FINAL PUBLISHABLE SUMMARY REPORT

Scanning Tunneling Microscopy (STM) is one of the most powerful tools for investigating the atomic and electronic structure of conductive surfaces with extremely high spatial resolution. The technique uses a sharp tip or probe that ideally ends in a single atom, which is brought close to the surface being measured, a voltage is placed on the surface and a current flows. The value of this current is determined by the makeup of the sample, the tip and the distance between them. By scanning the tip over the surface, a map is produced which reflects the local atomic and electronic structure.

The major objectives of this Marie Curie project ("Orbital Imaging") were: the reliable fabrication of functionalized STM probes with well-defined structures for use in high-resolution STM studies; investigation of the atom-atom interaction at small tip-surface distances; and selective imaging of electron orbitals with different angular momentum projections in distance-dependent STM experiments. These goals were achieved, and in some cases exceeded, and the main results of the project are summarized below.

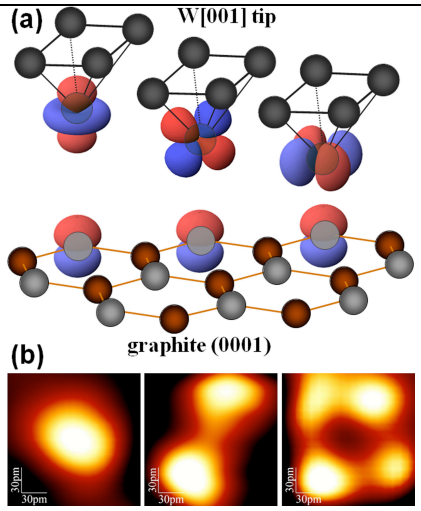

Fig. 1. (a) Schematic model of the W[001] probe approaching the hexagonal graphite surface. (b) STM images of the W 5*d* electron orbitals measured using the simpler 2*p* carbon orbitals of the surface. Changing the tip-surface distance allows us to select 5*d* electron orbitals with different momentum projections (d_{z^2}, d_{xy}, d_{xz}). The size of the images is 150 × 150 pm^2 (0.15 × 0.15 nm^2). (*Appl. Surf. Sci.*, 2013; *Sci. Rep.*, 2014)

1. Orbital Imaging

Procedures for fabricating sharp tungsten probes with well-defined structures have been developed. The structure of the chemically etched, [001]-oriented single crystalline tungsten probes sharpened in ultra-high vacuum using electron beam heating and ion sputtering has been studied using electron microscopy (EM). EM proves that tips with a single nanoscale pyramid apex grained by the {011} planes can be reproducibly fabricated. These sharp, [001]-oriented tungsten tips can be utilized in high-resolution STM studies of various complex surface atomic structures.

The electronic structure of the interacting W tip and graphite surface atoms has been studied experimentally and theoretically using STM and density functional theory (DFT) calculations. It is demonstrated that at small tunneling gaps (2–3 Å) the overlap of the tip and sample wave functions is responsible for the suppression of further extended orbitals with lower momentum projections on the z-axis (p_z, d_{z^2}, d_{xz}), leading to the direct visualization of the electron states in STM experiments (Fig. 1) The EM characterization performed before and after these STM experiments demonstrates the high stability of the W[001] tips and provides a direct correlation between the tip structure and picometer-scale (1 pm = 0.001 nm) spatial resolution achieved in the experiments.

This result is very important for STM analysis of multi-component systems. In particular, it shows that atomically resolved, chemically selective imaging at different gap resistances can be controlled using a general knowledge of the surface electron orbitals' shapes.

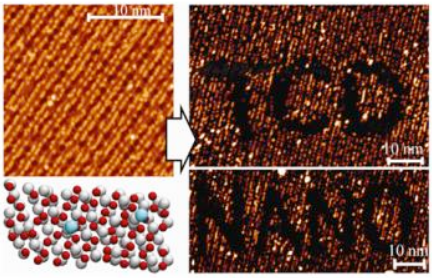

Fig. 2. *Left panel*: STM image and fully-relaxed model of the oxygen-rich MoO_{2+x}/Mo(110) surface. Blue spheres indicate the two oxygen adatoms. *Right panel*: The words TCD (Trinity College Dublin) and NANO written by the STM tip on the MoO_{2+x}/Mo(110) surface with a 3 V bias applied. (*Nano. Res.*, 2013)

2. Nanoscale Lithography

Single crystalline W[001] probes have been successfully utilized in STM studies of: the Si(557) atomic structure (*in preparation*); the dynamics of C_{60} molecules on the oxidized W(110) surface (*Nanoscale* **5** (2013) 3380); and the atomic structure of an oxygen-rich MoO_{2+x}/Mo(110) surface (*Nano Res.* **6** (2013) 929). The atomic structure of MoO_2(010)/Mo(110) has been determined from STM data and DFT calculations. It is demonstrated that stable W[001] probes can be used for the controllable desorption of oxygen adatoms from the surface at positive sample biases greater than 1.5 V. Tip movement along the surface was used for controlled lithography (writing) at the nanoscale, with a minimum feature size of just 3 nm (Fig. 2).

This result paves the way to use W[001] probes for atomic scale lithography utilizing the highly stable tip apex.

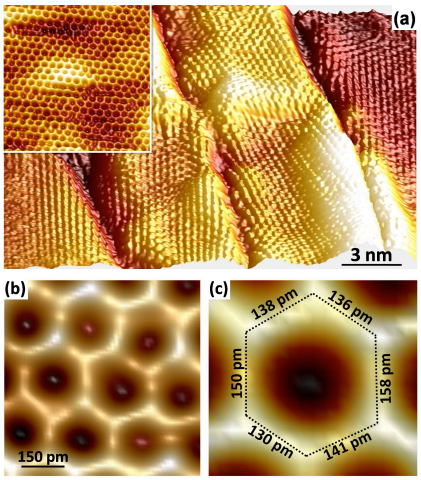

Fig. 3. STM images of the graphene on cubic-SiC(001). The images show the atomic structure of the top layer (a) and random picometer distortions of the carbon–carbon bond lengths (b,c) in the graphene lattice. (*Nano Res.*, 2013; *Nanotechnology*, 2014; *Pis'ma v ZhETF [JETP Letters]*, 2014)

3. Graphene on Silicon Carbide

The atomic structure of quasi-freestanding trilayer graphene synthesized on cubic-SiC(001)/Si(001) wafers has been studied with STM using single crystalline W[001] and W[111] tips. High-resolution STM data demonstrate that the top graphene layer consists of nanometer-sized domains with four different lattice orientations connected through the <110>-directed boundaries. Angle resolved photoemission studies reveal the typical electron spectrum of graphene with the Dirac points close to the Fermi level. The use of the technologically relevant SiC(001)/Si(001) wafers for graphene fabrication may represent a realistic way of large area graphene synthesis for electronics because of the low cost of the substrate and the possibility to open a transport gap in the graphene nanoribbon system (Fig. 3a).

STM experiments on graphene/SiC(001) show that higher tip stability can be achieved using a W[001] probe, yet higher spatial resolution with a W[111] probe. An example of picometer lateral resolution achieved with a W[111] probe is shown in Fig. 3(b,c). Similar resolution has been achieved so far only in rare non-contact atomic force microscopy (AFM) experiments.

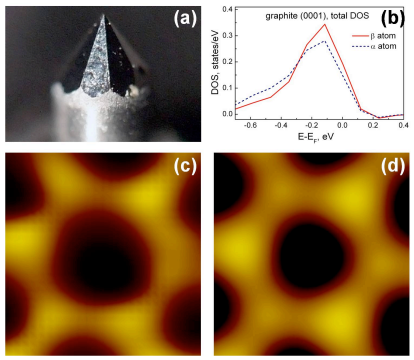

Fig. 4. Conductive single-crystal diamond probe (a). DOS associated with α and β atoms of the graphite (0001) surface (b). Comparison of the experimental STM image (3.8×3.8 Å^2) measured with the diamond probe (c) and the DFT-calculated charge density map (d). (*Nanotechnology*, 2014)

4. Diamond-probe STM

The advantages of STM imaging using a tip apex atom with frontier *p*-orbitals have been demonstrated in experiments performed on a graphite (0001) surface with a conductive, boron-doped, single-crystal diamond probe (Fig. 4a). The results of STM experiments and DFT calculations demonstrate that the highest spatial resolution can be achieved with diamond tips at tip–sample distances of 3–5 Å when the foremost *p*-orbitals of the tip provide their maximum contribution to the tunneling current. At these distances, modifications to the electronic structure of the interacting tip and surface atoms are negligible, allowing direct imaging of the minor difference in the density of electron states (DOS) of α and β atoms of the graphite surface (Fig. 4b-d).

Because of the extremely high stability of the diamond crystal lattice and defined orientation of the apex, these single crystal diamond probes can be considered as very promising probes for scanning tunneling microscopy and spectroscopy studies.

The results are novel and correspond to STM research of the highest quality. The picoscale lateral resolution achieved in STM experiments with [111]-oriented single crystalline tungsten probes is comparable to the best resolution obtained in AFM studies. The results represent an important step in the development of high-resolution scanning probe microscopy (SPM) methods and precise instruments for the examination of surface atomic structures. They are especially important for the improvement of the spatial resolution of SPM, fabrication of well-defined and stable probes for SPM studies of complex surfaces, atomically resolved chemical and spin-sensitive STM imaging. Surface analysis with extremely high spatial resolution is crucial for many different fields of science (physics, chemistry, biology) and technology since a large number of prospective materials consist of just one or several atomic layers (e.g., graphene, topological insulators, etc.).

The obtained results demonstrate how single-crystalline probes can be used for precise studies of technologically relevant low-dimensional systems (nanostructured graphene, metal oxides) and the modification of surfaces at the atomic level (nanolithography).

Our investigations of the graphene/SiC(001) system show the way towards the low-cost synthesis of graphene on technologically relevant, large-size SiC(001)/Si(001) wafers. These substrates are cheap and fully compatible with existing silicon lithographic technologies. Graphene/SiC(001)/Si(001) should be considered as a potential material for the development of graphene-based electronics.

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