Ultrafast Free Carrier Dynamics in Single Layer MoS_2

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Introduction

Single layer (SL) molybdenum disulfide (MoS_2) is a genuine two-dimensional (2D) semiconductor, which belongs to a class of transition metal dichalcogenides (TMDCs) with remarkable optical properties [1]. Unlike its bulk parent, SL MoS_2 has a direct band gap between the parabolic valence band (VB) and conduction band (CB) valleys located at the corners of the materials Brillouin zone (BZ) [2]. Excitations of electron-hole pairs in these valleys generate free carriers as well as strongly bound excitons [3]. The dynamic interplay between excitons and free carriers has been a central topic in conventional semiconductors such as GaAs and 2D quantum well systems for decades [4], and recently in SL MoS_2 the properties of the excitons have been extensively measured. In fact, the excitons completely dominate the optical response in photoluminescence or differential absorption spectroscopy techniques, thereby masking the properties of the free carriers [5,6,7,8]. In order for optoelectronic applications to exploit the optical properties of SL MoS_2 and other similar TMDCs it is essential that the bound electron-hole pairs that constitute the excitons are separated into free carriers that can be extracted by metallic electrodes. Here we provide the first direct femtosecond study of photoinduced free carriers around the VB and CB valleys in SL MoS_2 using time- and angle-resolved photoemission spectroscopy (TR-ARPES) at the Artemis facility. We reveal a direct band gap of 1.95 eV and an ultrafast (50 fs) decay of the carriers in to the supporting metal contact.

Tuning in on the Band Gap of MoS_2

In our experiment we employ an epitaxially grown film of SL MoS_2 on Au(111). The synthesis is achieved using a physical vapor deposition (PVD) approach where Mo atoms are evaporated onto a clean Au(111) substrate in a H_2S environment followed by annealing of the substrate. By cycling this process high quality SL MoS_2 films can be achieved. The crystal structure of this material consists of S-Mo-S atoms that are bonded in a trigonal prismatic configuration as sketched in Fig. 1(a).

The general idea of our experiment is illustrated in Fig. 1(a)-(b). We employ a Ti:sapphire amplified laser system to generate tunable pump pulses as well as high harmonic UV probe pulses with a photon energy of 25 eV in a pulsed jet of argon gas atoms. The time duration of both pulses is 30 fs, which provides access to the femtosecond dynamics of the excited free carriers. The pump pulse initially excites free carriers in the bandstructure of our sample, as illustrated for the MoS_2 VB and CB edges around K in Fig. 1(b). Photoemission from the excited states is then achieved along the entire high symmetry Γ-K direction in the Brillouin zone (BZ).

The first objective of the experiment is to find the optical excitation energy that efficiently generates free carriers around the MoS_2 VB and CB edges. In Figs. 1(c)-(e) we present the excited state signal for three different regimes of optical excitation. These plots show the intensity difference between a spectrum obtained before optical excitation and a spectrum acquired 30 fs after arrival of the pump pulse on the sample. To a first approximation, red (blue) can be interpreted as the electrons (holes) we induce with the pump pulse. As observed in Fig. 2(d) we are able to induce a significant population of electrons (holes) around the CB (VB) edge when we pump at 2.0 eV. In contrast, we observe no such population when we pump at 1.6 eV (Fig. 2(c)) or at 3.0 eV (Fig. 2(e)). Thus with a 2.0 eV pump pulse we are tuned close to the band gap of MoS_2.

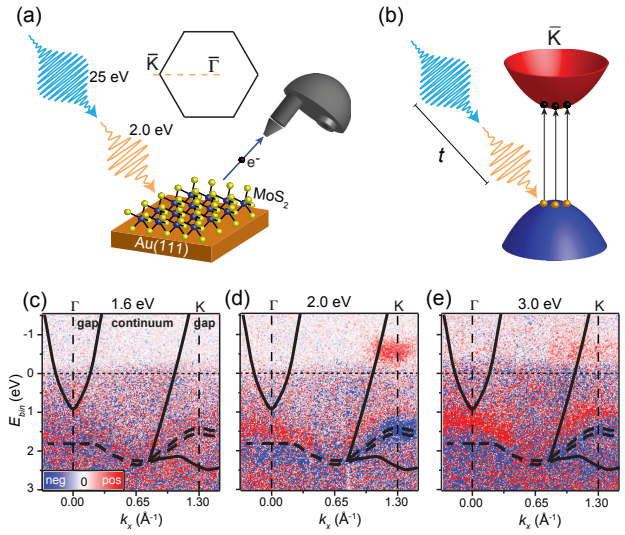

Figure 1 (a) *Pump-probe time- and angle-resolved photoemission experiment on epitaxial SL MoS_2 on Au(111). The excited electronic states are measured along the Γ-K direction in the materials Brillouin zone.* ***(b)*** *The electronic states of MoS_2 around K are excited by the pump pulse. This induces free carriers i.e. holes (yellow spheres) in the valence band (blue) and electrons (black spheres) in the conduction band.* ***(c)-(e)*** *Excited state signal at a time delay of 30 fs for pump pulse excitations of* ***(c)*** *1.6 eV,* ***(d)*** *2.0 eV and* ***(e)*** *3.0 eV. Solid black lines mark the boundaries of the bulk continuum of Au(111) states and dashed black lines illustrate the VB of MoS_2.*

Snapshots of Excited Free Carriers

By varying the time delay between the 2.0 eV pump pulse and the probe pulse we are able to record the snapshots of the excited free carriers shown in Fig. 2. Optical excitation of electrons and holes is visible around the VB and CB extrema as soon as the pump pulse arrives on the samle at $t = 0$ (Fig. 2(a)). The maximum excitation is observed after 30 fs (Fig. 2(b)), which is followed by a rapid decay of the free carriers with the signal halved after 60 fs (Fig. 2(c)). After 90 fs (Fig. 2(d)) the signal is close to the noise level and it is completely relaxed after 120 fs (Fig. 2(e)).

By analyzing the intense signals around the VB and CB edges at $t = 30$ fs it is possible to determine the band offsets with respect to the Fermi level. Intriguingly, this permits us to estimate a value of 1.95 eV for the direct quasiparticle band gap of SL MoS_2 on Au(111). This is somewhat lower than the theoretically predicted value of 2.8 eV [8] and remarkably close to the energy of the A exciton line determined for exfoliated SL MoS_2 on insulating SiO_2 substrates [6]. We interpret this strongly renormalized band gap to be a signature of efficient screening of the charge carriers in SL MoS_2 by the metal substrate.

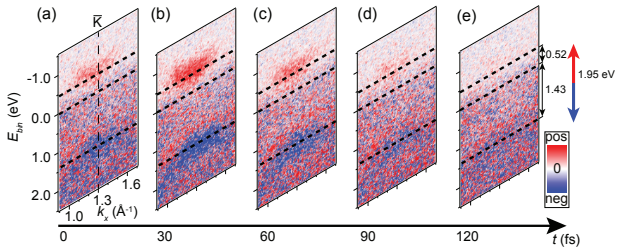

Figure 2 *TR-ARPES measurements of excited free carriers around the CB and VB edges at the K point of MoS_2. The spectra depict the difference between a spectrum taken before the pump beam arrives ($t < 0$ fs) and the spectrum at time delays of* ***(a)*** *0 fs,* ***(b)*** *30 fs,* ***(c)*** *60 fs,* ***(d)*** *90 fs and* ***(e)*** *120 fs. The dashed lines represent the onsets of the CB and VB and the position of the Fermi level at equilibrium. The offsets are given in electron volts to the right of panel* ***(e)****.*

Ultrafast Decay to the Metal Contact

In order to extract the lifetime of excited electrons and holes we integrate the intensity difference around the VB and CB edges for the data presented in Fig. 2. The time dependence is shown in Fig. 3(a)-(b). By fitting an exponential function to this data we obtain a time constant of 50 fs for both electrons and holes. This time scale is too short for lattice excitations to take place and can therefore only be explained by Auger type electron-electron interactions directly involving the metal contact as sketched in Fig. 3(c). Excited electrons in the bottom of the CB of SL MoS_2 can easily find a hole in the bulk continuum of states in the metal while simultaneously exciting an electron-hole pair in the Fermi sea of the metal. The reverse of this process accounts for the dynamics of holes in the VB.

Conclusions

Using the tunable pump pulses and high harmonic UV pulses available for time- and angle-resolved photoemission experiments at the Artemis facility we have been able to reveal the ultrafast dynamics of free carriers in SL MoS_2 contacted to a metal for the first time. We have shown that in order to generate free carriers around the CB and VB edges of this material it is necessary to use a 2.0 eV optical excitation. This allowed us to directly measure a direct quasiparticle band gap of 1.95 eV and to observe the relaxation of charge carriers into the metal substrate on a 50 fs timescale. [9]

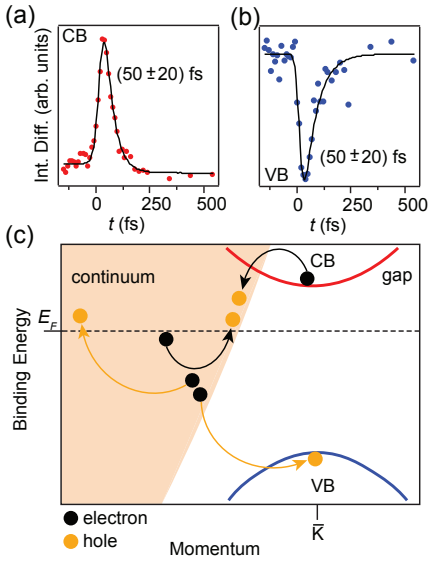

Figure 3 (a)-(b) *Intensity difference integrated* ***(a)*** *over the CB edge and* ***(b)*** *over the VB edge as a function of time delay. The black line is an exponential fit with the given time constant.* ***(c)*** *Interpretation of the free carrier dynamics. Electrons (black circles) rapidly scatter from the CB edge in to a hole (orange circles) in the continuum of states in the metal substrate while exciting electron-hole pairs in the metal. The reverse of this process accounts for the dynamics in the VB.*

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