Transactions of the Materials Research Society of Japan 28 [2] 481-484 (2003)

Secondary Ion Emission From Fullerene Films Bombarded by Fast Heavy Ions

Akio Itoh and Akifumi Yogo*
Quantum Science and Engineering Center, Kyoto University, Kyoto 606-8501, Japan
Fax: 81-75-753-5828, e-mail: itoh@nucleng.kyoto-u.ac.jp
*Department of Nuclear Engineering, Kyoto University, Kyoto 606-8501, Japan
Fax: 81-75-753-5828, e-mail: yogo@ nucleng.kyoto-u.ac.jp

Electronic sputtering of C60 thin films bombarded by 4 MeV Si^{3+} ions was investigated by means of a time-of-flight coincidence method. A variety of fullerene like secondary ions were observed strongly such as $C_{60\pm2n}{}^+$ and multiples of C_{60} ($C_{120}{}^+$, $C_{180}{}^+$). In order to elucidate the origin of these fullerene like ions, we have measured the energy and angular distributions of the emitted ions. It is found that the angular distribution varies strongly depending on the initial emission energy and are asymmetric with respect to the surface normal direction. The present result may be interpreted within the framework of the pressure pulse model developed in high impact energy region.

Key words: Secondary Ions, C60, Fullerene, Electronic

1. INTRODUCTION

Sputtering, or the emission of secondary particles from a solid surface bombarded by energetic particles is one of the most fundamental collision phenomena and has received a great deal of attention in the past. Mechanisms leading to the sputtering of target materials are primarily governed by the projectile velocity and can be, in general, divided into three regimes; single knock-on, linear cascade, and spike regime [1]. In collisions of fast heavy ions (spike regime) with velocities exceeding the Bohr velocity, ionization and excitation of target atoms are the predominant energy loss processes of projectile ions inside a solid, and hence the emission of secondary particles is referred to as electronic sputtering. To date, various theoretical models have been attempted to account for experimental results over a wide range of projectile velocity as reviewed by Johnson and Schou [2] and references therein. Nevertheless, little is known about emission mechanisms of secondary ions in the electronic sputtering regime. In particular, information is rather limited about emission energy and angular distributions of secondary ions which are thought to be produced via a combined mechanism between sputtering of neutrals and ionization near the solid surface [3].

Using various C60-containing film targets, Sundqvist and his coworkers have made pioneering work on the velocity distribution of secondary ions [4,5]. They employed a reflectron-type time-of-flight (TOF) spectrometer to obtain high-resolution data of radial velocity distributions and found asymmetric ion emission with respect to the surface normal. It is, however, important to know also axial velocity distributions of ions in order to achieve a better understanding of the emission mechanism. In the present work, we carried out measurements of secondary ions emitted from a thin C60 film by using a single-stage TOF spectrometer in conjunction with an emission-angle selection aperture. With the aid of simulation calculations of secondary ion trajectories, emission energy and angular distributions have been successfully obtained.

2. EXPERIMENTAL

A beam of 4 MeV Si^{3+} ions provided from a 1.7 MV tandem accelerator was well collimated to smaller than 1 mm in diameter and chopped with an electrostatic deflector before entering a collision chamber. The pulsed beam was achieved with a high-voltage pulse generator operated with 30ns in width and 10 kHz frequency. A trigger pulse from the pulse generator was used as the start pulse of the TOF coincidence measurement. A C60 film target of 200nm in thickness was prepared by vacuum sublimation of high purity powder on a Si(111) substrate at a temperature of 450°C and at a pressure below 1×10^{-5} Pa. A schematic sketch of our TOF spectrometer is shown in Fig. 1 [6]. The projectile beam impinges the target with an angle of 45degrees with respect to the surface normal (X-axis). The target was biased to +1kV and secondary ions were accelerated to the X-direction by the electric field between the target and a grounded mesh. Inside a drift tube we placed an electric deflector and an angle-selection aperture in order to make such ions pass through the aperture that were emitted into only limited angles. The aperture size used here were 1~4mm in Y-direction and 10mm in Z-direction as shown in the figure. Secondary ions were detected by a channel electron multiplier of which entrance part was biased to -4kV. By performing simulation calculations of flight trajectories of ions and fitting to TOF spectra measured, emission energy as well as angular distributions were deduced.

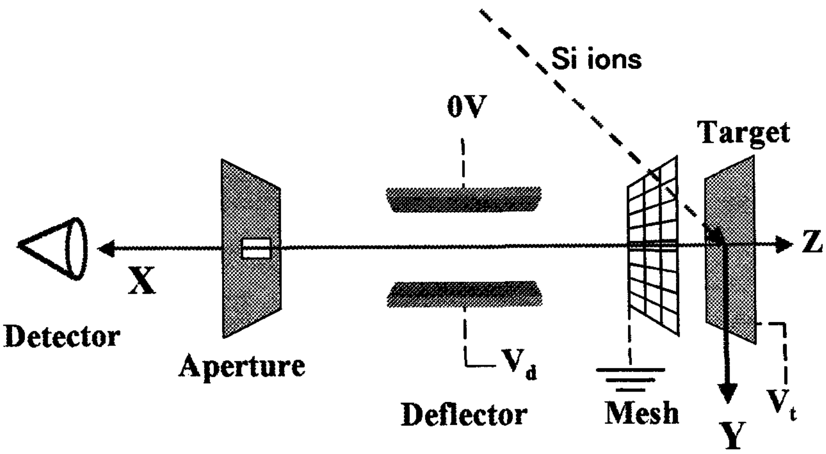

Fig. 1. A sketch of the TOF spectrometer

3. RESULTS AND DISCUSSION

Fig. 2 shows a time-of-flight mass distribution of secondary positive ions emitted from a C_{60} film. Various distinctive peaks appearing around a main peak of C_{60}^+ are attributed to C_{60-2n}^+ ions produced from C_{2n}-loss from parent C_{60} molecules and to C_{60+2n}^+ ions produced from addition of C_{2n} to C_{60}. The former so-called fragment daughter ions are commonly observed in experiments using a gas phase C_{60} target [7], and they are considered as products via evaporation processes of internally excited C_{60}^+ ions. By contrast, secondary ions like C_{60+2n}^+, heavier than C_{60}, have never been observed in gas target experiments. Thus, the present result indicates evidently a solid effect responsible for the production of these heavier fullerene-like ions. Namely, these ions are supposed to be produced via a recombination process taking place near the surface, in which C_{60}^+ ions combines with free C_{2n} molecules produced in highly excited tack zone along projectile ion trajectories. This recombination effect may also be proved by the presence of C_{60}-multiples such as C_{120}^+ and C_{180}^+ observed in the longer time-of-flight region. These multiples may be interpreted as a result of recombination of two or three C_{60} molecules. Note that broad peak profile of these multiples indicates that many neighboring cluster ions are also produced. Unfortunately, these peaks are unresolved with our spectrometer.

By placing appropriate voltage (V_d) on the deflector inside the spectrometer in conjunction with the angle-selection small aperture, only limited secondary ions whose flight trajectory satisfies the present geometrical condition can be measured selectively. Note that data shown in Fig.2 were taken with V_d =0 with a wide aperture size. Hence, intensity distribution of mass spectra is expected to change rather strongly, since the initial kinetic energy and emission angle may de different for different ions. The measurement of TOF spectra was carried out for deflection voltage between -100V and +100V. Examples are shown in Fig. 3. Note that spectral intensity vanished nearly completely beyond | V_d |>60V.

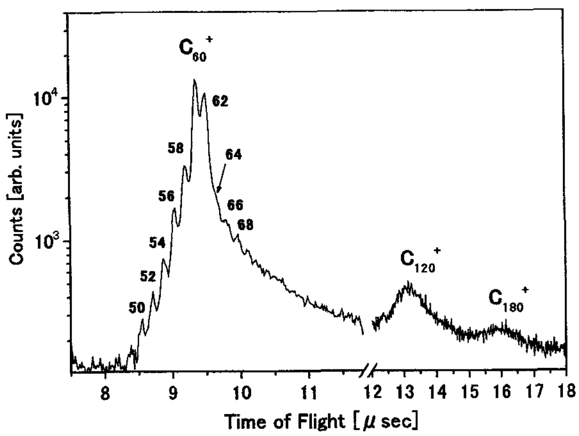

Fig.2. TOF spectrum from a C60 film.

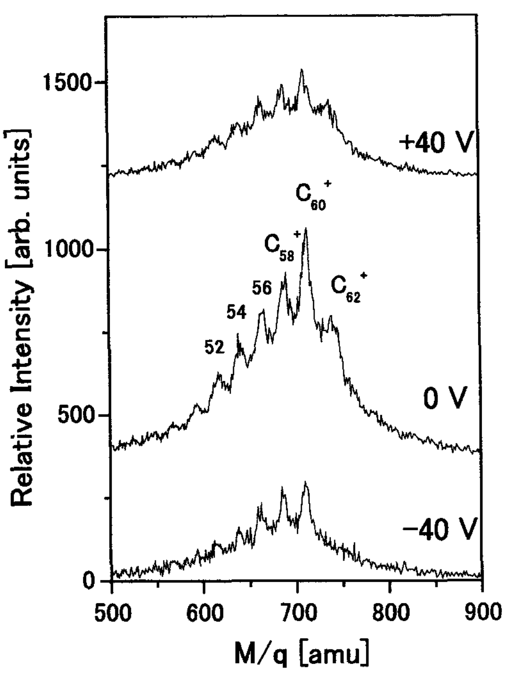

Fig.3. TOF spectra obtained at deflection voltages of 0, ±40V.

Characteristic features of the results are given as follows. First, the relative intensity of C_{60-2n}^+, with respect to C_{60}^+, changes drastically for different V_d. Second, all the fullerene-like fragment ions C_{60-2n}^+, C_{60}^+ and C_{62}^+ reveal asymmetric intensity distribution with respect to V_d=0, implying angular-asymmetric emission with respect to the surface normal. Third, compared to C_{60-2n}^+ (n=0,1,2...) ions, the peak intensity of C_{62}^+ decreases considerably faster for negative values of V_d than positive values. It implies evidently that the angular distribution of C_{62}^+ is more asymmetric in comparison with other C_{60-2n}^+ (n≧0) ions.

We performed simulation calculations of the flight trajectory of ions at various initial energies ε, and the transmission efficiency was calculated as a function of the emission angle θ at each value of ε. Fitting the experimental peak profile to these calculated values, the angular distribution at a fixed ε was deduced. The energy range calculated was from 0 to 24eV. For ε > 24eV, line overlapping with neighboring peaks prevented us from achieving accurate fitting. Note, however, that contributions from higher energies are estimated to be negligibly small. Fig. 4 shows the angular distribution obtained for C_{60}^+ (open circle) and C_{62}^+ (closed circle). The upper and lower parts of Fig. 4 are the distributions summed over ε from 0 to 10eV and from 10 to 24eV, respectively. Here, the direction (X) of angle 0 degrees is the surface normal and Y represents the surface plane, and the incident beam impacts the surface at 45 degrees. To make a better understanding of asymmetric angular distributions, we plotted two reference curves of cos θ and $\cos^3\theta$ by dashed and solid lines, respectively. The cosine like angular distribution of the form of $\cos^n\theta$ is generally recognized sputtering formula predicted

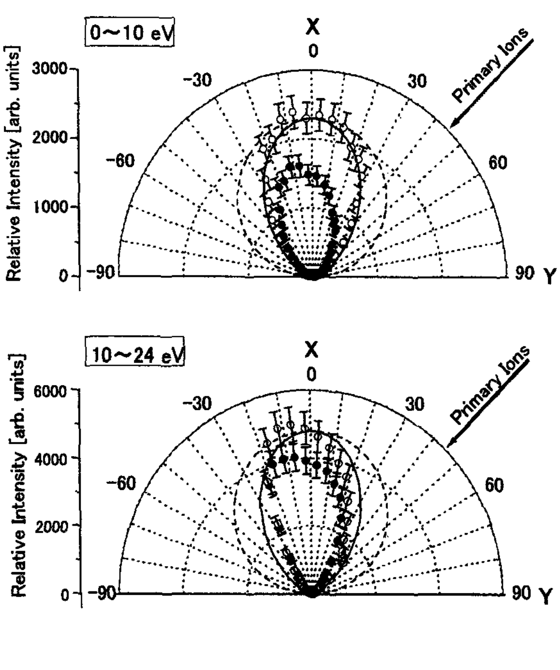

Fig. 4. Angular distributions of C_{60}^+ (○) and C_{62}^+ (●) with curves of cos θ (dashed line) and $\cos^3\theta$ (solid line).

by linear cascade models and the power n is typically between 1 and 2 [3]. The present results for C_{60}^+ seem to be well expressed by this distribution but with n =3 as shown in the figure. It is noted that the angular distribution varies somewhat strongly according to the initial energy ε and reveals preferential emission into the surface normal direction with increasing ε. A close inspection of Fig.4 shows this tendency. Namely, the power n for higher energy ions (lower part of Fig. 4) is obviously larger than that for low energy ions. Also, the degree of asymmetry is enhanced for higher ε. As for C_{62}^+, the degree of asymmetry is more prominent compared to C_{60}^+. Johnson et al [8] predicted characteristic emission angles, given by the following formula, from the pressure-pulse model.

$$\theta^{\pm} = \frac{\theta_{\rm inc}}{2} \pm \frac{\pi}{4}$$

Here, $\theta_{\rm inc}$ is the incident beam angle. In the present case, emission angles of 68° and -23° are obtained from this formula, which are different from our experimental mean value of -5±5°. However, if we bear in mind the fact that the theoretical model is valid for neutral particle emission, it may be stated reasonably that the present result has the similar tendency to this prediction. Production of charged particles may require an ionization process of neutrals near the surface close to ion track core created by the incident beam. Emission of charged particles then needs a driving force to leave the surface. In order to explain our result, we suppose that the driving force parallel to the normal direction may be predominant, resulting in a smaller average emission angle observed experimentally.

Kinetic energy distributions of C_{60}^+ and C_{62}^+ ions were found to have peak maxima at about 6 eV and 14 eV, respectively. It suggests evidently that the production mechanism of these fullerene-like ions is different from each other. At present we are performing more detailed analysis about the present experimental results.

4. CONCLUSIONS

Secondary ions from thin C60 films were measured using 4 MeV Si^{3+} incident ions. Various fullerene-like ions of $C_{60\pm2n}^+$ and C_{60}-multiples (C_{120}^+, C_{180}^+) were produced strongly. In particular, ions with mass heavier than C_{60} have never been observed so far in similar experiments but using a gas-phase C_{60} target, where only fragment ions (C_n^+, n≦60) are produced. The difference between solid and gas-phase targets suggests obviously the different production mechanisms in both cases. As one of the possible mechanisms, present results indicate the presence of recombination processes, occurring most probably near a surface, combining chemically two or more freed particles of C_{60} and C_{2n}. This is because the chance of chemical reaction between these particles is much higher in a solid target than a gas-phase target composed of single C_{60} molecules.

By placing an emission-angle selection aperture inside our TOF spectrometer, emission energy and angular distributions were obtained for individual secondary ions.

Angular-asymmetric emission with respect to the surface normal was clearly observed for most fullerene-like ions. We found that the angular distribution of C_{60}^+ is approximately cosine-like with a power of probably larger than 3, although a slight asymmetry exists. As for C_{62}^+ ions, the angular distribution was found to have a mean emission angle of about $-5 \pm 5°$. The present result can qualitatively be interpreted within the framework of the pressure-pulse model [8] developed in fast heavy ion collisions. Finally, it is interesting to note that the mean kinetic energy of C_{62}^+ was found to be about twice as large as that of C_{60}^+ ions.

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(Received December 21, 2002; Accepted March 26, 2003)