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μ-ARPES study of monolayer 1*T*-$TaSe_2$ and 1*T*-$NbSe_2$ films

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1 Introduction

The layered transition-metal dichalcogenide (TMD) 1*T*-TaS_2 is believed to be a special example of a bandwidth-controlled Mott transition material in the absence of magnetic order. Bulk 1*T*-TaS_2 undergoes a Mott transition accompanying a commensurate charge-density wave (CDW) characterized by the star-of-David cluster [Fig. 1(a)] with a $\sqrt{13}\times\sqrt{13}$ periodicity [Fig. 1(b)], at $T_{\text{CDW-Mott}} \sim$ 200 K. Although the Coulomb interaction U of Ta 5*d* electrons is relatively small (~0.7 eV), 1*T*-TaS_2 undergoes the Mott transition when the half-filled band is narrowed to the scale of U due to the band folding associated with the CDW in a similar manner to tilted bilayer graphene. More interestingly, it was shown that while it has a charge gap of ~0.3 eV, it shows gapless quantum-spin-liquid dynamics and no long-range magnetic order down to 70 mK. Recently, the exploration for Mott phases coexisting with CDW was extended to the atomic-layer limit in TMDs with the possible emergence of exotic quantum phenomena in the pure 2D limit. However, the nature of a pure 2D CDW-Mott phase, such as its robustness, possibility for magnetism, and differences if any, compared with the 3D bulk case, has been scarcely explored experimentally. To address all the above key issues, we performed a comprehensive angle-resolved photoemission spectroscopy (ARPES) study on epitaxially grown monolayer 1*T*-$TaSe_2$ and 1*T*-$NbSe_2$ films [1].

2 Experiment

Bilayer graphene was prepared by annealing an n-type Si-rich 6H-SiC(0001) single-crystal wafer, with resistive heating at 1100 °C in ultrahigh vacuum better than 1×10^{-10} Torr for 30 min. A monolayer $TaSe_2$ ($NbSe_2$) film was grown by evaporating Ta (Nb) on the bilayer graphene substrate kept at 560 °C (580 °C) under a Se atmosphere. The as-grown film was subsequently annealed at 400 °C for 30 min. After the fabrication by the MBE method, the films were transferred to the ARPES-measurement chamber without breaking the vacuum.

ARPES measurements were carried out using μ-ARPES system at the beamline BL-28A in Photon Factory, KEK [2], as well as using home-built ARPES system at Tohoku University and synchrotron-based ARPES system at Taiwan Light Source (TLS). The energy and angular resolutions were set to be 12.5–40 meV and 0.2°, respectively.

3 Results and Discussion

Figure 1(c) displays the 3D ARPES intensity plotted as a function of 2D wave vector (k_x and k_y) and binding energy E_B measured at T = 40 K. One can clearly recognize a nearly flat band at $E_B \sim$ 0.3 eV and dispersive holelike bands topped at the Γ point, which are ascribed to the Ta 5*d* and Se 4*p* bands, respectively. The topmost Ta 5*d* band does not cross the Fermi level (E_F) and exhibits an insulating gap of ~0.3 eV below E_F at the Γ point. This gap

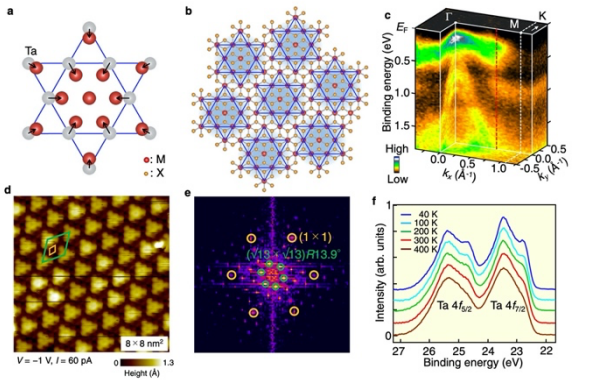

Fig. 1 (a) Schematics of the displacement of Ta atoms in the star-of-David cluster. (b) Crystal structure for monolayer 1*T*-$TaSe_2$ and star-of-David clusters with the $\sqrt{13} \times \sqrt{13}$ periodicity. (c) 3D ARPES-intensity plot for monolayer 1*T*-$TaSe_2$ at T = 40 K. Hybridization gap ($k_x \sim$ 2/3 ΓM) is indicated by red dashed line. (d) STM image in a surface area of 8 × 8 nm^2 for monolayer $TaSe_2$. (e) Fourier transform image of (d). (f) Ta-4*f* core level measured with $h\nu$ = 260 eV for monolayer $TaSe_2$ [1].

is assigned to a Mott-Hubbard gap which is associated with the enhancement of U/W caused by the hybridization of backfolded bands and the resultant band narrowing due to the $\sqrt{13}\times\sqrt{13}$ commensurate CDW [Fig. 1(b)]. The gap size below E_F, called here Δ_{Mott}, roughly corresponds to a half of the full Mott-gap size $2\Delta_{Mott}$ because E_F is nearly located at the midpoint between the lower Hubbard band (LHB) and the upper Hubbard band (UHB). As shown in Fig. 1(c), a signature of the CDW is clearly seen as an apparent hybridization-gap discontinuity in the band dispersion at $k \sim 2/3$ ΓM (see red dashed line of Fig. 1c). The STM image in Fig. 1(d) obtained in a spatial region of 8×8 nm^2 on a monolayer $TaSe_2$ island signifies a clear periodic modulation associated with the formation of CDW containing the hexagonal lattice of star-of-David clusters. We have confirmed that this lattice has a periodicity of $\sqrt{13}\times\sqrt{13}$R13.9° expected for the formation of star-of-David lattice, as well visible as superspots in the Fourier transform image shown in Fig. 1(e).

The Ta 4*f* core-level spectroscopy in Fig. 1(f) signifies that the Ta $4f_{5/2}$ and $4f_{7/2}$ spin-orbit satellite peaks split into two subpeaks, as is clearly visible in the energy-distribution curve (EDC) at $T = 40$ K. Since the additional splitting of Ta-4*f* peak is attributed to the different electron density at each Ta site and/or the change in the chemical bonding of Ta atoms due to the formation of the star-of-David clusters, the core-level spectrum is consistent with our STM data that support the formation of the star-of-David clusters. On elevating temperature, we found that the lower-binding-energy subpeak of both the Ta$4f_{5/2}$ and $4f_{7/2}$ components is gradually weakened, but the shoulder feature still remains even at $T = 400$ K. This implies that the Mott phase survives much above the room temperature.

Figure 2a shows temperature dependence of EDC at the Γ point for monolayer 1*T*-$TaSe_2$, together with the EDC for bulk 1*T*-$TaSe_2$ and bulk 1*T*-TaS_2. Intriguingly, the LHB survives even up to $T = 450$ K, whereas the overall spectral feature becomes less clear. In bulk $TaSe_2$, the LHB essentially vanishes at room temperature and a large metallic spectral weight emerges at E_F, in contrast to the low-temperature (70–220 K) data that display a peak associated with the LHB. Our ARPES data for monolayer 1*T*-$TaSe_2$ at room temperature resemble that of bulk $TaSe_2$ at low temperature in Fig. 2(a), suggestive of the persistence of a Mott gap at $T = 450$ K.

We show in Fig. 2(b) the Δ_{LEM} (binding energy of the leading-edge midpoint) vs T plot. Δ_{LEM} for monolayer 1*T*-$TaSe_2$ shows a nearly linear behavior as a function of T near $T_{CDW\text{-}Mott}$, and exhibits a finite value even at 450 K. This nearly linear behavior is also seen in bulk 1*T*-TaS_2 as shown in Fig. 2(b). From the numerical fittings, the transition temperature was estimated to be $T_{CDW\text{-}Mott} \sim 530$ K for monolayer 1*T*-$TaSe_2$, and this is much higher than that obtained for bulk 1T-TaS_2.

We compare the characteristic energy scales between monolayer $TaSe_2$ and $NbSe_2$ in in Figs. 2(c) and 2(d). One

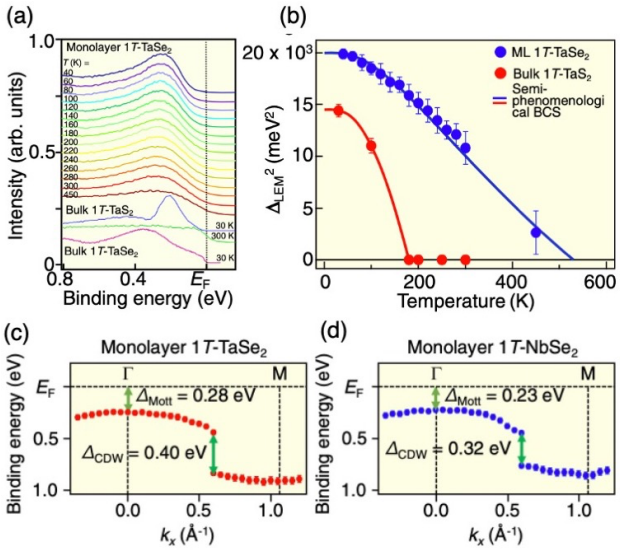

Fig. 2 (a) Temperature dependence of EDC at the Γ point. EDC for bulk 1T-TaS2 (T = 30 and 300 K) and bulk 1T-$TaSe_2$ ($T = 30$ K) is also shown as a reference. (b) Squared leading-edge midpoint Δ_{LEM} at the Γ point plotted against T for monolayer 1*T*-$TaSe_2$ (blue circles), together with the numerical fitting results. (c), (d) Experimental band dispersion extracted from the ARPES data for monolayer $TaSe_2$ and $NbSe_2$, respectively [1].

can see that a half of the full Mott gap, Δ_{Mott}, in $TaSe_2$ (0.28 ± 0.02 eV) is slightly larger than that in $NbSe_2$ (0.23 ± 0.02 eV). Also, the hybridization gap Δ_{CDW} in $TaSe_2$ (0.40 ± 0.03 eV) is larger than that in $NbSe_2$ (0.32 ± 0.03 eV). The general trend of 3*d*–4*d*–5*d* electron systems, it is expected that a larger U/W and a resultant more stable CDW–Mott phase in $NbSe_2$ than in $TaSe_2$, the observed smaller Δ_{Mott} (0.23 eV) in $NbSe_2$ apparently contradicts with such trend [1]. This discrepancy may be reconciled by taking into account the observed larger Δ_{CDW} (0.40 eV) in $TaSe_2$, which suggests a smaller intralayer hopping and as a result a larger U/W compared with $NbSe_2$. This suggests that the lattice displacement in the star-of-David cluster is stronger in monolayer $TaSe_2$, which is also inferred from the stronger metallic-bonding character of Ta than that of Nb. All these arguments suggest that the robust CDW–Mott insulator phase of monolayer $TaSe_2$ and $NbSe_2$ is caused by the disappearance of interlayer hopping assisted by a strong lattice distortions.

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