SIMS Methodology for Individual Nanoparticles

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Isolated nanoparticles, NPs, of dimensions too small for complete energy deposition by an impacting projectile, exhibit size-dependent sputter and ion yields [1-4]. The secondary ion, SI, signal may be further affected by ionization probabilities modulated by the NPs size, composition and environment. The impact parameters are not all equivalent and complicate the accurate characterization. Yet the latter is crucial for small size NPs since they can exhibit notable changes in chemical reactivity.

The present study examines innovative means for extracting a maximum of information from NPs of 5-20 nm in diameter. The samples consisted of decanethiol-functionalized Au and Ag NPs dispersed in single layers on Si wafers coated with polydiallyldimethyl ammonium chloride, PDDA, or on 1-6 monolayers of graphene. The negatively biased targets were bombarded with 520 keV Au_{400}^{4+} . This projectile generates high ion multiplicity, which makes it practical to run experiments in the impact-by-impact bombardment-detection mode. Thus isolated NPs are probed one by one, avoiding problems due to ensemble averaging. The pool of individual records (typically ~ 1M) likely comprises sets of data from alike impacts, allowing to identify molecules co-located within their respective ~ 15 nm areas of emission [5].

The experiments presented here focus on: a) identifying direct vs. grazing impacts, i.e. identifying SIs related to core vs. outer shell composition; b) maximizing information from NPs which fragment in one impact. We show in the case of 20 nm Au NPs, distinct co-emission of multiple small Au_n^- clusters with higher kinetic energy than in impacts resulting in emission of only one Au_n^-. The multiple Au_n^- events are attributed to emission from the NP core. Grazing impacts are identified by co-emission of SIs from the outer shell of the NP and the substrate. The distinction in impact parameters becomes blurred for NPs < 10 nm in size. The latter can be examined in the *transmission* mode. This novel approach is illustrated with transmission mass spectra from 5 nm NPs deposited on graphene.

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