Symmetric domain segmentation in WS$_2$ flakes: correlating spatially resolved photoluminescence, conductance with valley polarization

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Abstract
The incidence of intra-flake heterogeneity of spectroscopic and electrical properties in chemical vapour deposited (CVD) WS$_2$ flakes is explored in a multi-physics investigation via spatially resolved spectroscopic maps correlated with electrical, electronic and mechanical properties. The investigation demonstrates that the three-fold symmetric segregation of spectroscopic response, in topographically uniform WS$_2$ flakes are accompanied by commensurate segmentation of electronic properties e.g. local carrier density and the differences in the mechanics of tip-sample interactions, evidenced via scanning probe microscopy phase maps. Overall, the differences are understood to originate from point defects, namely sulfur vacancies within the flake along with a dominant role played by the substrate. While evolution of the multi-physics maps upon sulfur annealing elucidates the role played by sulfur vacancy, substrate-induced effects are investigated by contrasting data from WS$_2$ flake on Si and Au surfaces. Local charge depletion induced by the nature of the sample-substrate junction in case of WS$_2$ on Au is seen to invert the electrical response with comprehensible effects on their spectroscopic properties. Finally, the role of these optoelectronic properties in preserving valley polarization that affects valleytronic applications in WS$_2$ flakes, is investigated via circular polarization discriminated photoluminescence experiments. The study provides a thorough understanding of spatial heterogeneity in optoelectronic properties of WS$_2$ and other transition metal chalcogenides, which are critical for device fabrication and potential applications.

Supplementary material for this article is available online

Keywords: WS$_2$, domain segmentation, defects, optoelectronic heterogeneities, valleytronics

(Some figures may appear in colour only in the online journal)
which lacks scalability. CVD-grown TMDCs offer a scalable alternative though reproducibility remains a challenge and the optical, electrical and optoelectronic properties of such samples show a fair degree of variability, not only between flakes but often within single flakes [6, 13–22]. While generalized correlations between the growth parameters and the local properties like disorder, stoichiometry and doping are established, causal relationship and control remain non-trivial. Photo-luminescence (PL) maps within a single flake of TMDC [13, 15–17, 20, 22, 23], often evidence 3-fold symmetric segmented domains with high and low emissive regions, designated as the $\alpha$ and $\beta$ domains [15, 17, 18, 22]. This domain segmentation is distinct from polymorphism and coexisting 1T (metallic) and 2H (semiconducting) phases observed in TMDC flakes [10, 24, 25]. Any spatial variation in PL likely originates from local variation in strain or native defects (S or W) that modulate the local bandstructure or electron doping in the system [13, 15, 22, 26]. Spatially resolved Raman studies have evidenced the role of lattice defect and strain in determining the differences between the domains. However, significant variations between reported observations [15, 22] have hindered the emergence of a unified picture, which has been further complicated by the electronic nature of the substrates and effects like sample delamination [20, 27–29]. Atomic force microscopy (AFM) based techniques have been used to probe domain segmentation with higher spatial resolution correlating topographic variation with current maps that have shown both negative [17, 30] and positive[31] correlations between local defect density and local current. Together with results from complementary scanning probe techniques like scanning near field optical microscopy [32, 33] and tip-enhanced Raman spectroscopy [34, 35] it is evident that charge impurities [29], surface roughness [36, 37], the substrate and local strain [32, 37] play crucial roles in the optoelectronic properties of these 2D materials that need further exploration. Comprehending the luminescence properties vis-à-vis the above parameter assumes added significance while exploring valleytronics, especially preservation of polarization in emission properties. Exploiting valleytronics requires selective control over valley populations and long valley lifetimes ($\tau_v$) compared to other scattering timescales of the device, which are determined by the band structure, defects and the carrier density of the system [38–42]. Against this backdrop, we have investigated spatial heterogeneity and domain segmentation in WS$_2$ flakes employing electrical, electronic and optical probes on as-grown samples on Si, as well as those transferred onto polycrystalline Au substrates. In this multi-physics investigation, the symmetric domain segmentation observed in WS$_2$ flakes is mapped by spatially resolved PL and Raman spectroscopy in conjunction with spatially resolved electrical, electronic and optoelectronic investigations, using a conducting AFM (CAFM) coupled with optical excitation. Correlation among these various maps, along with topography and phase map elucidates the role of defects, strain, and substrate in determining the optoelectronic properties of the flakes. Our results demonstrate that for WS$_2$ on Si, the high luminescent ($\alpha$) domains are accompanied by higher local conductance, understood to originate from intrinsic defects. The defects also result in a spectral redshift of the PL emission [5, 14, 43] and the excitation of strong $\text{LA(M)}$ Raman mode [44] of WS$_2$, selectively within the higher conducting $\alpha$-domains. Differences between the samples’ response, prior and post annealing in vacuum and in sulfur rich environment, provide evidence that quenching of sulfur defects lead to near-complete disappearance of the characteristic segmented domains, across all the correlated multi-physics maps [19, 21, 30]. Investigating the effects of physical transfer, and the role of a highly conducting substrate (Au) with high $e^-$ density, on the local optoelectronic properties of the flakes show interesting differences from their as-grown counterparts. Notably lower intensity PL domains ($\beta$) show relatively higher local conductivity compared to the $\alpha$-domains. While some of these differences may originate from strain, induced during the transfer process, the role of the Au surface in modulating the local luminescence properties is not clear. Further, the helicity resolved PL (HRPL) experiments that yield the degree of circular polarization (DCP) parameter for WS$_2$/Au provides more insights into the relative abundances of direct radiative recombination vis-à-vis valley scattering, likely through modification of the exciton decay and intervalley scattering lifetimes. It is anticipated that this cohesive multi-physics investigation, mapping spectroscopic, electrical, electronic, and optoelectronic properties on these segmented domains will provide better comprehension of the spatial heterogeneities in determining the optoelectronic properties of these CVD grown WS$_2$ samples. The results also can be utilized for better design and exploitation of the material properties for future device applications.

**Experimental methods**

*Growth and transfer of WS$_2$*

The WS$_2$ flakes were controllably synthesized on a p-type Si substrate with a naturally grown surface oxide by chemical vapour deposition [45]. WO$_3$ powder drop casted on cleaned substrate provided the tungsten source, and 500 mg of sulfur powder kept at the upstream end of the quartz tube provided the sulfur. Growth proceeded in argon atmosphere at 900 °C. (Further details about the growth process can be found in section 2 of supplementary information (SI) (available online at stacks.iop.org/NANO/33/495203/mmedia).) Some of the as-grown WS$_2$ flakes were subsequently transferred to 50 nm Au coated Si wafer by PMMA based wet transfer technique. Details about the transfer technique are discussed in section 3 of SI. Section 1 in SI tabulates details of the various samples investigated here.

*Photoluminescence and Raman studies*

Spatially resolved PL and Raman studies were conducted at room temperature (RT) with HORIBA XPLORA PLUS micro-Raman setup. The PL and Raman mapping were acquired with 532 nm excitation focused on the sample
through a 100× objective with NA ~ 0.9, resulting in spatial resolution of ~720 nm. All PL spectra were recorded with 600 grooves mm⁻¹ grating, and 2400 grooves mm⁻¹ grating was used for conducting the Raman studies. Spectra were recorded using a CCD camera cooled to ~60 °C. The typical laser power was used 1 mW for both PL and Raman experiments.

**AFM studies**

All AFM based experiments were conducted using a Bruker Multimode 8 AFM in the ambient. Topography and phase map were recorded in TM AFM with silicon probe from MikroMasch (HQ: NSC15/Cr-Au BS) having a resonance frequency ~325 kHz, stiffness of ~40 N m⁻¹ and tip radius ~8 nm. The current maps and conductance (dl/dV) maps along with topography were recorded in the conducting AFM (CAFM) mode, equipped with a preamplifier (TUNA2) and gain of 10¹¹ V A⁻¹ with Cr/Au coated silicon cantilever having force constant ~0.1 N m⁻¹ and probe diameter ~35 nm. During the measurement, bias was applied to the sample keeping the cantilever virtually grounded. The dl/dV maps were recorded by modulating the dc sample bias with a small ac-signal (Vac < 5% Vdc) and detecting in phase ac output voltage using a built-in lock-in amplifier [46].

**Sulfur annealing**

Sulfur annealing of as-grown samples was conducted inside a CVD furnace at a temperature ~650 °C for 30 min under continuous Argon flow.

**DCP measurements**

DCP measurements were carried out using a home built HRPL set-up consisting of a Horiba-Jobin Yvon iHR320 spectrometer with a 300 gr mm⁻¹ grating, a 532 nm diode laser, a 633 nm He–Ne laser in a confocal geometry. The laser was focused on the sample using a 50× objective with NA ~ 0.9, which gave an excitation spot size of ~1 μm diameter. Laser power was kept constant throughout the experiment. The experiments were performed at RT.

**Results and discussions**

The WS₂ flakes investigated here, with thickness varying from one to a few monolayers, were grown on Si substrates using CVD [8, 45] (see methods section for details). While the majority of the flakes showed homogeneous physical and spectroscopic properties (figure S1 in supplementary information (SI)), some showed signatures of 3-fold symmetric domain segmentation. Figure 1(a) shows the AFM topography of a WS₂ flake, sample S1 (section in SI tabulates the details of all samples discussed in manuscript) of thickness 2.9 nm, with a flat topography (rms roughness: 0.5 nm), except for surface debris evidenced as bright blobs, and wrinkles. The corresponding AFM phase map (figure 1(b)) shows contrast between the α and β domains having alternating low and high phases with 3-fold symmetry, similar to that observed in the PL map (figure 1(d)). A careful examination of topography also shows a difference in the height between the α and β domains, especially nearer to the centre of the flake as shown in the line scan in figure 1(g). Both PL and phase maps discriminate the alternating α and β domains. However, the PL map depicts a continuous bright edge [6, 14, 43] that is not well differentiated in the phase map. Further, the PL intensity variation is accompanied by a systematic variation of PL peak wavelength (λp), as shown in figure 1(e). Across the domains, λp varies from 650 nm (1.9 eV) at the low-intensity PL regions (β) to 670 nm (1.85 eV) at the high-intensity PL regions (α), with linewidths in the range of 100–150 meV. Figure 1(f) plots the PL spectra at various locations (numbered in figure 1(d)), which along with the map for λp (figure 1(e)) shows that emission from the center (location 2) and at the edges (location 1) are more intense and red-shifted compared to emission from the darker β domains (location 3 and 4). λp from the β domains is closest in energy corresponding to direct band gap excitonic decay in WS₂ [1, 3, 47]. These observations broadly follow earlier reports and reiterate the critical role played by defects in the spatial variation of the PL properties of a flake. These characteristics are induced by local doping that favors trion formation through increased doping [3, 18], either via defects [5, 6] or local strain in the lattice or a combination thereof [26]. Variation in the local carrier concentration is also reflected in the local electronic and electrical properties. Figure 1(c) shows the spatially resolved CAFM junction dl/dV (conductance) map for a sample bias (Vdc) of +10 V. The conductance map again exhibits the 3-fold symmetric segmentation with α domains having higher conductance interleaved with the three β domains of lower local conductance, along with a peripheral high conductance band. Note, the irregular low conductance patches at the truncated corners which likely originate from surface debris and low conductance regions at the wrinkles in figure 1(a). The conductance and phase maps better resolve the boundaries between the α and β domains than those acquired by optical techniques. Defects at the sample surface can give rise to unsaturated dangling bonds leading to relatively stronger adhesion than defect-free domains. Therefore, the higher relative phase shift in the α-domains compared to the β-domains, indicates stronger tip-sample adhesion [19, 48, 49] that likely stems from higher defects in the α-domains. The highly correlated nature of the CAFM and PL maps, which otherwise originate from distinctly different physical interactions on the sample is further elucidated in the correlated line scans (figure 1(g)), showing height, phase, conductance and PL intensity variation along the white dashed lines in figures 1(a)–(d). The three color-coded regions, blue, orange and green, correspond to the edge, β and α regions respectively. Figure S2 in SI shows the spatial maps of the various measurements discussed above on three other flakes (samples S2, S3, S4 details of which are tabulated in section 1 in SI) exhibiting domain segmentation, demonstrating the overall reproducibility of the individual observations and the correlated nature of the same. Across all the samples, the PL, phase and conductance maps all evidence 3-fold symmetric, triangular
domains extending from the center to the truncated corners, which have higher conductance and PL intensity along with higher tip-sample adhesion. The coincidence of the high PL intensity and red-shifted emission, along with higher conductance and adhesion intensity and red-shifted emission, along with higher tip-sample adhesion. The coincidence of the high PL intensity along with red-shifted emission spectrum, evidences red-shifted emission, along with higher conductance and red-shifted emission, along with higher tip-sample adhesion.

Figure S11 in the SI shows the schematic of a likely growth process that illustrates the nucleation and migration of defects resulting in 3-fold segmentation, which is discussed later. Further, previous investigations have also explored the role of defects and other factors in the nucleation process, e.g. nature and abundance of local defects.

To investigate the above, some of the as-grown 2D WS$_2$ flakes were subsequently transferred to Au (50 nm) coated Si wafers using a wet-transfer method [51].

Figure 2(a) shows the spatially resolved PL map of a WS$_2$ flake (sample S5), with the inset showing the optical image. Domain segmentation, akin to the PL intensity maps of WS$_2$/Si, is evident, with the α domains connecting the center to the truncated edges and having the highest luminescence. Figure 2(b) shows the corresponding map of peak wavelength, $\lambda_p$ varying in the range 620 – 640 nm. Representative PL spectra from three points in figure 2(a) are shown in figure 2(c). Intensity from the α domains is significantly higher than that from the β domains. Further, emission from both the α and β domains show maximum intensity around $\lambda_p \sim 630$ nm (1.97 eV) in contrast to flakes on Si, except for the center that evidences red-shifted emission spectrum, $\lambda_p \sim 660$ nm. The elongated tail at lower energies in all spectra indicates the presence of multiple emission channels attributable to decay of neutral excitons ($A^+$), negative trions ($A^-$) and defect (D) state mediated emission [19, 33]. Spectral deconvolution identifies the contribution from the exciton and trion fractions that centred at $\sim 629$ nm and $\sim 645$ nm respectively and their mean separation of $\sim 50$ meV, justifying their identification [5, 18, 19, 33]. Variation in intensity associated with the excitons and trions across the α and β domains changes systematically as shown in figure 2(d), which co-plots intensity variation, peak emission wavelength and the $I_A/I_D$ ratio along the black dashed line shown in figure 2(a), extending across α–β–α domains. The smaller $I_A/I_D$ values across the α domains indicate lower relative contribution of trion to the overall PL intensity, compared to the β domains, which evidence relatively higher contribution from trions compared to excitons. The observation appears counterintuitive to the previous reports identifying the α domains as negatively doped, electron-rich regions induced by the defects [33, 52] and substrate-induced doping [3, 27].

Figure 3(a) shows the AFM topography of the sample S5 on Au, which now depicts 3-fold symmetric variation in height, along with nanobubbles, and wrinkles at the edges. The regions of α domains extending from the centre to the truncated corners have a higher topographic height ($\sim 20$ nm at the highest point) than the intervening β domains which are $\sim 4$ nm above the substrate, showing a large height difference $\sim 16$ nm between regions of α and β domains. The higher topography of the α domains, which is also evidenced across other transferred samples (figure S4), may originate from multiple
sources, e.g. (i) additional WS$_2$ layers, (ii) delamination [20, 53] from the surface or (iii) local adsorbates. PL from de-excitation of neutral excitons in WS$_2$ flakes decrease in intensity with increasing number of layers along with a spectral red-shift [1, 14]. Spectra presented in figure 2(c) shows little difference between the peak position acquired at the $\alpha$ and $\beta$ domains, which along with the significantly higher intensity at the $\alpha$ domains is not commensurate with additional layers at the $\alpha$ domains. The high correlation between the radial variation in PL intensity (figure 2(a)) and topography (figure 3(a)) within each $\alpha$ domain is also notable. In both cases, intensity is high at the centre, decreases outwards and rises again at the edges. The CAFM measurements of current and conductance maps recorded at a sample bias of $+1.2$ V, again evidence the 3-fold symmetry of segmented domains as shown in figures 3(b) and (c). However, in both cases the $\alpha$ domains show lower current and local conductance compared to those in the $\beta$ domains, in contrast to that observed in the as-grown flakes on Si. The contrast in the local electrical properties is better quantified from the point IV characteristics (figure 3(d)) and the corresponding $dI/dV$ spectra (figure 3(e)) obtained from the different domains.

Figure 4(a) shows a schematic of the CAFM measurement configuration, i.e. a WS$_2$ flake lying on a Au substrate with the CAFM tip atop, forming two junctions one at the bottom and another at the top surfaces of WS$_2$. If the flake is homogeneous with ohmic sample-substrate contact, the IV characteristics are typically dominated by electrical transport across the top junction formed between the Au-coated tip and the WS$_2$ flake. Perhaps both these assumptions are questionable in the present scenario. Neither is the WS$_2$ flake homogeneous as far as electrical and electronic properties are concerned nor is the sample-substrate junction ohmic, especially if the topographic height difference arises from local delamination of $\alpha$ domains. Symmetric segmentation in PL maps [20, 50], has been reported before in monolayer flakes and attributed to delamination of alternating domains due to strain induced in the sample from the high temperature growth and subsequent cooling and differential thermal expansion of the sample and substrate. However, transferred flakes of similar size were reported to have strain relaxed, leading to disappearance of segmentation [50], contrary to the present observations. The IV characteristics shown in figure 3(d) are representative of two back-to-back metal–semiconductor–metal Schottky junctions, which are asymmetric under bias reversal. Assuming that the WS$_2$ flake is nominally $n$-doped, for $-$ve substrate bias the sample-substrate junction is reverse biased, whereas the tip-sample junction is forward biased and vice versa for $+$ve substrate bias. Consequently, the overall IV characteristics will be dominated by the reverse bias characteristics of the top and bottom junctions under $+$ve and $-$ve bias, respectively. Figure S3 in the SI shows a series of current and conductance maps acquired on the same flake at $-1.0$ V, $+1.0$ V, $+1.4$ V and $+2.0$ V. At $-1$ V the current and conductance maps show little contrast between the domains, and improves upon increasing positive bias. Even at $+2$ V bias, the outer edges of the $\alpha$ domains carry practically zero current with conductance

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**Figure 2.** Spatially varying photoluminescence of a WS$_2$ flake on Au (sample S5) (a) PL map showing segmented domains, (b) map of PL peak wavelength, (c) PL spectra at points 1, 2 and 3 shown in (a), and (d) correlated plots showing the variation of PL intensity, peak wavelength, the intensity ratio of trion and exciton, along the black dashed line shown in (a). Scale bar: 2 $\mu$m.
below the detection threshold of the current amplifier. It’s worth mentioning that the CAFM IV characteristics and $dI/dV$ spectra are not tunneling spectra and hence they do not represent the bandgap of WS$_2$.

In the α domain, the coincidence of intense PL, dominated by excitonic contribution and lower conductance, points towards depletion in local electron density compared to that in the β domains. To elucidate the statement further we refer to the band diagrams shown in figure 4(b). The first and the second columns show the band alignment during contact formation between the WS$_2$ flake and the Au substrate in both the α and β domain interfaces. In drawing the band diagram band edge values of $-3.9$ eV and $-5.4$ eV for the conduction band minima and the valence band maxima for multilayer WS$_2$ [54] have been used with the Fermi level ($E_F$) of the Au substrate at $-5.2$ eV. From the spatially resolved optical and electrical data (CAFM) for the WS$_2$ flakes on Si it may be extrapolated that in a free-standing segmented WS$_2$ flake, the α domains would have higher electron density compared to the β domains. Consequently, the former will have a higher $E_F$ than the latter i.e. $E_F(\alpha) > E_F(\beta)$, as shown in the first row of figure 4(b). This is commensurate with Kelvin probe measurements on domain segmented WS$_2$ reported before, where the contact potential difference recorded on the α domains is higher than that on the β domains [17, 50]. Thus, even within a free-standing WS$_2$ flake, there would be band bending in the azimuthal direction to equilibrate the differences in the local chemical potential across the 3-fold symmetric domains. However, once placed in contact with the Au substrate, that equilibrium would be replaced by a new one dominated by the chemical potential of the Au substrate. Since the absolute difference between the Fermi level of Au ($E_F$ (Au)) and $E_F(\alpha)$ will be higher than that of the β domain i.e. $|E_F(\text{Au}) - E_F(\alpha)| > |E_F(\text{Au}) - E_F(\beta)|$ band bending will be higher at the Au-α domain interface compared to the Au-β domain interface. In effect, the electron depletion in the α domain will be more compared to depletion in the β domain. Finally, the Au-substrate induced equilibrium will ensure that the Fermi level of both the α and the β domains are pinned to that of the substrate, as shown in the bottom panels of figure 4(b). The WS$_2$ flake achieves this via $e^-$ transfer from α to β domain. In the CAFM device configuration, where the Au coated AFM tip forms another Schottky junction on the top WS$_2$ surface, the electron depleted α domain evidence lower conductance compared to the β domain. Thus, the regions of high and low current and

Figure 3. Spatial maps of WS$_2$ flake on Au (sample S5) (a) AFM topography, (b) CAFM current map, (c) conductance map at $+1.2$ V and (d) point IV characteristics and corresponding (e) $dI/dV$ spectra at different locations in the α and β domains identified in (a). Scale bar: 2 μm.
conductance map contrast of the segmented domains for WS$_2$ flakes on Si are inverted for the flakes on Au. This also explains the progressively increasing contrast in the current and conduction maps with an increase in $+$ ve bias, as seen in figure S3. Indeed, these observations have been replicated across multiple WS$_2$ flakes (samples S6, S7) transferred onto Au substrate, which displays domain segmentation, as shown in figure S4 of SI, and thus are understood to be generic in nature. This differential electron depletion across the $\alpha$ and $\beta$ domains also explains the variation in the PL spectra observed across the WS$_2$ flake. The $\alpha$ domains depleted of free electrons inhibit negative-trion formation resulting in the PL spectrum being dominated by excitonic decay relative to the $\beta$ domain. As mentioned before, the 3-fold segmentations observed have been attributed to local delamination at the $\alpha$ domains, which though commensurate with the low current and conductance at the $\alpha$ domains, does not conform with the evolution of the current and conductance maps with increasing bias (figure S3). The present investigations remain inconclusive as to the origin of the large height difference between the domains.

Raman measurement has been used effectively not only to understand the lattice dynamics of 2D TMDCs but also to investigate perturbations like adjacent layers [55, 56], strain [57, 58], and defects [44, 52, 59]. Figure 5(a) shows the Raman spectra acquired over $\alpha$ and $\beta$ domains of WS$_2$/Si substrate (sample S4) with 532 nm excitation. Both spectra show the two characteristic peaks of the semiconducting 2H phase of WS$_2$, at $\sim$417 cm$^{-1}$ which corresponds to the $A_g(\Gamma)$ mode and the other around 350 cm$^{-1}$, which is a convolution of three Raman modes, $E_{2g}(M)$, $2LA(M)$ and $E_{2g}(\Gamma)$ [55].

Figure S5(A) in SI shows the spectral deconvolution of the peak resolving the three constituent modes, $E_{2g}(M) \sim 344$ cm$^{-1}$, $2LA(M) \sim 350$ cm$^{-1}$, and $E_{2g}(\Gamma) \sim 354$ cm$^{-1}$. The $LA(M)$ and $LA(K)$ are zone edge modes, of which the $LA(M)$ mode is activated by lattice defects [44, 52, 59] and the phonons associated with $LA(K)$ enhances inter-valley ($KK'$) scattering impacting valley polarization [60–63]. The $2LA(M)$ mode denotes a second order 2-phonon scattering associated with resonant Raman scattering [55]. Figure 5(b) shows the Raman spectra on the $\alpha$ and $\beta$ domains for WS$_2$ on Au sample (sample S5), corresponding to the PL and CAFM data presented in figures 2 and 3. The differences between the Raman spectra across the domains and on different substrates are accentuated when comparing the spatially resolved modal maps. The spatial maps of the $LA(M)$, $[E_{2g}(M) + 2LA(M) + E_{2g}(\Gamma)]$, and the $A_{2u}(\Gamma)$ modes are shown in figures 5(c)–(e) and (f)–(h) for WS$_2$ on Si and Au substrates, respectively. On both substrates, the $LA(M)$ and $[E_{2g}(M) + 2LA(M) + E_{2g}(\Gamma)]$ maps show the 3-fold symmetric variation of intensity. The defect-related $LA(M)$ mode is more intense at the $\alpha$ domains in both systems (figures 5(c) and (f)), which further entrenches the positive correlation between defects, enhanced PL and local conductance (also see SI figure S5(B)). The correlation between the maps of the $[E_{2g}(M) + 2LA(M) + E_{2g}(\Gamma)]$ and PL is expected since higher intensity PL is indicative of stronger light–matter interaction, which would benefit resonant Raman scattering processes like the $2LA(M)$ mode. The correlation is also evident in the synchronous line scans taken across both flakes, along the dashed lines extending across the $\alpha = \beta$ domains (figures 5(d) and (g)) as shown in SI figure S5(B)). The maps for the $A_{2u}(\Gamma)$ modes, corresponding to the out-of-plane vibrations, are markedly different between the flakes on the two different substrates. While the modal intensity is almost uniform over the entire flake on Si (figures 5(e) and S5(B)), the map for the flake on Au (figure 5(h)) shows the 3-fold segmentation. Spatially the mode intensity is strongest at the truncated edges of its $\alpha$ domains (figure S5B(b)) but without any spectral shift, which might arise from weak substrate interaction. Overall, the above results establish a strong spatial correlation between the local conductance, PL intensity and the Raman modal maps, all of which carry signatures of higher defect density in the $\alpha$ domains compared to the $\beta$ domains, within single WS$_2$ flakes. As mentioned earlier, previous reports have associated sulfur vacancies at the edge of WS$_2$ flakes with the incidence of higher intensity PL, especially with increasing contribution from trions due to higher local.

**Figure 4.** (a) Schematic of the conducting AFM measurement configuration showing the segmented domains in a WS$_2$ flake, on an Au substrate and Au coated CAFM tip on top. The dashed line denotes the substrate-sample junction. (b) Energy band diagram of the junction between the $\alpha$ and $\beta$ domains of WS$_2$ with the Au substrate before and after junction formation.
Figure 5. Spatially resolved Raman investigation. Raman spectra over $\alpha$ and $\beta$-domain on (a) WS$_2$ on Si (sample S4) and (b) WS$_2$ on Au (sample S5). Raman map of (c) LA($M$) mode, (d) $[E_{2g}^1(M) + 2LA(M) + E_{2g}^1(\Gamma)]$ mode, (e) $A_{4g}(\Gamma)$ mode for sample S4 (scale bar: 1 $\mu$m) and (f) LA($M$) mode, (g) $[E_{2g}^1(M) + 2LA(M) + E_{2g}^1(\Gamma)]$ mode, (h) $A_{4g}(\Gamma)$ mode for the sample S5. Inset of figure (c) and (f) shows the optical image of the flakes (scale bar: 2 $\mu$m).

Figure 6. Spatially resolved maps and PL spectra of a WS$_2$ flake on Si (sample S2) (a), (b) PL intensity (c), (d) PL spectra (e), (f) Raman LA($M$) mode (g), (h) phase (i), (j) conductance maps. Top row corresponds to as-grown sample and bottom row corresponds to post sulfur annealing.
carrier densities and defect state mediated de-excitation. In both cases, the PL spectra are red-shifted compared to that of unperturbed samples suggesting higher defect density preferentially at the flake edge [6, 14]. To test the hypothesis that the domain segmentation may arise from sulfur vacancies, selected WS2 flakes on Si were annealed at 650 °C for 30 min in a sulfur-rich environment with Ar as the carrier gas.

Figures 6(a) and (b) show the PL intensity map of a WS2 flake (sample S2, S2A) before and after annealing in a sulfur environment with the corresponding PL spectra recorded at three points (figure 6(a)) at the centre, and the α and β domains shown in figures 6(c) and (d). Post annealing, the PL intensity contrast between the domains decreases significantly along with an overall reduction in the emission intensity across all regions. These observations are replicated across the other domain segmented WS2 flakes (samples S1A, S3A, S4A) that were annealed, as shown in SI figure S6. The spectra in figure 6(d) also shows the appearance of a shoulder at around 630 nm (1.97 eV) that was absent prior to annealing (figure 6(c)), which is attributable to excitonic recombination [5, 33, 41]. The drastic reduction in the primary peak intensity at 660 nm after sulfur annealing indicates that the emission in the as-grown sample is indeed associated with sulfur vacancy in the system. Further, a comparison between the Raman maps of the LA(M) mode (figures 6(e) and (f)), shows weakening within the α domains, providing further evidence for the decrease in defects within the region. Perhaps the most distinct change between the flakes brought about by sulfur annealing is evidenced in the AFM phase maps. The 3-fold symmetry of the phase map prior to annealing (figure 6(g)) is lost in the annealed sample (figure 6(h)), though the topography of the sample before and after annealing (figure S7) remain unchanged, ensuring integrity of the sample. Similarly, the conductance map also loses contrast upon annealing, providing indirect proof that the original spatial contrast arose due to sulfur vacancy induced local carrier density variation. Overall, sulfur annealing elucidates the role of defects in realizing the spectroscopic, optical, and electronic properties of these segmented films. Earlier studies have investigated the intermediate growth stages of TMDCs grown via CVD [64–66]. Often in triangular flakes, growth nucleates and progresses in a 3-fold symmetric manner where three individual triangular flakes grow radially along the three symmetry axes and finally merge azimuthally to form a layer [64]. Under such a growth and strain relaxation process, defects at the growing crystal edges diffuse radially and azimuthally, as shown schematically in SI figure S11. Finally, the residual defects are swept out radially to the outermost edge and azimuthally squeezed along the 3-symmetry axes, the latter forming the α-domains with high defect density.

In order to explore the performance of domain segmented flakes for application in valleytronics, helicity resolved PL measurements were performed with CW laser excitation at 633 nm (~1.96 eV) and 532 nm (~2.33 eV), at RT. At both wavelengths, the samples were excited with right circularly polarized (RCP/σ+) light and the polarization states of the emitted PL were discriminated as RCP/σ+ or left circularly polarized (LCP/σ−). The degree of circular polarization (DCP) parameter, as given below then quantifies the degree of valley polarization in the system,

\[
DCP[\%] = \frac{I_{\sigma^+} - I_{\sigma^-}}{I_{\sigma^+} + I_{\sigma^-}} \times 100 \tag{1}
\]

Here, \(I_{\sigma^+}\) and \(I_{\sigma^-}\) are the RCP and LCP emission intensities. For the WS2 flake on Au (sample S5) the overall PL spectrum is dominated by emission from the α domains with a peak near 630 nm. Figures 7(a), (b) shows the intensities of the RCP \((I_{\sigma^+})\) and LCP \((I_{\sigma^-})\) polarized PL along with the calculated DCP for 633 nm excitation from the α and β domains, respectively. The wavelength range 630 – 645 nm (shaded region) has been removed since it represents the stopband of the notch filter used to block the laser light from reaching the detector. The β domains show DCP ~50% while α domains show DCP ~10% for the same RCP (σ+) excitation. The PL spectra and DCP for two other WS2 flakes on Au (samples S6 and S7) are shown in SI figure S8, which are commensurate with the data presented above. The coincidence of higher DCP with low PL intensity in the β domains and low DCP with high PL intensity in the α domains has been reported before [40, 67]. For excitation with RCP (σ+) 532 nm light the PL and DCP obtained on samples S5 and S6 are shown in figure S9. Expectedly, the PL shows a single peak around

![Figure 7. HRPL spectra obtained by using right circularly (σ+) polarized, near-resonant (633 nm) excitation from the heterogeneous WS2 flake (sample S5), and the corresponding DCP at RT for (a) β and (b) α domains. The shaded region represents the stopband of the notch filter used to block the laser light from reaching the detector.](image-url)
630 nm but with negligible DCP for both the α and β domains. Thus, near resonant with A0 exciton excitation strongly favors DCP in comparison to excitations at higher energies. Weak DCP alludes to high intervalley scattering such that electrons optically excited to the spin-up states, under σ+ excitation, are scattered to the spin-down states and decay giving σ− PL, and vice-versa. Thus the observed DCP also quantifies the relative strength of the two associated processes, i.e. scattering rates of carrier recombination (e.g. excitonic decay rate) and intervalley scattering, and the DCP may be expressed in terms of the corresponding lifetimes as

\[ DCP[\%] = \frac{P_0}{1 + 2 \frac{\tau_l}{\tau_e}}. \]  

In equation (2), is the initial polarization, \( \tau_c \) denotes the valley lifetime and \( \tau_e \) denotes the exciton lifetime, including both radiative and non-radiative recombination processes and suggests that the DCP is increased by factors that decrease the \( \tau_l/\tau_e \) ratio. Thus intrinsic factors which influence the luminescence properties of TMDCs i.e. defects and doping, play a major role in deciding the DCP. Along with extrinsic parameters like the substrate and the excitation wavelength (\( \lambda_{\text{exc}} \)) significantly influence the observed DCP, as seen above in the difference between the DCP obtained with 532 nm and 633 nm excitation. Significant overlap between the excitation and emission line-widths increases DCP by disadvantaging intervalley scattering. While the difference in the overall DCP, in both the α and β, for the two excitations may be explained due to the difference in selectivity rules affecting the system, the difference in the spatial dependence of PL and DCP under the two excitation are non-trivial to reconcile. Firstly, for RCP excitation at 532 nm the ratio of \( I_{\sigma^+} \) between the domains i.e. \( I_{\sigma^+}(\alpha)/I_{\sigma^+}(\beta) \) is \( \sim 100 \), which for 633 nm excitation is \( \sim 10 \) (both calculated at the peak emission wavelength). Thus the PL contrast is also significantly reduced as \( \lambda_{\text{exc}} \) approaches the A0 resonant energy. Further, the LA(Κ) Raman mode is much stronger over the α domains (figure S10 in the SI) compared to that at the β domains. As discussed earlier, the phonons associated with the LA(Κ) Raman mode are responsible for intervalley scattering and thus decrease valley depolarization, as observed here, i.e. the stronger LA(Κ) mode at the α domains is correlated with lower local DCP value. Further, deconvolution of the PL spectrum (figures 2(c), (d)) from the β domain show relatively higher trion contribution than in the α domains, which is commensurate with the relatively higher carrier density in the β domains. Proximity of the WS2 sample with Au-substrate may also introduce parallel non-radiative relaxation pathways for photo-generated carriers [70], which may lead to a significant reduction in exciton lifetime (\( \tau_e \)) hence affect the DCP. Indeed, any potential valleytronics applications with TMDCs will involve an optimal hierarchy of three timescales \( \tau_c, \tau_e \) and a charge transport (drift-diffusion) timescale \( \tau_r \). Note \( \tau_c \) is not the same as the carrier scattering timescale that decreases with increasing disorder. Evidently, for simultaneous preservation of valley polarization and realization of high photovoltage upon illumination, the associated timescales should be in the order \( \tau_c \ll \tau_e \ll \tau_r \). The coincidence of high DCP regions with regions of lower disorder (β domains) is not only consistent with the dynamics of the system, i.e. phonon and impurity scattering, and lays out the design principles in realizing optically stimulated valleytronics applications.

**Conclusion**

In conclusion, this investigation explored spatially resolved optical, spectroscopic, topographic, electrical and electronic properties of 3-fold symmetric domain segmentation observed in WS2 flakes, grown on Si by CVD. The spatial maps highlight the common origins of the different physical properties, observed across domains within single flakes, and the circumstances that promote segmentation, especially the role of defects and substrates. Symmetric distribution of defects is understood to dictate the luminescence, electronic and electrical properties across domains. Further, annealing WS2 flakes in sulfur-rich environment is shown to quench domain contrast, not only in photoluminescence but also in local conductance, phase imaging and even spatial variation of Raman modes that are sensitive to native defects. Thus, sulfur vacancies appear to be a leading parameter in nucleating domain segmentation in the system. Later, the role of metal substrate on segmentation is probed for flakes transferred onto Au. In spite of the relatively uniform topography of as grown, domain segmented, WS2 flakes on Si, once transferred to Au the flakes show height variation across domains. Spatially varying electrical and optical properties in transferred samples directly demonstrate the difference in interactions between high and low electron density regions with the substrate and how that affects the resulting optical and spectroscopic properties of the flakes. Notably, on Au substrate the electronic α-domains exhibit carrier depletion far stronger than the β domains, resulting in inverting the correlation between the spatially resolved spectroscopic and electrical properties for Si substrates. The substrate-induced spatial variation in carrier density is reflected in the spectral composition of the photoluminescence spectra and leads to variation in relative abundance of trion formation across the segments. Evolution of the characteristic Raman modes and their differences across the domains, on either substrates and pre- and post-annealing in sulfur were analyzed to develop a comprehensive picture of the phonon modes which are crucial to preserving valley polarization in these systems. Finally, photoluminescence measurements quantifying spectrally resolved degree of circular polarization demonstrate that regions harboring higher defect density and having higher photoluminescence efficiency, do not preserve valley polarization, in contrast to regions of lower defect density.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Associated content

The Supplementary Information is available free of charge on the journal website.

Authors’ contribution

AK, PKB, PVS performed the experiments. All authors contributed to writing the manuscript.

Notes

The authors declare no competing financial interest.

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