Quaternary Alloys



Thermally Induced 2D Alloy-Heterostructure Transformation in Quaternary Alloys

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Composition and phase specific 2D transition metal dichalogenides (2D TMDs) with a controlled electronic and chemical structure are essential for future electronics. While alloying allows bandgap tunability, heterostructure formation creates atomically sharp electronic junctions. Herein, the formation of lateral heterostructures from quaternary 2D TMD alloys, by thermal annealing, is demonstrated. Phase separation is observed through photoluminescence and Raman spectroscopy, and the sharp interface of the lateral heterostructure is examined via scanning transmission electron microscopy. The composition-dependent transformation is caused by existence of miscibility gap in the quaternary alloys. The phase diagram displaying the miscibility gap is obtained from the reciprocal solution model based on density functional theory and verified experimentally. The experiments show direct evidence of composition-driven heterostructure formation in 2D atomic layer systems.

2D transition metal dichalcogenides (2D TMDs) have been an important research topic in the past few years due to exciting properties in the fields of photonics, optoelectronics, valleytronics, spintronics, catalysis, and flexible electronics.^[1–8] However, the fixed bandgap of 2D TMDs limits their scope of potential applications, and has pushed researchers to find new ways to tailor the bandgap by methods like mechanical straining, doping, electrical gating, alloying, and designing heterostructures.^[9–25] Out of these techniques, doping and alloying have resulted in extensive bandgap tunability (in Mo_{1–x}W_xS₂, MoS_{2(1–x})Se_{2x}, WS_{2(1–x})Se_{2x}, Mo_{1–x}W_xSe₂),^[17–21] and imparting

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interesting phase transformations and magnetic properties $(\text{Re}_{x}\text{Mo}_{(1-x)}\text{Se}_{2})^{[22]}$ without significantly complicating the synthesis process. Ordered arrangements (Janus monolayers) and intrinsic strain in $MoS_xSe_{(1-x)}$ alloys have shown good piezoelectric and catalytic properties.^[23,24] On the other hand, TMD heterostructures create abrupt interfaces of different 2D materials (MoS₂/WS₂, MoSe₂/WSe₂, MoS₂/WSe₂) and provide a platform to manipulate generation, confinement, and transport of excitons, photons, and phonons at the interfaces to facilitate the design of unique devices for ultrafast charge transport.^[6,11–15,26]

Since entropic mixing generally favors alloy formation, direct growth of hetero-

structures is challenging. Hence, lateral and vertical heterostructures of TMDs have been previously synthesized by either mechanical stacking or chemical vapor deposition (CVD) via adding catalysts, switching precursors/gases, and adopting two-step CVD processes.^[12,27–30] However, in all of these studies, only up to ternary systems were considered. Increasing the number of components introduces the possibility of existence of miscibility gap, when for certain compositions an alloy phase becomes unstable and can decompose into heterostructure, thus making heterostructure thermodynamically stable. Although this concept has been proven to be true for III–V semiconductors, the corresponding studies in 2D TMDs are missing.^[31]

Herein, we demonstrate a phase transition from a metastable alloy to stable heterostructure via thermal annealing of 2D quaternary alloys. The driving force behind the transformation is the existence of miscibility gap in quaternary alloys, as seen from the random alloy model based on density functional theory (DFT) calculations. The calculated phase diagram of the quaternary alloys was experimentally verified by thermal annealing of the different compositions of quaternary alloys. The formation of a lateral heterostructure is observed by Raman spectroscopy, Photoluminescence (PL) and atomic force microscopy (AFM), and the sharp interface between the phases is examined via scanning transmission electron microscopy (STEM). Since the transition is thermodynamically favorable, the obtained heterostructures are stable. Devices fabricated on the transformed alloy heterostructure showed p-n diode type behavior.







Figure 1. Schematic diagram showing main steps for heterostructure formation in the quaternary alloys. Following the CVD growth (left panel), transition metals preferentially segregate under annealing (center panel), forming a lateral heterostructure (right panel).

Quaternary alloys were grown using CVD at 700 °C in presence of Ar/H₂ as per previously reported method.^[25] Details about the growth setup are given in the Experimental Section. These quaternary alloys were then annealed at 250 °C for 5 h under pressure 20 mtorr. The annealing was also performed for other time periods, that is, 1, 2, 3, and 10 h, with results displayed in the Supporting Information (Figures S1 and S2, Supporting Information). Annealing the alloys at 5 h yielded the most stable phase-segregated heterostructures. The schematic in **Figure 1** summarizes the experimental procedure. **Figure 2**a shows a typical optical image of the quaternary alloy (25 μ m) after the annealing with no noticeable change in the contrast of the samples. Figure 2bi,ii shows the AFM images of the alloy pre- and post-annealing. Small bilayer domains of



Figure 2. Structural characterization of as-annealed samples. a) Optical image of as-grown quaternary alloy $M_{(1-x)}S_{y}Se_{(1-y)}$. b) Corresponding AFM image of the sample (i) before and (ii) after the annealing. c) Raman spectra taken before and after the annealing. The post-annealed sample shows formation of MoSSe (olive) and WSSe (blue) heterostructure at the center and edge, respectively. d) PL spectra showing the optical bandgap difference 1.75 eV (MoSSe) and 1.90 eV (WSSe) at the center and edge, respectively, as compared to uniform bandgap of 1.8 eV before the annealing. e) Normalized Raman maps. f) Normalized PL maps of as-grown quaternary alloy before and after the heat treatment indicating the formation of heterostructure due to annealing. The corresponding wavenumbers/optical bandgap values of the Raman/PL maps are indicated as an inset in the maps.





nanometer size were observed at the interface of lateral heterostructure of the monolayer flake in the post-annealed samples. Figure 2c shows the Raman spectra taken on the sample before and after the annealing. The spectrum of the pre-annealed sample exhibits the characteristic Q-peak of quaternary alloys as reported previously (red curve).^[25] The post-annealed samples show different Raman spectra for the central and edge regions indicating the potential formation of a heterostructure (blue and green curves). The spectrum for the central region shows four peaks at 406, 376, 348, and 271 cm⁻¹ indicating the formation of homogenous $MoS_{2(1-x)}Se_{2x}$ alloy^[23,24] whereas the edges show peaks at 416, 338, and 168 cm⁻¹ resembling that of a $WS_{2(1-\nu)}Se_{2\nu}$ alloy.^[20] The Raman maps of the post-annealed samples shown in Figure 2e clearly delineate the heterostructure with central $MoS_{2(1-x)}Se_{2x}$ (376 cm⁻¹; green region) and edge $WS_{2(1-\nu)}Se_{2\nu}$ regions (338 cm⁻¹ red regions) . The optical bandgap modification due to heterostructure formation was investigated using PL spectroscopy. The PL spectra and maps of the quaternary alloys pre- and post-annealing in Figure 2d,e show that the bandgap changes from uniform 1.85 eV (mixed alloy) to that with bandgaps of 1.75 eV (center) and 1.90 eV (edge), respectively, indicating a lateral heterostructure formation. The heterostructure interface shows an optical bandgap of 1.80 eV. It is interesting to note that at this interface, we saw the formation of bilayer domains in AFM. The composition of the alloys derived from X-ray photoelectron spectroscopy (XPS) do not indicate substantial change (Table S1, Supporting Information) in the pre- and post-annealed samples. The post-annealed sample showed p-n diode behavior due to heterostructure formation (Figure S5, Supporting Information).

To study segregation of the post-annealed samples in detail, they were examined via STEM. **Figure 3**a shows a large field-of-view high-angle annular dark field (HAADF) STEM image of a quaternary alloy flake exhibiting lateral phase segregation. HAADF imaging is dominated by Z-contrast, meaning that heavier atoms result in higher intensity in the image. The



Figure 3. STEM-EELS and atomic resolution analysis. a) STEM-HAADF image of quaternary alloy flake exhibiting lateral phase segregation. b) Higher resolution HAADF image of the area from the white box in (a), showing three regions with distinct differences in intensity (labeled R1-top, R2-middle, and R3-bottom). c) EEL spectra from each of the three regions in (b). d,e) Reference spectra for W O-edge and Mo N-edge, respectively, from ref. [12]. EELS shows R1 and R2 are dominated by W, while the reduced separation between the W edge peaks indicates that R3 is Mo-rich. f) HAADF image of the area from the white box in (b), showing atomic-resolution image of the sharp interface between the phase segregated W-rich (R2) and Mo-rich (R3) regions. g) Atomic-resolution HAADF image of monolayer interface between R2 and R3. h) Atomic positions of A-sites and B-sites in hexagonal 2H lattice for image in (g). i,j) Historgrams of HAADF intensities for atomic positions shown in (h) for the A-sites (i) and B-sites (j) showing clear division between the different constituent atoms in the quaternary alloy. k) Using divisions shown in (i,j) atoms in (h) are labeled by species. Atom labeled image shows that W atoms are present in Mo-rich region and vice versa, but the transition between W-rich and Mo-rich regions is almost atomically sharp.



flake in Figure 3a exhibits many regions with distinct contrasts, however some of the changes in contrast can be due to difference between monolayer and bilayer, or bilayer and trilayer, as opposed to phase segregation. To verify the nature of the changes in contrast, we examine the outer edge of the flake in higher resolution. Figure 3b shows a HAADF image of the area highlighted by the dashed box in Figure 3a possessing three distinct regions in terms of Z-contrast: top (R1), middle (R2), and bottom (R3). Electron energy loss spectroscopy (EELS) is performed in each of the three regions and the background subtracted EELS signals are plotted in Figure 3c. The W O-edge (onset at 36 eV) and the Mo N-edge (onset at 35 eV) overlap significantly, but have distinctly different fine structure.^[12] Figure 3d,e shows reference spectra of the W and Mo edges, respectively, taken from ref. [12]. The W edge exhibits two clearly resolved peaks, while the Mo edge has only one. The EEL spectra from the top and middle regions (R1 and R2) both show the two-peak structure of the W edge indicating that they are both mostly W, while in the bottom region (R3) the prepeak has vanished and the separation between the two main peaks is reduced, indicating that this region contains a high concentration of Mo while still being alloyed with W. Additionally, the total intensity of the Mo/W peak is significantly higher in the middle and bottom regions (R2 and R3) than it is in the top region (R1) indicating that R2 and R3 are bilayer regions while R1 is a monolayer. With the compositions of the three regions established, the phase segregation can be seen more clearly in Figure 3a. Just as the Raman and PL from Figure 2 showed, the STEM-EELS analysis shows W-rich areas on the outer edge and center of the flake with an Mo-rich region in between.

The Z-contrast of HAADF imaging can also be used to examine the interface between the phases at atomic resolution. Figure 3f shows the region highlighted by the box in Figure 3b, where a hole in the bilayer has exposed a monolayer region of the interface between the W-rich region in R2 and the Mo-rich region in R3. For a HAADF image, like that in Figure 3g, of a monolayer material, the species in the monolayer can be directly identified by their Z-contrast. First, the atomic peak positions of each atom in the monolayer region (i.e., excluding the crumpled

particulates or bilayer atoms) are identified, then they are sorted into A-sites and B-sites by their nearest-neighbor configuration. The resulting A-B sorted image is shown in Figure 3h, and the histograms of HAADF intensities are shown in Figure 3i for the A-sites and 3j for the B-sites. The peaks in the histogram match well to the atomic numbers and effective atomic numbers of the different species in the alloy (S₂: Z_{eff} = 22.6, S+Se: $Z_{\text{eff}} = 37.6$, Mo: Z = 42, Se₂: $Z_{\text{eff}} = 48.1$, and W: Z = 72). Thus, by using the minima between HAADF intensity peaks as a threshold we can identify the most likely element/elements for each atomic column in the HAADF image and show the physical distribution of those elements. The atom-labeled image is shown in Figure 3k, where it can be seen that the different chalcogenides are evenly distributed across the two regions, but that the W-atoms are highly localized to the top (R2) and the Mo-atoms to the bottom (R3). Partial alloying is still observed in each region (as we expected from the EELS in Figure 3c), but the transition between the Mo- and W-rich regions is extremely abrupt, occurring over the space of only a few atomic planes, demonstrating that the interfaces between the lateral phases in these heterostructures are almost atomically sharp.

The influence of annealing on the samples was further studied with respect to composition variation. A total of 15 quaternary batches were synthesized (by varying the concentrations of Mo/W and the positions of the S/Se boats) and same exercise (Raman, PL, and XPS measurements) as explained above was performed (**Figure 4a**). It is interesting to note that the lateral heterostructure formation of $MoS_{2(1-x)}Se_{2x}$ and $WS_{2(1-y)}Se_{2y}$ is selective to only a few compositions (b1, b4, b6) (indicated in green). For some compositions (b5, b7, b15, b10) segregation (green markers) was already present before annealing whereas for some compositions (b2, b3, b8, b9, b11, b13, b14) segregation does not happen at all (red). Detailed compositions of all the batches are indicated in Table S2 (Supporting Information).

This composition-selective transformation of the quaternary Mo–W–S–Se compound can be explained by comparing free energies of different phases. The free energy *G* of a random alloy $Mo_xW_{(1-x)}S_{2\gamma}Se_{2(1-\gamma)}$ includes mixing energy at 0 K and an entropy term. The alloy is represented by atoms



Figure 4. Influence of composition on heterostructure formation. a) Various compositions of quaternary alloys indicating the compositions which transform into heterostructure. b) Miscibility gaps in $Mo_x W_{(1-x)} S_{2y} Se_{2(1-y)}$ alloy. The free energy of the alloy is based on the nonideal reciprocal solution model described in the text. The miscibility gap extends along the $MoSe_2$ -WS₂ diagonal. Miscibility gaps at different temperatures are shown, with miscibility gap at T = 523 K shaded green.



occupying two sublattices-transition metal and chalcogenwith no interactions on each of the sublattices, and pairwise, nearest-neighbor-only interaction between the sublattices (for a detailed description of the model, see the Supporting Information). The mixing energy G_{mix} is then given by $G_{\text{mix}} = xy\Delta\mu$, for x+y < 1, and $(1-x)(1-y)\Delta\mu$ for x+y > 1. Here, $\Delta \mu = (\mu_{MoS2} + \mu_{WSe2}) - (\mu_{MoSe2} + \mu_{WS2})$ is the measure of the nonideality of the solution. MoSe₂, WS₂, and WSe₂ (MoS₂) phases are used as a reference for x+y < 1 (x+y > 1). From a DFT calculation $\Delta \mu = 0.264$ eV is obtained, and free energy evaluated after including configurational entropy. The resulting miscibility gaps are shown in Figure 4b for different temperatures, with the miscibility gap for T = 523 K shaded green. The inner green region corresponds to higher stability of the reference phases. Phase separation occurs along the MoSe₂-WS₂ diagonal, where reference phases have greatest stability. The miscibility gap region obtained from the model parameterized from DFT results agrees qualitatively with experimental data.

In conclusion, we show that facile annealing of the quaternary $Mo_{1-x}W_xS_{2(1-y)}Se_{2y}$ alloys results in segregation to a $MoS_{2(1-x)}Se_{2x}/WS_{2(1-y)}Se_{2y}$ lateral heterostructures, with nearly atomically sharp interfaces. This phenomenon of phase segregation is explained by spinodal decomposition due to the existence of miscibility gap. The miscibility gap, as shown by the experimental and DFT calculated phase diagram favors the transformation from alloy to heterostructure. This phenomenon is common to all the 2D alloys that have a metastable nature. The generation of the $MoS_{2(1-x)}Se_{2x}/WS_{2(1-y)}Se_{2y}$ structure allows for the combination of tunability of alloying and doping with the device characteristics of heterostructures in 2D materials, presenting a wide range of potential applications in flexible electronics.

Experimental Section

Growth of Quaternary Alloys: Quaternary alloys were grown using CVD as previously reported.^[25] Sulfur (S, 99.99% Sigma Aldrich) and selenium (Se, 99.99% Sigma Aldrich) were mixed in equimolar ratio using mortar and pestle. Molybdenum oxide (MoO₃) and tungsten oxide (WO₃) were taken in 1:1 ratio by weight and separately placed at the center of the heating zone of the furnace. 300 nm SiO₂/Si substrates (1×1 cm) precleaned with acetone and isopropyl alcohol were placed inverted on top of the WO₃ precursor. The furnace was heated to 700 °C at 50 °C min⁻¹ in the presence of 100 sccm Ar/H₂ and held at that temperature for 20 min followed by natural cooling.

Annealing Setup: Different compositions (batches b1-b8) of as-grown quaternary alloys were annealed at 250 °C for varying duration (1, 3, 5, and 10 h) under 20 mtorr pressure.

Sample Transfer: The samples for STEM imaging and device measurements were transferred using wet-chemical transfer method. Poly(methyl methacrylate) (PMMA 950 A4, Micro CChem) was spin-coated on the as-grown samples. The PMMA-coated samples were placed in 0.1 $\,$ M KOH to etch the underlying SiO₂ layer. The floating PMMA+sample film was scooped using a new SiO₂/Si substrate/TEM grid for the device/TEM measurements, respectively, after dissolving the PMMA on the sample using acetone.

Characterization: Raman and PL spectra/maps were taken using Renishaw inVia Raman spectroscopy with a 532 nm laser at 748 and 60.4 μ W powers for Raman and PL measurements, respectively. The data were processed using the Wire 4.2 software. X-ray photoelectron measurements were carried out using PHI Quantera XPS with 200 eV

Al K α X-rays. The XPS spectra were curve-fitted using Multipak software. AFM images were obtained on a Bruker Multimode 8. Microscopy was performed using a Nion aberration-corrected UltraSTEM 100 operated at an accelerating voltage of 60 kV, which is equipped with a Gatan Enfina EEL spectrometer. The experiments were performed with a convergence semiangle of 30 mrad, and an EELS collection semiangle of 48 mrad. The HAADF image in Figure 2d was a 2048 \times 2048 pixel image with a 16 μ s pixel dwell time, a Gaussian blur with σ = 1.5, to improve the signal-to-noise ratio, the other HAADF images in Figure 2 were 1024×1024 pixels with an 8 µs dwell time, and are displayed as acquired. The HAADF detector used for all images had a collection half-angle ranging from 86 to 200 mrad. EELS for R1, R2, and R3 were taken from a 100 spectra line scan extending between the three regions, with a spectrum acquisition time of 2 s. The three spectra shown in the main text are each the average of five consecutive spectra from the line scan (corresponding to a distance of 20 nm) far from the interfaces between the different regions. The background was subtracted with a power-law fitting.

Device Fabrication/Measurements: FET device was fabricated on the transferred sample using electron beam lithography on FEI Quanta 400 ESEM followed by evaporation of 40 nm Au and lift-off. Electrical measurements were carried out on a vacuum probe station. The electrical signals were collected by a Keithley 2634B sourcemeter.

Calculations: DFT calculations were performed within the local-density approximation (LDA) to the exchange-correlation potential, using normconserving pseudopotentials, as implemented in the Quantum Espresso package.^[32] The kinetic energy cutoff for the plane-wave basis set was set to 816 eV in all calculations, and spin–orbit interactions were neglected. The vacuum region was represented by a cell with a size of 15 Å in z-direction. System geometries were relaxed until the maximum force on any atom was less than 0.001 eV Å⁻¹.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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