Layer-dependent electronic structure of an atomically heavy two-dimensional dichalcogenide

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We report angle-resolved photoemission spectroscopic measurements of the evolution of the thickness-dependent electronic band structure of the atomically heavy two-dimensional layered dichalcogenide, tungsten diselenide (WSe2). Our data, taken on mechanically exfoliated WSe2 single crystals, provide direct evidence for shifting of the valence-band maximum from Γ (multilayer WSe2) to K (single-layer WSe2). Further, our measurements also set a lower bound on the energy of the direct band gap and provide direct measurement of the hole effective mass.

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Single layers of two-dimensional metal dichalcogenides (TMDCs) such as MoS2 have emerged as a new class of noncentrosymmetric direct-band-gap materials with potential photonic and spintronic applications [1,2]. Among the TMDC family, tungsten-based dichalcogenides, such as WSe2, exhibit high in-plane carrier mobility and allow electrostatic modulation of the conductance [3,4], characteristics that make them promising for device applications. For example, bulk WSe2 possesses an indirect band gap of 1.2 eV [1,5] and has been used as the channel of a field-effect transistor (FET) with an intrinsic hole mobility of up to 500 cm2/V s [6]. By comparison, WSe2, in its monolayer form (ML), should have a direct band gap, as predicted by theory [7–12], and a promising intrinsic hole mobility of 250 cm2/V s, as recently demonstrated in the performance of top-gated FETs [4]. In addition, ML WSe2 has been demonstrated to be the first TMDC material possessing ambipolar, i.e., both p-type and n-type, conducting behavior [4,12], thus making it possible to design additional electronic functionality, such as p–n junctions or complementary logic circuits.

Despite these intriguing characteristics, measurements of ML WSe2 have generally been limited to probing of optical and transport properties [4–6]. In this Rapid Communication, we report thickness-dependent measurements of the surface and electronic structure of exfoliated WSe2, using low-energy electron microscopy (LEEM), diffraction (LEED), and micrometer-scale angle-resolved photoemission spectroscopy (µ-ARPES) of samples supported on a native-oxygen-terminated silicon substrate. Our experimental results provide direct evidence for a predicted valence-band maximum (VBM) symmetry-point change, which leads to an indirect-to-direct band-gap transition. Because TMDCs have a large carrier effective mass and reduced screening in two dimensions, electron-hole interactions are much stronger than in conventional semiconductors [13–15]. Our results allow us to obtain a direct measurement of the hole effective mass. Finally, our measurements allow us to directly infer a lower bound on the energy of the direct band gap.

Our measurements were performed using the spectroscopic photoemission and low-energy electron microscope (SPELEEM) system at the National Synchrotron Light Source (NSLS) beamline USUA [16,17]. The spectrometer energy resolution of this instrument was set to 100 meV at 33 eV incident photon energy with a beam spot size of 1 μm in diameter. The momentum resolution is ∼0.02 Å−1. Exfoliated WSe2 samples were transferred to a native-oxygen covered Si substrate; prior to measurements, these samples were annealed at 350 °C for ~12 h under UHV conditions. The layer number of the sample is determined by Raman and photoluminescence spectroscopy [18,19]. Additional experimental details can be found in the Supplemental Material [20], which includes Refs. [21,22].

Sample quality and crystal orientation were examined using both LEEM and µ-LEED (Fig. 1). Diffraction patterns (at a primary electron energy of 48 eV) of exfoliated WSe2 flakes of 1–3 ML and bulk are shown in Figs. 2(a)–2(d), respectively, and clearly display the sixfold crystal symmetry. At an electron energy of 48 eV, the mean free path of the low-energy electrons is ∼5.2 Å [23], which is comparable to the thickness of a single covalently bound Se-W-Se unit of monolayer WSe2 (∼7 Å) [24,25]. With increasing WSe2 thickness, the LEED spots become sharper, due in part to decreased scattering from the substrate [25]. This assertion is supported by the monotonically decreasing full width at half maximum (FWHM) of the (00) diffraction spot, plotted for different electron energies in Fig. 2(e) [25].

The electronic structure of the top-lying valence bands of WSe2 is derived from the W 5d and Se 4p orbitals [26,27], each of which possesses a strongly varying photon-energy-dependent photoionization cross section [28], as displayed in Fig. 3(b). Prior work [28] has shown that the cross section of the W 5d subshell is an order of magnitude larger than that of Se 4p at the photon energy of 33 eV used in our experiments [indicated by the vertical line in Fig. 3(b)]. Thus the primary contributions to our µ-ARPES measurements, shown in Fig. 4, are from the W 5d orbitals. Angle-integrated photoemission spectra of 1 ML WSe2 along high-symmetry directions and over the full Brillouin zone (BZ) are shown in Fig. 3(c). These spectra show a clear energy cutoff at about 1.8±0.1 eV above the VBM, which we identify as the position of the Fermi level EF. The band gap of ML WSe2 has been previously reported to be in the range of 1.4–2.3 eV [19,29,30]. Based on our identification of the Fermi energy, the minimum band-gap value of WSe2 must be greater than at least 1.8 eV; this
result also suggests that our exfoliated ML WSe$_2$ is heavily electron doped, i.e., the Fermi level falls near the conduction-band minimum \cite{31,32}. The energy differences between the Fermi level ($E_F$) and the VBM for 2 ML, 3 ML, and bulk are approximately 1.5, 1.5, and 1.1 eV, respectively. Taking into account the previously reported band-gap energies of these materials, we find that these energy differences are consistent with our samples being heavily electron doped, regardless of thickness. This result suggests that our electron doping is more likely to be intrinsic to the layered material and not due to charge transfer from the substrate.

Our µ-ARPES measurements of 1–3 ML and bulk WSe$_2$ along the high-symmetry directions $\bar{M} - \tilde{\Gamma} - \bar{K}$, given in Fig. 4, clearly show a change in the occupied electronic structure with a change in layer thickness. Superimposed on the measured data are the corresponding density functional theory–local density approximation (DFT-LDA) band calculations, computed using ABINIT without a spin-orbit interaction \cite{33,34}. In the spectra, the distinctive features include the VBM at $\tilde{\Gamma}$, derived from the W $d_{z^2}$ and Se $p_z$ orbitals, the VBM at $\bar{K}$, derived from the W $d_{x^2-y^2}$ and Se $p_x/p_y$ orbitals, and the valley between $\tilde{\Gamma}$ and $\bar{K}$, derived from a crossover to the W $d_{z^2}$/$d_{xy}$ orbitals from the W $d_{z^2}$ and Se $p_z$ orbitals \cite{11,35,36}, as shown and labeled in Fig. 4(a). Bands of higher binding energies and along other high-symmetry directions have been previously calculated and discussed in the literature \cite{11,26,27,35-37}. These features are further displayed in the corresponding energy distribution curves (EDCs) [see Fig. 4(b)] and momentum distribution curves (MDCs) [see Fig. 4(c)]. Note that several of the WSe$_2$ bands are not detected in our ARPES measurements due to matrix-element selection rules as well as the above-mentioned difference in the photoionization cross section between W- and Se-derived states. In our experiments, the incident photon flux was directed normal to the sample surface so that its polarization is in the plane of the WSe$_2$ crystal, thus suppressing excitation of states with out-of-plane character. This result explains why the W- and Se-derived states with a $z$ or out-of-plane component, i.e., $d_{z^2}$ or $p_z$ orbital, in the uppermost valence band (UVB) near $\tilde{\Gamma}$ have a consistently relatively weaker, but nonzero, intensity for 1–3 ML and bulk WSe$_2$.

An important feature of our measurements is the change in the energy of the uppermost valence band (UVB) at $\tilde{\Gamma}$ and $\bar{K}$ for 1 ML WSe$_2$ compared to that of few-layer WSe$_2$. Our µ-ARPES spectra show that the valence-band maximum is at $\bar{K}$ for 1 ML WSe$_2$ and shifts to $\tilde{\Gamma}$ for multilayer WSe$_2$. Previous reports \cite{38-42} using traditional ARPES and inverse photoemission instruments have confirmed that the location of the VBM in bulk WSe$_2$ is at $\tilde{\Gamma}$; note that for bulk WSe$_2$, ARPES measurements over a large enough photon energy range are required in order to take into account the $k_z$ dependence of the observed states. To fully quantify the VBM transition as a function of thickness, we used curvature analysis \cite{43}, or the second-derivative method, to help delineate the electronic band structure, as shown in Fig. 5. Figures 5(a)–5(d) give the bands for the 1–3 ML and bulk WSe$_2$ samples, derived from the data in Fig. 4 using this method, and with the zero energy referenced to the VBM. The UVB of exfoliated WSe$_2$ closely matches the corresponding calculated bands (white curves), except for the monolayer case, where the measured energy difference between $\tilde{\Gamma}$ and $\bar{K}$ is less than that predicted by theory, and where the dispersion at $\tilde{\Gamma}$ is greater than that in the calculated bands. The experimentally measured and theoretically predicted \cite{11} energy differences between $\tilde{\Gamma}$ and $\bar{K}$ for monolayer and multilayer WSe$_2$ are plotted in Fig. 5(e). The measured energy differences are 0.21, −0.14, and −0.25 eV for 1–3 ML; the value for bulk WSe$_2$ has been reported previously to be −0.3 eV \cite{39,41}. The error bars denote the standard deviation of the fittings from all six high-symmetry equivalent directions, and they are well under the detector error of ±0.10 eV. Thus, these results provide direct experimental evidence for a thickness-dependent shift...
FIG. 3. (Color online) (a) Brillouin zone and high-symmetry points of WSe$_2$. (b) Atomic photoionization cross section for W 5$d$ and Se 4$p$ subshells as a function of ARPES photon energy [28]. At 33 eV, the cross section between W 5$d$ and Se 4$p$ has an order-of-magnitude difference. Therefore, the dominant features in our ARPES measurement are the contribution of the W 5$d$ subshell. Note that the Cooper minimum of the Se orbital is $\sim$50 eV. (c) Angle-integrated photoemission spectra of monolayer WSe$_2$ extracted from high-symmetry directions $K$-$\Gamma$-$K$ and $M$-$\Gamma$-$M$, and over the full BZ, referenced with respect to the Fermi level.

in the relative energy of the VBM at $\Gamma$ and at $\bar{K}$ and, hence, strong support for a shift from an indirect to a direct band gap in going from 2 to 1 ML WSe$_2$.

An analysis of the curvature of the bands from the $\mu$-ARPES measurements also allows us to deduce the effective mass of monolayer and bilayer WSe$_2$. For monolayer WSe$_2$, we determined an experimentally derived hole effective mass of $1.4 \pm 0.6m_0$ [44] (where $m_0$ is the electron mass) at $\bar{K}$, which is $\sim$3 times larger than theoretical predictions, and a hole effective mass of $3.5 \pm 1.8m_0$ [44] at $\bar{\Gamma}$. The latter quantity is approximately half as large as theoretical predictions ($7.1 \pm 0.2m_0$) [7–10,45]. For the case of bilayer WSe$_2$, however, we determined an experimentally derived hole effective mass of $0.4 \pm 0.1m_0$ at $\bar{K}$, which agrees well with theoretical predictions.

FIG. 4. (Color online) $\mu$-ARPES band mapping of exfoliated WSe$_2$ for (a) 1 ML, (d) 2 ML, (c) 3 ML, and (f) bulk along the high-symmetry path $M$ -- $\Gamma$ -- $K$ in the Brillouin zone. $E = 0$ denotes the Fermi level. The overlaid white lines are our DFT-calculated band structures. The calculations do not include the effect of spin-orbit coupling. (b), (c) Corresponding EDCs and MDCs of 1 ML WSe$_2$, respectively.
monolayer MoS2. Thus, resolving the spin-orbit splitting in widths, that the transfer process introduces corrugation in linewidth [51] of the spin-orbit split bands, leading to a broad roughness, induced in the transfer process, is broadening the clear peaks in the vicinity of¯KΓ0. We conjecture that the sample roughness, induced in the transfer process, is broadening the clear peaks in the vicinity of¯KΓ0. We expect that this observation provides support for an indirect-to-direct band-gap transition. For monolayer WSe2, we have found a lower bound of 1.8 eV for the band gap and measured a hole effective mass of 1.4m0 at K and 3.5m0 at Γ. We expect that these results will provide insight for understanding the optical and electronic properties of monolayer and multilayer WSe2 that is important for devices made from this transition-metal dichalcogenide material.

In conclusion, we have probed the surface structure and occupied electronic bands of one- to three-layer exfoliated WSe2 crystals prepared by transfer to a native-oxide-terminated Si substrate. LEEM and µ-LEED provided real-space and reciprocal-space structural measurements of WSe2, revealing clearly resolved thickness-dependent contrast and diffraction spot widths, respectively. Our µ-ARPES measurements have probed the occupied valence-band structure and confirmed the transition of the valence-band maximum from Γ to K as the thickness is reduced from few-layer to 1 ML WSe2; this observation provides support for an indirect-to-direct band-gap transition. For monolayer WSe2, we have found a lower bound of 1.8 eV for the band gap and measured a hole effective mass of 1.4m0 at K and 3.5m0 at Γ. We expect that these results will provide insight for understanding the optical and electronic properties of monolayer and multilayer WSe2 that is important for devices made from this transition-metal dichalcogenide material.

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[44] The estimated error here is a combination of the standard error in parabolic fitting and the standard deviation of the effective mass along different high symmetry directions.

[45] Based on our DFT-LDA calculation.


