Van der Waals Schottky barriers as interface probes of the correlation between chemical potential shifts and charge density wave formation in 1T-TiSe$_2$ and 2H-NbSe$_2$

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Layered transition metal dichalcogenide (TMD) materials, i.e. 1T-TiSe$_2$ and 2H-NbSe$_2$, harbor a second order charge density wave (CDW) transition where phonons play a key role for the periodic modulations of conduction electron densities and associated lattice distortions. We systematically study the transport and capacitance characteristics over a wide temperature range of Schottky barriers formed by intimately contacting freshly exfoliated flakes of 1T-TiSe$_2$ and 2H-NbSe$_2$ to n-type GaAs semiconductor substrates. The extracted temperature-dependent parameters (zero-bias barrier height, ideality and built-in potential) reflect changes at the TMD/GaAs interface induced by CDW formation for both TMD materials. The measured built-in potential reveals chemical-potential shifts relating to CDW formation. With decreasing temperature a peak in the chemical-potential shifts during CDW evolution indicates a competition between electron energy re-distributions and a combination of lattice strain energies and Coulomb interactions. These modulations of chemical potential in CDW systems, such as 1T-TiSe$_2$ and 2H-NbSe$_2$ harboring second-order phase transitions, reflect a corresponding conversion from short to long-range order.

I. INTRODUCTION

Understanding the mechanism of charge density wave (CDW) formation in low-dimensional correlated systems is of fundamental importance in condensed matter science, where studies of layered transition metal dichalcogenides (TMDs) harboring CDWs, such as 1T-TiSe$_2$ and 2H-NbSe$_2$, have revealed critical insights. The conventional weak-coupling mechanism driving the CDW state, known as the Peierls instability in 1-D, derives from Fermi surface nesting in which the energy gain associated with the formation of an energy gap separating filled and empty states is greater than the energy cost of forming a lattice distortion. On the other hand CDW formation in 1T-TiSe$_2$ and 2H-NbSe$_2$ is believed to be a consequence of strong-coupling, where electron-electron or electron-phonon coupling is considered to be essential.

Direct observations by scanning tunneling spectroscopy/microscopy (STS/STM), angle-resolved photoemission spectroscopy (ARPES), X-ray powder diffraction (XRD), etc, have facilitated a better understanding of the physics of strong-coupling CDW systems. For example, in 2H-NbSe$_2$ with a temperature-independent CDW wave vector, a short range CDW sets in at a temperature almost three times higher than the CDW transition temperature $T_{\text{CDW}}$ (33 K) where long range CDW order dominates. Accordingly, for 2H-NbSe$_2$ the amplitude of the CDW order parameter is well defined within nanosized domains at higher temperature and the phase coherence gradually increases as the temperature is lowered towards an onset of long-range order with global phase coherence at $T_{\text{CDW}}$. The TMD, 1T-TiSe$_2$, exhibits a different behavior. Here, although a short range coherent CDW state has been reported as well [2, 3], the mechanism for CDW formation is associated with the opening of an indirect gap accompanied by the formation of excitons [4]. The amplitude of the order parameter is proportional to the gap and thus with decreasing temperature (for $T < T_{\text{CDW}}$) the amplitude increases towards saturation. For $T > T_{\text{CDW}}$, 1T-TiSe$_2$ is a semimetal and the CDW does not exist.

Transport measurements on CDW materials have traditionally provided evidence for a translational motion of the bulk CDW condensate in the presence of pinning to the underlying lattice. In this work we report systematic temperature-dependent current-voltage ($I$-$V$) and capacitance-voltage ($C$-$V$) measurements on Van der Waals junctions of 1T-TiSe$_2$ and 2H-NbSe$_2$ intimately contacted to moderately-doped n-type GaAs substrates. Specifically we find that mechanically exfoliated thin flakes of 1T-TiSe$_2$ and 2H-NbSe$_2$ form high quality Schottky barriers when placed into intimate contact with n-GaAs substrates with a nominal room-temperature doping concentration of $4.1 \times 10^{16}$ cm$^{-3}$. Advantageously our Schottky junctions serve as surface state probes that are sensitive to quasistatic chemical potential shifts that are associated with CDW formation in bulk.

II. SAMPLE FABRICATION AND EXPERIMENTAL METHODS

Mechanically exfoliated thin flakes of 1T-TiSe$_2$ and 2H-NbSe$_2$, with nominal thicknesses in the range 5-20 $\mu$m, were transferred onto chemically cleaned n-type GaAs wafers as shown in Fig. 1(a). An RCA-I clean followed by a 3:1:50 HNO$_3$:HF:H$_2$O rinse for 2 minutes removed most native organics and oxides on the GaAs. According to our Hall measurements, the commercially available Si-doped GaAs(100) wafer had a nominal doping concentration of $4.1 \times 10^{16}$ cm$^{-3}$ at room temperature. Low resistance ohmic contacts to the GaAs wafers,
robust to temperatures as low as 5 K, were made by rapid thermal annealing using a series of previously described recipes [15]. As shown in Figs. 1(b) and (c), clean and flat flakes of cleaved 1T-TiSe₂ and 2H-NbSe₂, with root mean square surface roughness’s around 4 Å from AFM images, guarantee intimate contact to the GaAs substrate. All measurements in the temperature range from 5 K to 300 K were carried out using a custom low-noise shielded chamber mounted in a Quantum Design Physical Properties Measurement System (PPMS). Four-terminal in-plane transport measurements for intrinsic crystals were performed using lock-in techniques at 526 Hz. DC I-V and AC C-V characteristics at kilohertz frequencies were acquired by a Keithley 2400 source meter and HP 4284A LCR meter. More than 10 devices for both 1T-TiSe₂/n-GaAs and 2H-NbSe₂/n-GaAs junctions were tested and shown to exhibit reproducible features. In Figs. 1(c) and (d), we plot the in-plane resistance as well as the derivative with respect to temperature for thin flakes of 1T-TiSe₂ and 2H-NbSe₂ as a function of temperature, the CDW transition temperatures \( T_{CDW} \) of 1T-TiSe₂ and 2H-NbSe₂ are respectively 193 K and 33 K.

III. SCHOTTKY BARRIERS AS INTERFACE PROBES

As shown in Fig. 2, the measured built-in potential \( V_{bi} \) ideally is equal to the difference between the work functions \( \phi_m \) of the TMD metallic electrode and \( \phi_s \) of the adjacent semiconductor [16]. In the presence of a correction for Fermi level pinning (FLP), the work function \( \phi_s \) of the semiconductor is modified to be \( \phi_s' \) and \( V_{bi} \) becomes,

\[
V_{bi} = \phi_m - \phi_s' = -\mu - \phi_s',
\]

where the chemical potential \( \mu \) is referred to the vacuum level where \( \mu = 0 \). There are two contributions to a temperature-dependent \( V_{bi}(T) \): the first derives from the semiconductor side where \( \xi(T) = E_C - E_F = k_BT \ln(N_C/N_D) \) with \( N_C \) and \( N_D \) denoting the intrinsic (donor dopant) density and the second derives from the TMD side where the chemical potential \( \mu \) or work function \( \phi_m \) shifts associated with CDW formation occur.

Accordingly, after normalizing out the well known \( V_{bi}(T) \) changes arising from the temperature dependence of \( \xi(T) \) in GaAs, we are able - as shown in the paragraphs below - to utilize Eq. 1 to isolate and study the chemical potential shifts due to CDW formation in our 1T-TiSe₂ electrodes. At low temperatures, 1T-TiSe₂ is like a heavily doped semiconductor with a small gap and can be treated as a metallic electrode for this analysis. Similar signatures are also observed in 2H-NbSe₂ based junctions indicating CDW-induced chemical potential shifts in 2H-NbSe₂. For 2H-NbSe₂, the observed \( V_{bi}(T) \) evolves with decreasing temperature, suggesting a crossover from short range to long range CDW order below 90 K in accord with transport and STM measurements [3]. Unexpectedly, for 1T-TiSe₂, the short-to-long range CDW formation feature also appears when we closely analyze the temperature-dependent chemical potential shift in accord with Eq. 1. This common feature for two different materials with demonstrably different CDW formation mechanisms is somewhat surprising and presents a unifying theme embracing the nature of second-order CDW phase transitions in layered 2D TMD materials.
characteristics, described by $I(T) \propto \exp(-e \Phi_{SB}(T)/k_B T) \cdot \exp[(V - I \cdot R_s)/\eta(T) k_B T]$ [15], where the contact resistance $R_s$ is negligible as it is for our junctions. These parameters $\Phi_{SB}(T)$ and $\eta^{-1}(T)$ for both 1T-TiSe$_2$/n-GaAs and 2H-NbSe$_2$/n-GaAs junctions, are extracted by fitting from the linear regime of semi-log scaled $I$-$V$ curves indicated in insets of Figs. 3(a) and (b) and are shown in Figs. 3(c) and (d) respectively.

The deflection or kink delineated by slope changes seen in Fig. 3(c) for the 1T-TiSe$_2$/GaAs junction in the 140 K and 200 K range reveals CDW-induced changes in $\Phi_{SB}(T)$ and $\eta^{-1}(T)$ corresponding to changes of the barrier profile. Such changes are the result of the transition from semimetal to semiconductor in 1T-TiSe$_2$ related to the CDW formation [2]. A similar, although less pronounced, kink signature is also apparent in the vicinity of $T_{CDW}$ $\approx$ 33 K for 2H-NbSe$_2$ as shown in Fig. 3(d), thereby corroborating the correlation between barrier profile change and CDW formation in 2H-NbSe$_2$.

Complementary to forward-bias transport through the interface, capacitance measurements in reverse bias provide a direct measurement of $V_{bi}$ and therefore a quasistatic method to characterize the depletion region and hence the Schottky barrier profile. Firstly, we notice the temperature-dependent zero-bias capacitance, as shown in the upper panels of Fig. 4(a) and (b), experiences a step-like anomaly spanning the range 150 K-200 K for 1T-TiSe$_2$/n-GaAs and begins at 33 K-60 K for 2H-NbSe$_2$/n-GaAs junctions with an upper bound determined below with further analysis. Here, $V_{bi}$ at each temperature is extracted from extrapolated abscissa intercepts of linear $1/C^2$ versus reverse bias voltage $V$ plots [16] $(1/C^2 \propto (V-V_{bi}))$ shown for both 1T-TiSe$_2$/n-GaAs and 2H-NbSe$_2$/n-GaAs junctions at selected temperatures in the insets of Figs. 4(a) and (b).

Central to this paper is the understanding that measured built-in potentials $V_{bi}$ for both metal/semiconductor (see Fig. 2) and heterojunctions reflect the difference between the work functions of the two materials in contact [15]. For our doped GaAs substrates we calculate that deep within the GaAs the energy difference between the conduction band minimum and the chemical potential (Fermi energy) $\xi(T)$ is small ($\xi \approx 60$ mV at 300 K and near zero at low temperature) compared to $V_{bi}$, thereby justifying the use of the measured $V_{bi}$ as a good estimate of the Schottky barrier height. The work functions of 1T-TiSe$_2$ and 2H-NbSe$_2$ at room temperature are around 5.4 eV and 5.6 eV [21], which for the 4.07 eV electron affinity of GaAs together with the Schottky-Mott law for ideal Schottky barriers [21] gives Schottky barrier heights ($\phi_{Mott}$) of 1.33 eV and 1.53 eV for 1T-TiSe$_2$/n-GaAs and 2H-NbSe$_2$/n-GaAs junctions respectively. However, the barrier heights from our $V_{bi}$ measurements at room temperature are somewhat lower at 1.182±0.025 eV and 1.054±0.010 eV respectively (the term $\xi$ is also included), indicating the presence of Fermi level pinning (FLP) effects [22].

To minimize these unavoidable FLP effects in our analysis, a certain temperature range with less FLP origins but overlapping the CDW transition regime is needed.
The pinning coefficient $\gamma$ is calculated by using the FLP relation $\phi = \gamma \phi_{\text{Mott}} + (1 - \gamma) E_g/2$ with the charge neutrality level $\phi_{\text{CNL}} \sim E_g/2$ for simplicity [22], where $\phi$ is the barrier height from measurement, $\phi_{\text{Mott}}$ is the barrier height from the Schottky-Mott law [21], and $E_g = 1.42$ eV is the semiconductor band gap. As seen in the lower panels of Fig. 4, the temperature-dependent relative built-in potentials $\Delta V_{bi} = V_{bi}(T) - V_{bi}(T_{ref})$ for both junctions are depicted as solid green squares. We note, as discussed earlier, that the background increase of $V_{bi}$ with decreasing $T$ is due to the monotonic changes in $\xi(T)$ in the semiconductor whereas the kink is due to CDW induced rearrangement of electron energy distributions in the TMD electrode. For the 1T-TiSe$_2$/n-GaAs junction, we choose the reference temperature $T_{ref}$ as 250 K, $V_{bi}(250K)=1.208\pm0.005$ eV and $\gamma \sim 0.88$, whereas $T_{ref} = 90$ K, $V_{bi}(90K)=1.353\pm0.003$ eV and $\gamma \sim 0.79$ for the 2H-NbSe$_2$/n-GaAs junction. As a procedural check of these similarly calculated pinning coefficients, the results here for the tested devices are not sensitive to the chosen reference temperatures within the vicinity of $\pm 20$ K.

To further interpret our observed step-like anomalies in $V_{bi}(T)$, we use graphite/n-GaAs junctions as reference junctions that are characterized by the same method as already discussed. The red dashed lines shown in Fig. 4 are data scaled by manually shifting the measured $V_{bi}$ for the graphite/n-GaAs junction, with $V_{bi}(250K)=1.082\pm0.008$ eV and $V_{bi}(90K)=1.252\pm0.005$ eV, to the scale of 1T-TiSe$_2$/n-GaAs and 2H-NbSe$_2$/n-GaAs junctions respectively. Here, we consider highly ordered pyrolytic graphite (HOPG) to serve as the “ideal” Van der Waals featureless electrode for the following two reasons: Firstly, HOPG is also a 2D-layered material with a similar honeycomb crystal structure of TMD materials and secondly, HOPG exhibits no phase transition within the temperature range of 5 K to 300 K.

Since metal-induced gap states (MIGS) are strongly suppressed in Van der Waals junctions [20], we justifiably exclude the MIGS induced FLP effect at lower temperatures. In addition, since the lattice distortion’s amplitude during CDW formation in 1T-TiSe$_2$ and 2H-NbSe$_2$ is small compared to the in-plane distance between Se/Ti(Nb)-Se atoms $[5, 22]$, we can also rule out the change of barrier height due to significant breaking of chemical bonds at the Schottky barrier interface. Moreover, with carrier density much higher than moderately doped semiconductors for both materials $[12, 24]$, we exclude the possibility of the observed changes originating from the modulation of interfacial dielectric properties during the CDW formation, a more pronounced mechanism that has already been reported in 1T-TaS$_2$ harboring first-order CDW phase transitions $[25]$.

We consequently interpret the $\Delta V_{bi}$ kink feature existing in both junctions as a chemical potential shift accompanying CDW formation in 1T-TiSe$_2$ and 2H-NbSe$_2$. Although the explicit correlation between CDW formation and chemical potential has already been discussed and confirmed in 1T-TiSe$_2$ owing to the change of the associated order parameter’s amplitude during CDW formation $[14, 26]$, a corresponding shift in 2H-NbSe$_2$ has to our knowledge not been reported.

In both 1T-TiSe$_2$ and 2H-NbSe$_2$, the CDW wave vector $\mathbf{q}$ is temperature independent $[3, 4, 17]$. Therefore, only the CDW energy gap $\Delta$ and the relative phase $\phi$ of the charge displacements characterize the CDW formation in both materials $[6]$. From ARPES studies of 1T-TiSe$_2$ at low temperatures $[14]$ the change of the energy gap $\Delta$ is associated with CDW formation raising the chemical potential by around 40 meV. However, a slight deviation of the experimental result from an exciton condensate model at temperatures ranging from 150 K to 200 K is noticed $[14, 26]$, which when combining with the signature of short range coherent CDW $[12, 13]$, indicates that changes in phase coherence are also significant for CDW formation in 1T-TiSe$_2$. The case for CDW formation in 2H-NbSe$_2$ is conversely, somewhat different. During the CDW formation in 2H-NbSe$_2$, phase coherence is gradually developed and completed down to $T_{CDW}$ (from short range to long range CDW), whereas the amplitude of the CDW order parameter is well-defined with a finite amplitude over the temperature range starting from higher temperature as shown in a systematic work by Chatterjee et al. $[4]$.

In this paper we are addressing evidence in support of the hypothesis that chemical potential shifts in a CDW
material are linked with the evolution of a CDW’s complex order parameter comprising both amplitude and phase. To our knowledge there are no experiments that can simultaneously detect the amplitude and phase of the CDW order parameter. Our evidence (Fig. 5) for effective chemical potential shifts $\Delta \mu_{eff}$ of graphite/n-GaAs junction (red) and $\Delta V_{bi}$ for both junctions (green) shown in Fig. 4. The red dashed lines are guides to the eye for the temperature dependent phase coherence of CDW formation.

In summary, by use of “simple” Van der Waals Schottky barriers between layered TMD materials and the moderately doped semiconductor n-type GaAs, we have found common features of CDW formation in 1T-TiSe$_2$ and 2H-NbSe$_2$. These common features suggest that similar considerations may apply to other layered TMD strong-coupling CDW materials. Our insights provide a complementary understanding of the mechanism of CDW formation in low-dimensional correlated systems and have shown a promising route for detecting and analyzing collective interfacial phenomena arising from strong correlation. The use of Schottky barriers as surface state probes not only enlightens our understanding of the electronic states in low dimensional correlated systems but also suggests technological applications.

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