Charge Density Wave Vortex Lattice Observed in Graphene-Passivated 1T-TaS$_2$ by Ambient Scanning Tunneling Microscopy

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ABSTRACT

The nearly commensurate charge density wave (CDW) excitations native to the transition-metal dichalcogenide crystal, 1T-TaS$_2$, under ambient conditions are revealed by scanning tunneling microscopy (STM) and spectroscopy (STS) measurements of a graphene/TaS$_2$ heterostructure. Surface potential measurements show that the graphene passivation layer prevents oxidation of the air-sensitive 1T-TaS$_2$ surface. The graphene protective layer does not however interfere with
probing the native electronic properties of 1T-TaS$_2$ by STM/STS, which revealed that nearly-commensurate CDW hosts an array of vortex-like topological defects. We find that these topological defects organize themselves to form a lattice with quasi-long range order, analogous to the vortex Bragg glass in type II superconductors, but accessible in ambient conditions.

KEYWORDS: STM, CDW, graphene, 1T-TaS$_2$, oxidation, topological order, Bragg glass,

INTRODUCTION

The nature of ordering in two dimensions is a decades-old problem.[1] Berenzinski-Kosterlitz-Thouless (BKT) theory shows that quasi-long range order (or “topological order”) is maintained in 2D systems through the generation of topological defects of the 2D ordered state.[2] Famous examples include vortices in type-II superconductors and dislocations in 2D charge density waves (CDWs).[3] BKT theory shows that these topological defects are interacting and capable of forming a lattice of their own in 2D (e.g. flux line lattices in superconducting films) which unbind above a critical melting temperature. Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory extends BKT theory by considering the interactions between topological defects, identifying a theoretically predicted but rarely observed intermediate hexatic phase between the 2D solid and liquid.[4] The topic continues to draw interest as the interaction between topological defects and pinning impurities leads to novel, glassy phases like those observed in the vortex lattices of type II superconductors.[5, 6]

1T-TaS$_2$ is a layered transition metal dichalcogenide (TMD) which exhibits a wide range of phenomena arising from strong correlations and spin-orbit coupling, including metastable quantum states,[7] layer dependent charge density wave symmetry,[8] superconducting ground states upon doping and pressure,[9, 10] and a potential quantum spin liquid state.[11] 1T-TaS$_2$ has
attracted much attention from the research community for decades due to its rich phase diagram and non-linear transport properties with applications for next-generation electronic devices.[12-14] However, the room temperature transport behavior of 1T-TaS₂ is not understood, such as the large in-plane resistivity and its negative temperature coefficient, the high depinning threshold energies compared to quasi-1D CDWs, and peculiar scaling of current fluctuations with applied DC electric fields.[15-18]

Strong electron-phonon (e-ph) coupling leads to several quasi-2D CDW phases including a unique nearly commensurate CDW (NC-CDW) state at room temperature. In the NC-CDW state, the competition between CDW commensuration energy and CDW strain causes long-range periodic phase shifts and amplitude modulations of the CDW order parameter, forming a network of domains (hexagons in Fig. 1a) separated by domain walls (simulated in Fig. 1a-d). Inside the domains, the CDW is locally commensurate with the atomic lattice, forming clusters of 13 Ta atoms in the shape of a “star of David” (SD) (simulated in figure 1a inset).[19-22] The line defects, which make up the domain wall network, are fundamental topological defects of the CDW in two dimensions whose intersections form a lattice resembling those formed by Abrikosov vortices in type II superconductors.[19, 21, 23-25] Despite being accessible at room temperature and ambient pressures, this lattice of topological “CDW vortices” (and “CDW anti-vortices” ) is seldom looked at and has not yet been analyzed or compared with other topologically ordered systems. This is due, in part, to the material’s susceptibility to oxidation in ambient conditions. Furthermore, the sample surface tends to be unstable when subjected to various scanning probes (SI-A).[26] This limits studies of its microscopic properties by scanning probe methods to only a handful, such as low temperature scanning tunneling microscopy (STM) of cleaved bulk crystals in ultra high vacuum.[21, 27-30]
In this work, we show that a monolayer graphene blanket provides a highly effective impermeable gas barrier\cite{31} that protects the air-sensitive 1T-TaS$_2$ from surface oxidation while allowing electronic characterization of its intrinsic NC-CDW phase by ambient scanning probe methods. Using Kelvin probe force microscopy (KPFM), the chemical properties of the graphene-covered surface are shown to be stable over long periods of exposure to air, making it possible to probe the electronic properties of the structure by using STM in ambient conditions. These STM measurements reveal the CDW structure intrinsic to 1T-TaS$_2$ at room temperature, exhibiting details of the NC-CDW phase (including domain walls and CDW vortices). By computing the spatial correlation functions from the measured positions of the CDW vortices, we find that these form a quasi-long range ordered glassy lattice akin to flux line lattices in type-II superconducting films. This work not only demonstrates elements of exotic quasi-long range ordering in a 2D electron system which is accessible in ambient conditions but also demonstrates the power of graphene passivation to enable probing of hitherto inaccessible electronic properties.
Figure 1: a) Simulated model of the nearly commensurate charge density wave with several domains highlighted by black hexagons as well as a vortex-antivortex pair highlighted in red and green. Inset: Star of David-shaped Ta clusters (outlined in white) are commensurate with the CDW modulation near the center of the domains. Inset scale bar is 4nm. b) Fourier transform of the NC-CDW state given in (a) shows coherent peaks due to the nearly commensurate charge density wave as well as satellite peaks, as observed experimentally c) Amplitude of the CDW modulation shown in (a). The amplitude is maximized in the center of domains and minimized at the CDW vortices/antivortices (red and green highlights). d) Phase of the CDW modulation shown in (a). Domain walls are marked by a local phase shift of the CDW order parameter. The intersection of three domain walls marks the locations of CDW vortices and antivortices. Details of the simulation are given in Supporting Information (SI-B).

RESULTS AND DISCUSSION

Like many transition metal dichalcogenides, the top surface (approx. 2nm deep) of 1T-TaS$_2$ readily oxidizes in air, forming amorphous tantalum oxide. To measure the surface oxidation rate and to identify the presence of tantalum oxide, we perform atomic force microscopy (AFM) and KPFM measurements on the surface of bulk 1T-TaS$_2$ and graphene-passivated 1T-TaS$_2$ in ambient conditions as a function of time. Figure 2a shows the change in surface potential (measured by KPFM) due to the ambient oxidation of 1T-TaS$_2$ as a function of time. An exponential fit gives a characteristic lifetime of the material surface ($\tau \approx 46.8$ minutes). As detailed in the Supporting Information (SI-A), the graphene cover layer passivates the surface of the sample, preventing the oxidation of the 1T-TaS$_2$ surface and making it possible to probe its electronic properties in ambient conditions by using STM/STS. We show that the graphene layer acts as a highly effective gas barrier, protecting the 1T-TaS$_2$ from deteriorating under exposure to oxygen, consistent with earlier findings on other surfaces.[31, 32]
Figure 2: a) Change in the surface potential of bare 1T-TaS$_2$ in ambient conditions as a function of time. An exponential fit gives a characteristic timescale for the oxidation of the 1T-TaS$_2$ surface without graphene passivation. b) Cartoon diagram of the graphene on 1T-TaS$_2$ (G/TaS$_2$) device on SiO$_2$. A gold contact is used to apply a bias voltage during KPFM and STM measurements. c) AFM topography of the edge of the G/TaS$_2$ heterostructure. d) Local work function, determined from KPFM measurement, in the same region as (c). e) Diagram describing the charge transfer and observed work function difference between graphene on SiO$_2$ and on 1T-TaS$_2$.

**Contact Doping of Graphene on TaS$_2$.** Our AFM and KPFM measurements additionally probe the charge distribution at the surface of the G/TaS$_2$ heterostructure (depicted in fig. 2b). By comparing the work function of graphene on insulating SiO$_2$ (the left part of fig. 2c,d) and G/TaS$_2$ (fig. 2c,d, right half), we observe that the graphene becomes hole doped by approximately
102±2mV when placed on 1T-TaS$_2$. When two metallic materials contact each other, electrons will flow between them until the Fermi levels of the two metals to align with each other. The amount of charge carriers needed to move the Fermi energy is determined by the density of states at the Fermi level. Because the carrier density at the Fermi level of graphene is 3-4 orders of magnitude smaller than that of 1T-TaS$_2$, a small amount of charge transfer between these materials will produce a much larger shift of the band structure of graphene than that of 1T-TaS$_2$ (see figure 2e and SI-C). Such contact doping effect is trivial when taking place between two normal metals, however, the presence of the correlated electronic state of 1T-TaS$_2$ begs the question of how the transferred charge is distributed on the atomic scale.

**Figure 3:** a) Simulation of the charge density wave and graphene lattice showing the nearly commensurate CDW modulation as well as the contributions of the graphene and 1T-TaS$_2$ lattices. Inset: Fourier transform of (a) shows peaks associated with the NC-CDW, graphene lattice, and
the 1T-TaS$_2$ lattice (not resolved experimentally at room temperature). b) Schematic diagram of the ambient STM measurement scheme: a metallic STM tip is brought close to the G/TaS$_2$ heterostructure which is supported on an SiO$_2$ substrate. The presence of atmospheric oxygen does not affect the sample surface during measurement. c) Constant-height atomic resolution topography of G/TaS$_2$ at room temperature ($V_b$=100mV, I=60pA, measured in air). Inset: Fourier transform of the topography image (c) displays two sets of coherent peaks corresponding to the graphene lattice ($a_g = 0.245(3)$ nm) and the CDW in 1T-TaS$_2$ ($\lambda_{CDW} = 1.20(1)$ nm). d) dI/dV measured at the surface of G/TaS$_2$ shows a dip near zero bias and a shoulder near 550mV, consistent with previous reports of bare 1T-TaS$_2$ (without graphene). Data shown is the average of 16 spectra taken with a bias of -200mV and a current set point of -120pA. Inset: Fourier filtered STM topography image of G/TaS$_2$ at the location where dI/dV is measured (marked with square).

**Ambient STM Measurement of Graphene on TaS$_2$.** With protection from oxidation by a graphene layer, we image the CDW state(s) of 1T-TaS$_2$ by STM at room temperature both in vacuum and in air, using Pt/Ir tunneling tips[33-35]. Figure 3c gives an atomically resolved, constant-height STM image of the heterostructure surface measured in ambient conditions. As illustrated in the schematics of the experimental setup (figure 3b), the STM measurement is performed at the surface of the G/TaS$_2$ flake supported on an insulating SiO$_2$ substrate. A bias voltage ($V_b$) is supplied between the heterostructure and grounded STM tip and the tunneling current is recorded as a function of tip position. STM imaging is performed in constant-height mode, rather than the typical constant-current mode, to mitigate the effects of a large thermal drift rate in our system in ambient conditions (see SI-D). Figure 3c inset displays the fast Fourier transform (FFT) of the topography image showing two sets of 6 peaks which correspond the periodic structures seen in figure 3c. The outer set of peaks in the inset of fig. 3c (circled) correspond to the honeycomb lattice expected of graphene ($a_g = 0.245(3)$ nm) while the inner set of peaks (marked with arrows) correspond to the CDW modulation expected in 1T-TaS$_2$ ($\lambda_{CDW} = 1.20(1)$ nm). The honeycomb appearance of the graphene lattice indicates that the large lattice spacing mismatch between the two materials as well as the smooth variation of the CDW
does not break the sublattice symmetry in graphene which would lead to the appearance of a triangular graphene lattice in STM measurements.

The observation of the CDW modulation through the graphene layer is striking, but the mechanism by which we observe it is not immediately apparent. To investigate the electronic properties of the heterostructure, we perform scanning tunneling spectroscopy (STS). At the surface of G/TaS2 (figure 3d (right panel)), a typical spectrum shows two low energy features: a dip in density of states near zero bias and a shoulder (or a shallow dip) around 550mV. The dip near zero bias is a stable feature across the entire surface, however, the dip at positive bias varies slightly in depth between spectra taken at different locations. Importantly, the spectra observed here are consistent with previous STM experiments taken on bare 1T-TaS2 at this temperature.[29, 36] The fact that the spectrum of G/TaS2 mirrors that of bare 1T-TaS2, and not the expected shifted Dirac spectrum of doped graphene, suggests that the tunneling rate between the tip and the graphene layer is appreciably smaller that the transition rate between the tip and 1T-TaS2, possibly due to graphene’s much smaller carrier density compared to that of 1T-TaS2. This differs qualitatively from previous work, where imaging through a semiconductor encapsulant was only possible within the energy range defined by the semiconductor’s band gap.[37] Thus, as an atomically thin semimetal, the graphene cover is quite unmatched in its utility as it both protects the air sensitive surface while at the same time allowing to image the electronic properties over a wide energy range.

**CDW Vortex Lattice of 1T-TaS2**
Figure 4: a) Large scale STM topography image of G/TaS$_2$ showing the CDW lattice through the graphene layer (measured in high vacuum). Inset: a zoomed in image of the CDW lattice (scale bar is 2 nm) b) Fourier transform of (a) shows six peaks corresponding to the NCCDW ($Q_{NC}$) with satellite peaks nearby ($Q_{sat}$), associated with the long range domain structure with period $2\pi/|k_d|$ c) Slope map (magnitude of the gradient) of the topography image (a) (described in SI-D) highlights domain walls where the CDW amplitude is reduced (some are highlighted in white). Intersection of domain walls form topological vortices and anti-vortices (highlighted with red dots) d) Orientational (black) and translational (red) correlation functions are measured (squares) and fit to a power law (dashed lines) indicating quasi-long range ordering (plotted on linear scales in Supporting Information)

Figure 4a displays a large area STM topography map of G/TaS$_2$ taken at room temperature exhibiting a periodic modulation consistent with that of the CDW of bare/bulk 1T-TaS$_2$. [21, 25, ...]
The expected modulation from the NCCDW phase is subtle and can be difficult to see in large area scans with the naked eye. The fast Fourier transform of the drift corrected STM topography map (given in Supporting Information) is shown in figure 4b. There is a main set of peaks associated with the NCCDW wavevectors as well as nearby satellite peaks which are indicative of the presence of CDW domains. The wavevector which links adjacent domains ($k_d$) is given by the difference between the NCCDW wavevector ($Q_{NC}$) and the satellite wavevector ($Q_{sat}$) so that the domain period is given by $\lambda_d = 2\pi / |k_d| = 6.305(8)$ nm. In figure 4c, we plot a slope map (the gradient) of the topography image (figure 4a). In the slope map, individual CDW peaks appear as small white rings while the periodic reduction of the CDW amplitude at domain walls can be seen as dark lines with spacing approximately equal to $\lambda_d$. Adjacent domains (highlighted with white hexagons in figure 4c) interlock with each other and are rotated with respect to the CDW wavevector. The corners of the domain walls form topologically protected “vortices” and “antivortices” which, like their analogs in type II superconductors, can be removed from the system by annihilating one another. Note that these domains are fundamentally different from the extended domains and domain walls which have been induced within the low temperature, CCDW phase using pulses from an STM tip. The domains in the NCCDW phase are more ordered, due to interlayer interactions, and arise from commensuration strain-induced CDW rearrangements rather than quenched disorder within an insulting background. The CDW domains observed here are consistent with previous X-ray scattering and STM data as well as the theoretical model proposed by Nakanishi and Shiba describing the NCCDW phase of 1T-TaS$_2$. Although previous studies have observed the distortion or loss of equilibrium CDW phases in critically thin 1T-TaS$_2$ films exfoliated onto SiO$_2$, the flake presented here (approximately 14nm thick) is above this thickness and expected to display intrinsic, bulk...
qualities.[13, 40-42] The preservation of the intrinsic spatial ordering of the CDW structure in G/TaS$_2$ suggests that it is possible to study the collective excitations and complex CDW structure of this thin, air-sensitive material through the graphene layer.

Taking advantage of the imaging technique, we perform a correlation analysis of the CDW vortex lattice. First, we determine the vortex/antivortex positions from Voronoi decomposition of the domain lattice.[43] From these we calculate the translational and six-fold orientational correlation functions, $G_T$ and $G_6$, respectively:

$$G_T(r) = \langle \rho_T(r) \rho_T^*(0) \rangle$$

and

$$G_6(r) = \langle \psi_6(r) \psi_6^*(0) \rangle$$

where $\rho_T(\vec{r}) = \sum \exp(-i \mathbf{k}_d^{(i)} \cdot \mathbf{r})$ and $\psi_6(\mathbf{r}) = \sum_{nn} \exp(i 6 \theta(\mathbf{r}))$ are the translational and orientational order parameters, respectively, $\theta(\mathbf{r})$ is the bond angle between neighboring lattice sites (with respect to a fixed axis), $\mathbf{r}$ is a vector connecting two CDW vortex lattice points. The sum in the translational order parameter is over reciprocal lattice vectors of the vortex lattice, $\mathbf{k}_d^{(i)}$, and the sum in the orientational order parameter is over the nearest neighbors of the vortex at each lattice point.[44-46] These functions correlate the spacing and bond orientations between vortex lattice points as a function of distance between them. An arbitrary crystal, with evenly spaced particles, gives a constant $G_T(\mathbf{r})$ and $G_6(\mathbf{r})$, indicating long-ranged ordering, whereas a liquid gives an exponentially decaying $G_T(\mathbf{r})$ and $G_6(\mathbf{r})$. However, in two dimensions, thermal fluctuations prevent the formation of long-range positional order. Instead, a 2D crystal exhibits quasi-long range translational order, characterized by a power law decay of $G_T(\mathbf{r})$, and long range orientational order ($G_6(\mathbf{r}) \sim \text{const.}$). In 2D, there exists a rarely observed hexatic phase between the 2D solid and liquid phases which is characterized by quasi-long range orientational order
The resulting correlation functions for the CDW vortex lattice are plotted in figure 4d on a log-log scale (linear scale is given in Supporting Information). The bond-orientational correlation function, $G_6(r)$, decays as a power law ($\sim r^{-\eta_6}$) with $\eta_6 = 0.03(1)$ indicating quasi-long range orientational order. This is consistent with a 2D hexatic phase, however, in such a case, the translational order correlations are expected to decay exponentially. The translational correlation function, $G_T(r)$, does decay much faster than $G_6(r)$, however the decay shows a power-law dependence with $\eta_T = 0.77(1)$. Thus, the CDW vortex lattice is not a hexatic liquid as described by KTHNY theory. The power law dependence of the translational correlation function suggests instead that the CDW vortex lattice orders as either a Bragg glass or hexatic glass which describe a 2D solid or hexatic liquid which is disordered by pinning impurities.[5, 6, 47-51] Indeed, CDW lattice-size defects are seen in the real space topography and slope images (fig. 4a,c and Supporting Information) which cause local distortions of the CDW vortex lattice. Such pinning defects have been shown to have a small effect on $G_6(r)$ but a large effect on $G_T(r)$ in 2D, consistent with the observations made here.[49, 51, 52] However, a hexatic glass maintains quasi-long range orientational order through the proliferation of dislocations which are rarely observed in the CDW vortex lattice measurement (Fig. 4c and Supporting Information). It is likely that ordering of CDW vortices in the out-of-plane direction stabilizes the Bragg glass phase over the hexatic glass phase as dislocations are not favorable in three dimensions.[53] The presence of quasi-long range translational order without dislocations leads us to conclude that the ordering of CDW vortex
lattice observed here is consistent with that of a Bragg glass, rather than a 2D crystal or hexatic, analogous to that observed in weakly disordered superconducting vortex lattices.

Carrying this analogy further could test our theoretical understanding of topologically ordered systems as well as shed light on the intriguing transport properties of this material. For example, as in-plane electric fields in CDW systems play the role of out-of-plane magnetic fields in superconductors, it would be interesting to probe transitions into less ordered phases as a function of electric field strength, similar to what has been done for superconducting vortex lattices. In addition, varying the thickness of this layered material from single layer to bulk to probe the effect of dimensionality on the CDW vortex ordering as could further extend the phase diagram and help explain why the NCCDW phase is stabilized to lower temperatures in thin, disordered 1T-TaS$_2$ flakes and with rapid cooling.[41, 42, 54] Moreover, reframing the discussion of the transport properties of 1T-TaS$_2$ to include details of the motion and disordering of the CDW vortex lattice may help explain the high pinning energy, in-plane resistivity, negative temperature coefficient and peculiar current fluctuations observed in room temperature transport measurements.[15-18]

SUMMARY

In conclusion, ambient scanning probe measurements of an exfoliated 1T-TaS$_2$ surface were made possible by using a graphene passivation layer to prevent oxidation. These measurements revealed the topological excitations of the NCCDW phase of 1T-TaS$_2$ and brought forth their resemblance to vortex lattices in type II superconductors. By analyzing the spatial correlation functions, we found that these topological excitations organize themselves into a state with quasi-long range order, similar to a Bragg glass state that emerges in superconducting vortex lattices in the presence of pinning defects.
ASSOCIATED CONTENT

Methods used to determine oxidation rate of bare and graphene-covered 1T-TaS$_2$, model simulating the charge density modulation in the NCCDW phase, discussion of contact doping between graphene and 1T-TaS$_2$, drift corrected STM topography used in FFT analysis, CDW vortex lattice points used in correlation analysis, and STM/STS characterization of the graphene layer on SiO$_2$.

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Author Contributions

M. A. A. and E. Y. A. wrote the manuscript, M. A. A. constructed the STM measurement system, performed sample fabrication and KPFM measurements and analysis, M. A. A. and N. T. performed STM and STS measurements and analysis, S. P. and M. A. A. performed correlation analysis of CDW vortices, C. J. W. and S. W. C. grew TaS$_2$ crystals, and G. L. and E. Y. A. provided invaluable motivation and guidance throughout the work.

Notes

The authors declare no competing financial interest.

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