Ultrafast Charge Separation in Bilayer WS\(_2\)/Graphene Heterostructure Revealed by Time- and Angle-Resolved Photoemission Spectroscopy

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Efficient light harvesting devices need to combine strong absorption in the visible spectral range with efficient ultrafast charge separation. These features commonly occur in novel ultimately thin van der Waals heterostructures with type II band alignment. Recently, ultrafast charge separation was also observed in monolayer WS\(_2\)/graphene heterostructures despite the type I band alignment (see Figure 1B). These heterostructures combine the benefits of a direct gap semiconductor with strong spin-orbit coupling [14, 15] and a semimetal with high-mobility carriers and long spin lifetimes [16] with great potential for novel optoelectronic and optospintronic applications [17].

1. INTRODUCTION

Solar energy conversion plays an important role in satisfying mankind’s ever-increasing energy usage in an environmentally friendly way. Despite several decades of optimization Silicon solar cells still lack efficiency. On the other hand, highly efficient III-V multijunction solar cells are expensive and not sustainable [1, 2]. Recently, van der Waals (vdW) heterostructures made of different monolayer (ML) transition metal dichalcogenides (TMDs) have emerged as a promising new solar cell platform due to their strong excitonic absorption in the visible spectral range [3, 4] followed by efficient ultrafast charge separation due to type II band alignment [5–10] (see Figure 1A). Interestingly, ultrafast charge separation was also found to occur in ML WS\(_2\)/graphene heterostructures despite the type I band alignment [11–13] (see Figure 1B).
One simple way to improve the efficiency of WS$_2$/graphene-based light harvesting devices might be to enhance the thickness and therefore the absorption of the WS$_2$ layer [18–20]. It is not a priori clear, however, if ultrafast charge separation survives when direct-gap monolayer WS$_2$ is replaced by thicker WS$_2$ layers with an indirect band gap (Figure 1C). In this work we address this issue by exciting carriers across the direct gap at the $K$-point of BL WS$_2$ in an epitaxial BL WS$_2$/graphene heterostructure on SiC(0001) and tracing the relaxation of the photogenerated electron-hole pairs as a function of time, energy, and momentum using time- and angle-resolved photoemission spectroscopy (tr-ARPES). We find that photoexcited holes in BL WS$_2$ are transferred to the graphene layer within 100 fs. The photoexcited electrons are found to remain in the conduction band of BL WS$_2$ for 420 fs resulting in the formation of a charge separated transient state with a lifetime of 770 fs. These timescales are consistent with the microscopic charge transfer model recently proposed for ML WS$_2$/graphene heterostructures [13] indicating that also in the case of BL WS$_2$ on graphene the timescale for charge separation is determined by direct tunneling at the points in the Brillouin zone where WS$_2$ and graphene bands intersect.

2. METHODS

2.1. Sample Preparation and Characterization

Commercial N-doped 6H-SiC(0001) wafers from SiCrystal GmbH were etched in hydrogen atmosphere and then graphitized by annealing at 1,300°C for 8 min [27]. The resulting carbon buffer layer was decoupled from the substrate by hydrogen intercalation at 800°C yielding a completely $sp^2$-hybridized quasi free-standing hole-doped graphene monolayer [22]. WS$_2$ was grown on top of this graphene layer by low pressure chemical vapor deposition (LPCVD) in a standard hot-wall reactor at a pressure of 1 mbar [23, 24]. Argon served as carrier gas with a flow of 80 sccm. WO$_3$ and S precursors with a mass ratio of 1:100 were kept at 900 and 120°C, respectively. The WO$_3$ powder was placed close to the substrate. After growth, the sample was characterized with secondary electron microscopy (SEM), Raman and photoluminescence (PL) spectroscopy, as well angle-resolved photoemission spectroscopy (ARPES).

The SEM picture in Figure 2A shows dark triangular WS$_2$ islands that cover ~80% of the graphene layer. The orientation of the triangles reveals the presence of two rotational domains with an angle of 60° between them. From previous low energy electron diffraction measurements on similar samples [11] we deduce that either the $\Gamma K$- or the $\Gamma K'$-direction of the WS$_2$ islands are aligned with the $\Gamma K$-direction of graphene. Further, the topological contrast reveals that ~90% of the islands consist of bilayer WS$_2$. This is consistent with the Raman spectrum shown in Figure 2B where the energy of the $A_{1g}$ peak at 417 cm$^{-1}$ and the intensity ratio between the central peak at 351 cm$^{-1}$ $(2L\hbar + E_g)$ and the $A_{1g}$ peak of ~6 are indicative of bilayer WS$_2$ [25]. From the PL spectrum in Figure 2C we find a quenched A-exciton resonance at 635 nm (1.95 eV) which confirms the presence of bilayer WS$_2$ [26]. The ARPES spectrum in Figure 2D was taken along the along the $\Gamma K$-direction. We find that the band structure of the heterostructure is a superposition of the band structures of the constituting materials that are indicated by the white dashed lines [15, 27]. The Dirac cone of graphene is found to be hole-doped with the Dirac-point 300 meV above the Fermi level, $E_F$. As expected for bilayer WS$_2$ [15] the maximum of the WS$_2$ valence band is found to be located at the $\Gamma$-point.

2.2. Tr-ARPES

Tr-ARPES experiments were performed at the Artemis user facility at the Rutherford Appleton Laboratory in Harwell, UK. We used a Ti:Sa amplifier with a central wavelength of 795 nm, a repetition rate of 1 kHz, 30 fs pulse duration, and 12 mJ pulse energy to generate visible pump and extreme ultraviolet (XUV) probe pulses. Two mJ of output energy were focused into an Argon gas jet for high harmonics generation. A single harmonic at $\hbar \omega_{\text{probe}} = 31.8$ eV was selected with a time-preserving grating...
monochromator [28] to be used as the probe. Ten mJ of output power were used to seed an optical parametric amplifier. The signal beam with a photon energy of 1 eV was frequency doubled yielding 2 eV pump pulses matching the A-exciton resonance in WS$_2$. The kinetic energy of the photoelectrons emitted from the sample by the XUV probe pulse were measured with a homemade Time-of-Flight analyzer with an angular acceptance of 2$^\circ$ [29]. The static ARPES spectrum in Figure 2D was obtained by rotating the sample. We measured the energy dependence of the photocurrent at two different emission angles (energy distribution curves, EDCs) as a function of pump-probe delay. The energy and temporal resolution of the experiment were 450 meV and 66 fs, respectively.

3. RESULTS

To investigate ultrafast charge transfer in our BL WS$_2$/graphene heterostructure we excited carriers across the direct band gap at the K-point of BL WS$_2$ using 2 eV pump pulses and probed the response of the heterostructure using tr-ARPES. In detail, we investigated the time dependence of two representative energy distributions curves (EDC 1 and EDC 2 in Figure 2D) to obtain the population and band structure dynamics of the WS$_2$ conduction and valence bands (CB and VB) and the graphene Dirac cone, respectively. The pump fluence was 6.6 mJ/cm$^2$ for EDC 1 (WS$_2$) and 9.1 mJ/cm$^2$ for EDC 2 (graphene).

Figures 3A,B show EDC 1 and EDC 2, respectively, as a function of pump-probe delay. The corresponding pump-induced changes obtained by subtracting the respective EDC at negative pump-probe delay from the transient EDCs are shown in Figures 3C,D. Upon arrival of the pump pulse the WS$_2$ VB is found to shift toward the Fermi level in Figure 3A. This upshift is responsible for the strong gain (red) and loss (blue) signal around −2 eV in Figure 3C. Figure 3C also reveals a transient gain of photoelectrons in the CB of WS$_2$ around +1 eV following photoexcitation. The graphene π-band in Figure 3B is found to...
FIGURE 3 | Time- and angle-resolved photoemission spectroscopy (tr-ARPES). (A,B) Time-resolved EDCs measured along the orange (EDC 1) and red lines (EDC 2), respectively, in Figure 2D as a function of pump-probe delay after photoexcitation at $\hbar \omega_{\text{pump}} = 2\,\text{eV}$. (C,D) Pump-induced changes of EDC 1 and EDC 2, respectively, obtained by subtracting the equilibrium EDC taken at negative pump-probe delay from all transient EDCs. Red and blue correspond to gain and loss of photoelectrons with respect to negative pump-probe delay, respectively. Colored brackets indicate the integration ranges for the data presented in Figure 4.

broaden and to shift down which—together with the up-shift of the WS$_2$ VB at lower energy—produces the gain-loss-gain signal in the energy range between $+1$ and $-2\,\text{eV}$ in Figure 3D.

To analyze the transient population dynamics of the individual bands we integrated the EDCs in Figure 3 over the energy range indicated by the colored brackets yielding the pump-probe traces in Figure 4. Panel A shows the transient population of the WS$_2$ VB and CB in green and orange, respectively. The population of the WS$_2$ VB is found to be unaffected by the photoexcitation within the experimental signal-to-noise ratio. The WS$_2$ CB on the other hand exhibits a clear gain of electrons. An exponential fit to the data yields a lifetime of $\tau = 420 \pm 20\,\text{fs}$.

Figure 4B shows the gain above and the loss below the Fermi level in graphene. We find a short-lived gain ($\tau = 97 \pm 3\,\text{fs}$) and a long-lived loss ($\tau = 840 \pm 30\,\text{fs}$). The transient up-shift of the WS$_2$ VB gives rise to a gain of photoelectrons above its equilibrium position that is plotted as a function of pump-probe delay in Figure 4C. An exponential fit to the data yields a lifetime of $\tau = 770 \pm 30\,\text{fs}$.

In agreement with Aeschlimann et al. [11] and Krause et al. [13], we interpret these timescales as follows: The absence of holes in the WS$_2$ VB together with the short-lived gain in graphene indicates that the photogenerated holes in the WS$_2$ VB are rapidly (within $\sim 100\,\text{fs}$) refilled by electrons from the Dirac cone. The photoexcited electrons are found to remain in the WS$_2$ CB for $\sim 400\,\text{fs}$, indicating the formation of a charge-separated transient state where the holes reside in the graphene layer and the electrons reside in the WS$_2$ layer. This charge-separated state is expected to decrease the binding energy of the WS$_2$ states and to increase the binding energy of the graphene states [11, 13].

Figures 5A,B illustrate the fitting procedure used to determine the transient peak positions of the WS$_2$ VB and CB and the graphene Dirac cone, respectively. Details are provided in the figure caption. The transient positions of the WS$_2$ CB and VB are shown in Figures 5C,D, respectively. We find that the WS$_2$ VB shifts up by $\sim 110\,\text{meV}$ with a lifetime of $\tau = 600 \pm 20\,\text{fs}$ (Figure 5D). The transient WS$_2$ band gap at $k \approx 1.1\,\text{Å}^{-1}$ obtained by subtracting the transient position of the VB from the transient position of the CB is displayed in Figure 5E. An exponential fit yields a transient band gap reduction of $\sim 230\,\text{meV}$ with a lifetime of $\tau = 140 \pm 40\,\text{fs}$. Note that the equilibrium gap size of 2.7 eV at $k \approx 1.1\,\text{Å}^{-1}$ is bigger than the direct band gap at the K-point [13, 30]. In good agreement with Chernikov et al. [31], Liu et al. [32], Ulstrup et al. [33], and Pogna et al. [34], we attribute this band gap renormalization to the presence of photoexcited carriers that screen the Coulomb interaction.
The transient band gap renormalization results in shifts of the WS$_2$ VB and CB that are symmetric with respect to the center of the WS$_2$ band gap (see inset of Figure 5E). By subtracting $|\Delta E_{\text{gap}}|/2$ from the transient position of the WS$_2$ VB we obtain the transient VB shift shown in green in Figure 5F that shows a remaining up-shift of $\sim 90$ meV with a lifetime of $\tau = 560 \pm 30$ fs.

At the same time the $\pi$-bands of graphene shown in red in Figure 5F shift down by $\sim 110$ meV with a lifetime of $\tau = 900 \pm 50$ fs. As discussed previously, these shifts are a direct consequence of the transient charge-separated state where excess negative charge on the WS$_2$ layer decreases the binding energy of the WS$_2$ states and the corresponding excess positive charge on
At this point we are able to attribute the pump-probe signal in which is linked to the lifetime of the charge-separated state [6]. Frontiers in Physics | www.frontiersin.org

The observed lifetimes for electron and hole transfer are in good agreement with previous tr-ARPES [11, 13] and time-resolved optical techniques [12] on similar WS₂/graphene heterostructures. Next we will discuss if the microscopic model for ultrafast charge separation across the interface between monolayer WS₂ and monolayer graphene [13] also applies to heterostructures made of bilayer WS₂ and monolayer graphene. In this model [13], the timescale for ultrafast charge separation in the heterostructure is determined by direct tunneling of hot carriers from WS₂ to graphene at those points in the Brillouin zone where the respective bands intersect. The associated energy barrier is smaller for holes than for electrons which, combined with a larger tunneling matrix element and a larger scattering phase space, results in hole transfer being faster than electron transfer. The lifetime of the charge-separated state, on the other hand, is determined by defect-assisted tunneling via in-gap states originating from S vacancies inside the WS₂ layer. This decay channel is extremely sensitive to the number of S vacancies in the sample, resulting in lifetimes of the transient charge-separated state between ∼ 1 ps in high-quality epitaxial samples [11, 13] and > 1 ns in commercial manually assembled heterostructures [12]. In this model ultrafast charge transfer occurs close to the K-point of WS₂ where the WS₂ VB maximum and CB minimum are located.

It is not a priori clear whether this model also applies to heterostructures made of bilayer WS₂ and monolayer graphene because, in this case, the maximum of the WS₂ VB and the minimum of the WS₂ CB are located at Γ and K (in between Γ and K), respectively. The observed timescales for hole transfer from WS₂ to graphene within ∼ 100 fs and a lifetime of the electrons inside the WS₂ CB at K of ~ 400 fs are perfectly consistent with direct tunneling via band intersections close to the K-point. The lifetime of the charge-separated transient state of ~ 800 fs observed in the present heterostructure is consistent with defect-assisted tunneling via S vacancies in similar high-quality epitaxial samples [11, 13]. Therefore, we conclude that, despite the band structure differences, the microscopic model for ultrafast charge transfer developed for the interface between monolayer WS₂ and monolayer graphene [13] also applies for heterostructures made of bilayer WS₂ and monolayer graphene (see sketch in Figure 6).

In summary, we have shown that ultrafast charge separation also occurs at the interface between bilayer WS₂ and monolayer graphene. Together with the enhanced absorption in the visible spectral range compared to monolayer WS₂ our findings provide important insights that will guide the design of novel optoelectronic applications.

**DATA AVAILABILITY STATEMENT**

The raw data supporting the conclusions of this article will be made available by the authors upon request.

**AUTHOR CONTRIBUTIONS**

IG, CCa, ES, and CCo organized the project. SF, FF, AR, and CCo prepared the sample. RK, MC-C, SA, SF, FF, AR, YZ, PM, RC, CCa, and IG prepared and conducted the tr-ARPES experiments. RK analyzed the data. RK and IG wrote the manuscript. All authors contributed to manuscript revision, read, and approved the submitted version.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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