

Functionalized two-dimensional vdW multijunction MoS₂-MoS₂/WS₂-WS₂/WS₂-WS₂ platform for defect-related carrier dynamics studies

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Defect engineering plays a critical role in two-dimensional (2D) semiconductor devices, especially for 2D transition-metal dichalcogenides (2D-TMDs) due to their extraordinary optoelectronic properties. However, directly comparing defect-related effects on various devices presents challenges, as it requires multiple growth processes and device fabrication procedures including stacking. Here, we have designed and produced one platform for 2D-TMD multijunction MoS₂-MoS₂/WS₂-WS₂/WS₂-WS₂ on a single flake via chemical vapor deposition (CVD) growth to investigate its photoexcited carrier dynamics. Ultrafast pump-probe transient transmittance measurements at four junctions reveal the defect-related effects on fast and slow relaxation processes and further uncover passivation occurring at the MoS₂/WS₂ junction, with a longer relaxation time of 25 ps. This work paves the way to establish a paradigm for examining charge-carrier dynamics in functionalized 2D van der Waals multijunctions via CVD growth and a unique microscopic method.

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I. INTRODUCTION

Transition-metal dichalcogenides (TMDs) have recently attracted enormous attention due to their intriguing physical properties, such as strong Coulomb interactions, distinctive spin-valley physics, and unique magnetic, optical, and electronic characteristics [1–6]. As fundamental building blocks for two-dimensional (2D) optoelectronic devices, 2D van der Waals (vdW) TMD lateral and vertical heterostructures have been widely adopted to tune the properties of 2D materials, and they have been extensively investigated in both theoretical and experimental studies [7–12]. Among various approaches to optimize the performance of 2D TMD-based devices, defect-engineering has attracted researchers the most, not only due to its intrinsic role for semiconductor properties, but also for its ability to control electrical, optical, vibrational, magnetic, and chemical properties, enabling new

functionalities. Theoretical studies on point defects and disorder, defect-induced experimental optical/electrical responses, and applications such as doping and single photon sources have been reported with growing interest [13].

2D crystals can exhibit various types of defects. With a high number of defects, different kinds of combinations are likely to occur. Extrinsic disorders include strain, adsorbates, surface roughness, charged impurities in the substrate, and oxidation, while intrinsic defects consist of atomic defects such as vacancies, antisites, substitutions, edges, and grain boundaries [14]. In general, sulfur vacancies are the most common intrinsic defects in CVD-grown monolayers [15]. These vacancies facilitate oxygen substitution, forming active sites for molecular species [16]. Next to sulfur vacancies, the most common defect in as-grown CVD samples of WS₂ is oxygen replacing sulfur atoms [17]. Previous studies have shown that aging WS₂ monolayers lead to gradual oxidation and absorption of organic materials at sulfur vacancies [18]. In our work, this oxygen passivation was observed in the photoluminescence spectra, which showed an enhancement [19]. Grain boundaries, another common defect in CVD-grown MoS₂, have also been reported to enhance photoluminescence, as they can act as charge-carrier sinks or increase scattering [20]. For MoS₂, nonoccupied sulfur vacancies introduce sharp point defects, while adsorbates create a continuum of defect

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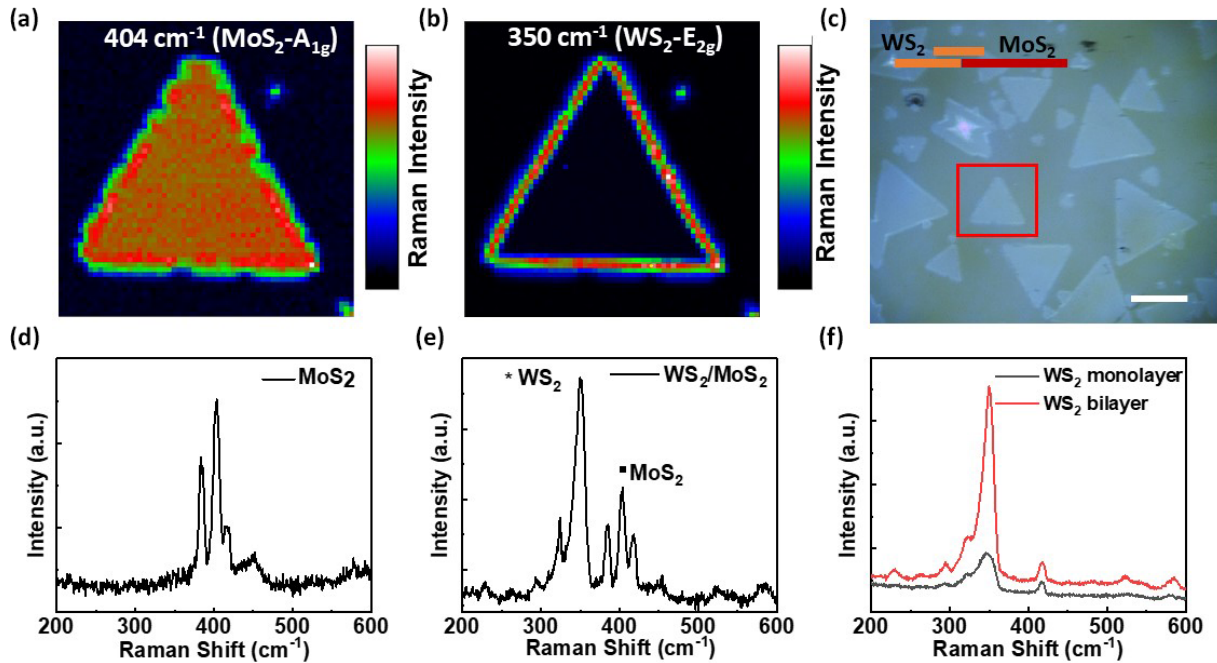


FIG. 1. The Raman intensity mapping centered at 404 cm^{-1} (a) and 350 cm^{-1} (b) taken from the area marked by a red square in (c). The WS_2 is around a MoS_2 flake and covers $1\text{ }\mu\text{m}$ of MoS_2 . (c) The optical microscopy image of TMDs-multisample. The stacking structure is indicated in the inset. (d)–(f) The Raman spectra taken from MoS_2 (d), WS_2/MoS_2 (e), and WS_2 (f). The scale bar in (c) is $50\text{ }\mu\text{m}$.

states [16]. Similarly, vacancy defect states in WS_2 can lead to nonradiative recombination of charge carriers, as well as for the more common sulfur vacancies and the less common tungsten vacancies [21]. In contrast, oxygen substitution of sulfur does not introduce in-gap states [22,23]. Comparing calculation results for WS_2 and MoS_2 shows that sulfur vacancies and atomic defects generate gap states closer to the valence band in WS_2 and closer to the conduction band in MoS_2 [24].

The degree of disorder can be assessed using Raman spectroscopy, particularly by analyzing the peak distances of the $\text{E}_{2\text{G}}$ and $\text{A}_{1\text{G}}$ modes, as well as the area percentage of the WS_2 2LA mode [25]. The Raman spectra (Fig. 1) show disorder-activated peaks for MoS_2 and WS_2 , confirming defect presence. For MoS_2 , the peak around 415 cm^{-1} has been previously associated with disorder and the out-of-plane mode [26]. This peak has been observed in multiple studies using ion irradiation to induce defects. The generated defects include molybdenum and sulfur vacancies with varying numbers of missing sulfur atoms, as well as sulfur and molybdenum substitutions [27–29]. Reducing sulfur vacancies has been shown to enhance long-term stability [30]. Theoretical calculations indicate that defect states created by molybdenum vacancies are closer to the valence band, whereas those related to sulfur vacancies lie closer to the conduction band [31]. Defect-bound excitons are enabled from unoccupied defect states deep in the band gap, introduced by sulfur vacancies [32]. For WS_2 , defect levels can be assessed based on the area percentage of the 2LA mode [25]. Peak-Lorentz fitting reveals a contribution of the 2LA mode to the WS_2 Raman spectrum in both monolayer and bilayer regions.

However, a direct comparison of defect-dependent electrical and optical properties in monolayer, multilayer, and

heterostructures of 2D TMDs with single growth on the same substrate is still lacking. Due to these constraints, researchers must either fabricate multiple devices to assess their electric transport response or test different samples to analyze their optical behaviors [33–35]. Research efforts are underway by multiple groups to rectify this issue, including advancements in transfer techniques and complicated growth procedures [36,37]. This work aims to create a functionalized 2D TMDs-based platform including monolayers, bilayers/multilayers, and heterostructures constructed as MoS_2 - MoS_2/WS_2 - WS_2/WS_2 - WS_2 in a single growth process with consecutive steps. Our primary goal in fabricating this structure is to demonstrate that different stacking orders and designs are feasible using our growth procedure. It is well known that the properties of TMD-vdW heterostructures can be tuned by modifying the stacking order, composition, and layer number [38]. By varying these parameters, the band gap can be adjusted [39], absorption increased [40], interlayer excitons can be generated [41], and ultrafast charge transfer can be enabled [42]. Recently, multilayered structures have been developed to further enhance light absorption and interlayer excitons lifetimes [43]. Potential applications of these structures include detection [44–46], photovoltaic devices [47], and water-splitting [48] devices.

Our heterostructure combines an ultrathin p - n heterojunction in both vertical and lateral directions, along with a vertical homojunction. These types of junctions are particularly promising for fabricating nanoscale optoelectronic devices such as photodetectors, photovoltaics, and light emitting diodes. By combining different layers and junctions together, the absorption/emission range can be modulated and extended. Moreover, additional phenomena can arise in multilayered structures, such as enhanced photoconductivity due to

spatial carrier confinement [12]. Recent studies have demonstrated shape-dependent properties in CVD-grown TMDs, which are attributed to different levels of defects in the tailored morphologies, making them ideal defect-dependent junctions for optoelectronics [19,20]. Therefore, we prepare this pristine 2D TMDs multijunction by applying the CVD technique and allow the sample to naturally deteriorate for defect growth as a platform for defect-related carrier dynamics studies.

While various techniques including micro-Raman scattering, photoluminescence (PL), x-ray photoelectron spectroscopy, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and scanning tunneling microscopy (STM) have been extensively used for defect studies [49–51], they do not enable visualization of the dynamics of charge carriers, which is a crucial requirement for photonic applications. As a result, there is a need to utilize nondestructive and efficient methods like scanning ultrafast time-resolved optical pump-probe spectroscopy (UPPS) to directly investigate and observe the dynamics of charge carriers in TMDs. Understanding excited-state lifetimes is crucial for practical applications: short photocarrier lifetimes are advantageous for optical switches [52], while long radiative lifetimes enhance luminescence quantum yield, benefiting light-emitting devices [53]. A recent report on scanning-UPPS reveals the carrier dynamics distribution in various shapes of 2D TMD junctions and undoubtedly serves as a critical experimental technique for investigating carrier dynamics in our MoS_2 - MoS_2/WS_2 - WS_2/WS_2 platform [54].

II. METHODS

A. Chemical vapor deposition growth

The MoS_2 - WS_2 -heterostructure sample was manufactured using a two-step chemical vapor deposition (CVD) process inside of a quartz-tube furnace. The heterostructure was synthesized on oxidized silicon wafers and subsequently transferred to a sapphire substrate.

In the first step, MoS_2 monolayer triangles were grown. By dissolving the molybdenum precursor Na_2MoO_4 in DI water, spincoating could be used to obtain evenly distributed structures on the substrate surface. To promote the growth process and to achieve a more uniform distribution of the precursor, NaCl and the readily available density gradient Opti were added to the spincoating solution [55,56]. Subsequently, the coated substrate was placed inside of a quartz boat in the center of a two-zone furnace. Upstream of the sample, in the second heating zone, the sulfur precursor was placed. It consisted of sulfur pellets inside of a second quartz boat. After evacuation of the quartz tube, the carrier gas flow was introduced and the furnace was heated up to 500°C to anneal the substrate. The carrier gas used consisted of an argon-hydrogen mixture with 2.5% of H_2 . Hydrogen acts as a reducing agent as well as an etchant for unnecessary nuclei. For the growth of MoS_2 , the temperature of the furnace was set to 865°C and the gas flow to 60 sccm. The heating of the second heating zone, with the sulfur precursor, was delayed by 5 min. After reaching the growth temperature, it was kept for 6 min. Afterwards, the oven was switched off and opened to cool down fast.

For the second growth step, a solution with the tungsten precursor (Na_2WO_4) was spin-coated onto a second silicon wafer. Here, NaOH and the density gradient Opti were added to the solution. NaOH works as a density gradient, a growth catalyst, and reduces the surface energy of the hydrophobic surface of the substrate. The sample was placed together with the as-grown MoS_2 sample in the center of the furnace. The sample with the tungsten precursor was placed upside down on top of the MoS_2 sample, leading to both coated surfaces facing each other at a distance of 1.7 cm. The growth steps are equivalent to the MoS_2 growth, using a growth temperature of 840°C and a duration for the deposition of 4 min.

B. ADF-STEM sample preparation and characterization

Initially, the sample was coated with PMMA by spin-coating at 3000 rpm for 1 min. Subsequently, the edges of the substrate were carefully scratched using a razor blade to expose the sapphire surface, facilitating faster etching.

Next, the prepared substrate was floated onto a sodium hydroxide (NaOH) solution with a volume ratio of 1:10 for NaOH and H_2O , respectively. After the substrate was completely etched by the solution, the PMMA film with WS_2 flakes adhered to the solution. The sapphire substrate was then immersed in the solution to separate the film.

The film was rinsed in deionized (DI) water three to four times to remove any residual solution, and then it was transferred onto a TEM grid and air-dried. The TEM grid was subsequently annealed in a CVD tube furnace under a mixture of 90% N_2 and 10% H_2 at a flow rate of 200 sccm to remove the PMMA. The annealing process involved ramping up the temperature to 40°C at a rate of 1°C per minute, maintaining it at 40°C for 2 h, and then cooling it down to room temperature.

All annular dark-field scanning transmission electron microscopy (ADF-STEM) images were acquired using a Thermo Fisher Titan Themis microscope operated at 300 kV.

C. Pump-probe microscopy

The spatial-resolved pump-probe measurements were performed using a commercial Ti:sapphire laser (repetition rate: 5.1 MHz, wavelength: 800 nm, pulse duration: 200 fs) and a homemade dual-color pump-probe system with a laser-scanning confocal microscope (LSCM) at room temperature. To focus the pump and collect the signal in the backward direction, a $20\times$ (CFI Plan Fluor $20\times$, Nikon) objective with a numerical aperture of 0.5 was used in the LSCM for measurements. The pump spot size (FWHM) used under this $20\times$ objective was measured as $2\text{ }\mu\text{m}$, and the probe spot size was $1\text{ }\mu\text{m}$. The samples were pumped with a 400 nm (3.1 eV) pulse and probed with 800 nm (1.55 eV). The fluences of the pump and probe beams are 200 and $20\text{ mJ}/\text{cm}^2$, respectively.

D. PL and Raman microscopy

The spatially and spectrally resolved photoluminescence (PL) and Raman spectra were acquired by using a home-built multiwavelength laser-scanning confocal microscope and a spectrometer equipped with a thermoelectrically cooled charge-coupled detector (DV420A-BU2, Andor). The spectral

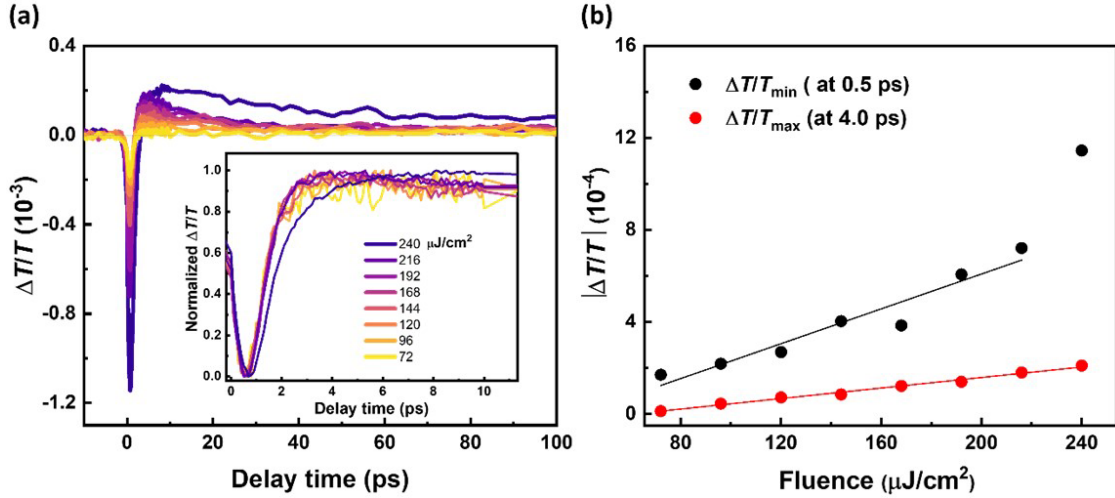


FIG. 2. (a) The $\Delta T/T$ spectra of MoS_2 at various pump fluences. Inset: Normalized $\Delta T/T$ spectra of (a). (b) The magnitude of negative ($\Delta T/T_{\min}$ at 0.5 ps) and positive ($\Delta T/T_{\max}$ at 4.0 ps) changes of $\Delta T/T$ spectra in (a).

resolution of the spectrometer in the LSCM is approximately 0.1 nm. A fiber-coupled CW laser diode (NDV4316, NICHIA/LDH-D-C-405, PicoQuant) was used for photoluminescence measurements. Also, an ultralow noise laser at 532 nm was used for photoluminescence and Raman measurements. To focus the pump and collect the signal in the backward direction, a $50\times$ (MPLN50 $\times$, Olympus) objective with a numerical aperture of 0.75 was used in the LSCM for all optical measurements.

III. RESULTS AND DISCUSSION

The pristine monolayer-vertical heterostructure-bilayer-monolayer platform, (I) MoS_2 -(II) MoS_2/WS_2 -(III) WS_2/WS_2 -(IV) WS_2 , is designed and produced via CVD growth within two consecutive steps (see Methods). This multijunction sample (TMDs-multi) is characterized using micro-Raman spectroscopy, micro-photoluminescence (PL) spectroscopy, and HAADF-STEM to verify the proposed sample structure (see Figs. 1(a) and 1(b) of the Supplemental Material (SM) [57]). The clear atomic structure, without rotational stacking, is further confirmed in Fig. 2 of the SM [57]. The homogeneous MoS_2 monolayer center is revealed from Fig. 1(a) of the SM, exhibiting uniform micro-Raman mapping at its core. The lateral ring structure from WS_2 growth is more complex due to the overlapping area with MoS_2 and the intrinsic Raman intensity difference in the outer region, as depicted in SM Fig. 1(b). Therefore, the point Raman spectrum at all four locations with the PL spectrum are extracted for comparison. As shown in SM Fig. 1(d), the Raman spectrum at the center (location 1) exhibits only MoS_2 responses at 387 and 404 $1/\text{cm}$; in the overlapping area (location 2), both MoS_2 (387 and 407 $1/\text{cm}$) and WS_2 (350 and 420 $1/\text{cm}$) peaks are present; in the outer region, WS_2 intensity differences determine the bilayer junction (location 3) and the monolayer junction (location 4). Similarly, we conducted a micro-PL experiment at the same locations plotted in SM Fig. 1(c) [57]: location 1 shows PL solely from MoS_2 , whereas location 2 exhibits PL responses from both

MoS_2 and WS_2 with lower intensities for both; locations 3 and 4 reveal PL from WS_2 but lower intensity at location 4, supporting the bilayer WS_2 at location 3 and monolayer WS_2 at location 4. The proposed structure is hence verified as sketched in Fig. 1(c): MoS_2 - MoS_2/WS_2 - WS_2 - WS_2 multijunction. Previous studies reported conflicting results regarding the relationship between defect density and PL intensity in TMD monolayers, with some observing an increase and others a decrease in PL as defect concentration rises [16]. Enhancements have been associated with S-rich areas and strained edges, which may modify the band gap or lift off the material from the substrate [58], as well as with oxygen-passivated sulfur vacancies [19]. While at low temperatures additional optical emissions arise in the signal, the reported measurements were carried out at room temperature. The discussed findings concerning the defect concentration are based on observations from optical microscopy, Raman spectroscopy, and UPPM measurements.

As the material undergoes natural degradation, defects form, as evidenced by the micro-Raman mapping in Fig. 1. The same TMDs-multijunction structures remain while additional defect-induced Raman peaks appear, consistent with previous reports for MoS_2 [28,59] and WS_2 [60]. Optical microscopy in Fig. 1(c) further supports the structural integrity of the multijunction structure, as suggested by white-light absorption contrast. We further verify the core center of monolayer MoS_2 with increasing defects-related inhomogeneity by micro-Raman mapping with the peak position at 404 $1/\text{cm}$ constructed in Fig. 1(a). Figure 1(b) confirms the lateral-ring connection of the WS_2 junction with micro-Raman mapping centered at 350 $1/\text{cm}$ from the second consecutive CVD growth for a total width of close to 3.5 μm . Additional defect-related Raman modes are observed at all four junctions, as shown in Fig. 1(d) for MoS_2 , Fig. 1(e) for MoS_2/WS_2 vertical heterojunction, and Fig. 1(f) for WS_2 bilayer and monolayer. These defect-related peaks include the peak to the right of the MoS_2 A_{1G} peak and the 2LA mode of WS_2 . The MoS_2 peak has been previously observed after helium ion beam irradiation and linked to generated vacancies [28]. The 2LA mode,

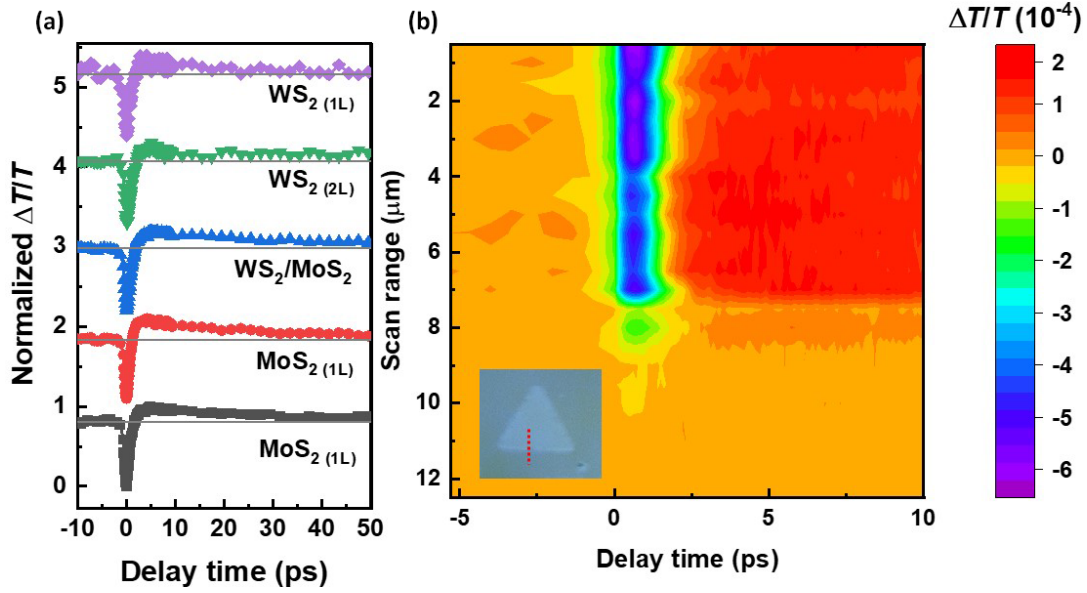


FIG. 3. (a) The $\Delta T/T$ as a function of delay time at different positions of the red line in the inset of Fig. 2(b). (b) Line-scan $\Delta T/T$ of the sample shown in the inset. The red line indicates the line-scan range (12 μm) of pump-probe measurements. The $\Delta T/T$ after 10 μm shows no signal, confirming the scan passes the edge of TMDs-multi flake and reaches the substrate.

associated with disorder, serves as an indicator of defect density by examining the $2LA/A_{IG}$ area ratio [25]. However, the prominent Raman peaks like SM Fig. 1(d) remain consistent [57], confirming that the TMDs-multistructure remains unaffected and the ring lateral junctions are estimated to be 1 μm for a MoS_2/WS_2 vertical heterojunction, 1 μm for a WS_2/WS_2 bilayer junction, and 1.5 μm for a WS_2 monolayer junction by our spatial resolution.

To investigate spatially resolved ultrafast carrier dynamics in MoS_2 or WS_2 , a scanning microscope is utilized alongside an ultrafast pump-probe system (see Methods). We first performed the pump fluence-dependent $\Delta T/T$ measurements as shown in Fig. 2. When increasing the pump fluence, the magnitudes of both negative (at 0.5 ps) and positive (at 4.0 ps) changes of $\Delta T/T$ increase linearly below the pump fluence of 240 $\mu\text{J}/\text{cm}^2$ [see Fig. 2(b)]. Besides, all $\Delta T/T$ spectra with various pump fluences significantly overlap together in the normalized plot in the inset of Fig. 2(a) to show the fluence-independent dynamics in the linear regime (pump fluence $< 240 \mu\text{J}/\text{cm}^2$). To avoid complicated processes and nonlinear effects, such as structural relaxation, etc., as the reviewer mentioned, we carried out all pump-probe spectroscopy in this study under the condition of weak perturbation, i.e., within the linear regime in Fig. 2(b) with the pump fluence of 200 $\mu\text{J}/\text{cm}^2$. This value is in the same order of magnitude as the conditions used in many TMDs studies [61,62].

This setup allows mapping of the materials. By adjusting the time delay between pump and probe pulses, one can capture location-dependent changes in transient transmittance ($\Delta T/T$), although the intraband transition in TMDs can be revealed by our nonresonant pump-probe spectroscopy (i.e., 400-nm pump and 800-nm probe) [61], which is similar to the THz-probe spectroscopy in semiconductors, e.g., GaAs [63]. In the case of our experiments, when the probe photon energy (1.55 eV) is much larger than the exciton binding energies (~ 0.2 eV) and smaller than the optical band gap (~ 1.9 eV),

the photoexcited and free carriers in the valence band mainly contribute to intraband absorption. These changes are quantified through the measured $\Delta T/T$, as detailed in Ref. [64]:

$$\frac{\Delta T}{T} \approx -2\eta_0 \frac{\Delta\sigma_r}{1+n_s} - 2\eta_0^2 \frac{(\sigma_r\Delta\sigma_r + \sigma_i\Delta\sigma_i)}{(1+n_s)^2}, \quad (1)$$

where σ_r (σ_i) represents the real (imaginary) part of the sample's optical conductivity, $n_s \approx 1.45$ is the refractive index of the substrate, and η_0 is the free-space impedance.

When $\eta_0\sigma_r$ and $\eta_0\sigma_i$ are much less than 1 at the probe energy [61], the second term on the right-hand side of Eq. (1) becomes significantly smaller than the first term. Consequently, the differential transmission is primarily influenced by variations in the real part of the optical conductivity, which is represented by the first term on the right-hand side. This effect arises from intra-conduction-band and intra-valence-band processes as discussed in previous results [54].

A spatial line scan of $\Delta T/T$ measurements is performed at distinct locations crossing the TMDs-multistructure: from the center to the outmost junction as depicted in the inset of Fig. 3(b). Five representative single-point $\Delta T/T$ measurement results from MoS_2 (one close to the center in black and the other close to the second junction in red), MoS_2/WS_2 (one in blue), WS_2/WS_2 bilayer (one in green), and WS_2 monolayer (one in purple) are plotted in Fig. 3(a). These measurements reveal variations in absorption intensity and transmittance decay characteristics. We observe nonuniform behaviors of photoexcited carriers across these four junctions, both in absorption intensity difference and relaxation trends. This suggests that defect-related photoexcited carriers experience varying defect trapping mechanisms. We will discuss the mechanisms responsible for the relaxation behaviors in each junction in the following graphs. Additionally, the $\Delta T/T$ heatmap line scan shown in Fig. 3(b) supports the same lateral junction structure of the TMDs-multistructure: (I) core- MoS_2 , (II) 1 μm MoS_2/WS_2 vertical heterojunction (at 7 μm), (III) 1

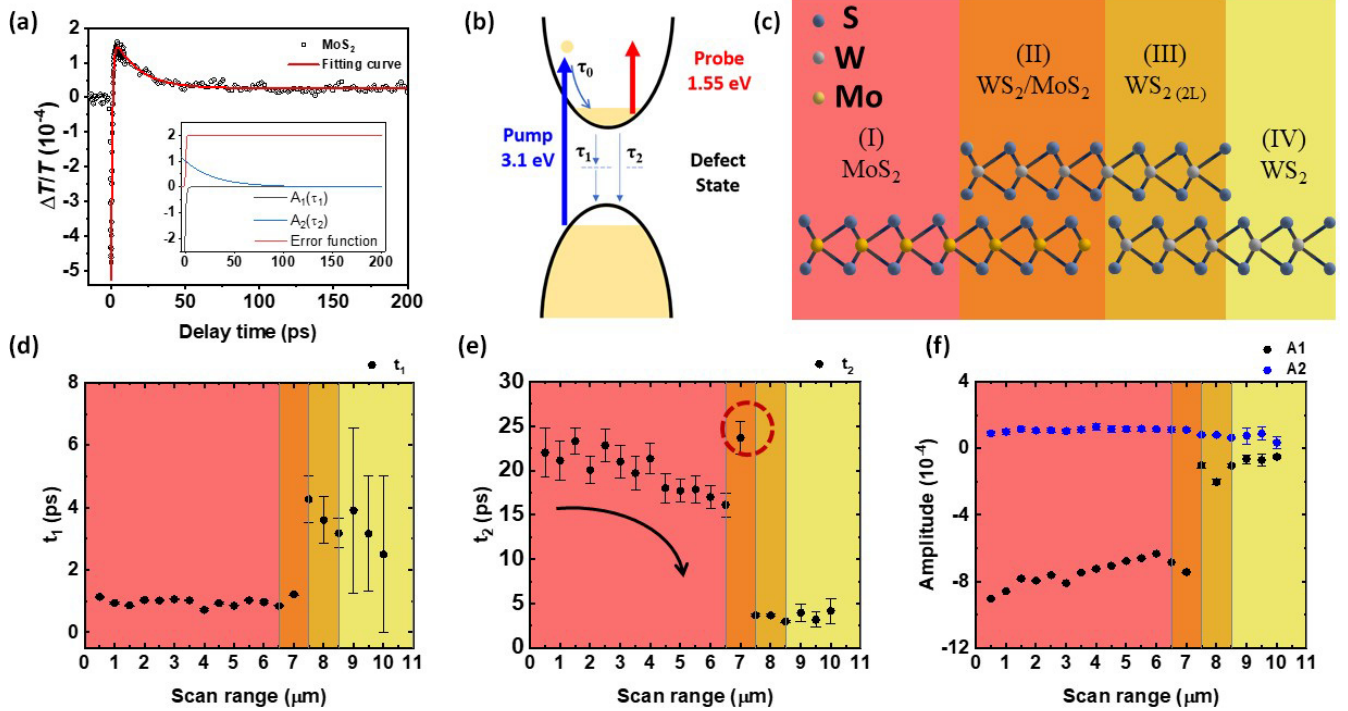


FIG. 4. (a) The fitting results of a typical $\Delta T/T$ spectrum of MoS_2 . The inset shows the fitting components. (b) Band structure and relaxation processes of photoexcited carriers after pumping. (c) Sample structure of TMDs-multi. (d) The relaxation time τ_1 , (e) the relaxation time τ_2 , and (f) the amplitude of $\Delta T/T$ spectra at different areas of Fig. 3(c) are categorized by the corresponding junctions.

μm for WS_2/WS_2 bilayer junction (at $8\ \mu\text{m}$), and (IV) $1.5\ \mu\text{m}$ for WS_2 monolayer junction (from 8.5 to $10\ \mu\text{m}$). These findings are consistent with our micro-Raman mapping reported in Fig. 1(b), further validating the spatial resolution and measurement capability of our microscopic ultrafast pump-probe system.

First, we analyze $\Delta T/T$ from MoS_2 plotted in Fig. 4(a) as an example. The transient signal exhibits a quick relaxation of negative $\Delta T/T$ before $5\ \text{ps}$ and a positive $\Delta T/T$ that persists for a relaxation time longer than $50\ \text{ps}$ after $5\ \text{ps}$. The initial drop of $\Delta T/T$ is dominated by the instrumental response function of the pump-probe spectroscopy system (for details, see SM Figs. 3 and 4 [57]). Therefore, we neglected the initial drop of $\Delta T/T$ and only focused on analyzing the processes with the time constants greater than the time resolution ($\sim 110\ \text{fs}$) of our pump-probe spectroscopy system after the minimum. The spectra are all fitted by a double-exponential decay to extract two distinct relaxation times: τ_1 for the quick relaxation and τ_2 for the persistent relaxation. The inset in Fig. 4(a) illustrates the double-exponential decay functions: one in black fits the negative component to acquire τ_1 and the other one in blue fits the positive component to acquire τ_2 . The final fitting curve presents a good agreement with our experimental data, confirming the validity of our approach. The τ_1 is attributed to electron-phonon scattering and trap-assisted capture of excitons into shallow defect states near the conduction-band minimum (CBM) [61]. In materials like MoS_2 and WS_2 , such defects are known to form during growth or transfer processes and can act as efficient traps. The fast depletion of electrons from the CBM into these defect states or to the valence band via nonradiative

recombination accounts for the rapid decay observed in $\Delta T/T$. The τ_2 is associated with carrier recombination from deeper trap states, defect-assisted intraband transitions, or longer-lived photoexcited carrier populations that experience reduced recombination pathways [61]. When the samples possess higher defect densities (as evidenced by spatial variation in τ_2), carriers can be temporarily trapped in localized states and released slowly via phonon-assisted processes, contributing to the positive $\Delta T/T$ signal. All the other transient transmittances are analyzed in the same fashion. The consistent sign change indicates defects spreading across all four junctions in our TMD-multistruature sample. This sign change is attributed to partially filled shallow defect states near the CBM, as previously reported [54,61,65]. We would like to elaborate on this mechanism as sketched in Fig. 4(b): the pump laser pulse excites electrons from the valence band (VB) to the middle of the conduction band, filling the energy states near the CBM with relaxation time τ_2 . At the same time, the electrons at the CBM relax into shallow defect states with a shorter relaxation time τ_1 or directly to the VB via phonon-assisted or defect-assisted transitions (or to deeper defect states) with longer relaxation time τ_2 . Due to the slow intraband relaxation of the photoexcited electrons in CB and the fast relaxation of the electrons from the CBM into shallow defect states, the transient unbalance (output rate > input rate) and missing CBM electrons contribute to a positive $\Delta T/T$, as observed after $2\ \text{ps}$.

Next, we investigate the defect-related carrier dynamics across the four 2D vdW junctions in our functionalized MoS_2 - MoS_2/WS_2 - WS_2/WS_2 multijunction platform. The core junction, MoS_2 monolayer in red, as illustrated in

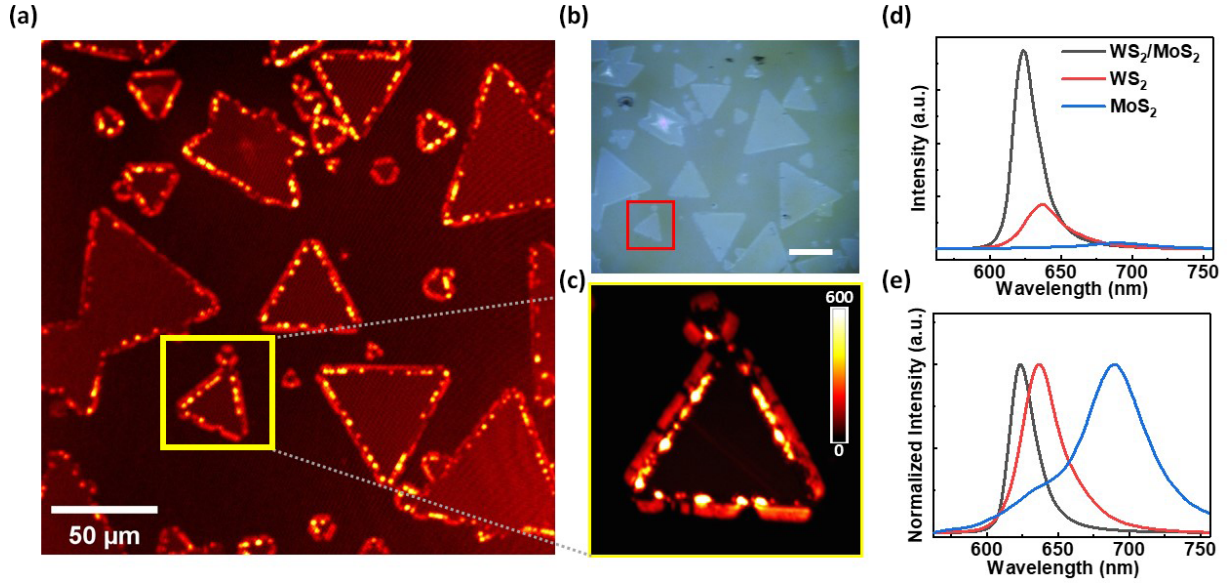


FIG. 5. (a) The PL intensity mapping of TMDs-multi after natural degradation. (b) The optical microscopy image of TMDs-multi in the same area as Fig. 1. (c) The PL intensity mapping of the yellow-square marked area in Fig. 4(a). (d) PL spectra of MoS₂, WS₂, and WS₂/MoS₂ junctions. (e) Normalized PL spectra revealing the PL peak shifts.

Fig. 4(c), reveals the decreasing trend of τ_2 from the center to the edge of the core junction, as plotted in Fig. 4(e). This suggests that the edge region of the core junction contains a higher density of defect states. A greater number of defects can drain more electrons at CBM and accelerate the defect-assist relaxation process from CBM to VB, resulting in the shorter τ_2 . For the WS₂/WS₂ bilayer and WS₂ monolayer junctions, the relaxation time τ_2 remains almost constant, indicating that both the defect state levels and the number of defect states are similar. The relaxation time τ_1 for WS₂/WS₂ bilayer and WS₂ monolayer junctions also shows a similar range, close to 3.5 ps, as plotted in Fig. 4(d), but the large error bars make definitive conclusions difficult. This significant fitting uncertainty is due to the lower absorption amplitude signal, as shown in Fig. 4(f). However, in comparison with the relaxation times from the MoS₂ junction, τ_1 is larger, indicating the degradation process of WS₂ progresses further than MoS₂ and defect numbers are increased. In this case, additional deeper defect levels provide channels for the electrons at the CBM to relax, resulting in an increase of τ_1 . Conversely, electrons with more defect assistance need to relax from channels involving relaxation time τ_2 and therefore τ_2 is smaller.

Surprisingly, at the junction WS₂/MoS₂ we have observed an intriguing relaxation behavior. Both relaxation times τ_1 and τ_2 are larger than those extracted from the MoS₂ junction, as shown in Figs. 4(d) and 4(e). The relaxation process related to τ_1 for the WS₂ top layer takes longer because the defect level is deeper than the defect level in MoS₂. The relaxation process related to τ_2 , however, suggests that the defect states at this vertically stacked junction decreased to slow down the defect-assist relaxation of electrons from CBM to VB and therefore τ_2 becomes longer. Although junctions II, III, and IV all contain WS₂ layers, the carrier dynamics vary due to differences in defect distributions. Notably, the junction II

has fewer defects, possibly due to oxygen passivation. This observation is intriguing because this was not observed on the other junctions, suggesting a different influence of oxygen passivation in O₂ environment on the defect states. To explore this further, we analyze the PL optical responses from each junction, given that the oxygen-passivation effect on PL peak enhancement and shift is well established [66].

We further reexamine the PL microscopy of our TMDs-multistructure sample as depicted in Fig. 5(a). The intensity contrast at junction II is clearly observed. Focused on one flake, the optical microscope image shown in Fig. 5(b) and the micro-PL mapping in Fig. 5(c) provide detailed views. To analyze the passivation effect on the sample, we extract PL spectra at three locations and compare them to the PL results from our previous pristine sample, as reported in SM Fig. 1(c) [57]. At junction II, the PL intensity is four times higher than the intensity from the WS₂ monolayer and ten times higher than the intensity from the MoS₂ monolayer, as depicted in Fig. 5(d), which is consistent with the PL mapping observations. This behavior is, however, in contrast to the PL response from the previous pristine TMDs-multistructure sample in SM Fig. 1(c), where the PL intensity at junction II was the lowest for the vertical WS₂/MoS₂ heterostructure compared to the PL intensity from the WS₂ monolayer and MoS₂ monolayer, consistent with previous reports [8]. After natural degradation, the PL intensity should typically decrease at all junctions. However, the fact that junction II exhibits higher PL intensity indicates that the passivation in the O₂ environment (room environment) occurs most prominently in this junction. It is worth noting that the relative PL intensity ratio between WS₂ monolayer and MoS₂ monolayer remains unchanged before and after degradation. Moreover, the PL peak shift of around 40 meV from the WS₂ PL peak shown in Fig. 5(e) suggests O-doped behavior, further supporting the oxygen passivation process.

IV. CONCLUSION

In summary, we have designed and produced a functionalized 2D vdW multijunction, including monolayer, bilayer, and vertical stacking structures, for defect-related carrier dynamics studies via CVD growth. We investigated these junctions using an ultrafast pump-probe microscopy system. The results reflect the defect-related carrier dynamics, and we discuss the analysis of two fast and slow relaxation mechanisms for all four junctions in this work. Moreover, a passivation effect on the vertical heterostructure junction is observed and the slower relaxation time extracted, supporting a reduction in defects due to passivation, consistent with PL verification. Our work provides a platform for future 2D semiconductor defect-engineering for desired optoelectronics.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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- [1] X. Xu, W. Yao, D. Xiao, and T. F. Heinz, Spin and pseudospins in layered transition metal dichalcogenides, *Nat. Phys.* **10**, 343 (2014).
 - [2] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, and A. Kis, Ultrasensitive photodetectors based on monolayer MoS₂, *Nat. Nanotechnol.* **8**, 497 (2013).
 - [3] T. Scrace, Y. Tsai, B. Barman, L. Schweidenback, A. Petrou, G. Kioseoglou, I. Ozfidan, M. Korkusinski, and P. Hawrylak, Magnetoluminescence and valley polarized state of a two-dimensional electron gas in WS₂ monolayers, *Nat. Nanotechnol.* **10**, 603 (2015).
 - [4] M. Cetina, Ultrafast many-body interferometry of impurities coupled to a Fermi sea, *Science* **354**, 96 (1979).
 - [5] Y. J. Zhang, T. Oka, R. Suzuki, J. T. Ye, and Y. Iwasa, Electrically switchable chiral light-emitting transistor, *Science* **344**, 725 (1979).
 - [6] Y. Ma, Y. Dai, M. Guo, C. Niu, Y. Zhu, and B. Huang, Evidence of the existence of magnetism in pristine VX₂ monolayers (X = S, Se) and their strain-induced tunable magnetic properties, *ACS Nano* **6**, 1695 (2012).
 - [7] S. Tongay, Tuning interlayer coupling in large-area heterostructures with CVD-grown MoS₂ and WS₂ Monolayers, *Nano Lett.* **14**, 3185 (2014).
 - [8] Y. Gong, Vertical and in-plane heterostructures from WS₂/MoS₂ monolayers, *Nat. Mater.* **13**, 1135 (2014).
 - [9] C. Lee, G. Lee, A. M. van der Zande, W. Chen, Y. Li, M. Han, X. Cui, G. Arefe, C. Nuckolls, T. F. Heinz, J. Guo, J. Hone, and P. Kim, Atomically thin p–n junctions with van der Waals heterointerfaces, *Nat. Nanotech.* **9**, 676 (2014).
 - [10] X. Zhang, Z. Zhang, D. Wu, X. Zhang, X. Zhao, and Z. Zhou, Computational screening of 2D materials and rational design of heterojunctions for water splitting photocatalysts, *Small Methods* **2**, 1700359 (2018).
 - [11] C. Zhang, Systematic study of electronic structure and band alignment of monolayer transition metal dichalcogenides in van der Waals heterostructures, *2D Mater.* **4**, 015026 (2016).
 - [12] Y. Tsai, Z. Chu, Y. Han, C. Chuu, D. Wu, A. Johnson, F. Cheng, M. Chou, D. A. Muller, X. Li, K. Lai, and C. Shih, Tailoring semiconductor lateral multijunctions for giant photoconductivity enhancement, *Adv. Mater.* **29**, 1703680 (2017).
 - [13] Q. Liang, Q. Zhang, X. Zhao, M. Liu, and A. T. S. Wee, Defect engineering of two-dimensional transition-metal dichalcogenides: Applications, challenges, and opportunities, *ACS Nano* **15**, 2165 (2021).
 - [14] D. Rhodes, S. H. Chae, R. Ribeiro-Palau, and J. Hone, Disorder in van der Waals heterostructures of 2D materials, *Nat. Mater.* **18**, 541 (2019).
 - [15] H.-P. Komsa, J. Kotakoski, S. Kurasch, O. Lehtinen, U. Kaiser, and A. V. Krasheninnikov, Two-dimensional transition metal dichalcogenides under electron irradiation: Defect production and doping, *Phys. Rev. Lett.* **109**, 035503 (2012).
 - [16] E. Mitterreiter, B. Schuler, A. Micevic, D. Hernangómez-Pérez, K. Barthelmi, K. A. Cochrane, J. Kiemle, F. Sigger, J. Klein, E. Wong *et al.*, The role of chalcogen vacancies for atomic defect emission in MoS₂, *Nat. Commun.* **12**, 3822 (2021).
 - [17] M. G. Bianchi, F. Risplendi, M. Re Fiorentin, and G. Cicero, Engineering the electrical and optical properties of WS₂ monolayers via defect control, *Adv. Sci.* **11**, 2305162 (2024).
 - [18] J. Gao, B. Li, J. Tan, P. Chow, T.-M. Lu, and N. Koratkar, Aging of transition metal dichalcogenide monolayers, *ACS Nano* **10**, 2628 (2016).
 - [19] W. Zhao, J. Ma, P. Sun, K. Zhang, and Y. Yuan, Strong photoluminescence enhancement of MoS₂ monolayer via low-power Ar/O₂ plasma treatment, *Mater. Lett.* **235**, 129 (2019).
 - [20] X. Zou, Y. Liu, and B. I. Yakobson, Predicting dislocations and grain boundaries in two-dimensional metal-disulfides from the first principles, *Nano Lett.* **13**, 253 (2013).
 - [21] Y. Wang, H. Ho, X. Ho, L. Lu, S. Hsieh, S. Huang, H. Chiu, C. Chen, W. Chang, J. D. White, Y. Tang, and W. Woon,

- Photoluminescence enhancement in WS₂ nanosheets passivated with oxygen ions: Implications for selective area doping, *ACS Appl. Nano Mater.* **4**, 11693 (2021).
- [22] B. Schuler, J. Lee, C. Kastl, K. A. Cochrane, C. T. Chen, S. Refaely-Abramson, S. Yuan, E. van Veen, R. Roldán *et al.*, How substitutional point defects in two-dimensional WS₂ induce charge localization, spin-orbit splitting, and strain, *ACS Nano* **13**, 10520 (2019).
- [23] S. Barja, S. Refaely-Abramson, B. Schuler, D. Y. Qiu, A. Pulkín, S. Wickenburg, H. Ryu, M. M. Ugeda, C. Kastl, C. Chen *et al.*, Identifying substitutional oxygen as a prolific point defect in monolayer transition metal dichalcogenides, *Nat. Commun.* **10**, 3382 (2019).
- [24] S. Salehi and A. Saffarzadeh, Atomic defect states in monolayers of MoS₂ and WS₂, *Surf. Sci.* **651**, 215 (2016).
- [25] J. Li, W. Su, F. Chen, L. Fu, S. Ding, K. Song, X. Huang, and L. Zhang, Atypical defect-mediated photoluminescence and resonance Raman spectroscopy of monolayer WS₂, *J. Phys. Chem. C* **123**, 3900 (2019).
- [26] S. Mignuzzi, A. J. Pollard, N. Bonini, B. Brennan, I. S. Gilmore, M. A. Pimenta, D. Richards, and D. Roy, Effect of disorder on Raman scattering of single-layer MoS₂, *Phys. Rev. B* **91**, 195411 (2015).
- [27] S. Bertolazzi, S. Bonacchi, G. Nan, A. Pershin, D. Beljonne, and P. Samorì, Engineering chemically active defects in monolayer MoS₂ transistors via ion-beam irradiation and their healing via vapor deposition of alkanethiols, *Adv. Mater.* **29**, 1606760 (2017).
- [28] F. Aryeetey, T. Ignatova, and S. Aravamudan, Quantification of defects engineered in single layer MoS₂, *RSC Adv.* **10**, 22996 (2020).
- [29] Y. Chen, S. Huang, X. Ji, K. Adepalli, K. Yin, X. Ling, X. Wang, J. Xue, M. Dresselhaus, J. Kong, and B. Yildiz, Tuning electronic structure of single layer MoS₂ through defect and interface engineering, *ACS Nano* **12**, 2569 (2018).
- [30] H. Şar, A. Özden, İ. Demiroğlu, C. Sevik, N. K. Perkgoz, and F. Ay, Long-term stability control of CVD-grown monolayer MoS₂, *Phys. Rapid Res. Lett.* **13**, 1800687 (2019).
- [31] W. Zhou, X. Zou, S. Najmaei, Z. Liu, Y. Shi, J. Kong, J. Lou, P. M. Ajayan, B. I. Yakobson, and J.-C. Idrobo, Intrinsic structural defects in monolayer molybdenum disulfide, *Nano Lett.* **13**, 2615 (2013).
- [32] H. Bretscher, Z. Li, J. Xiao, D. Y. Qiu, S. Refaely-Abramson, J. A. Alexander-Webber, A. Tanoh, Y. Fan, G. Delport, C. A. Williams, S. D. Stranks *et al.*, Rational passivation of sulfur vacancy defects in two-dimensional transition metal dichalcogenides, *ACS Nano* **15**, 8780 (2021).
- [33] A. L. Elías, Controlled synthesis and transfer of large-area WS₂ sheets: From single layer to few layers, *ACS Nano* **7**, 5235 (2013).
- [34] D. O. Dumcenco, H. Kobayashi, Z. Liu, Y.-S. Huang, and K. Suenaga, Visualization and quantification of transition metal atomic mixing in Mo_{1-x}W_xS₂ single layers, *Nat. Commun.* **4**, 1351 (2013).
- [35] Z. Lin, M. T. Thee, A. L. Elías, S. Feng, C. Zhou, K. Fujisawa, N. Perea-López, V. Carozo, H. Terrones, and M. Terrones, Facile synthesis of MoS₂ and Mo_xW_{1-x}S₂ triangular monolayers, *APL Mater.* **2**, 092514 (2014).
- [36] M. Cai, J. Yang, X. Lu, and X. Lu, Layer-by-layer self-assembly strategies of atomically thin two-dimensional nanomaterials: Principles, methods, and functional applications, *ACS Appl. Nano Mater.* **7**, 27940 (2024).
- [37] P. V. Pham, T.-H. Mai, S. P. Dash, V. Biju, Y.-L. Chueh, D. Jariwala, and V. Tung, Transfer of 2D films: From imperfection to perfection, *ACS Nano* **18**, 14841 (2024).
- [38] F. Chen, X. Jiang, J. Shao, S. Zhao, W. Su, and Y. Li, Multilayered vertical heterostructures comprised of MoS₂ and WS₂ nanosheets for optoelectronics, *ACS Appl. Nano Mater.* **4**, 9293 (2021).
- [39] J. Kang, S. Tongay, J. Zhou, J. Li, and J. Wu, Band offsets and heterostructures of two-dimensional semiconductors, *Appl. Phys. Lett.* **102**, 012111 (2013).
- [40] D. Jariwala, A. R. Davoyan, J. Wong, and H. A. Atwater, Van der Waals materials for atomically-thin photovoltaics: Promise and outlook, *ACS Photon.* **4**, 2962 (2017).
- [41] Y. Jiang, S. Chen, W. Zheng, B. Zheng, and A. Pan, Interlayer exciton formation, relaxation, and transport in TMD van der Waals heterostructures, *Light Sci. Appl.* **10**, 72 (2021).
- [42] X. Hong, J. Kim, S.-F. Shi, Y. Zhang, C. Jin, Y. Sun, S. Tongay, J. Wu, Y. Zhang, and F. Wang, Ultrafast charge transfer in atomically thin MoS₂/WS₂ heterostructures, *Nat. Nanotechnol.* **9**, 682 (2014).
- [43] Y. Wan, J. Huang, C. Chu, W. Hsu, C. Lee, A. Aljarb, C. Huang, M. Chiu, H. Tang, C. Lin, X. Zhang, C. Wei, S. Li *et al.*, Strain-directed layer-by-layer epitaxy toward van der Waals homo- and heterostructures, *ACS Mater. Lett.* **3**, 442 (2021).
- [44] N. Huo, J. Kang, Z. Wei, S. Li, J. Li, and S. Wei, Novel and enhanced optoelectronic performances of multilayer MoS₂-WS₂ heterostructure transistors, *Adv. Funct. Mater.* **24**, 7025 (2014).
- [45] Y. Kim, S. Lee, J. Song, K. Y. Ko, W. J. Woo, S. W. Lee, M. Park, H. Lee, Z. Lee, H. Choi, W. Kim *et al.*, 2D transition metal dichalcogenide heterostructures for p- and n-type photovoltaic self-powered gas sensor, *Adv. Funct. Mater.* **30**, 2003360 (2020).
- [46] W. Wu, Q. Zhang, X. Zhou, L. Li, J. Su, F. Wang, and T. Zhai, Self-powered photovoltaic photodetector established on lateral monolayer MoS₂-WS₂ heterostructures, *Nano Energy* **51**, 45 (2018).
- [47] M. Tsai, M. Li, J. R. D. Retamal, K. Lam, Y. Lin, K. Suenaga, L. Chen, G. Liang, L. Li, and J. He, Single atomically sharp lateral monolayer p-n heterojunction solar cells with extraordinarily high power conversion efficiency, *Adv. Mater.* **29**, 1701168 (2017).
- [48] J. Ma, J. Pang, J. Yang, W. Xie, X. Kuang, and A. Mao, Prediction of high photoconversion efficiency and photocatalytic water splitting in vertically stacked TMD heterojunctions MX₂/WS₂ and MX₂/MoSe₂ (M = Cr, Mo, W; X = S, Se, Te), *J. Mater. Chem. A* **13**, 9312 (2025).
- [49] J. D. Fuhr, A. Saúl, and J. O. Sofo, Scanning tunneling microscopy chemical signature of point defects on the MoS₂ (0001) surface, *Phys. Rev. Lett.* **92**, 026802 (2004).
- [50] J. Lin, S. T. Pantelides, and W. Zhou, Vacancy-induced formation and growth of inversion domains in transition-metal dichalcogenide monolayer, *ACS Nano* **9**, 5189 (2015).
- [51] R. Addou, Impurities and electronic property variations of natural MoS₂ crystal surfaces, *ACS Nano* **9**, 9124 (2015).
- [52] Z. Sun, A. Martinez, and F. Wang, Optical modulators with 2D layered materials, *Nat. Photon.* **10**, 227 (2016).
- [53] M. Amani, Near-unity photoluminescence quantum yield in MoS₂, *Science* **350**, 1065 (2015).

- [54] S. Boandoh, F. Hsiao, B. Shin, M. Mack, L. P. Grote, R. Wang, Y. Han, J. Lou, N. Koch, N. H. Nickel, C. Luo, and Y. Tsai, Ultrafast pump–probe microscopy on 2D transition metal dichalcogenides, *Adv. Photon. Res.* **3**, 2200046 (2022).
- [55] J. Lei, Y. Xie, A. Kutana, K. V. Bets, and B. I. Yakobson, Salt-assisted MoS₂ growth: Molecular mechanisms from the first principles, *J. Am. Chem. Soc.* **144**, 7497 (2022).
- [56] L. Seravalli and M. Bosi, A review on chemical vapour deposition of two-dimensional MoS₂ flakes, *Materials* **14**, 7590 (2021).
- [57] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/b339-7j5f> for micro-Raman/PL characterization and annular dark-field scanning transmission electron microscopy (ADF-STEM) image of the sample, as well as the instrumental response function of pump-probe spectroscopy.
- [58] A. M. Zande, P. Y. Huang, D. A. Chenet, T. C. Berkelbach, Y. You, G.-H. Lee, T. F. Heinz, D. R. Reichman, D. A. Muller, and J. C. Hone, Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide, *Nat. Mater.* **12**, 554 (2013).
- [59] T. Huang, X. Cong, S. Wu, K. Lin, X. Yao, Y. He, J. Wu, Y. Bao, S. Huang, X. Wang, P. Tan, B. Ren *et al.*, Probing the edge-related properties of atomically thin MoS₂ at nanoscale, *Nat. Commun.* **10**, 5544 (2019).
- [60] H. Liu, T. Yang, Y. Tatsumi, Y. Zhang, B. Dong, H. Guo, Z. Zhang, Y. Kumamoto, M. Li, L. Li, R. Saito, and S. Kawata, Deep-ultraviolet Raman scattering spectroscopy of monolayer WS₂, *Sci. Rep.* **8**, 11398 (2018).
- [61] H. Wang, C. Zhang, and F. Rana, Ultrafast dynamics of defect-assisted electron–hole recombination in monolayer MoS₂, *Nano Lett.* **15**, 339 (2015).
- [62] T. Goswami, R. Rani, K. S. Hazra, and H. N. Ghosh, Ultrafast carrier dynamics of the exciton and trion in MoS₂ monolayers followed by dissociation dynamics in Au@MoS₂ 2D heterointerfaces, *J. Phys. Chem. Lett.* **10**, 3057 (2019).
- [63] J. Shah, *Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures* (Springer, Berlin, 1999), Vol. 115.
- [64] J. M. Dawlaty, S. Shivaraman, J. Strait, P. George, M. Chandrashekar, F. Rana, M. G. Spencer, D. Veksler, and Y. Chen, Measurement of the optical absorption spectra of epitaxial graphene from terahertz to visible, *Appl. Phys. Lett.* **93**, 131905 (2008).
- [65] A. Senkić, A. Supina, M. Akturk, C. Gadermaier, M. Maiuri, G. Cerullo, and N. Vujčić, Microscopic investigation of intrinsic defects in CVD grown MoS₂ monolayers, *Nanotechnology* **34**, 475705 (2023).
- [66] Q. Cui, Robust and high photoluminescence in WS₂ monolayer through in situ defect engineering, *Adv. Funct. Mater.* **31**, 2105339 (2021).