Observation of Layer Pseudospin Interference in Bilayer MoS_2

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Introduction

The energy-, momentum- and time-resolved excitation spectrum of charge carriers in semiconducting transition metal dichalcogenide bilayers can be optically and electrically tuned via intense ultrafast optical pulses and interlayer interactions involving a supporting substrate [1-3]. Here, we investigate the ultrafast dynamics of electron-hole pairs and the pseudospin associated with the layer-degree of freedom in single-domain bilayer (BL) MoS_2 synthesized on a Ag(111) substrate. The pseudospin can be understood as the selection rule for selectively exciting carriers in the conduction band valleys of the material. Using time- and angle-resolved photoemission spectroscopy (TR-ARPES) we observe a layer pseudospin polarization of excited electrons in the conduction band minimum, which we can optically control in momentum space using excitation pulses with variable polarization θ. Calculations of the excitation probabilities for transitions at the K- and K'-valleys of the material reproduce our measurements and reveal that the momentum-dependent excited charge carrier populations are highly dependent on interference effects between the two MoS_2 layers induced by the electric field.

Direct and in-direct gaps of MoS_2 bilayers

We access the electron-hole pair dynamics and associated layer-degree of freedom in momentum space using the TR-ARPES experimental configuration at Artemis, sketched in Fig. 1(a). A 32 eV extreme ultraviolet (XUV) probe pulse measures the BL MoS_2 excited state with a time-resolution of 40 fs following optical excitation with a 2 eV pump pulse. The photoemission intensity probed by XUV, BL MoS_2 dispersion and projected Ag(111) bulk band-structure along K – Γ are shown in Fig. 1(b) before excitation (time delay, $t < 0$). Fig. 1(c) displays the excited state via the intensity difference between the equilibrium spectrum in (b) and a similar spectrum at $t = 40$ fs. The dominant features are a strong excitation of electrons around the conduction band minimum (CBM) (positive intensity difference) at K and an excitation of holes along the entire valence band (VB), which is peaked at the valence band maximum (VBM) (negative intensity difference). Analysis of band offsets at Γ and K directly reveal an in-direct gap of 1.49 eV and a direct gap at K of 1.90 eV as sketched in Fig. 1(d). Our 2 eV optical excitation is thereby close to resonant with the direct gap of the system.

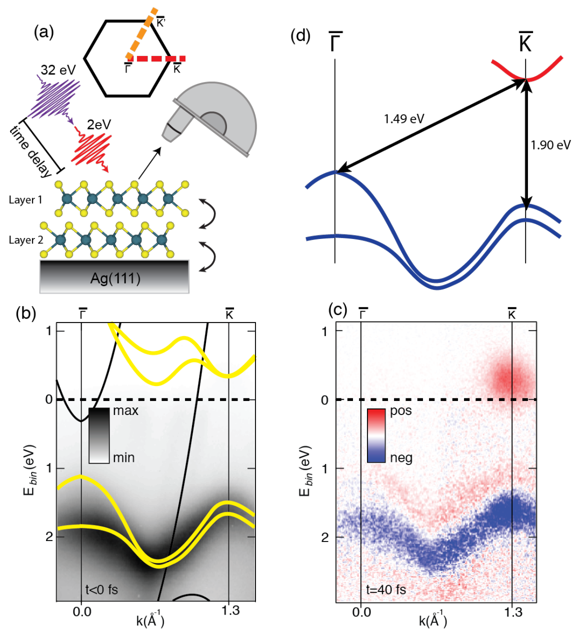

Figure 1 (a) *Pump-probe time- and angle-resolved photoemission experiment on epitaxial BL MoS_2 on Ag(111). The excited electronic states are measured along the Γ-K and Γ-K' directions in the materials Brillouin zone.* ***(b)*** *ARPES spectrum at equilibrium with overlaid BL MoS_2 bands (yellow curves) and the bulk continuum of Ag(111) (black curves).* ***(c)*** *Pump-probe difference spectrum at the peak of the optical excitation revealing excited electrons (red) at the K-valley and excited holes (blue) throughout the top-most valence band.* ***(d)*** *Alignment of valence and conduction bands with indication of direct and indirect gaps.*

Layer-dependent ultrafast dynamics

In Fig. 2(a) we present the t-dependence of the excited hole and electron dynamics in the VB and CBM, respectively. An ultrafast 50 fs single-exponential decay is observed throughout the VB, which resembles both the VB and CBM dynamics we previously observed in single-layer (SL) MoS_2 on Au(111) [7]. Interestingly, we find a similar fast component in the CBM but this is accompanied by slower 230 fs component. This may be explained by considering the phase space for electron-hole (e-h) recombination processes in the two layers, as shown in Fig. 2(b). The substrate interaction is weaker in layer 1 than in layer 2 such that inter- and intra-band e-h Auger processes in the MoS_2 are more dominant in layer 1. The out-of-plane d_{z^2}-

character of the CB minimum leads to a stronger interlayer coupling of these states. An excited electron in layer 1 can thereby recombine with a hole in layer 2, which accounts for the 230 fs interlayer dynamics seen in Fig. 2(a). In layer 2 this CB region is rapidly depleted via the substrate interaction, which leads to e-h excitations in the Ag(111) bulk states and the 30 fs time scale observed in the dynamics of both CBM and VB regions. The in-plane $d_{xy}/d_{x^2-y^2}$-character at the VB maximum at K leads to mainly intra-layer e-h dynamics and allows for the scattering of holes in the entire VB along Γ –K. Once the holes reach the d_{z^2}-like states around Γ they recombine via bulk states.

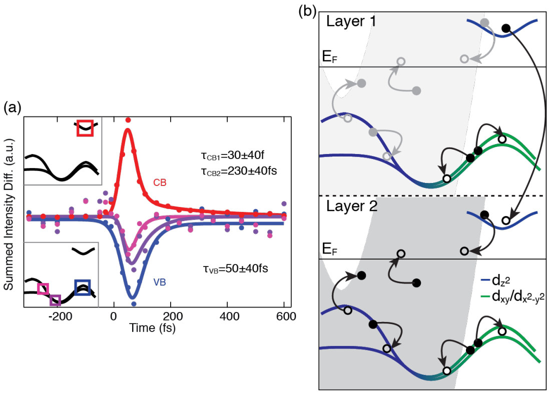

Figure 2 ***(a)*** *Time dependence of the intensity difference signal in the correspondingly colored boxed regions on the bands in the inserts. The data (filled circles) is fitted by an exponential increase and (one) two exponential decays in the (VB) CB with the provided decay times.* ***(b)*** *Layer dependence of electron (filled circles) and hole (open circles) recombination processes in the VB and CB states and involving the Ag(111) bulk states (gray-shaded part of (E,k)-space). Layer 2 is more strongly coupled to the substrate (darker gray-shading), while the layer 1 coupling is weaker (shaded e-h processes involving Ag(111) bulk state excitations). Orbital character of bands is given.*

Unexpected linear polarization of free carriers

The dispersions around K and K' were measured while varying the electric field polarization angle θ of the excitation pulse using half- and quarter-wave plates as sketched in Fig. 3(a). The integrated intensity of the CB marked by the red (K) and orange (K') data points in Fig 3(b) exhibits a striking polarization contrast for linear vertical ($\theta = 0$) and horizontal ($\theta = \pi/2$) polarized light, as seen by comparing to the thick gray and dashed gray calibration curves measured using a beamsplitter after the sample. The (E,k)-resolved contrast at the peak of the optical excitation along K and K' for $\theta = 0$ (Figs. 3(c)-(d)) and $\theta = \pi/2$ (Figs. 3(e)-(f)) polarizations reveal that the effect only pertains to the free electrons in the CB region. The free holes along the VB do not exhibit polarization contrast (see also bottom panel in Fig. 3(b)). We ascribe this to the rapid intra-layer scattering of holes along this band (see Fig. 2), which would lead to a depolarization on faster timescales than we can measure. Interestingly, we also observe an asymmetry in the CB signal between K and K' for $\theta = \pi/4$ and $\theta = 3\pi/4$ circularly polarized light. Furthermore, the amplitude of the difference signal at K' appears smaller than at K.

We can explain our observations by considering the theoretical expressions for the transition probabilities $|M|^2$ at the two valleys:

$$|\mathcal{M}_{\mathrm{K}}|^2 \propto 1 + T^2 + (1 - T^2)\sin(2\theta) - 2T\cos(2\theta), \qquad (1a)$$

$$|\mathcal{M}_{\mathrm{K}'}|^2 \propto 1 + T^2 - (1 - T^2)\sin(2\theta) - 2T\cos(2\theta)\cos(2\pi/3), \qquad (1b)$$

where T is a fit parameter that takes into account a different coupling between the two layers and substrate. For T=0 the layers would be completely isolated and non-interacting, recovering the circular dichroism effect for isolated monolayers. For $T = 1$ the layers are perfectly coupled and the system would be completely inversion symmetric without any circular dichroism. Instead we observe that the last interference term remains and gives a $\cos(2\theta)$ dependence, which can explain our observation of linear dichroism. We also have a phase factor of $\cos(2\pi/3)$ due to the act of rotating the crystal under a given applied pump laser field, which explains the switching and amplitude change between K and K'.

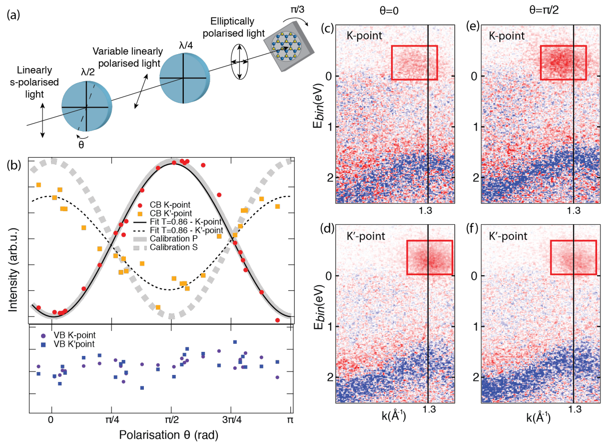

Figure 3 ***(a)*** *Experimental configuration for varying the electric-field polarization and for measuring the dispersion around the K- and K'-points.* ***(b)*** *Measured intensity difference (points) in the CB and VB regions and fits (full and dashed curves) to theoretical transition probabilities. The thick shaded curves are polarization calibrations curves.* ***(c)-(f)*** *Difference spectra at t = 40 fs at* ***(c)*** *K and* ***(d)*** *K' for s-polarization and* ***(e)*** *K and* ***(f)*** *K' for p-polarization. The red box marks the region where the CB data in* ***(b)*** *was obtained.*

Conclusions

Using excitation pulses with variable polarization θ we have demonstrated the possibility of inducing linearly polarized free carriers in the K and K' valleys of BL MoS_2. The effect is caused by an interference effect between the two layers and therefore constitutes a first example of layer pseudospin interference in BL dichalcogenides.

Acknowledgements

We thank Phil Rice for technical support during the Artemis beamtime. We gratefully acknowledge funding from VILLUM FONDEN through the Young Investigator Program (Grant. No. 15375) and the Centre of Excellence for Dirac Materials (Grant. No. 11744), the Danish Council for Independent Research, Natural Sciences under the Sapere Aude program (Grant No. DFF-4002-00029 and DFF-6108-00409) and the Aarhus University Research Foundation. Access to the Artemis Facility was funded by STFC.

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