Note: Mechanical in situ exfoliation of van der Waals materials

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Abstract
Exfoliation, namely, the peeling of layered materials down to a single unit-cell thin foil, opens promising avenues to fabricate novel electronic materials. New properties and original functionalities emerge in the single and few layer configurations of a number of layered compounds, in particular in transition metal dichalcogenides. However, many of these thin exfoliated materials are very sensitive to ambient conditions impeding the exploration of this new and fascinating parameter space. Here we describe a method of mechanical exfoliation in ultra-high vacuum (UHV). This technique is easily adaptable to any UHV system and allows preparing and studying air sensitive nanoflakes in situ. We present the basic design and proof-of-concept scanning tunneling microscopy imaging of VSe2 nanoflakes.

Reference

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Note: Mechanical in situ exfoliation of van der Waals materials

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Exfoliation, namely, the peeling of layered materials down to a single unit-cell thin foil, opens promising avenues to fabricate novel electronic materials. New properties and original functionalities emerge in the single and few layer configurations of a number of layered compounds, in particular in transition metal dichalcogenides. However, many of these thin exfoliated materials are very sensitive to ambient conditions impeding the exploration of this new and fascinating parameter space. Here we describe a method of mechanical exfoliation in ultra-high vacuum (UHV). This technique is easily adaptable to any UHV system and allows preparing and studying air sensitive nanoflakes in situ. We present the basic design and proof-of-concept scanning tunneling microscopy imaging of VSe$_2$ nanoflakes. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4993738]

Tuning material properties via size control is a very attractive scheme in fundamental research with great potential for applications. Transition metal dichalcogenides (TMDs) are of particular interest in this context. TMDs are layered materials with general chemical formula MX$_2$, where M is a transition metal (e.g., Mo, Ti, Ta, V) and X is a chalcogen (S, Se, Te). Each layer is composed of a covalently bonded sheet of metal atoms sandwiched between two hexagonal planes of chalcogen atoms. Adjacent layers are held together by weak van der Waals interactions enabling simple mechanical exfoliation of large area thin flakes. These compounds span the entire range of electronic phases, from insulator to semiconductor and metal, and host fascinating ground states such as charge density wave (CDW) phases and superconductivity. Many have been found to exhibit interesting novel electronic, mechanical, and optical properties when their thickness is reduced to the nanoscale (monolayer or few layers). Thus, adjusting their thickness offers a novel route to tune their actual properties to specific design and application requirements.

While exfoliated flakes and thin films of semiconducting TMDs are routinely studied and already integrated in practical device configurations, their metallic counterparts have been much less investigated. This is a direct consequence of their greater reactivity under ambient conditions, restricting their use to controlled atmosphere, vacuum, or encapsulated configurations. The latter makes it difficult to investigate their properties by surface sensitive techniques. One alternative to overcome this difficulty is in situ growth of van der Waals materials. However, they require sophisticated equipment and do not offer the wide thickness range from bulk to monolayer accessible in a single exfoliation experiment. Here, we present a device to prepare mechanically exfoliated metallic TMDs in ultra-high vacuum (UHV) that enables photoemission and scanning probe investigation of their bare surface.

The UHV exfoliation tool we present in Fig. 1(a) is built around a sample storage carousel mounted on a linear shift and a sample holder manipulator. It can in principle be adapted to any UHV system, be it in the load-lock, preparation, or STM chamber. The central part is an exfoliation wheel mounted on a standard sample holder. We fix an insulator, low outgassing, residue-free clean-room adhesive tape (UltraTape product) on the circumference of the wheel by means of a double sided adhesive tape, with the adhesive side facing outwards. This sticky surface is then loaded with freshly cleaved flakes in the following way: starting from a bulk single crystal, we perform 1-3 steps of standard exfoliation and then transfer the thinned crystals to the wheel. The loaded exfoliation wheel is then transferred to the UHV system load-lock and pumped to below 10$^{-8}$ mbar within less than 10 min.

The exfoliation process is done manually using standard manipulators. It starts after reaching the base pressure of the load-lock (<3 · 10$^{-8}$ mbar). We grab the exfoliation tool with the transfer arm and align it over a previously prepared substrate on the carousel. The substrate is then carefully raised until gently touching the exfoliation wheel [Fig. 1(a), step 1]. We then move the transfer arm horizontally to roll the cylinder over the substrate surface at an average speed of about 2 mm/s [Fig. 1(a), step 2]. Because the exfoliation tool is only loosely held with the transfer arm, the wheel self-aligns to roll perfectly flush over the substrate surface. When reaching the end of the substrate, we lower the carousel to get out of contact [Fig. 1(a), step 3] and withdraw the transfer arm [Fig. 1(a), step 4]. The complete cycle can be repeated to deposit more flakes on the substrate and/or further thin the already deposited ones. Ultimately, we distribute and thin the starting material on the surface of the substrate and on the exfoliation wheel resulting in a dense coverage of the substrate with thin flakes [Fig. 1(b)].

The procedure was tested exfoliating MoS$_2$ nanoflakes on a gold coated silicon substrate. MoS$_2$ is stable in air, allowing us to confirm the in situ deposition of nanoflakes from high magnification optical microscopy outside UHV [Fig. 1(b)]. We observe a suitable coverage after only three exfoliation cycles. Increasing this number will increase the coverage if needed.

During the exfoliation [Fig. 1(a), step 2], it is important to maintain a “rolling without slipping” condition by controlling the translation speed and contact force. This is crucial
FIG. 1. (a) *In situ* exfoliation setup: the substrate sits on the storage carousel that can be moved vertically. The exfoliation tool is loosely held on a linear transfer arm. The arrows 1-4 indicate the exfoliation sequence (refer to main text). Typical dimensions are given in mm. (b) Optical microscope image of MoS$_2$ flakes after three exfoliation cycles (scale bar 100 µm). Inset: the red rectangle represents a 4×100 µm$^2$ area that we automatically search for flakes overnight.

To obtain high quality flakes and to minimize the amount of glue transferred from the adhesive tape to the substrate, alternative implementations of our *in situ* exfoliation scheme include the use of an empty (covered with adhesive tape, but not loaded with crystals) wheel that can be loaded *in situ* by first rolling repeatedly over a thick single crystal before starting the exfoliation process. This method may prove critical to prepare single layer flakes of extremely air sensitive materials.

As a proof of principle, we demonstrate scanning tunneling microscopy and spectroscopy of a VSe$_2$ nanoflake. VSe$_2$ is a metallic TMD that grows in the 1T polymorph and is extremely sensitive to atmosphere. Each unit-cell layer consists of covalently bonded V atoms sandwiched between two layers of Se atoms in an octahedral configuration. These slabs are stacked by weak van der Waals forces and can be easily cleaved, exposing a triangular Se lattice to the surface. The in-plane and out-of-plane lattice constants are $a = 3.356$ Å and $c = 6.104$ Å, respectively.

VSe$_2$ nanoflakes of different thicknesses were prepared *in situ* (3·10$^{-5}$ mbar) on Au(111) using the method and device described in Fig. 1(a). Prior to the exfoliation, the Au(111) single crystal surface was cleaned and reconstructed by repeated cycles of Ar$^+$ sputtering and annealing at 450 °C in UHV. The VSe$_2$ single crystals were grown by chemical vapor transport using I$_2$ as transport agent and showed a clear CDW transition in resistivity measurements. Constant current STM micrographs were recorded at 77.6 K using a SPECS Joule-Thomson STM (base pressure <2·10$^{-10}$ mbar). We used STM tips electrochemically etched out of an annealed tungsten wire, and the bias voltage was applied to the sample. Tunneling $I(V)$ and differential conductance $dI/dV(V)$ curves were acquired simultaneously using a standard lock-in technique with a 14.1 mV rms bias modulation at 337.7 Hz.

Positioning the STM tip over the exfoliated nanoflakes is challenging. Indeed, they are too small to be seen in the

FIG. 2. (a) Large scale (4×4 µm$^2$) STM micrograph ($V_{\text{bias}} = 1$ V, $I_t = 100$ fA) of VSe$_2$ nanoflakes with different thicknesses. (b) 9×9 nm$^2$ high resolution STM micrograph ($V_{\text{bias}} = -100$ meV, $I_t = 10$ pA) of a VSe$_2$ nanoflake showing the atomic lattice and a strong CDW modulation (T = 77.6 K). (c) Fourier transform of the micrograph in (b). Red and green circles indicate the first-order atomic and CDW modulation peaks, respectively. (d) STM micrograph ($V_{\text{bias}} = 0.5$ V, $I_t = 100$ fA) of the edge of a VSe$_2$ nanoflake showing the undisturbed underlying Au(111) herringbone reconstruction (non-linear color scale). (e) Topographic traces marked in (a). (f) Tunneling spectra of a thick (46 nm) VSe$_2$ flake at 77.6 K.
optical setup of our UHV system. Even if we were able to identify a flake on the exfoliation stage, the long working distance and absence of an absolute sample position monitoring would make it impossible to reﬁnd it on the STM stage. We therefore relied on a systematic scan and search procedure to locate a suitable flake. We ﬁrst scan a large surface area [red rectangle in Fig. 1(b) inset] by recording a sequence of adjacent low resolution and large scale $4 \times 4 \mu m^2$ micrographs. These images are then analyzed to identify morphological characteristics expected for nanoflakes, such as large atomically ﬂat terraces and long straight edges. Once we identify an image with such features [Fig. 2(a)], the presence of a VSe$_2$ nanoflake is unambiguously conﬁrmed from high resolution STM micrographs (atomic and CDW lattices) and from tunneling spectra.

Figure 2(b) shows a high resolution atomic-scale STM micrograph of an in situ exfoliated VSe$_2$ flake. This image reveals the expected atomic lattice and the $4 \times 4$ CDW modulation developing below 105 K. The Fourier transform shows the perfect commensuration of the atomic and CDW lattices and their six-fold symmetry [Fig. 2(c)]. Tunneling spectroscopy of thick flakes [Fig. 2(f)], where bulk-like behavior is expected, shows a metallic $I(V)$ characteristic and the vanadium $d$-state derived band in the $dI/dV(V)$ spectrum, in agreement with bulk data. While we ﬁnd the freshly cleaved bulk surface is degrading within hours in air, we did not observe any sign of surface degradation of thin ﬂakes in situ, even after several weeks.

The spectroscopic and topographic fingerprints shown in Fig. 2 demonstrate that we have successfully prepared exfoliated VSe$_2$ nanoflakes which are stable and can be extensively studied in UHV. We ﬁnd that a few exfoliation cycles (6-10, this may be material dependent) are enough to obtain high quality VSe$_2$ ﬂakes on Au(111) with appropriate coverage to easily locate a suitable ﬂake with the STM tip using the scan and search scheme described above. The thickness of the exfoliated ﬂakes ranges from hundreds of nanometer to few (1-2) layers, enabling thickness dependent studies in a much broader range than in situ grown thin ﬁlms. We have perfect control over the exfoliation process as evidenced by the preservation of the herringbone reconstruction of the underlying Au(111) single crystal all the way to the edge of the exfoliated nanoflake [Fig. 2(d)].

In conclusion, we present a novel method for mechanical exfoliation of van der Waals materials in UHV that yields high quality nanoflakes with dense substrate coverage. Performance of the device is demonstrated by preparing and imaging in situ exfoliated VSe$_2$ nanoflakes by scanning tunneling microscopy. Our device can be easily adapted to any UHV system and offers possibilities for further development and ﬁne tuning. Monitoring the force applied between the cylinder and the substrate may increase reproducibility. The diameter of the exfoliation wheel, hence the cleaving angle, is another tunable degree of freedom to obtain ﬂakes of different size and thickness. Our method is applicable to a broad range of layered materials and opens new opportunities to study few layers to monolayer thin air sensitive materials with surface probes like tunneling and force microscopy and photoemission.

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