On the surface mapping using individual cluster impacts

F.A. Fernandez-Lima a,⇑, M.J. Eller a, J.D. DeBorda a, S.V. Verkhoturov a, S. Della-Negra b, E.A. Schweikert a

a Department of Chemistry, Texas A&M University, College Station, TX 77940-3012, United States
b Institut de Physique Nucléaire d’Orsay, Université Paris-Sud 11, CNRS/IN2P3, F-91406 Orsay, France

Abstract

This paper describes the advantages of using single impacts of large cluster projectiles (e.g., C60 and Au400) for surface mapping and characterization. The analysis of co-emitted time-resolved photon spectra, electron distributions and characteristic secondary ions shows that they can be used as surface fingerprints for target composition, morphology and structure. Photon, electron and secondary ion emission increases with the projectile cluster size and energy. The observed, high abundant secondary ion emission makes cluster projectiles good candidates for surface mapping of atomic and fragment ions (e.g., yield >1 per nominal mass) and molecular ions (e.g., few tens of percent in the 500 < m/z < 1500 range).

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The performance of SIMS for molecular analysis has been notably enhanced with large cluster projectiles, e.g., C60 and Au400 [1–3]. However for surface imaging purposes, the use of cluster beams has some disadvantages when compared to mono-atomic and poly-atomic beams (e.g., Cs, Au1–3, Bi1–3, etc.). For example, a C60 beam is constrained by limitations in source brightness; in the case of massive clusters, e.g. Au400, from liquid metal ion sources (Au-LMIS), their energy and angular emission are incompatible with tight focusing. In the present paper, we describe the potentialities of surface mapping by using spatially and temporally isolated events of individual projectile impacts for the case of C60 or Au400 projectiles. In particular, we present their advantage for surface molecule characterization, via electron emission microscopy (EEM), combined with the detection of secondary ions, SIs, and of photons emitted from a single cluster impact.

An experimental setup that comprises a cluster primary ion beam, an electron emission microscope, a photon detector and a ToF mass spectrometer was used for this study (Fig. 1). Two primary ion beams were used: (i) massive gold projectiles (e.g., Au400) from a Au-LMIS installed in a100 kV Pegasus Platform and (ii) C60+ from a 15 kV in-house-built effusion source [4,5]. The primary ion projectiles are massselected using a Wien filter and focused into the analysis chamber. To achieve the single event analysis mode, the primary ions were pulsed and/or collimated so that experiments were performed at <500 Hz. Emitted photons, electrons and secondary ions were collected per projectile impact. A photomultiplier (PMT, R4220P model from Hamamatsu Photonics), with an active window from 185 to 710 nm and a maximum 22% detection efficiency at 410 nm, was positioned behind the target for photon detection. Electrons emitted per impact were accelerated and then deflected using a weak magnetic field toward an electron emission microscope. Electron images were recorded per projectile impact using a position sensitive detector/fast digital camera, and after processing the images the x–y coordinates of the impact were determined [6]. The secondary ions were detected using a microchannel-plate based multi-anode detector and were stored on a multi-channel time-to-digital converter (TDC). Materials for neat targets were obtained from Sigma Aldrich (St. Louis, MO). Surface target homogeneity was achieved by applying and then deflecting using a weak magnetic field toward an electron emission microscope. Electron images were recorded per projectile impact using a position sensitive detector/fast digital camera, and after processing the images the x–y coordinates of the impact were determined [6]. The secondary ions were detected using a microchannel-plate based multi-anode detector and were stored on a multi-channel time-to-digital converter (TDC). Materials for neat targets were obtained from Sigma Aldrich (St. Louis, MO). A sagittal rat brain section was used for secondary ion yield comparison purposes (courtesy of Dr. Ami

Corresponding author.
E-mail address: ff.fernandez@chem.tamu.edu (F.A. Fernandez-Lima).

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case of a CsI/ITO target. In the case of C₆₀, we attribute the two fast components to the hollow nature of the projectile, which dissociates after penetrating a few layers and induces collision cascades involving projectile constituents and surface atom targets. A single component, fast photon emission is observed under massive gold projectile impacts associated with the projectile coherent motion. For the cases studied to date, the photon emission is target specific and increases with the projectile energy.

Multiple electron emissions are observed from a single impact, which enables the determination of the x–y coordinates of the impact site. Electron emission depends on the target composition, morphology and structure. For example, we have recently shown that the number of electrons emitted per C₆₀ impact increases from organics to semiconductors to metals to ionic salts [5]. Moreover, we have also observed differences in the number of electrons from targets of similar composition (e.g., between bulk Al oxide, 50 nm Al oxide particles and 2 nm Al bohemite whiskers) and from single layer vs multi-layer nano-structures [10]. The cluster size and energy also affect the number of electrons emitted. As an example, electron distributions from a Glycine target bombarded by individual C₆₀ and Au₄₀₀ cluster projectiles are shown in Fig. 3. The electron distributions follow a Poisson distribution, analogous to those observed from atomic ion bombardment [11,12]. A significant feature is that in the case of C₆₀ and Au₄₀₀ cluster bombardment, electron emission is observed where kinetic electron emission from comparable velocity atomic projectiles does not occur [13,14]. Moreover, due to C₆₀ and Au₄₀₀ charge states (q = 1, 2 and q = 1–4, respectively), the phenomenon cannot be attributed to potential electron emission mechanism. That is, the unexpected electron emission under individual cluster bombardment is related to a collective effect during the projectile impact. Our results suggest that electronic excitations at the impact site are responsible for the coincidental electron and photon emission, both being characteristic of the target.

The unique feature of positional mass spectrometry is the ability to identify ions co-emitted from a single projectile impact. This
information is spatially resolved in the size of the area of co-emission. As an example, total secondary ion and specific ion maps are shown in Fig. 4 for a CsI coated 400 mesh grid. An important feature of surface mapping is that the number of secondary ion per impact has to be significant. For the case of atomic and poly-atomic ions, due to lower secondary ion yields, this approach is mainly limited to low mass secondary ions (e.g., atomic ions and small fragments). Nevertheless, due to the high desorption yields observed with cluster ions, surface mapping of molecular ions can be attainable from single impacts and from undamaged areas.

A comparison of secondary ion yields from model and native biological targets can be found in Table 1 for: (i) 50 keV Au$_{3}^{+}$ (equivalent to commercially available 50 keV Bi$_{3}^{+}$), (ii) Cs$_{60}$ and (iii) massive Au$_{400}^{+4}$ projectiles. As a general trend, higher secondary ion emission and reduced fragmentation are observed for Cs$_{60}$ and Au$_{400}^{+4}$ relative to Au$_{3}^{+}$ projectiles. Previous studies have shown that for small gold cluster projectiles (e.g., Au$_{3}^{+}$), the secondary ion emission from organic samples reaches a maximum around 30–40 keV/atom [15]. The analysis of native biological samples shows that 130 keV Au$_{3}^{+}$ secondary ion yields are one and two orders lower when compared to 130 keV Au$_{3}^{+}$ and 520 keV Au$_{400}^{+4}$, respectively. A similar trend has been observed for biomolecular solids [16]. In the case of cluster projectiles, Cs$_{60}$, we have previously shown that the secondary ion yield increases with the projectile energy (15–43 keV) [8]. For massive 300–520 keV Au$_{400}^{+4}$ projectiles, multiple atomic and small fragment ions are observed per projectile impact (yield > 1 per nominal mass); moreover, molecular ion yields of few tens of percent are obtained from model targets (single component) and few percents from native biological surfaces in the 500 < m/z < 1500 mass range [17].

These results show the advantage of individual cluster impacts for surface characterization in comparison with atomic and polyatomic beam techniques. The event-by-event bombardment-detection localization mode offers as a unique feature the combined characterization of a target surface using co-emitted photons, electrons and secondary ions; this information can later be

### Table 1

<table>
<thead>
<tr>
<th>Target</th>
<th>m/z</th>
<th>Au$_{50}^{+}$ 50 keV</th>
<th>Cs$_{60}^{+}$ 43 keV</th>
<th>Au$_{400}^{+}$ 520 keV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_{60}$ target</td>
<td>127</td>
<td>3.84E–01</td>
<td>6.56E–01</td>
<td>14.59</td>
</tr>
<tr>
<td>Cs$_{60}$ target</td>
<td>387</td>
<td>1.61E–01</td>
<td>7.35E–01</td>
<td>12.54</td>
</tr>
<tr>
<td><strong>Model biological surfaces</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycine CN$^-$</td>
<td>26</td>
<td>1.08E–01</td>
<td>2.12E–01</td>
<td>4.55</td>
</tr>
<tr>
<td>Glycine M$^-$</td>
<td>75</td>
<td>8.87E–01</td>
<td>4.57E–01</td>
<td>3.04</td>
</tr>
<tr>
<td>PG18:0–18:1 PO$_{3}^{+}$</td>
<td>79</td>
<td>1.56E–01</td>
<td>2.75E–01</td>
<td>4.08</td>
</tr>
<tr>
<td>PG18:0–18:1 M$^+$</td>
<td>775</td>
<td>5.23E–03</td>
<td>3.14E–02</td>
<td>2.53E–01</td>
</tr>
<tr>
<td>YGGFL CN$^-$</td>
<td>26</td>
<td>6.64E–02</td>
<td>4.08E–01</td>
<td>5.26</td>
</tr>
<tr>
<td>YGGFL M$^+$</td>
<td>554</td>
<td>1.08E–02</td>
<td>7.55E–03</td>
<td>5.74E–01</td>
</tr>
<tr>
<td>Ang III CN$^-$</td>
<td>26</td>
<td>7.85E–02</td>
<td>1.32–E</td>
<td>4.59</td>
</tr>
<tr>
<td>Ang III M$^+$</td>
<td>929</td>
<td>1.06E–03</td>
<td>6.19E–3</td>
<td>1.54</td>
</tr>
<tr>
<td><strong>Native biological surfaces</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN$^-$</td>
<td>26</td>
<td>2.76E–02$^1$</td>
<td>7.89E–02</td>
<td>3.67</td>
</tr>
<tr>
<td>PO$_{2}^{+}$</td>
<td>79</td>
<td>2.77E–01$^1$</td>
<td>2.55E–01</td>
<td>3.11</td>
</tr>
<tr>
<td>Lipid 1 P38:4(ST24:1)</td>
<td>885.5</td>
<td>7.27E–03$^3$</td>
<td>7.05E–03</td>
<td>1.41E–01</td>
</tr>
<tr>
<td>Lipid 2 ST24:0(OH)</td>
<td>906.6</td>
<td>4.17E–03$^3$</td>
<td>3.27E–03</td>
<td>1.50E–01</td>
</tr>
</tbody>
</table>

$^1$ Data correspond to Au$_{3}^{+}$ at 130 keV.
used as a surface fingerprint for target composition, morphology and structure. This approach is promising for molecular ion mapping at the nanoscale level with large applications in materials science, as well as biological and nanotechnology studies.

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