Scanning tunnelling microscopy and spectroscopy investigation of rubidium-induced Mott–Hubbard transition on $1T$–TaS$_2$

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Abstract. The influence of rubidium deposition on structural and electronic properties of $1T$–TaS$_2$ was investigated by scanning tunnelling microscopy and spectroscopy at room temperature. The hexagonally ordered charge density wave (CDW) of the clean surface exhibits a rectangular symmetry upon rubidium adsorption. The spectroscopy data signals a Mott–Hubbard phase transition by an energy gap between upper and lower Hubbard bands giving rise to a Coulomb interaction energy of 1 eV. Owing to spatially resolved spectroscopy the energy gap can be directly related to the rectangular CDW phase. In addition, rubidium adsorption leads to the formation of a network of linear wires. Scanning tunnelling spectroscopy indicates that the wires are most likely not fabricated from rubidium.

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1. Introduction

Transition metal dichalcogenides have attracted considerable attention because of their quasi-two-dimensional character giving rise to unique electronic properties [1]. They present a material class with intriguing phase diagrams which include metal–insulator transitions, charge density waves (CDWs), and superconductivity [1, 2]. Owing to their peculiar geometric structure consisting of a periodic stacking of van der Waals-bonded transition metal dichalcogenide layers, dimensionality effects on the above mentioned phases can be investigated.

In this paper, particular interest is devoted to a Mott–Hubbard-type metal–insulator transition where the width of the involved electron bands decreases such as to render the on-site Coulomb repulsion between electrons dominant. As a result of this phase transition, a formerly partially filled band is split into an unoccupied and an occupied band. The latter are generally referred to as the upper and lower Hubbard bands. A phase transition of the Mott–Hubbard type may be induced by modifying the chemical composition [3], by the application of pressure [4], by changing the temperature of CDW systems [5], or by adsorption of alkali metals on transition metal dichalcogenides [6].

The two latter methods are particularly appealing since they allow control of the band width and the Coulomb correlation energy in the same crystal. A recent angle-resolved photoelectron spectroscopy experiment [6] was performed on 1T–TaS₂ and revealed the evolution of the electronic structure near the Fermi level across the metal–insulator transition. Upon rubidium deposition at room temperature a Ta 5d band was observed to shift to higher binding energies, and therefore was interpreted as the lower Hubbard band. The upper Hubbard subband, however, was not monitored since photoemission experiments are sensitive to occupied electronic states while unoccupied states are difficult to access.

Here, we present scanning tunnelling microscopy (STM) and spectroscopy data for the clean and rubidium-covered 1T–TaS₂ surface. As key results we show in direct space the rubidium-induced modification of the CDW from a hexagonal to a rectangular symmetry and, owing to the sensitivity of tunnelling spectroscopy to occupied as well as unoccupied electronic states, spectroscopic evidence for the rubidium-driven splitting of the upper and lower Hubbard bands. Thus, we directly relate the rectangular CDW phase to the Mott–Hubbard gap and provide a direct measure of the Coulomb interaction energy. By spatially resolved spectroscopy, we find indication that the rubidium-induced wire network is most likely not fabricated from rubidium.

2. Experiment

Experiments were performed using a home-built STM operated in ultrahigh vacuum at a base pressure of 10⁻⁹ Pa and at room temperature. Single crystal samples were grown by chemical vapour transport and clean surfaces were obtained by in vacuo cleavage. Rubidium was deposited on to freshly cleaved 1T–TaS₂ from commercial dispensers [7]. The deposition rate of ≈0.9 Å min⁻¹ was monitored by a quartz microbalance. Deposition was performed for 5 min to obtain a similar coverage to that reported in [6]. During deposition the pressure of the recipient stayed below 5 × 10⁻⁸ Pa. Prior to STM experiments the surfaces were characterized by low-energy electron diffraction (LEED). Spectroscopy of the differential conductance (dI/dV) was performed by superimposing a sinusoidal voltage (root-mean-square amplitude 1–2 mV and...
3. Results and discussion

To reveal the rubidium-induced changes in direct space most clearly, the CDW of clean and rubidium-covered $1T$–TaS$_2$ is presented in figures 1(a) and (b), respectively. The clean surface exhibits a CDW visible as the brightest protrusions in figure 1(a). The CDW superstructure is described by a $p(\sqrt{13} \times \sqrt{13})R13.9^\circ$ unit cell indicated by the lozenge with dimensions of $\approx 12 \text{ Å} \times 12 \text{ Å}$. This finding is in good agreement with electron diffraction results [8] and LEED patterns reported in [9]. Sulfur atoms appear as almost circular protrusions in a hexagonal frequency 4–8 kHz) on to the tunnelling voltage and measuring the current response with a lock-in amplifier. STM images were acquired in the constant-current mode and the voltage was applied to the sample.

Figure 1. (a) Atomically resolved CDW on clean $1T$–TaS$_2$ (current $I = 0.15$ nA and voltage $V = 75$ mV). The lozenge shows the CDW unit cell. The arrow indicates one crystallographic direction of the charge density wave unit cell. (b) STM image of the CDW of rubidium-covered $1T$–TaS$_2$ ($I = 25$ pA and $V = 75$ mV). The unit cell of the CDW is illustrated by the rectangle. Arrows indicate crystallographic directions of CDW unit cells of clean (dashed line, see also (a)) and rubidium-covered (full line) $1T$–TaS$_2$. The angle between these directions is $\approx 14^\circ$ and corresponds to the rotation angle of the CDW phase on clean $1T$–TaS$_2$. The STM image shows plane-subtracted raw data.
arrangement and with a mutual distance of $\approx 3.4\,\text{Å}$ in accordance with the in-plane lattice constant [10]. After deposition of rubidium for $\approx 5\,\text{min}$ the LEED pattern changed from a $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ to a three-domain $c(2\sqrt{3} \times 4)$ structure which has previously been observed [6, 9]. A typical STM image of this surface is presented in figure 1(b). We experienced an increase in the tunnelling current noise which we attribute to diffusing rubidium atoms [11] and therefore stable imaging was possible only for several scan lines. Nevertheless, in the case of stable imaging a rectangular structure as depicted in figure 1(b) was observed. We attribute the protrusions in figure 1(b) to the maxima of the CDW which exhibit a rectangular arrangement. By measuring the distances $a$ and $b$ for more than 100 protrusions we find $a = (12.0 \pm 0.6)\,\text{Å}$ and $b = (13.0 \pm 0.6)\,\text{Å}$ where the error margins correspond to standard deviations. These dimensions are close to the CDW unit cell dimensions reported in [9] ($a = 11.64\,\text{Å}$ and $b = 13.44\,\text{Å}$). We notice that images with larger lateral sizes (not shown) exhibit three $c(2\sqrt{3} \times 4)$ domains which are rotated by $60^\circ$ with respect to each other and which are in accordance with the above mentioned diffraction patterns [9]. On average, domain sizes are $\approx 150 \times 150\,\text{Å}$. In agreement with previous studies [9, 12, 13], we find that alkali metal adsorption on $1T$–TaS$_2$ induces strong modifications of the CDW phase. The mechanism of the transition from a hexagonal to a rectangular symmetry of the CDW phase has not been unraveled yet. In [9], the authors suggest that the rubidium-induced network of nanowires (to be discussed below) causes the CDW to align along the wires leading to the observed reduction of symmetry. For a similar system, namely TaS$_2$–Na, Pettenkofer and Jaegermann [12] found that the Ta d$_z^2$ band was populated by Na 3s electrons leading to a shift of the band below the Fermi level and thus giving rise to an increase of the Fermi surface. As a consequence, spanning vectors of nested Fermi surface contours were modified leading to the new superstructure. The relation between Fermi surface nesting vectors and CDW superstructures is discussed, for instance, in [14, 15].

Next, we discuss the electronic properties of clean and rubidium-covered $1T$–TaS$_2$. Rossnagel et al [6] showed by angle-resolved photoelectron spectroscopy that for the $c(2\sqrt{3} \times 4)$ CDW phase, the lower Hubbard band reached its lowest binding energy. In figure 2, we compare $dI/dV$ spectra of the clean and the rubidium-covered TaS$_2$ surface. For clean $1T$–TaS$_2$ a half-filled Ta 5d band lies close to the Fermi level and defines the Fermi surface [6, 16]. We interpret the spectroscopic structure in figure 2(a) as the signature of the Ta 5d occupied and unoccupied density of states (the Fermi level is located at $V = 0$). Rubidium adsorption leads to marked changes in the electronic structure as revealed by the spectrum shown in figure 2(b) which is representative for areas exhibiting the $c(2\sqrt{3} \times 4)$ CDW superstructure. The onsets of the Ta 5d band are split further away from the Fermi level and thus give rise to a depletion of the density of states in an energy interval of $\approx 0.4\,\text{eV}$ width around the Fermi energy. The middle of the d band onsets are located at $\approx \pm 0.5\,\text{eV}$. An analogous shift of spectral weight of the occupied Ta 5d band to $\approx 0.5\,\text{eV}$ below the Fermi energy was reported by Rossnagel et al [6] and interpreted as a result of a rubidium-induced Mott–Hubbard transition and consistently the photoemission peak as the spectroscopic signature of the lower Hubbard band. Adopting this interpretation, we attribute the onsets in the $dI/dV$ spectrum of figure 2(b) to the lower and upper Hubbard band. The width of the gap between the onsets is $\approx 1.0\,\text{eV}$. Pristine $1T$–TaS$_2$ is known to exhibit a temperature-induced Mott–Hubbard transition at $\approx 180\,\text{K}$ with the centroids of the Hubbard bands being separated by 0.3–0.4 eV [17]–[19]. Owing to the sensitivity to occupied as well as to unoccupied electronic states with tunnelling spectroscopy, we can measure the gap width without resorting to more sophisticated data evaluation and thus have
Figure 2. (a) \(dI/dV\) spectrum of clean 1\(T\)–TaS\(_2\). Feedback was opened at \(V = 610\) mV and \(I = 50\) pA. (b) \(dI/dV\) spectrum of rubidium-covered 1\(T\)–TaS\(_2\). Feedback loop parameters: \(V = 710\) mV and \(I = 80\) pA. Dashed lines indicate the position of the middle of the \(dI/dV\) signal onsets. Lines in (a) and (b) display smoothed data and serve as a guide for the eye.

direct access to the Coulomb interaction energy. The spectroscopic data gives complementary information to previously published photoemission data \[6\] and corroborates the conclusion of a rubidium-induced Mott–Hubbard transition.

To understand why rubidium adsorption may drive a Mott–Hubbard phase transition, it is helpful to understand the induced modifications of the Coulomb repulsion energy, the width and the filling of the involved electron bands. First, as can be deduced from the \(dI/dV\) spectra, the width of the energy gap between the lower and upper Hubbard band and thus the Coulomb repulsion energy is increased. Further, a previous STM investigation of rubidium-covered 1\(T\)–TaS\(_2\) by Schmidt \textit{et al} \[11\] showed that the adsorbate intercalates into the van der Waals gaps between the transition metal dichalcogenide layers, and therefore gives rise to an increased distance between the layers. As a consequence, the interlayer coupling may be reduced. This assumption is corroborated by an observed decreased width of electron bands perpendicular to the layers \[6\]. Calculations reported by Bovet \textit{et al} \[20\] indicate that the bandwidth perpendicular rather than parallel to the layers is an important parameter for the Mott–Hubbard transition. Moreover, Rossnagel \textit{et al} \[6\] concluded by analysing the evolution of the Fermi surface of 1\(T\)–TaS\(_2\)–Rb for various rubidium coverages that electron transfer from the alkali metal to the Ta 5d conduction band is negligible. As a consequence, the band filling is almost unaltered upon rubidium deposition. We therefore conclude that rubidium adsorption increases the ratio of the Coulomb repulsion energy and the band width giving rise to a critical value which induces a Mott–Hubbard transition.
Figure 3. (a) STM image of rubidium-covered 1$T$–TaS$_2$ at room temperature. The linear protrusions are part of an adsorbate-induced network of wires. ($V = 0.86$ V, $I = 0.04$ nA, $5400$ Å $\times 4000$ Å). (b) $dI/dV$ spectrum acquired at the site indicated by the arrow in (a). The line depicts smoothed data. Feedback loop parameters: $V = 1$ V, $I = 0.1$ nA.

Taking advantage of scanning tunnelling spectroscopy to provide information about the local electronic structure we explored the extent the Mott–Hubbard gap was influenced by surface modifications. Rubidium-covered TaS$_2$ exhibits a network of nanometre scale wires whose nature is still under debate. Similar honeycomb-like networks on rubidium-covered TiTe$_2$ [21] and copper-covered VSe$_2$ [22, 23] were reported previously. While in [21, 22] it was argued that the nanostructures consist of adsorbate material within cracks of the layered crystal surface, in [23] the nanostructures were interpreted as nanoscale folding patterns induced by adsorbate intercalation and strain relief.

Linear nanostructures observed on the rubidium-covered 1$T$–TaS$_2$ surface are shown in figure 3(a). The STM image shows a part of a network of wires whose width is $\approx 400$ Å and whose apparent height is $\approx 30$ Å. As the composition of these structures is a topic of discussion (see above), we acquired $dI/dV$ spectra on top of the wires. A generally noisy tunnel current hampered spectroscopy data collection. However, several curves were successfully obtained. In figure 3(b) a representative spectrum is shown. The spectrum shows a depletion of the $dI/dV$ signal close to the Fermi level. Therefore, the wires are probably not fabricated from rubidium as then one would expect an almost constant $dI/dV$ signal around the Fermi level.
4. Conclusion

In summary, rubidium adsorption on $1T$–TaS$_2$ leads to marked structural and electronic modifications. The symmetry of the CDW phase changes from hexagonal to rectangular and concomitantly the surface undergoes a Mott–Hubbard transition. Using scanning tunnelling spectroscopy a direct relation between the rectangular CDW phase and the Mott–Hubbard gap was established. A Coulomb interaction energy of 1 eV was obtained. The adsorbate-induced network of linear wires is most likely not fabricated from rubidium.

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