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Correspondence and requests for materials should be addressed to A.N.C. (chaika@issp.ac.ru)

Fabrication of [001]-oriented tungsten tips for high resolution scanning tunneling microscopy

A. N. Chaika[1,2], N. N. Orlova[1], V. N. Semenov[1], E. Yu. Postnova[1], S. A. Krasnikov[2], M. G. Lazarev[1], S. V. Chekmazov[1], V. Yu. Aristov[1,3], V. G. Glebovsky[1], S. I. Bozhko[1] & I. V. Shvets[2]

[1]Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow district 142432, Russia, [2]Centre for Research on Adaptive Nanostructures and Nanodevices, School of Physics, Trinity College, Dublin 2, Ireland, [3]HASYLAB at DESY, D-22607 Hamburg, Germany.

The structure of the [001]-oriented single crystalline tungsten probes sharpened in ultra-high vacuum using electron beam heating and ion sputtering has been studied using scanning and transmission electron microscopy. The electron microscopy data prove reproducible fabrication of the single-apex tips with nanoscale pyramids grained by the {011} planes at the apexes. These sharp, [001]-oriented tungsten tips have been successfully utilized in high resolution scanning tunneling microscopy imaging of HOPG(0001), SiC(001) and graphene/SiC(001) surfaces. The electron microscopy characterization performed before and after the high resolution STM experiments provides direct correlation between the tip structure and picoscale spatial resolution achieved in the experiments.

The atomic structure of a scanning tunneling microscopy (STM) probe is crucial for enhancement of the spatial resolution and reliable interpretation of experimental data. Shortly after the invention of STM[1,2] it was realized that only sharp tips having single atom at the apex can provide stable and reliable atomically resolved imaging. Although several-atom-terminated tips can produce atomic resolution on metal surfaces[3], the ultimate resolution can be reached only with sharp tips collecting most of the tunneling current through the electron orbitals of a single front atom closest to the surface.

STM tips are usually prepared from low-cost polycrystalline tungsten wires using electrochemical etching[4]. To reach atomically resolved imaging, STM probes are cleaned and sharpened *in-situ* in ultra-high vacuum (UHV) by high temperature annealing[5], electric field restructuring[6–10], co-axial ion milling[11–14], controllable crashing using voltage pulses or a contact between the tip and the sample[15,16]. Enhanced spatial resolution can also be achieved using metallic tips terminated by molecules consisting of light-element atoms[17–21]. However, most of these tip treatments cannot produce stable apexes with defined atomic and electronic structure. The experiments with *in-situ* control of the apex geometry demand a combination of STM and field emission or electron microscopy which can hardly be considered as a routine practice. Therefore, the controlled fabrication of STM tips with a well-defined apex suitable for experiments with ultimate spatial resolution is one of the most critical issues in STM research.

Recently, it has been demonstrated that oriented single crystalline tungsten tips can produce high-quality atomically resolved images of surfaces with complicated atomic structure[22–25]. Furthermore, the orbital contribution of the front tungsten atom at the tip apex can be controlled in precise distance-dependent STM experiments[26–28] to achieve ultimate, picometer-scale lateral resolution[25–28]. However, all STM data presented in previous papers were measured with W[001] tips, which apex structure had not been characterized by electron microscopy techniques before or after the experiments. This leaves some room for contention and speculation about the origin of the observed subatomic features[26–29] and the actual structure of the tips' apexes responsible for picoscale resolution.

In this manuscript we present detailed tip preparation procedure, from chemical etching to UHV sharpening, and complete step-by-step characterization of the W[001] tips by scanning (SEM) and transmission (TEM) electron microscopy. These experimental results reveal the structure of the apex on the nanometer scale and prove that sharp W[001] tips with well-defined geometry can be reproducibly fabricated. The STM data presented in this manuscript were obtained using the W[001] tip characterized by TEM before and after the STM experiments

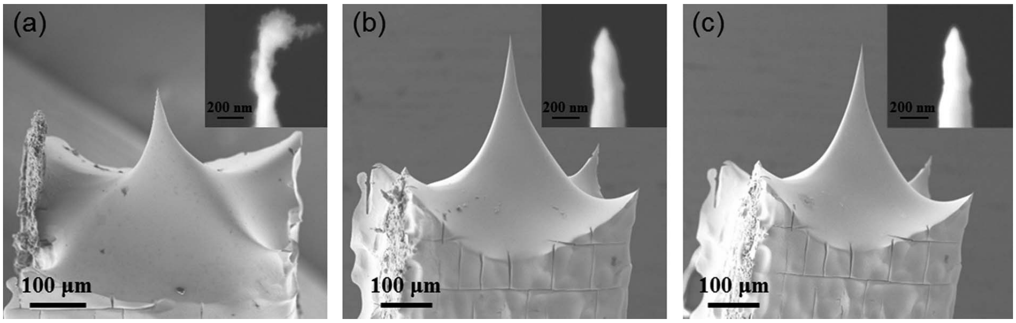

Figure 1 | SEM images of the electrochemically etched [001]-oriented tungsten tip before (a) and after electron beam heating at 1000°C (b) and 1500°C (c) and co-axial ion sputtering in UHV. Insets show magnified views of the contaminated (a) and clean (b and c) apex before and after the UHV treatment.

on HOPG(0001). The electron microscopy studies show that high resolution STM data were obtained using the W[001] tip having a nanoscale pyramid grained by the {011} planes at the apex thus providing a correlation between the tip structure and the spatial resolution obtained in STM experiments.

Results

For the reproducible W[001] tip fabrication we used chemical etching followed by special sharpening procedure in the UHV STM chamber. SEM data [Fig. 1(a)] show that the typical radius of curvature of the W[001] tips after chemical etching was in the range of 5–20 nm. The SEM images in Fig. 1(a) taken prior to UHV cleaning reveal some contamination of the apex as well as defects (rips) in the <001> crystallographic directions (along and perpendicular to the tip axis) that were formed during the spark cut of the tungsten ingots. After initial SEM characterization, the etched W[001] tips were loaded into the STM chamber and sharpened using several cycles of electron beam flash heating and co-axial Ar^+ ion sputtering. The SEM images of the tip after flash heating at 1000°C [Fig. 1(b)] and 1500°C [Fig. 1(c)] reveal that its shape including the radius of curvature at the apex is not changed substantially. This effect was observed on all tungsten tips subjected to the same UHV cleaning and sharpening procedure at tip annealing temperatures between 900°C and 1500°C. Furthermore, the insets in Figs. 1(b) and 1(c) show that most of contaminants have been removed and the tip has a single, nanometer-sized pyramid at the apex.

More detailed information about the shape of the W[001] tips was obtained from high resolution TEM characterization. Figs. 2 and 3 show TEM images of two different W[001] tips sharpened in UHV. Although the shape of the probes is not the same, both tips have nanometer-sized pyramids at the apexes grained by the {011} planes. Bright-field TEM image in Fig. 2(a) shows the pyramid at the tip apex formed after UHV sharpening. Electron diffraction pattern taken from the apex [Fig. 2(b)] exhibits characteristic diffraction reflexes, which correspond to the {011} and {001} crystallographic planes forming the pyramid. This is further illustrated by the dark-field TEM images taken from two different diffraction spots [marked by C and D in Fig. 2(b)], which allow to achieve better contrast in different regions of the tip. The dark-field image in Fig. 2(c) reveals that the angle at the tip apex is close to 90° that corresponds to the [001]-oriented tungsten apex grained by the {011} planes. Double-spot reflexes (C and D) in Fig. 2(b) indicate the presence of slightly misoriented single crystalline blocks at the tip apex. This misorientation is most likely caused by the stress applied to the apex at the final stage of chemical etching.

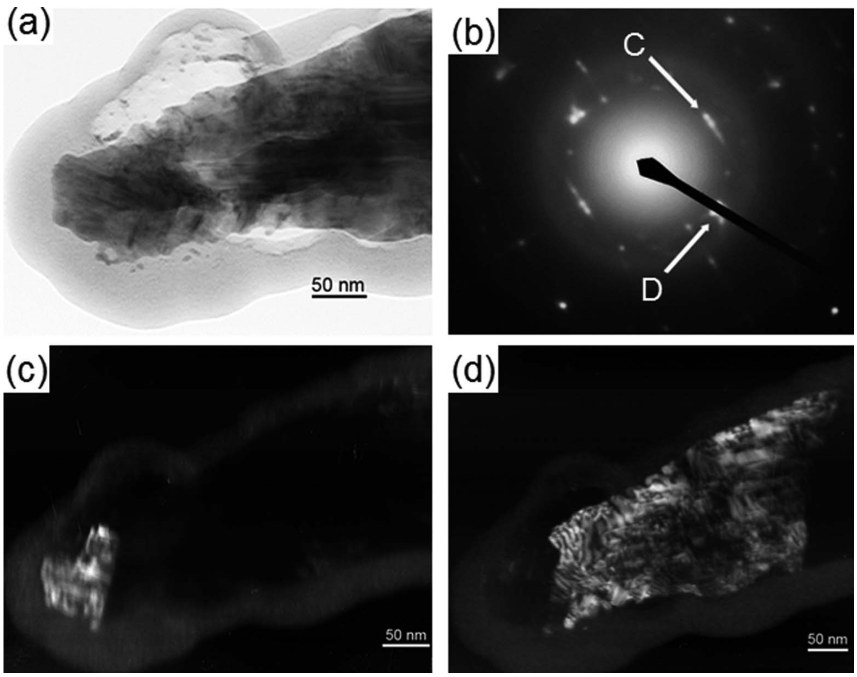

Figure 2 | **Images of the W[001] tip apex after electron beam heating at 1000°C and ion sputtering.** (a) Bright-field TEM image and (b) electron diffraction pattern taken from the apex. (c and d) Dark-field TEM images of the apex taken with the C and D diffraction spots on panel (b).

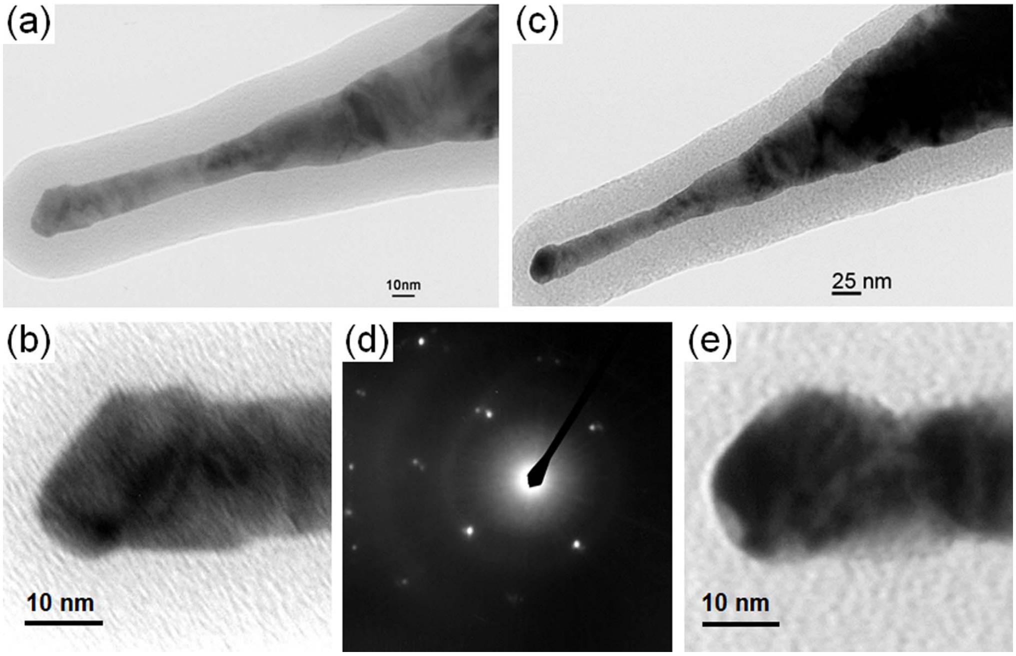

Figure 3 | Bright-field TEM images of the W[001] tip sharpened using electron beam heating and ion sputtering before (a and b) and after (c and e) STM experiments on HOPG(0001). (d) Electron diffraction pattern taken from the tip apex.

Fig. 3 shows TEM images of another W[001] tip taken before and after utilizing it in atomically resolved STM experiments. TEM images obtained after UHV sharpening [Figs. 3(a) and 3(b)] illustrate that the tip apex has a shape of a pyramid grained by the {011} planes, similar to the tip shown in Fig. 2. After TEM characterization the tip shown in Figs. 3(a) and 3(b) was used in STM experiments on highly oriented pyrolitic graphite (HOPG) surface and corresponding results are shown in Fig. 4. Atomic resolution was easily achieved on HOPG(0001) with this tip. Furthermore, the STM images measured at different gap resistances [Fig. 4(b–d)] reveal qualitatively the same subatomic features as reported previously[26–28]. The images shown in Fig. 4(b–d) were measured with the W[001] tip at the unchanged tip state, fixed bias voltage and various tunneling currents. They reveal the transformation of spherically symmetric atomic features to multiple subatomic features reproducing the shape of the tungsten atom *d*-electron orbitals with increasing tunneling current (decreasing tip-surface distance), as schematically shown in Fig. 4(a). TEM images of this W[001] tip taken after STM experiments on HOPG(0001) demonstrate almost no changes of the apex pyramid [see Figs. 3(c) and 3(e)]. Minor modification of the apex is, presumably, related to additional ion sputtering applied to the tip prior to the STM experiments. The TEM images shown in Figs. 3(a) and 3(c) prove safe tip to sample approach without a transfer of material from the sample to the tip and almost unchanged atomic structure of the apex during the STM experiments.

After experiments on HOPG and second TEM characterization the W[001] tip shown in Fig. 3 was utilized in high resolution studies of the graphene growth on cubic-SiC(001)[25]. Figs. 5(a) and 5(b) show typical atomically resolved STM images of the c(2×2) and (3×2) reconstructions of the SiC(001) surface[30,31]. The cross-sections in Figs. 5(c) and 5(d) demonstrate that the atomic corrugations observed in these experiments were about several picometers. Fig. 5(e) proves that the extreme sharpness of the tip found in TEM studies (Fig. 3) correlates with its ability to resolve the SiC(001)-c(2×2) reconstruction, extra carbon atoms, diamond-like atomic chains[30] on the surface and single atomic defects in the surface layer. All the features observed in the STM image shown in Fig. 5(e) could only be resolved using very sharp and stable tip with high aspect ratio and small radius of curvature at the apex (Fig. 3). In turn, STM images of the graphene/SiC(001) system[25] measured with the same W[001] tip [see Figs. 5(f) and 5(g)] reveal well-resolved carbon honeycomb pattern typical of the rippled quasi-freestanding graphene layer.

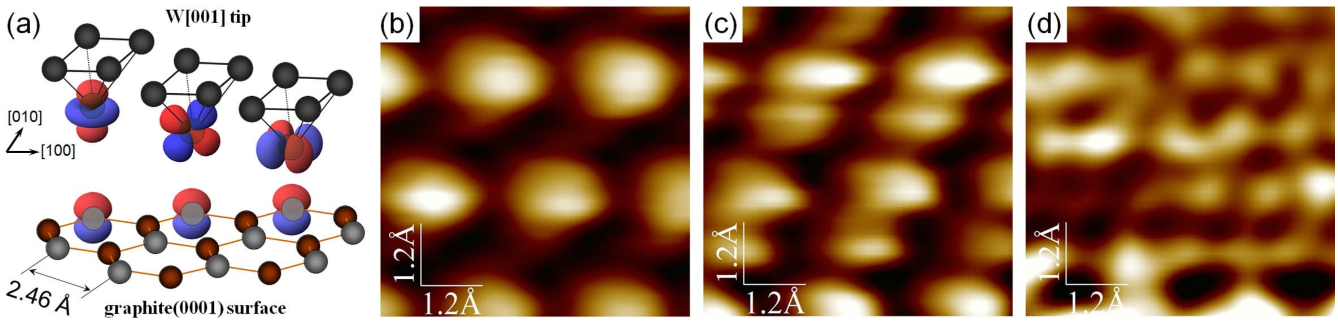

Figure 4 | A schematic model of the STM experiment on HOPG(0001) with the [001]-oriented W tip (a). STM images (6×6 Å^2) measured with the W[001] tip shown in Fig. 3 at a sample bias voltage of −50 mV and tunneling currents of 0.15 nA (b), 0.2 nA (c) and 0.4 nA (d). The [100] and [010] crystallographic directions of the tungsten tip in the experiment coincide with the *x* and *y* axes of the STM scanner.

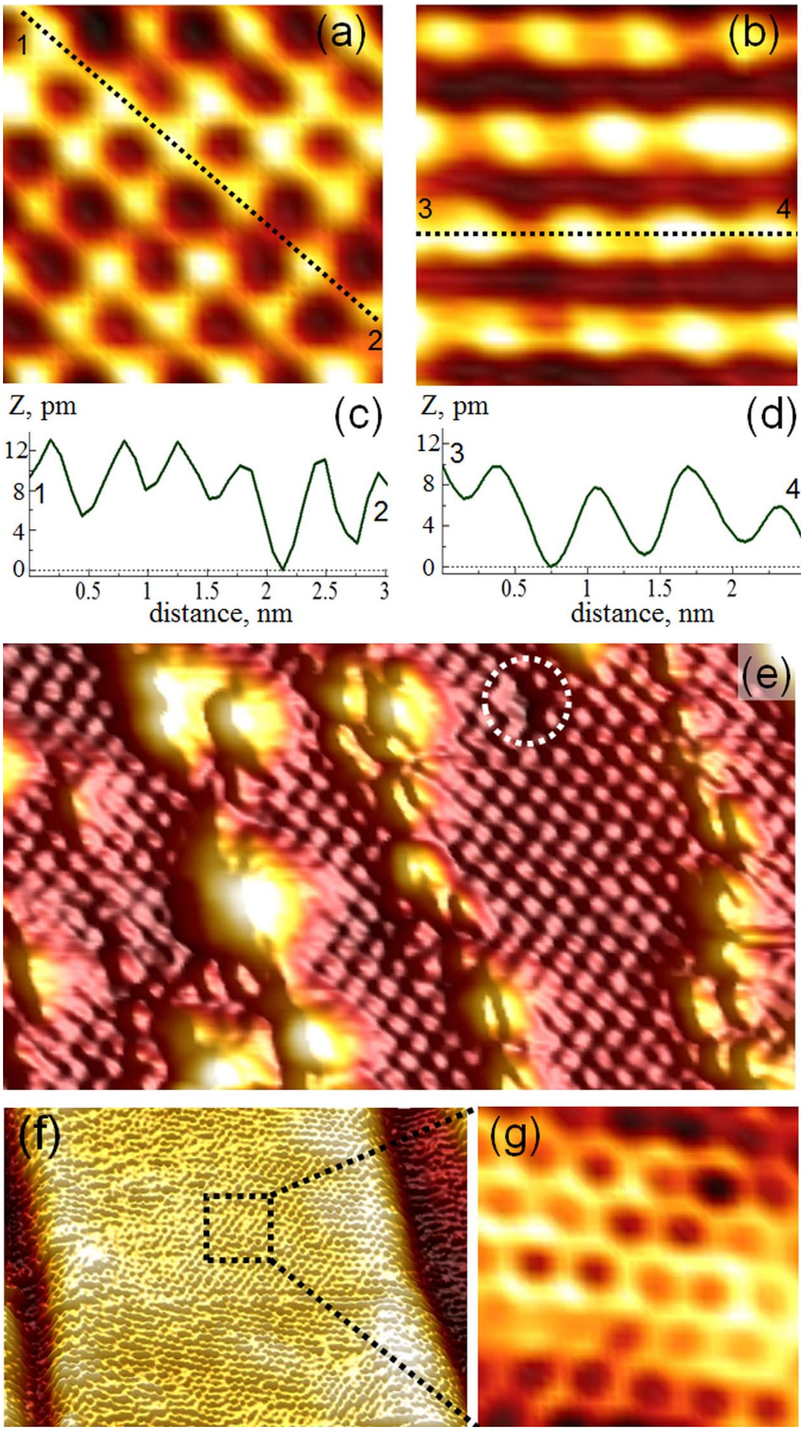

Figure 5 | 25×25 Å² STM images of the SiC(001)-c(2×2) (a) and SiC(001)-(3×2) (b) surfaces. (c and d) The corresponding cross-sections 1–2 and 3–4 taken from the images in panels (a) and (b). (e) A 16×9 nm² STM image revealing single atomic defect (highlighted by white circle) and carbon atomic chains on the SiC(001)-c(2×2) reconstruction. 15×10 nm² (f) and 15×15 Å² (g) STM images of the graphene/SiC(001) system measured with the same tip. The tunneling parameters are: U=−3 V, I=60 pA (a and e); U=−3 V, I=70 pA (b); U=50 mV, I=60 pA (e); and U=50 mV, I=60 pA (f). All images were measured with the W[001] tip shown in Fig. 3.

Discussion

The SEM and TEM data obtained from several tips prepared using the same procedure (Figs. 1–3) show reproducible fabrication of sharp W[001] tips, which have nanoscale pyramids at the apex grained by the {011} planes. According to the diffraction patterns measured from the tips' apexes (Figs. 2(b) and 3(d)), deflection of the pyramids from the [001] crystallographic direction does not exceed several degrees. Step-by-step characterization of the W[001] tips' structure (Figs. 1 and 3) demonstrates that the UHV sharpening procedure can be repeated on the same tip without inducing substantial changes of the apex structure. Furthermore, the data shown in Fig. 3 prove that the tip structure is not changed after STM experiments. The electron microscopy studies and STM data obtained with the well-characterized W[001] tip emphasize an exceptional quality of STM research that can be achieved with oriented single crystalline tungsten probes sharpened by consecutive electron beam heating and ion bombardment. The stability of the tip apex structure during the tip treatment and STM experiments (Fig. 3) and high resolution data obtained with clean tips (Figs. 4 and 5) prove the possibility to perform STM experiments with picometer vertical and lateral resolution using the probes with well-defined structure.

The difference in the gap resistances responsible for the transition from spherically symmetric atomic features to two-fold and four-fold split subatomic features observed in the STM experiments on HOPG [Figs. 4(b–d)] is in full agreement with results of our previous studies[26–28]. Furthermore, the crystallographic orientation of the tungsten tip was the same in the current experiments on graphite (Fig. 4) and earlier studies[26–28]: the [100] and [010] directions coincide with the side planes of the tungsten tip ingots. Because of rectangular shape of the ingots (Figs. 1–3), in both cases the [100] and [010] directions of the tungsten crystal coincided with the x and y axes of the STM scanner. Therefore, the orientation of the four-fold split subatomic features shown in Fig. 4(d) is in agreement with the results of fully-relaxed density functional theory calculations[27] suggesting the domination of the d_{xy} electron orbital at the front tungsten tip atom at tunneling gaps of 2.0–2.5 Å when the tip-sample interaction reduces the partial contribution of the d_{z^2} and $d_{xz,yz}$ orbitals. The almost unchanged tip shape after measurements at such small tip-sample distances proves the extreme stability of the W[001] tips sharpened in UHV which is very important both for measurements in topography mode and for scanning tunneling spectroscopy experiments.

In conclusion, the electron microscopy data presented in this work prove the reproducible fabrication of sharp [001]-oriented single crystalline tungsten tips with well-defined nanoscale pyramids at the apex. The STM experiments carried out with the well-characterized tip show that the front tungsten atom of sharp [001]-oriented tips is responsible for the subatomic contrast observed in scanning probe microscopy experiments on HOPG(0001)[26–29]. STM studies show that such tips provide high resolution images of various surfaces, even those which are far from being ideally flat. Furthermore, the W[001] tips fabricated using consecutive electron and ion bombardment can be easily refurbished using the same UHV treatment in the case of minor contaminations of the tip apex by the surface atoms during STM experiments.

Methods

W[001] STM tips were fabricated from single crystalline tungsten ingots by electrochemical etching in 2M NaOH with controllable cut-off adjusted by the current jump that allows to switch off the voltage between electrodes with a minimal delay. [001]-oriented tungsten ingots ($0.5\times0.5\times10$ mm^3) for chemical etching have been cut from a high quality single crystal using the spark cut. To minimize the radius of curvature at the apexes, the length of the ingot immersed into the etchant was in the range of 2.5–3 mm and the voltage applied between two electrodes was in the range of 4.0–4.5 V[4]. Prior to electron microscopy characterization and UHV sharpening, the etched tips were cleaned in hot distilled water. Other cleaning procedures like ultrasonic rinsing in ethanol or acetone were avoided since they could lead to breaking the tip apex[32]. According to SEM data the success rate in preparation of sharp tungsten tips using the etching parameters indicated above exceeds 85%. In particular, only three chemically etched tips, from the 30 characterized by electron microscopy, showed the radius of curvature at the apex in the range between 20 and 100 nm. The radii of curvature for all other apexes were below 20 nm.

The chemically etched W[001] tips were further sharpened in UHV STM chamber to fabricate well-defined nanoscale pyramid at the apex using consecutive electron beam heating and ion sputtering. During heating the voltage between the tungsten cathode and STM tip was adjusted to 1 kV while the emission current was varied depending on the tip-cathode distance and the temperature used. To avoid melting or possible field-induced blunting of the apex[33], the flash heating was usually no longer than 15 seconds at temperatures of 900–1000°C and shorter at higher temperatures (up to 1500°C). The temperature of the W[001] tips during flashing was measured by a pyrometer focused on the area of the ingots close to the apex. The exact temperature at the apex could not be measured precisely because of its nanometer size (Figs. 1–3) and temperature gradients during the electron bombardment. Therefore, it could be slightly higher at the apex, but the temperature difference most likely cannot exceed 100°C because of high thermal conductivity of the metallic ingot. The co-axial Ar^+-sputtering has been performed with a 600-eV ion beam and typical sputtering time was in the range of 15–20 minutes.

Scanning and transmission electron microscopy characterization of the W[001] tips after chemical etching, UHV sharpening, and STM experiments have been performed using Zeiss Supra 50VP and JEM-100CX-II microscopes, respectively. The tip cleaning and sharpening and atomically resolved STM experiments have been carried out in the UHV chamber of a room temperature scanning tunneling microscope GPI-300. The base pressure in the STM chamber was in the range of 4-6×10^{-11} mbar. Atomically resolved STM experiments on HOPG and graphene/SiC(001) were started approximately 1 hour after the ion sputtering of the W[001] tips to prevent the apex from possible contamination.

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Author contributions

V.N.S., S.I.B., V.G.G. and S.V.C. prepared single crystalline tungsten ingots. A.N.C. and M.G.L. prepared sharp tips by chemical etching. A.N.C. performed UHV sharpening of the tips and STM experiments. A.N.C. and V.Y.A. prepared SiC(001) and graphene/SiC(001) surface reconstructions. E.Y.P. made SEM characterization of the tips. N.N.O. performed TEM experiments. I.V.S. gave scientific advices. A.N.C. and S.A.K. analyzed the data and wrote the paper. All authors discussed the results.

Additional information

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