PCSI
Room Ballroom South - Session PCSI-2TuM

Atomic Scale Characterization

Moderator: Javier García de Abajo, ICFO-Institut de Ciencies Fotoniques

9:25am **PCSI-2TuM-12 Surface Potential and Hydrophilicity Measurements on Titanium Dioxide before and after Ultraviolet Irradiation**, ***Takuya Furukawa***, *K Noda,* Keio University, Japan

Surface properties of titanium dioxide (TiO_2) have been studied extensively due to their attractive phenomena such as photocatalysis and photo-induced superhydrophilicity. However, relations between these phenomena and photo-induced carriers in TiO_2 have not been fully understood yet. In this work, we discuss the relationship between surface potential (SP) and hydrophilicity on various TiO_2 surfaces before and after ultraviolet (UV) irradiation, by investigating the relaxation process of SP with Kelvin probe force microscopy (KFM) and water contact angle measured with an inkjet deposition system.

9:30am **PCSI-2TuM-13 Atomic-scale Observations of Reduced Graphene Oxide Nanosheets Dispersed on HOPG Substrates**, ***Shaoxian Li***, *T Hirano, K Kawai, K Yamamura, K Arima,* Osaka University, Japan

Reduced graphene oxide (rGO) is a promising catalyst in both an electrode for fuel cells and a chemical tool for a semiconductor surface. In order to obtain higher catalytic performances, we need to control the structure of an rGO sheet on the atomic-scale. In this study, we aimed at obtaining highly resolved images of rGO sheets on HOPG by scanning tunneling microscopy (STM). First, we found four kinds of nanostructures in rGO. Secondly, both edges and defect sites of the rGO sheet implied to have high local density of states around the Fermi level.

9:35am **PCSI-2TuM-14 Diamond Coated Tips for Scanning Tunneling Microscopy**, *J Owen,* Zyvex Labs; ***Ben Stein***, *O Auciello,* University of Texas at Dallas

Scanning Tunneling Microscopy (STM) has shown promise as an emerging tool for nanotechnologists to enable atomically-precise control over surface modification in the nanometer regime via surface lithography for device fabrication, and atomic-scale surface imaging and microanalysis. However, researchers have reported tip performance issues such as wear, oxidation and damage from electrostatic discharge, among other effects. While polycrystalline tungsten (W) wires have been typically used for tip fabrication via KOH-etching, diamond has long been considered an ideal potential candidate for numerous applications in scanning probe microscopy due to its well-documented hardness, chemical inertness and corrosion resistance, high Young's modulus, low coefficient of friction, and potential for controlled conductivity through selective doping via either Boron or Nitrogen atom insertion in grain boundaries. Numerous methods have been developed for fabricating diamond-based STM probes. However, no standardized practices have been established due to lack of repeatability, scalability and doping requirements. Clearly, there is room for improvement in the design and fabrication of diamond-based STM tips.

In this presentation, we report the development, application, and characterization of diamond coated STM tips and demonstrate their superior functionality in scanning imaging and lithography modes. Polycrystalline tungsten probe tips are prepared using the established method of electrochemical etching terminated at drop-off automated by the Zyvex ZEtcher system, followed by a secondary self-limiting Field-Directed Sputter Sharpening (FDSS) step, which utilizes an unfocused Ar^+ ion beam directed at a positively biased tip. Ultra-nanocrystalline diamond (UNCD) is then directly grown onto the tips without prior seeding in a microwave plasma chemical vapor deposition (MPCVD) process utilizing Bias Enhanced Nucleation (BEN) and Bias Enhanced Growth (BEG). We have found that by lowering the process temperature and plasma pressure, the extreme point of the tip can be quickly coated with a UNCD film tapering to a point with a radius of curvature <10 nm. While further sharpening of the diamond tip is possible with a lower energy FDSS step, it has been found that with ideal growth conditions no further sharpening is needed, nor is any extra doping step required to achieve tip conductivity. Furthermore, the tip can be used immediately for surface scanning and hydrogen depassivation lithography. UNCD film-based tips exhibit excellent durability, maintaining consistent scanning performance over very large scan areas. Tip morphology is characterized via STEM and ED.

9:40am **PCSI-2TuM-15 Surface Physical and Chemical Processes with an Optical Scanning Tunneling Microscope**, ***Shaowei Li***, University of California, Irvine; *W Ho,* Northwestern University

The desire for observing finer details using optical microscopy particularly in bio-science has pushed technology developments toward the joint spatial-temporal resolution. The combination of optical excitation with scanning probe techniques provides a new window for viewing the unique properties of individual nano-scale objects. The optically excited atoms or molecules can be locally probed by a scanning probe microscope (SPM). The combination of a femtosecond (fs) laser with the scanning tunneling microscope (STM) would enable the study of laser photochemistry to attain simultaneous spatial and temporal resolutions.

Here, we demonstrate the laser photochemistry at single molecule level with a femtosecond laser STM, and ultimately probe the coherence molecular dynamics with joint fs-Å sensitivity. Irradiation of the STM junction with femtosecond laser pulses can generate energetic photo-assisted tunneling electrons. The coupling of laser to the electron tunneling process can shatter the diffraction limited resolution in light induced phenomena and reach the atomic scale resolution of the STM. We show that photo-assisted tunneling electrons can selectively activate individual C-H bonds in an azulene molecule adsorbed on a Ag(110) surface at 8.6 K. Electron energy required to break the bond decreased by 1.5 eV under 820 nm laser illumination, indicating that an electron can be coupled with one photon to induce the reaction. The C-H bond to be activated can be chosen by positioning the tip over the molecule with sub-Å resolution. The inelastic tunneling probe (itProbe) images taken before and after the reaction provide unambiguous structural identifications of the reaction products.

The coupling of femtosecond laser pulses to the tunneling process enables the investigation of coherence chemistry with joint fs-Å resolution. We observed the coherent vibration driven structural transition of single pyrrolidine molecules adsorbed on a Cu(001) surface with joint fsÅ resolution. The molecular dynamics, including vibrational frequency and lifetime, are determined to drive the coherent structural transition in the molecule. When two molecules are spatially close to each other, the intermolecular interactions lower the vibrational lifetime and downshift the vibration energy. We expect our work with joint fs-Å resolution to open a new avenue into probing single molecule coherent chemistry.

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