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Layer-dependent electronic structure of an atomically heavy 2D dichalcogenide

Po-Chun Yeh,1 Wencan Jin,2 Nader Zaki,2 Datong Zhang,2 Jonathan T. Liou1, Jerzy T. Sadowski,3 Abdullah Al-Mahboob,3 Jerry I. Dadap,2 Irving P. Herman,2 Peter Sutter,3 and Richard M. Osgood, Jr.1,2,*

1 Department of Electrical Engineering, Columbia University, New York, New York 10027, USA
2 Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027, USA
3 Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, USA

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Abstract

We report angle-resolved photoemission spectroscopic measurements of the evolution of the thickness-dependent electronic band structure of the heavy-atom 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.

Single layers of two-dimensional metal dichalcogenides (TMDCs) such as MoS₂, have emerged as a new class of non-centrosymmetric direct-bandgap 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, which make them promising for device applications. For example, bulk WSe₂ possesses an indirect bandgap 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][8][9][10][11][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][5][6] In this paper, 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-oxide 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 bandgap 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][14][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 (SPE-LEEM) system at the National Synchrotron Light Source (NSLS) beamline U5UA.\cite{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 WSe\(_2\) samples were transferred to a native-oxide covered Si substrate; prior to measurements, these samples were annealed at 350\(^\circ\)C for ~12 hours under UHV conditions. The layer number of the sample is determined by Raman and photoluminescence spectroscopy.\cite{18,19} Additional experimental details can be found in the Supplemental Materials section.

Sample quality and crystal orientation were examined using both LEEM and \(\mu\)-LEED (Fig. 1). Diffraction patterns (at a primary electron energy of 48eV) of exfoliated WSe\(_2\) flakes of 1-3ML and bulk are shown in Fig. 2a-d, respectively, and clearly display the six-fold crystal symmetry. At an electron energy of 48eV, the mean free path of the low-energy electrons is ~5.2Å,\cite{20} which is comparable to the thickness of a single covalently bound Se-W-Se unit of monolayer WSe\(_2\) (~7Å).\cite{4,21} With increasing WSe\(_2\) thickness, the LEED spots become sharper due, in part, to decreased scattering from the substrate.\cite{22} 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. 2e.\cite{22}

The electronic structure of the top-lying valence bands of WSe\(_2\) is derived from the W 5d and Se 4p orbitals\cite{23,24}, each of which possesses a strongly varying photon-energy-dependent photoionization cross-section,\cite{25} as displayed in Fig. 3b. Prior work\cite{25} 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 33eV used in our experiments (indicated by the vertical line in Fig. 3b.) Thus the primary contributions to our \(\mu\)-ARPES measurements, shown in Fig. 4, are from the W 5d orbitals. Angle-integrated photoemission spectra of 1ML WSe\(_2\) along high symmetry directions and over the full Brillouin Zone (BZ) are shown in Fig. 3c. These spectra show a clear energy cut-off at about 1.8±0.1eV above the VBM, which we identify as the position of the Fermi level \(E_F\). The bandgap of ML WSe\(_2\) has previously been reported to be in the range of 1.4 to 2.3eV.\cite{19,26,27} Based on our identification of the Fermi energy, the minimum bandgap value of WSe\(_2\) must be greater than at least 1.8eV; 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{28,29} The energy differences between the Fermi level (\(E_F\)) and the VBM for 2ML, 3ML, and bulk, are approximately 1.5eV, 1.5eV, and 1.1eV, respectively. Taking into account the previously reported bandgap 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 \(\mu\)-ARPES measurements of 1-3ML and bulk WSe\(_2\) along the high symmetry directions \(\bar{M}\rightarrow\bar{\Gamma}\rightarrow\bar{K}\), given in Fig. 4, clearly show a transition in the occupied electronic structure with change in layer thickness. Superimposed on the measured data are the corresponding DFT-LDA band calculations, computed using ABINIT without spin-orbit interaction.\cite{30,31} In the spectra, the distinctive features include the VBM at \(\bar{\Gamma}\), derived from the W \(d_z^2\) and Se \(p_z\) orbitals, the VBM at \(\bar{K}\), derived from the W \(d_{x^2-y^2}/d_{xy}\) and Se \(p_x/p_y\) orbitals, and the valley between \(\bar{\Gamma}\) and \(\bar{K}\), derived from a crossover to the W \(d_{x^2-y^2}/d_{xy}\)
orbitals from the W $d_{xy}$ and Se $p_z$ orbitals,[11][32][33] 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.[11][23][24][32][33][34] 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., $d_{xy}$ or $p_z$ orbital, in the uppermost valence band (UVB) near $\Gamma$ have a consistently relatively weaker, but non-zero, intensity for 1-3ML and bulk WSe$_2$.

An important feature of our measurements is the change in the energy of the upper-most valence band (UVB) at $\Gamma$ and $K$ for 1ML WSe$_2$ compared to that of few-layer WSe$_2$. Our $\mu$-ARPES spectra show that the valence band maximum is at $K$ for 1ML WSe$_2$ and shifts to $\Gamma$ for multilayer WSe$_2$. Previous reports[35][36][37][38][39] using traditional ARPES and inverse photoemission instruments have confirmed that the location of the VBM in bulk WSe$_2$ to be at $\Gamma$; 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,[40] or the second-derivative method, to help delineate the electronic band structure, as shown in Fig. 5. Figures 5a-d give the bands for the 1-3ML 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 $\Gamma$ and $K$ is less than that predicted by theory, and where the dispersion at $\Gamma$ is greater than that in the calculated bands. The experimentally measured and theoretically predicted[11] energy differences between $\Gamma$ and $K$ for monolayer and multilayer WSe$_2$ are plotted in Fig. 5e. The measured energy differences are: 0.21eV, -0.14eV, and -0.25eV for 1-3ML; the value for bulk WSe$_2$ has been reported previously to be -0.3eV.[36][38] 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 ±0.10eV. Thus, these results provide direct experimental evidence for a thickness-dependent shift in the relative energy of the VBM at $\Gamma$ and at $K$, and, hence, strong support for a shift from an indirect to a direct bandgap 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±0.6$m_0$[41] (where $m_0$ is the electron mass) at $K$, which is $\sim$3x larger than theoretical predictions, and a hole effective mass of 3.5±1.8$m_0$[41] at $\Gamma$. The later quantity is approximately half as large as theoretical predictions (7.1±0.2$m_0$)[7][8][9][10][42]. For the case of bilayer WSe$_2$, however, we determined an experimentally derived hole effective mass of 0.4±0.1$m_0$ at $K$, which agrees well with theoretical predictions.[7][9] The origin of the discrepancy between experiment and DFT calculations for the case of a monolayer is uncertain at this time. Our
finite energy resolution does contribute to the measurement error. However, it is also apparent that there is an overall difference in band dispersion between our relatively simple theory calculation and experiment. This reasoning indicates that the above discrepancy is more complicated than simple instrumentation limits. Note that our DFT-derived effective-mass value of 0.44m₀ for monolayer WSe₂ at K̅ is in reasonable agreement with previous theoretical reports. Also since $m_{\text{eff}} \propto \frac{g^2 E}{\hbar^2 k}$, slight measurement errors are accentuated by the flat-like dispersion curve in the vicinity of Γ̅.

“Renormalization” in bands of other 2D dichalcogenides have also been reported, though the reason for this remains in question. Other possible explanations beyond that of an intrinsic nature of WSe₂ include effects of substrate interaction, such as strain, dielectric screening, etc.

In comparison to monolayer MoS₂, monolayer WSe₂ is expected to have an even larger spin-orbit splitting in the vicinity of K̅, with a theoretically predicted value of $\sim 0.46$ eV v.s. $\sim 0.16$ eV of MoS₂. The expected splitting of the valence band along the Γ̅-K̅ direction of monolayer WSe₂ is due to the strong spin-orbit coupling originating from the high mass of the constituent elements and the lack of inversion symmetry. The theoretically predicted value ($\sim 0.46$ eV) is larger than our experiment energy resolution and thus, should have been resolved directly in our measurements. However, despite the presence of an increasing linewidth of the UVB in the direction of Γ̅-K̅, which may be attributed to spin-orbit-splitting of the bands, we do not see two clear peaks in the vicinity of K̅. We conjecture sample roughness, induced in the transfer process, is broadening the linewidth of the spin-orbit split bands, leading to a broad unresolved band in our ARPES measurements. We have shown in previous works, using an analysis of LEED spot widths, that the transfer process introduces corrugation in monolayer MoS₂. Thus, resolving the spin-orbit-splitting in monolayer dichalcogenides is demanding in terms of a flat transfer procedure.

In conclusion, we have probed the surface structure and occupied electronic bands of 1 – 3 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 K̅ as the thickness is reduced from few-layer to 1ML WSe₂; this observation provides support for an indirect-to-direct bandgap transition. For monolayer WSe₂, we have found a lower bound of 1.8 eV for the bandgap and measured a hole effective mass of 1.4 m₀ at K̅ and 3.5 m₀ at Γ̅. We expect that these results will provide insight to the understanding of the optical and electronic properties of monolayer and multilayer WSe₂ that is important for novel devices made from this transition-metal-dichalcogenide material.
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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.

Based on our DFT-LDA calculation.


Figure 1 (a) Side view and (b) top view of the trigonal prismatic coordination of the atoms in 2H-WSe$_2$. (c) LEEM image of 1ML WSe$_2$ after transfer (detector artifacts and background signal have been removed.) The inset is the corresponding optical microscope image of the same sample. LEEM images were taken at an electron energy of 1.8eV.

Figure 2: (a)-(d) Micro-LEED patterns at 48eV electron energy on exfoliated WSe$_2$ 1 ML (a), 2 ML (b), 3 ML (c), and bulk (d) after transfer to Si. The halo around 1ML (00) spot came from edge deflection of electrons due to a limited sample size. (e) Measured FWHM of the (00) LEED spot for 1-3ML WSe$_2$ flakes relative to that of bulk, measured at 20.5, 30, and 40eV electron energy. The FWHM decreases with increasing number of layers, since electrons elastically backscattered from the Si substrate are progressively decreased.
Figure 3: (a) Brillouin zone and high-symmetry points of WSe$_2$. (b) Atomic photoionization cross-section for W 5d and Se 4p subshells as a function of ARPES photon energy.$^{[25]}$ At 33eV, the cross-section between W 5d and Se 4p has an order-of-magnitude difference. Therefore, the dominant features in our ARPES measurement are the contribution of W 5d subshell. Note that the Cooper minimum of the Se orbital is ~50eV. (c) Angle-integrated photoemission spectra of monolayer WSe$_2$ extracted from high symmetry directions K-Γ-K and M-Γ-M, and over the full BZ, referenced with respect to the Fermi level.
Figure 4: µ-ARPES band mapping of exfoliated WSe$_2$ for (a) 1ML (d) 2ML (c) 3ML and (f) bulk along the high-symmetry path M-Γ-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 1ML WSe$_2$, respectively.
Figure 5 (a)-(d) Second derivatives of the low-energy valence bands along high symmetry points of exfoliated 1-3ML and bulk WSe\(_2\), respectively, generated from the \(\mu\)-ARPES band maps of Fig. 4. The white lines are the corresponding DFT-calculated bands as in Fig. 4. The dashed-white lines refer to the top valence bands, which illustrate the layer-number dependence of the electronic structure near the VBM. Here the energy scale is set to zero at the VBM. (e) Layer-number-dependent VBM transition in terms of energy difference between K and \(\Gamma\) points. 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 \(\pm 0.10\text{eV}\). The theoretical and experimental results are plotted for comparison.