

TOF.SIMS 5 (ION-TOF GmbH, Germany, 2010)

► General Description

The Time of Flight Secondary Ion Mass Spectrometer (TOF-SIMS) is essentially an ultra-high resolution mass spectrometer. It possesses both surface (few atomic layers) and elemental (up to parts-per-billion) sensitivity that no other spectroscopic technique does. Extremely versatile, a TOF-SIMS instrument can be used to analyze solid samples from virtually any scientific field (physics, chemistry, biology, medical science, etc.). ***The principle of time of flight secondary ion mass spectrometry consists in producing a yield of secondary ions from a surface which is bombarded by a low current pulsed ion beam and measuring their mass with a so called time of flight detector.*** At the core of the TOF-SIMS technique is the fact that by sputtering a solid surface in ultra-high vacuum (UHV) with a *high energy* (30 keV) *pulsed* (10 – 20 ns) ion beam (i.e. *primary ion beam*) short bursts of debris representative for that surface will emerge following the impact of the incident ion pulses. Statistically, up to 1% of that debris is electrically charged (i.e. *secondary ions*). Most of the charged debris consists of ions with one electric charge (i.e. fragments that either lost or gained an electron). By applying a high voltage in between the sample surface and a so-called *flight tube* situated in close proximity (about 1.5 mm away from the surface) the secondary ions are directed within a few tens of nanoseconds into the flight tube while gaining the same amount of kinetic energy, independent of their mass, since the electrostatic potential energy is only proportional to the charge. However, due to their mass difference, at the entrance of the flight tube the secondary ions will gain different velocities as the kinetic energy is proportional to the product of mass and velocity squared. In other words: the smaller the mass of an ion fragment the higher its gained velocity such that the kinetic energy is maintained constant. Thus, at the entrance of the flight tube different species will possess different velocities. To further separate these species in time they are left to drift for a long distance (few meters, translating into tens to hundreds of microseconds travel time, i.e. *time of flight*, depending on their mass/velocity) until they reach a detector where they are logged by intensity, position of impact on the detector and arrival time with respect to their generating primary ion pulse' position and time of impact on the sample. A plot of the secondary ion intensity as function of the arrival time at the detector represents the mass spectrum. Such time of flight technique is able to separate species with masses as close as 0.001 a.m.u. depending on the corrugation and conductivity of the sample. Besides spectra one can record maps of the species' distribution at the surface (imaging) with high lateral resolution (up to 70 nm), depth profiles with a depth resolution better than 1 nm and, if combining the two, 3D depth profiles.

As a practical example of what one can do with such instrument we have the semiconductor industry where it is used for micro-devices analysis and diagnose. Many high tech companies like Intel, AMD, Samsung, IBM, etc. own not one but many TOF-SIMS machines. It is pretty much the only instrument that can give with high accuracy the depth profile and/or amount of doping or contamination in a semiconductor device at parts-per-billion level. Chemists use TOF-SIMS to verify the composition of complex organic or inorganic compounds that they synthesize. Another example is coming from biology and medicine where scientists use TOF-

SIMS to look at tumors in animal tissues for a better understanding of how to fight different types of cancer. In criminal investigations TOF-SIMS is used to detect traces of drugs or gun powder in fingerprints otherwise invisible to any other detection instrument or technique. Related, nuclear scientists use TOF-SIMS to detect the presence of enriched uranium isotopes in hot places around the world thus preventing the wrong people to produce the so called “dirty bombs”. Even more, TOF-SIMS has started to become a very important tool for detecting forgeries in old documents or paintings. In geology and paleontology scientists base their research on TOF-SIMS to date fossils and determine their mass composition. And these are only few examples. Some of the TOF-SIMS research performed in our facility is presented below.

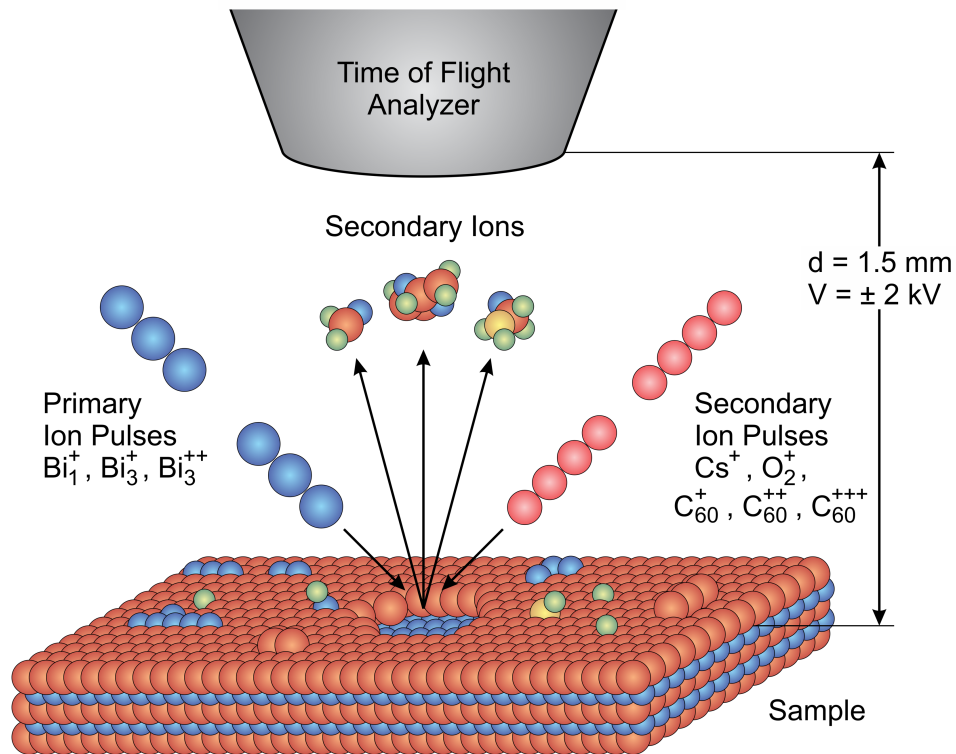


Figure Legend: The principle of Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS).

► Main directions of research using TOF-SIMS

1. Graphene related research

Q. Li et al., *Nano Letters* **13**, 486 (2013)

(link: <http://pubs.acs.org/doi/abs/10.1021%2Fnl303879k>)

The chemical vapor deposition (CVD) growth of bilayer and multilayer graphene on copper foils was studied by using isotopic (^{12}C vs. ^{13}C) labeling of the methane precursor. TOF-SIMS spatial mapping (high lateral resolution, ~ 200 nm) and depth profiling (atomic layer resolution) of the ^{12}C and ^{13}C isotopes revealed the stacking order of the graphene adlayers.

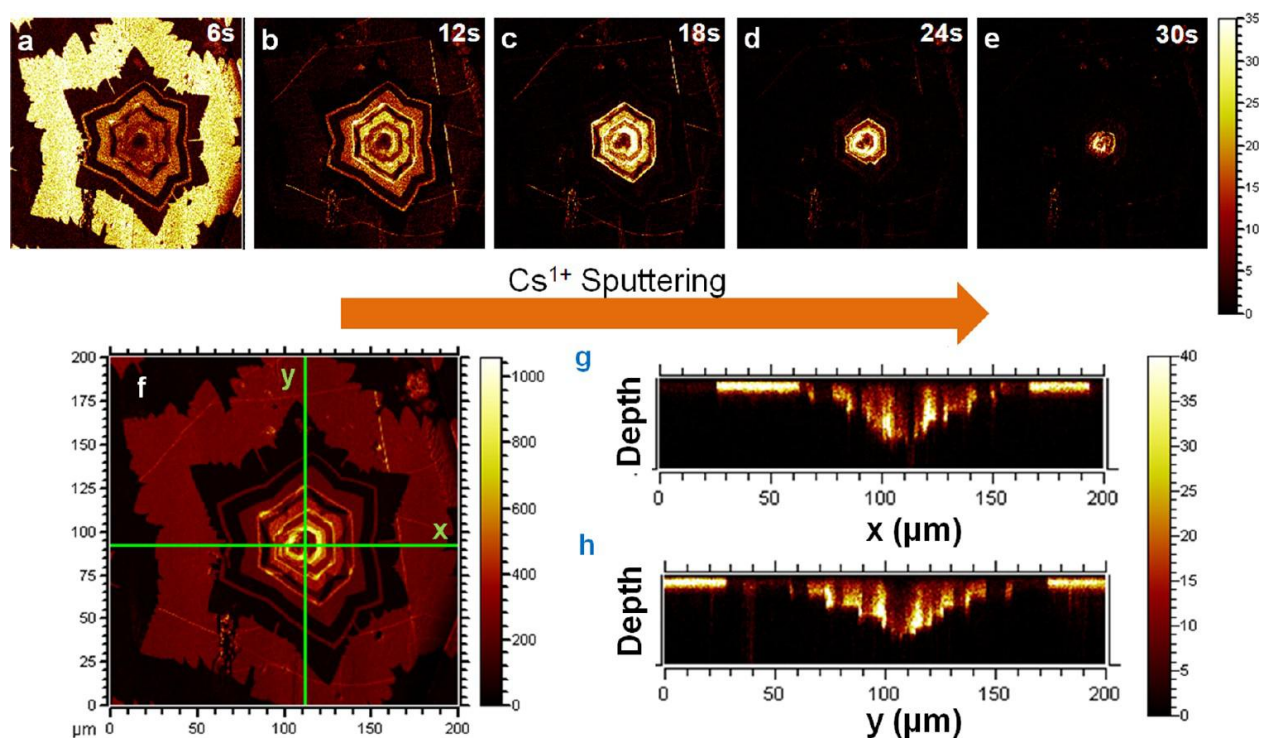


Figure Legend: High lateral resolution (~ 200 nm) TOF-SIMS mapping ($200 \times 200 \mu\text{m}^2$) of isotopically labeled multilayer graphene on Cu foil. (a–e) The ^{12}C isotope distribution images of graphene by TOF-SIMS after 6 s (a), 12 s (b), 18 s (c), 24 s (d), and 30 s (e) 1 kV Cs_1^+ ion beam sputter. (f) The overall sum image of 36 total images. (g,h) The cross-section views of ^{12}C graphene from the marked x (g) and y (h) lines in (f). The color scale represents secondary ion intensity.

2. Hexagonal Boron Nitride (h-BN) related research

Avinash P. Nayak et al., *NANO*, DOI: 10.1142/S1793292014500027 (2013)
(link: <http://www.worldscientific.com/doi/abs/10.1142/S1793292014500027>)

By acoustically irradiating pristine, white, electrically insulating h-BN in aqueous environment its material properties are inverted. The resulting dark, electrically conductive h-BN (referred to as h-BNO) shows a significant decrease in optical transmission (> 60%) and band-gap (from 5.46eV to 3.97eV). By using TOF-SIMS high resolution spatial mapping (~ 200 nm) and dynamic depth profiling (atomic layer resolution) the basic mechanism leading to the dramatic changes following the acoustic treatment is revealed.

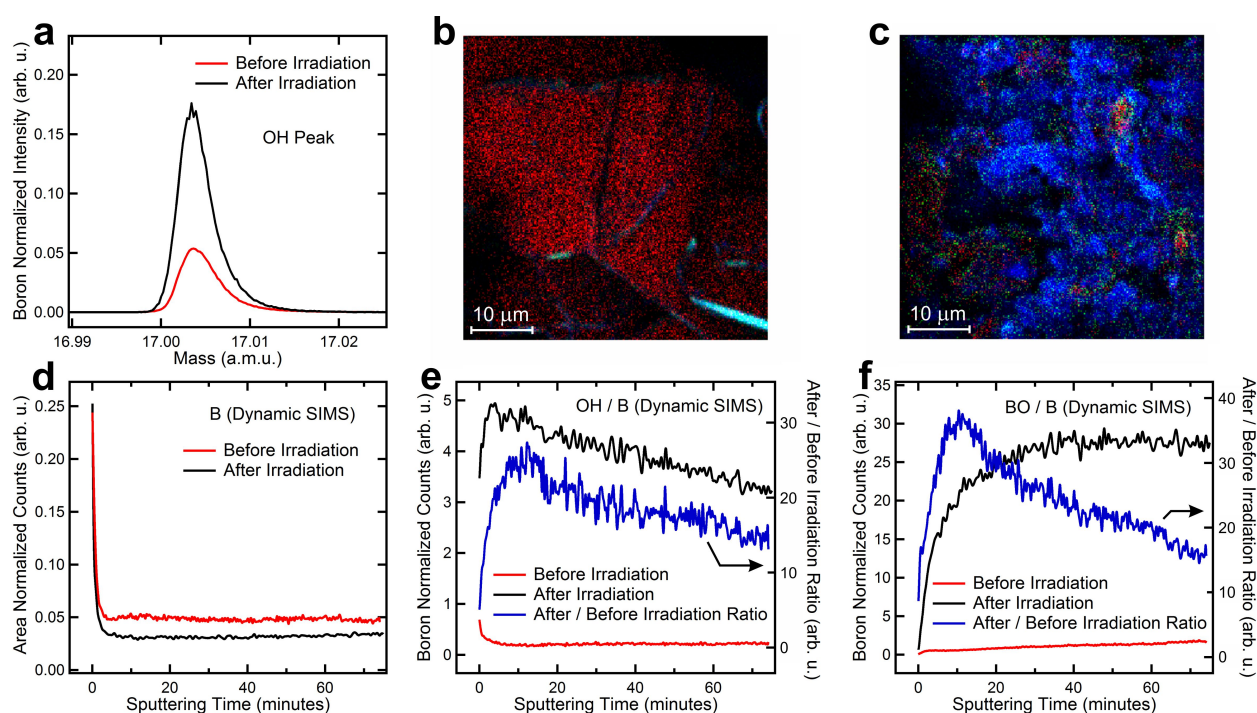


Figure Legend: (a) Comparison of the OH signal normalized to the total boron count for pristine and irradiated h-BN samples. (b) Overlay of B (red), BO (green) and OH (blue) signals for the pristine and (c) irradiated h-BN sample. The irradiated h-BN platelets reveal coverage by OH species. (d) Dynamic SIMS depth profiles of the boron signal normalized to its coverage area for the pristine (red curve) and irradiated (black curve) h-BN. A steady state is reached after 5 – 10 minutes of sputtering. Dynamic SIMS depth profiles of the (e) OH and (f) BO signals normalized to their corresponding B signals for pristine (red curve) and irradiated (black curve) h-BN. The ratios of the irradiated and pristine curves in each plot are shown in blue.

3. Lithium-Ion Batteries related research

D. W. Shin et al., *Chemistry of Materials* **24**, 3720 (2012)
(link: <http://pubs.acs.org/doi/abs/10.1021%2Fcm301844w>)

The high-voltage doped spinel oxides $\text{LiMn}_{1.5}\text{Ni}_{0.5-x}\text{M}_x\text{O}_4$ ($\text{M} = \text{Cr}, \text{Fe}, \text{and Ga}; 0 \leq x \leq 0.08$) synthesized at 900°C have been investigated systematically before and after post-annealing at 700°C . TOF-SIMS data reveal that the dopant cations $\text{M} = \text{Cr}, \text{Fe}, \text{and Ga}$ segregate preferentially to the surface, resulting in a more stable cathode–electrolyte interface and superior cyclability at both room temperature and 55°C with conventional electrolytes. Regardless of the post-annealing process, the Cr-, Fe-, and Ga-doped spinels show segregation of each dopant ion at the surface possibly because of the structural stabilization driven by the surface energy.

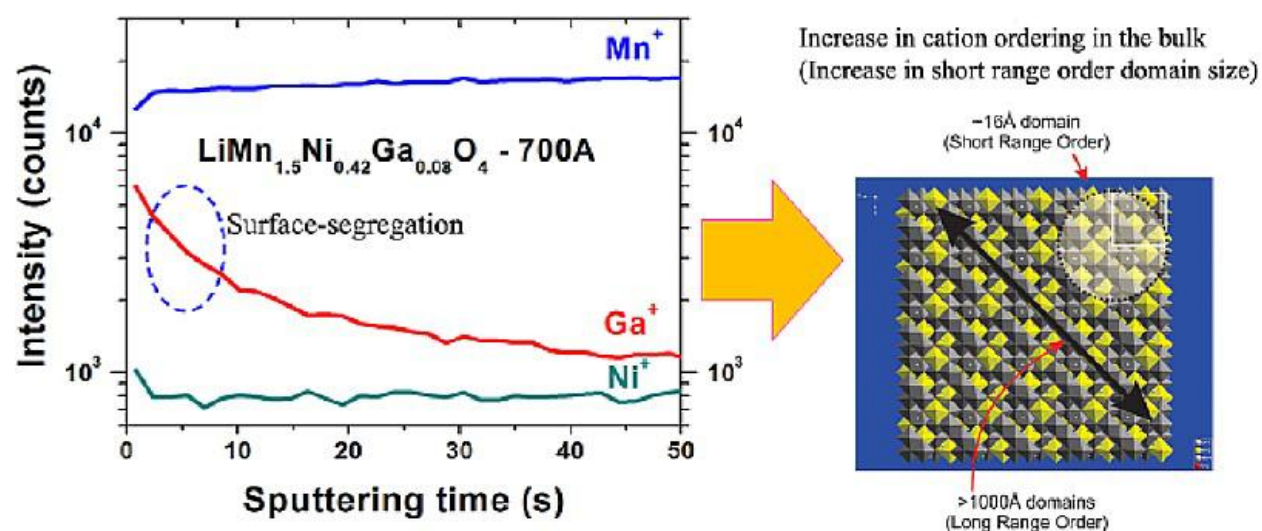


Figure Legend: TOF-SIMS depth profile of Gallium doped Lithium Manganese Oxide spinel (left) and illustration of the scale of the cation-ordered domain size, with the ordered P4_332 structure (right).

4. Organic Solar Cells (Organic Interfaces) related research

4.a. N. Sai et al., *The Journal of Physical Chemistry Letters* **3**, 2173 (2012)

(link: <http://pubs.acs.org/doi/abs/10.1021%2Fjz300744r>)

TOF-SIMS depth profiling of organic bilayer stacks consisting of C₆₀ and Copper-Phthalocyanine (CuPc) shows that when C₆₀ is deposited on top of CuPc the mixing length at the interface of the two organic materials is roughly twice larger than in the case of CuPc on top of C₆₀. This result reveals a much more complex interfacial structure than the one normally assumed in layered models. The effect of this complexity must be taken into account to gain a better understanding of the interfacial electronic structure.

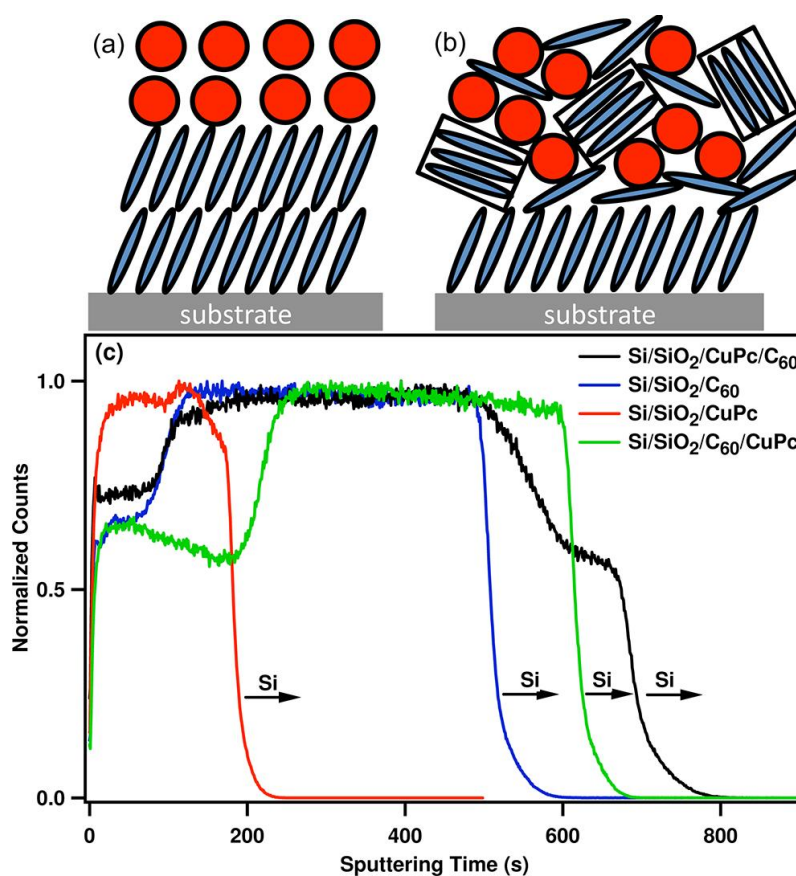


Figure Legend: Schematic representation of an ideal standing-up interfacial configuration (a) and molecular intermixed CuPc/C₆₀ interface (b). (c) Normalized TOF-SIMS profiles of the C₉⁻ marker for the CuPc, C₆₀, C₆₀/CuPc, and CuPc/C₆₀ films on Si/SiO₂ substrate.

4b. J. Zimmerman et al., *ACS Nano* **7**, 9268 (2013)
(link: <http://pubs.acs.org/doi/abs/10.1021/nn403897d>)

Solvent vapor annealing (SVA) of blends of two archetype functionalized squaraines, the asymmetric [2-[4-(N,N-diphenylamino)-2,6-dihydroxyphenyl]-4-[4-diphenyliminio] squaraine] (DPASQ), and the symmetric, 2,4-bis[4-(N,N-diphenylamino)-2,6 dihydroxyphenyl] squaraine (DPSQ), leads to their phase separation, alignment to, and ultimately interdiffusion with a nanocrystalline fullerene (C_{60}) cap. The SVA technique improves dramatically the power conversion efficiency of organic solar cells based on squaraine/ C_{60} junctions. TOF-SIMS depth profiling shows complete intermixing of the squaraine and C_{60} in the squaraine layer (C_{60} up to 20% of the total squaraine volume) for SVA samples. In addition, in case of a 4:6 DPASQ to DPSQ blend the SVA treatment leads to a squaraine penetration into the C_{60} layer of more than 30 nm.

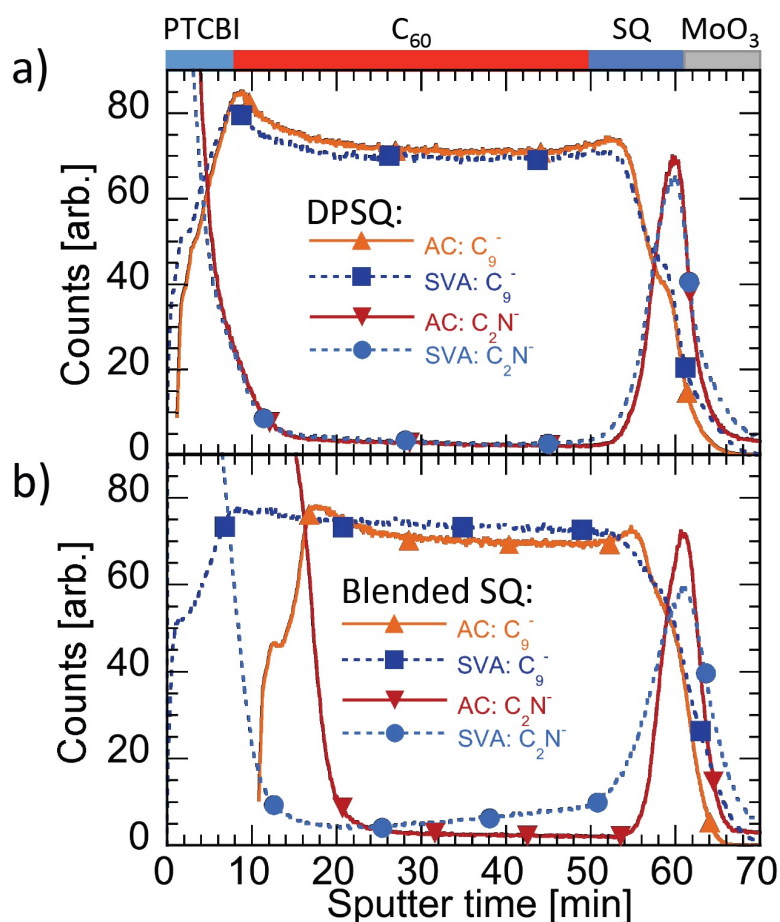


Figure Legend: Interdiffusion of squaraine/ C_{60} junctions. (a) Depth profile of DPSQ/ C_{60} /PTCBI films and (b) for blended squaraine/ C_{60} /PTCBI films before and after SVA measured using TOF-SIMS. The C_2N^- fragment tracks the squaraine and PTCBI concentrations, and C_9^- tracks mostly the C_{60} concentration. The intense C_2N^- signal at the beginning of the scans arises from the PTCBI overlayer.

5. Nanoparticles and quantum dots related research

S. Garcia et al., *Chemical Communications* **49**, 4241 (2013)

(link: <http://pubs.rsc.org/en/content/articlelanding/2013/cc/c3cc40387d>)

Microwave-assisted heating allows convenient and reproducible synthesis of defined Au–Rh core–shell metallic nanoparticles with tunable shell thicknesses. Such gold nanoparticles with rhodium shells as thin as a few atomic layers exhibit significantly higher catalytic activities with respect to single Rhodium nanoparticles. By using TOF-SIMS depth profiling both the spatial separation of Rh shells with respect to Au cores and the shell thicknesses were studied.

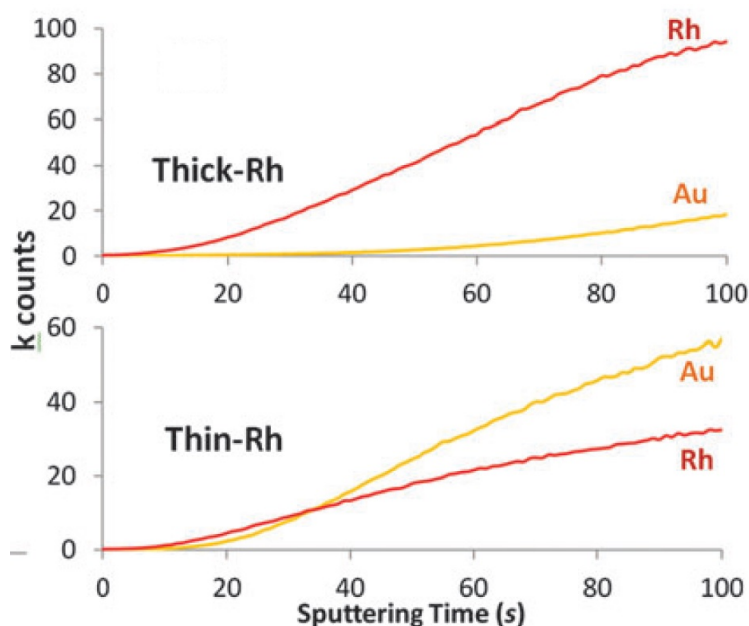


Figure Legend: First 100 seconds TOF-SIMS depth profiles of Au and Rh for thick (upper graph) and thin (lower graph) Rh shells Au nanoparticles.

6. Electrochemistry/Catalysis related research

S. P. Berglund et al., *Journal of the American Chemical Society* **136**, 1535 (2013)
(link: <http://pubs.acs.org/doi/abs/10.1021/ja411604k>)

Platinum coated p-doped Silicon (p-Si) substrates are highly active catalysts for solar induced hydrogen production by photoelectrochemical water splitting (that is, hydrogen evolution reaction (HER)). This research shows that tungsten semicarbide (W_2C) ultrathin films grown on p-Si can reduce the amount of platinum coating required for HER by a factor of 9 without reducing the overall catalytic activity. TOF-SIMS was employed to investigate the chemical composition of the W_2C films and the corresponding W_2C/p -Si interfaces. It was found that both surface contamination and atomic intermixing at the W_2C/p -Si interface increase upon annealing at 450°C , which might explain the improved stability and photocatalytic activity of platinum coated samples with annealed W_2C/p -Si substrates.

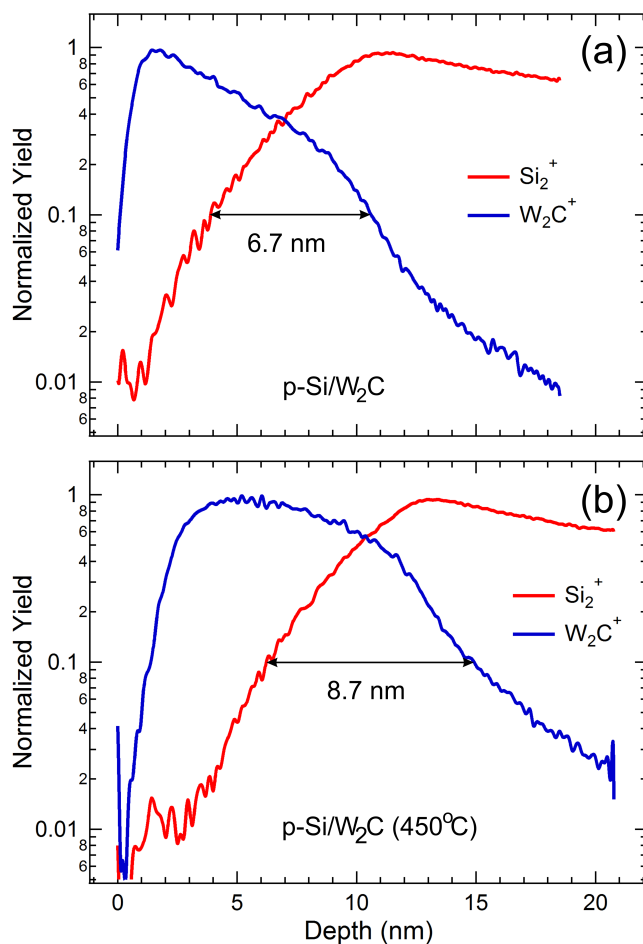


Figure Legend: Dynamic depth profiles of W_2C^+ and Si_2^+ markers for p-Si/ W_2C photocathodes (a) as deposited and (b) after annealing in Ar at 450°C .

7. Biology/Paleontology related research

L. Orlando et al., *Nature* **499**, 74 (2013)

(link: <http://www.nature.com/nature/journal/v499/n7456/full/nature12323.html>)

The genome of a horse bone recovered from permafrost dated to approximately 560–780 thousand years before present was sequenced. This represents the oldest full genome sequence determined so far by almost an order of magnitude. TOF-SIMS surface mapping was used to determine the presence of amino acids (the building blocks of proteins) specific for collagen in the ancient bone matrix thus proving its endogenous nature.

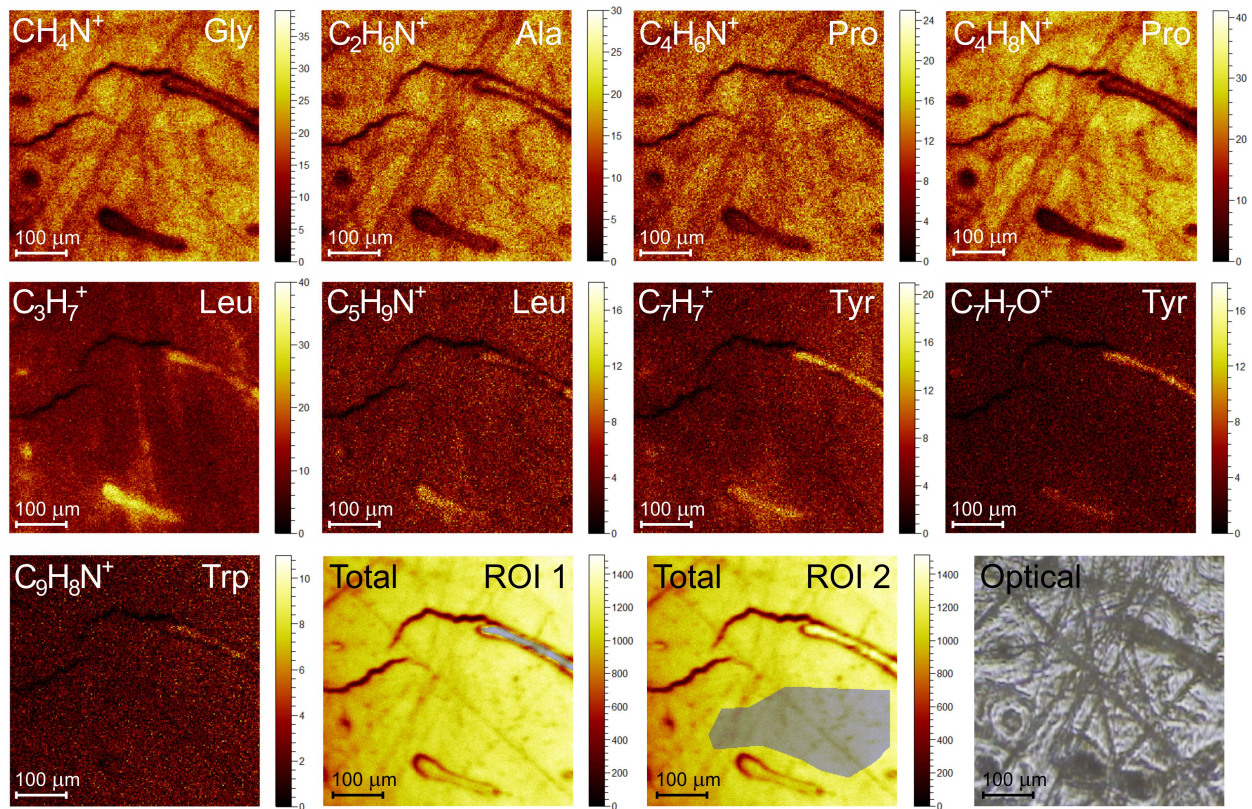


Figure Legend: TOF-SIMS secondary ion maps of the most intense markers detected in the bone matrix (ROI 2: Gly (G), Ala (A) and Pro (P)) and the vascular canals (ROI 1: Leu (L), Tyr (Y) and Trp (W)). The size of the secondary ion maps is 500 x 500 μm^2 with a resolution of 256 x 256 pixels. The grey picture represents an optical view of the analyzed area.

► TOF-SIMS publications acknowledging the NSF Award DMR-0923096

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9. Avinash P. Nayak, Andrei Dolocan, Jongho Lee, Hsiao-Yu Chang, Twinkle Pandhi, Milo Holt, Li Tao and Deji Akinwande, "Inversion of the Electrical and Optical Properties of Partially Oxidized Hexagonal Boron Nitride", *NANO*, DOI: 10.1142/S1793292014500027 (2013).
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