pulse energy. The output pulses are amplified to reach 3.5 mJ/per pulse energy at a 1 kHz repetition rate. The laser beam is coupled into the mass spectrometer 1 mm above the sample surface with a CaF_2 lens which has a 25 cm focal length. After focusing to a laser spot of about 570 μm in diameter, the peak laser power density reaches 5.4×10^{12} W/cm^2. The beam position can be controlled by an x, y and z manipulator outside the vacuum.

The Ag sample (Aldrich) was etched with 30% (v/v) HNO_3 for 30 s, then rinsed with water and methanol and allowed to dry in air. In order to achieve reproducible yields and kinetic energy distributions, the surface was bombarded using C_{60}^+ ions until all of the peaks in the mass spectrum reached a steady state value, usually after a dose of 10^{15} to 10^{16} ions/cm^2.

3. Results and discussion

Laser postionization mass spectra of Ag bombarded with 15 keV Ga^+ and 15 keV C_{60}^+ ions are shown in Fig. 1. In order to compare the partial sputtering yields of the different ejected species, the spectra have been normalized to the current of the respective primary ion source. In both cases, C, Ag, Ag_2 and Ag_3 are readily observed. The low mass peaks except the C signal exist without primary ion beam bombardment, therefore, they originate from laser photoionization of residual gas components and are therefore

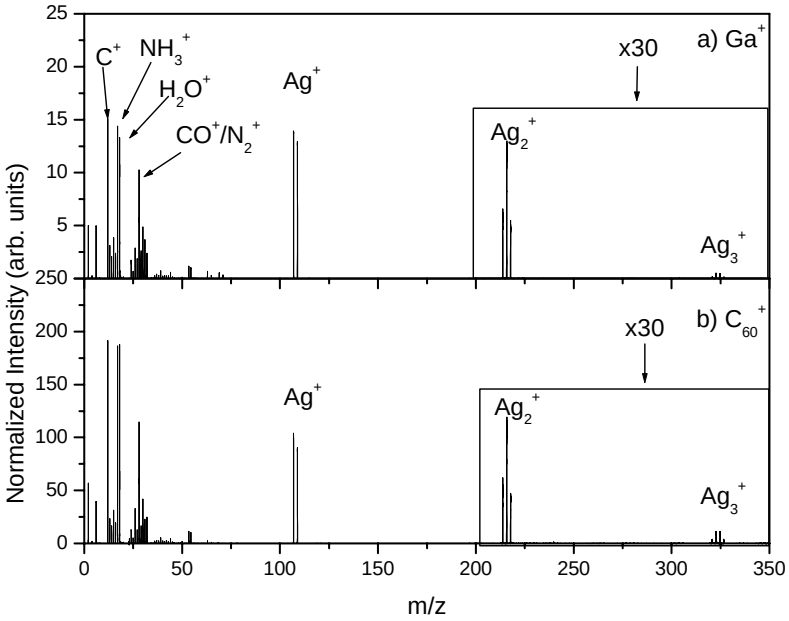

Fig. 1. Ag postionization spectra of (a) 15 keV Ga^+ sputtering (b) 15 keV C_{60}^+ sputtering. The C^+ intensity arises primary from atomic carbon resulting from C_{60} implantation.

Table 1
Ag_n ion and neutral relative yields due to C_{60}^+ and Ga^+ bombardment

	Enhancement factor (Y_{C60}^+/Y_{Ga}^+)		
	Ag	Ag_2	Ag_3
Experiment (45° incidence)			
SIMS	3.7	12.5	25
Laser Postionization	5.6	9.1	23.5
MD Simulation (normal incidence)	7	25	35

The calculated yield of Ag is 327.1.

independent of the primary ion beam. The relatively high C signal results from the fact that the surface has been pre-bombarded with a high dose of C_{60}^+ ions prior to the spectra acquisition. The Ag cluster yields decrease by roughly one order of magnitude with incorporation of each additional Ag atom, in agreement with previous observations [7]. It is obvious that C_{60}^+ ion bombardment results in a much higher overall yield than Ga^+ bombardment at the same kinetic energy.

In order to compare the neutral Ag_n relative yields produced by Ga^+ and C_{60}^+ ions, the peak area from each individual Ag cluster ion is integrated, and the ratio of the peak areas obtained with both projectiles are listed in Table 1 as enhancement factors. For example, for Ag^+ resulting from laser postionization, the total peak area of Ag_{107}^+ and Ag_{109}^+ is integrated and reported as Y_{C60}^+ and Y_{Ga}^+ depending upon the primary ion beam used. The secondary ion yields are also compared between C_{60}^+ and Ga^+ bombardment in Table 1 and are calculated in an identical fashion.

Molecular dynamics simulations were also carried out for bombardment of Ag{111} with C_{60} and Ga projectiles at 15 keV. Details of this simulation have been described elsewhere [8]. Briefly, a total of 300 trajectories were calculated for Ga and 83 trajectories were calculated for C_{60} using a crystallite containing 166,530 atoms. The average number of ejected Ag_n particles is recorded for Ga and C_{60} bombardment and the resulting enhancement factors are listed in Table 1. Fragmentation of internally excited Ag_2 and Ag_3 clusters has been considered in the simulation. The simulations show values that are generally in agreement with experiment. The small difference arises in part due to the fact that the simulations were performed at normal incidence, whereas the experiments were performed at an incidence angle of 45° with respect to the surface normal. The MD simulations predict that sputtering yields decrease when the incidence angle changes from 0° to 45° for C_{60}, but increase for Ga. Therefore, the enhancement factors should be lower for off-normal angles. Detailed calculations are underway to more clearly elucidate this point. In any case, the results suggest that the effects observed for secondary ions have their origin in the sputtering of neutral species. It is interesting that Fuoco et al. report a 2× enhancement in the sputter yields for PPMA under SF_5 bombardment but a 10-fold enhancement for the secondary ion yield when compared to Ar^+ ion bombardment [9]. Wucher and coworkers also report that SF_5^+ bombardment increase the number of secondary ions more than corresponding number of neutral species [10]. It is possible that the presence of the fluorine atoms in the SF_5^+ cluster contribute to the ionization enhancement, but more experiments would be needed to establish this point.

The kinetic energy of Ag and Ag_2 neutral species can be measured by varying the delay time τ between the primary ion beam and the laser beam. Flight time distributions are converted to kinetic energy distributions with the following relation [11]:

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

where $s(\tau)$ is the Ag_n signal intensity at delay time τ (ns), r denotes the distance between the sample surface and the laser ionization volume which is determined to be 1 mm in current experiment, Δr is the spatial extension of the laser beam in the direction along the surface normal (570 μm) and Δt is the laser pulse width (100 fs).

The resulting kinetic energy distributions of neutral Ag and Ag_2 from 15 keV Ga^+ bombardment and 15 keV C_{60}^+ bombardment are shown in Fig. 2. The distribution contains the neutral species desorbing from the target over a wide polar angle interval extending up to ±30°. The Ag atoms sputtered by 15 keV C_{60}^+ ions exhibit a most probable energy (energy at maximum) of 0.8 ± 0.1 eV, compared to 1.9 ± 0.4 eV for bombardment by 15 keV Ga^+ ions. This trend is well reproduced by the MD simulations for normal incidence bombardment [12]. The

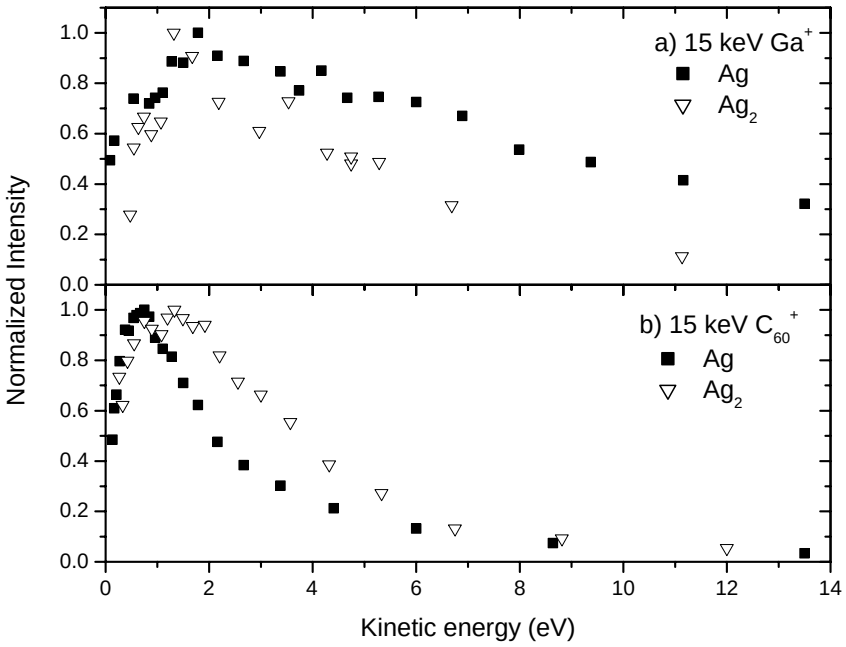

Fig. 2. The kinetic energy distributions of neutral Ag and Ag_2 produced by (a) 15 keV Ga^+ bombardment and (b) 15 keV $C_{60}{}^+$ bombardment.

observed shift to lower kinetic energies with cluster impact has been reported earlier [3,4], and is suggested to be a result of non-linear collision cascades. The mechanisms associated with C_{60} bombardment may well be quite different as suggested by graphical pictures of the impact event [8]. Of special interest is that the most probable kinetic energy of Ag_2 for both experiment and calculation (not shown) are larger than for the monomer. This trend is opposite from that found for atomic bombardment, and the mechanism behind this effect is currently unknown. From a visual inspection of the simulation results [8], one might speculate that the emission mechanism under cluster impact may resemble an adiabatic expansion from a superheated volume rather than a typical collision cascade. In that case, all particles would leave the surface with similar velocities, thus leading to larger kinetic energies of heavier ejectees.

Acknowledgements

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