Heterostructures of semiconductors and metals form fundamental building blocks of modern electronic and photonic devices. Atomically sharp, coherent and passivated interfaces in such heterostructures are particularly important in high mobility transistors, solid state lasers, light emitting devices, and solar cells where the performance is limited by interfacial defects. Implementation of heterostructures in low dimensional structures such as quantum dots, nanowires, and nanosheets is thus a key step toward enabling their integration into novel nanoscale devices. Single crystal heterostructures are typically realized with chemically dissimilar lattice-matched compounds via heteroepitaxy or solid-state reactions. For example, silicon forms coherent interface with metallic nickel silicide (NiSi) such that when Si nanowires are reacted with Ni, metal-semiconductor heterojunctions are achieved. Similarly, a lattice match of graphene and hexagonal boron nitride (hBN) enables hybrid structures in two dimensions. The atomically thin 2D sheet of molybdenum disulfide (MoS2) is unique in that it is chemically homogeneous but exhibits semiconducting and metallic polymorphs that are lattice matched. Here, we report that chemically exfoliated MoS2 single layers exhibit a hybrid structure of semiconducting and metallic phases that are coherently bonded such that the resulting single-layer heterostructure is chemically monolithic and single crystalline.

A single layer of molybdenum disulfide (SL-MoS2) consists of a 6.7 Å thick slab of a S—Mo—S sandwich layer. Recent reports on direct band gap photoluminescence properties, field effect transistor characteristics, gas sensitivity, and mechanical stability of SL-MoS2 have opened up new prospects for the technological applications of 2D materials derived from layered inorganic compounds. Polymorphism is one of the unique features of layered transition metal dichalcogenides. MoS2 and WS2 exist in both metallic and semiconducting phases. Our previous studies indicate that two phases coexist in chemically exfoliated sheets of MoS2 and WS2 (ref 14) pointing to the electronic heterostructural nature which may be exploited for realization of novel nanodevices with advanced functionalities. Solution-based exfoliation of graphite and inorganic layered compounds has been demonstrated to be a versatile route to the
bulk production of 2D sheets and could be a viable method for implementation into technology.\textsuperscript{15,16} Ultrasoundication of the bulk material in an appropriate organic solvent has also been reported as a simple approach to exfoliation for a number of layered compounds.\textsuperscript{16} The yield of single layers is typically low, but the crystal structure of the exfoliated layers remains undisturbed during the process.

Layered transition metal dichalcogenides can be efficiently exfoliated via lithium intercalation and subsequent addition of excess water which leads to hydrogen formation and forced separation of the layers.\textsuperscript{17,18} This process results in exfoliated layers in a metastable phase.\textsuperscript{19} For the case of MoS\textsubscript{2} and WS\textsubscript{2}, electron transfer from Li during intercalation causes a change in the electron count from d\textsuperscript{2} to d\textsuperscript{3}, leading to destabilization of the original crystal structure.\textsuperscript{20} Specifically, Li intercalation results in a change in the metal coordination from trigonal prismatic (2H) to octahedral geometry (1T).\textsuperscript{21} The 1T phase is metastable and persists after exfoliation and removal of Li until it is subject to heating or aging.\textsuperscript{22} The two phases exhibit substantially different electronic structures due to the changes in the crystal symmetry. 2H-MoS\textsubscript{2} is a semiconductor with a band gap between the filled d\textsuperscript{2} and empty d\textsuperscript{2}-,\textsuperscript{-\gamma} bands while the 1T phase is metallic with Fermi level lying in the middle of degenerate d\textsubscript{xy,\gamma} single band.\textsuperscript{23} We recently demonstrated that SL-MoS\textsubscript{2} obtained via Li intercalation exhibits a mixed phase structure and that the phase composition strongly influences the electronic properties of the material.\textsuperscript{14}

Our studies indicate that chemically exfoliated SL-MoS\textsubscript{2} exhibits a biphase structure with semiconducting and metallic regions. While a number of reports discuss the structural distortion induced during Li intercalation,\textsuperscript{19,22,24–26} the biphase nature and its influence on the physical characteristics of the material remains unexplored. Here, we report high resolution scanning transmission electron microscopy (STEM) imaging of chemically exfoliated SL-MoS\textsubscript{2}. We demonstrate direct observation of the heterogeneous phase structure consisting of both 2H and 1T phases. Our observations reveal that the structure is highly inhomogeneous consisting of nanometer-sized domains of each phase as well as other regions where the lattice is strongly distorted due to clusterization of the metal atoms.

High resolution scanning TEM (STEM) has proven to be an extremely powerful tool in revealing the atomic structure of 2D materials. In particular high angle annular dark-field (HAADF) imaging mode allows investigation of atomic arrangement in the thickness...
direction due to Z-contrast, which can be used for the identification of single layers and atomic scale edge structure. In this study, we utilize the Z-contrast in HAADF STEM to identify regions with different structures and their distribution over the 2D sheet.

RESULTS/DISCUSSION

An individual layer of MoS$_2$ consists of a slab of hexagonal Mo lattice sandwiched between two layers of hexagonally packed S. In 2H structure, the stacking sequence is BaB AbA, where capital and lower case letters denote S and Mo atoms, respectively. The coordination of Mo with S in 2H-MoS$_2$ is trigonal prismatic and the S atoms in the upper layer are located directly above those on the lower layer as schematically shown in Figure 1a. On the other hand, the stacking sequence for 1T-MoS$_2$ is AbC where S atoms in the upper and lower planes are offset from each other and the Mo atoms occupy the octahedral holes of the S layers as shown in Figure 1b. It can be seen that 2H to 1T transformation can be realized by gliding one of the S planes in the $\{2100\}$ direction by $a/\sqrt{3}$. Figure 1a shows an example of local S plane glide motion that leads to creation of the 2H-1T interface.

Chemically exfoliated MoS$_2$ is in metastable 1T phase and is also substantially distorted, deviating from the ideal 1T structure. Studies have indicated that the distorted 1T phase, denoted here as 1T', exhibits superlattice structure resulting from clusterization of Mo atoms into zigzag chains (Figure 1c) according to previous diffraction, X-ray absorption spectroscopy, and scanning tunneling microscope studies. The displacement of atoms from the equilibrium hexagonal lattice sites also results in departure from full planarity.

Owing to the different atomic arrangements of 2H, 1T, and the 1T’ structures, their direct identification is possible with HAADF STEM imaging. Figure 1 panels d and e show simulated HAADF STEM images of 2H and 1T MoS$_2$ single layers, respectively. The variations in the signal intensity show clear difference for the two structures. For 2H-MoS$_2$, the signal from the S sites are enhanced due to overlap of two sulfur atoms along the electron beam direction, making the contrast almost comparable to that of Mo sites despite the lower atomic number ($Z$). On the other hand, S atoms in the 1T-MoS$_2$ single layer are evenly distributed around the Mo sites resulting in the contrast almost comparable to that of Mo sites despite the lower atomic number ($Z$).

Figure 2 panels a–c show high resolution HAADF STEM images of various regions of chemically exfoliated SL-MoS$_2$ sheets. Crystalline order can be clearly observed despite the presence of vacancy defects.
It should be mentioned that some of the vacancy defects were formed during imaging due to high electron beam energy (120 keV) which is larger than the knock-on energy for MoS$_2$. Careful examination of the STEM images reveals that the MoS$_2$ sheets consist of structurally distinct domains. Honeycomb lattice intensity variations consistent with the simulated 2H-MoS$_2$ single layers were observed in various regions of the samples (Figure 2d). A predominant fraction of the as-exfoliated sheets exhibited hexagonal intensity variations in agreement with the simulated STEM image for 1T-MoS$_2$ single layer (Figure 2e). Typical intensity ratios between the 2S and Mo sites were found to be 0.6–0.7 and <0.3 for the 2H and 1T regions, respectively, in reasonable agreement with the simulation (Figure 2g,h). The deviation from simulation results can be readily explained by the effect of thermal vibrations and the presence of surface contaminations. These observations demonstrate that the chemically exfoliated MoS$_2$ is highly heterogeneous in structure consisting of 1T and 2H domains which are typically at least a few nanometers in size.

In addition to 1T and 2H phases, our STEM images also reveal the existence of distorted 1T' structure consisting of Mo zigzag chains in agreement with the previous studies. Interestingly, the orientation and the length of the zigzag chains are not uniform throughout individual sheets. Each chain is either disrupted by another chain or is merged with another chain via 60° or 120° kinks, resulting in overall maze-like structure (Figure 2b,c). Although the chain orientations were typically random with short coherence lengths (<5 nm), ordered arrays of zigzag chains were also observed as shown in Figure 2f. The structure of such ordered regions can be described by a $2a \times a$ superlattice in agreement with previous observations.

It is worth noting that the zigzag chains were unstable under electron beam exposure and relaxed to 1T structure during imaging. This suggests that the zigzag chain clusters are only formed on the 1T phase rather than on 2H phase. An electron beam did not induce further transformation from the 1T to 2H phase, suggesting that the activation barrier for the phase transformation is greater than the relaxation of the zigzag chain distortion. From earlier studies, it was believed that the 2H to 1T phase transformation during intercalation is always accompanied by lattice distortion. We observed that the distorted 1T' phase can be relaxed to the undistorted 1T phase with electron beam irradiation without fully transforming it to the 2H phase. Our observation indicates that transformation from 1T' to 2H phase is a multistep process which goes through an intermediate metastable 1T phase and that similar 1T' to 1T relaxation may be induced by other means such as mild heating. The activation energy for 1T to 2H phase transition in WS$_2$ was previously measured to be 0.85 eV/atom. It is known that the 1T phase of WS$_2$ is more stable than that of MoS$_2$. 

Figure 3. (a) STEM image of a region where a boundary between 2H (left) and 1T (right) phases is observed. The phase boundary is parallel to (-1100) planes and marked by a dashed line. (b, c) Fourier transform image of the (b) lower left and (c) upper right box of the STEM images. (d) Enlarged image of the region indicated by the green rectangle in image a. The intensity profile along the blue line is overlaid on the image. The width of the image corresponds to 3.9 nm.
Thus relaxation of the 1T’ structure in MoS₂ is expected to require energy significantly smaller than 0.85 eV/atom. It may also be noted that the energy difference ($\Delta E$) between the 1T and 2H phases of MoS₂ has been calculated to be 0.27 eV/atom.31

The boundary of two phases was observed to typically occur along the crystal direction. Figure 3a shows the boundary region between the 1T and 2H phases. The hexagonal arrangement of Mo and its orientation remains undisturbed across the boundary as confirmed by the nearly identical Fourier Transform image of the two phases (Figure 3b,c). The difference in the lattice constants of the two regions could not be resolved indicating that the phase boundary is largely strain-free despite the nonideal coordination of the Mo atoms at the interface region. The intensity profile across the boundary in Figure 3d shows sudden change where alternate S–Mo peaks are observed on the 2H phase side and only Mo peaks are observed on the 1T side demonstrating the atomically abrupt interface.

In our recent XPS study we observed two distinct sets of Mo3d and S2p peaks which we assigned to 2H and 1T-type phases.14 We found that relative fraction of the 1T-type component diminished with increasing annealing temperature from $\sim$0.5 for as-exfoliated material to <0.1 for samples annealed at 300 °C. Here, we examined the structures from randomly chosen areas in a total of $\sim$5,000 nm² and found that there is approximately equal amounts of 2H and 1T-type phases in the as-exfoliated samples in agreement with the XPS analysis. However, from a similar survey of phase content in the samples that were annealed at 100, 200, and 300 °C (not shown in the figures), no clear trend in the phase fraction change could be identified within the volume of the samples investigated. Instead, the observable trend was fewer 1T phases for a higher annealing temperature. Our STEM observation suggested that an appreciable amount (>0.1) of 1T phase resides in the 300 °C sample, while the 1T’ phase is nearly absent. The presence of 1T phase residues suggests that they are stabilized due to defects or electron donating surface adsorbates.31 While further statistical analysis is needed for conclusive quantitative analysis, these preliminary results suggest that the set of Mo3d and S2p peaks that we previously assigned to 1T-type phase primarily arise from the 1T’ component. Thus simplified analysis of the XPS results may lead to an underestimation of the fraction of residual 1T phase. These new findings prompt the need for refining the evaluation of the phase components by XPS.

It was recently shown32 that a suspended sheet of SL-MoS₂ exhibits intrinsic ripples similar to that of graphene.33 The height of the ripples was estimated...
to be on the order of 1 nm for both MoS$_2$ and graphene. Ripples in the 2D layers are expected to play an important role in the stabilization of the structure as well as charge transport across the sheet.\textsuperscript{34} Ripple structure in chemically exfoliated MoS$_2$ may be influenced by distortion due to clusterization of Mo atoms and the presence of phase boundaries. Figure 4a shows a high resolution TEM image of a single-layer sheet. It can be seen that the contrast fluctuates over a distance of a few nanometers, suggesting the presence of ripples with a length scale of similar magnitude. The reciprocal lattice space of corrugated sheet consists of a cone-shaped volume where the cone angle scales with the magnitude of undulations, or deviation of the surface normal from the mean. The electron diffraction spot becomes consistently blurred as the electron beam deviates from the surface normal (Figure 4b). The corrugation of a suspended 2D sheet can be quantitatively evaluated by studying the width of electron diffraction spots as a function of the tilt angle. Figure 4c shows the plot of peak center and full width at half maxima (fwhm) in the reciprocal space for the −1100 reflections. The data for mechanically exfoliated MoS$_2$ from ref 32 are also plotted for comparison. The cone angles were found to vary between 8°–13°, comparable to the values reported for the mechanically exfoliated sheets. Linear increase of the fwhm with tilt angle suggests uniform ripple structures across the probed regions (Figure 4d). The slope of the curve is on a similar order of magnitude as that in the case of mechanically exfoliated MoS$_2$ and graphene. The corrugation height is thus estimated to be around 1 nm. Thus our results indicate that the microscopic ripple structure of the sheets is not affected by the structural distortion in the atomic scale, heterogeneous phase structure, and high local pressure involved in the forced exfoliation of Li$_x$MoS$_2$.

CONCLUSION

Our STEM observations reveal that a 2D MoS$_2$ sheet consists of nanometer-sized domains of semiconducting 2H and metallic 1T phases that form coherent interfaces with each other. Local distortions due to clusterization of Mo atoms are also identified in the 1T phase. We also show that the microscopic ripple structure of chemically exfoliated SL-MoS$_2$ is comparable to that of mechanically exfoliated counterparts despite the structural inhomogeneities. The two polymorphs of SL-MoS$_2$ which allow formation of coherent electronic heterostructures represent a unique characteristic of the material that may be exploited for novel molecular functionalities.

METHOD

A colloidal suspension of SL-MoS$_2$ was prepared and the particles were deposited on a TEM grid using the previously reported transfer method.\textsuperscript{15} Both as-deposited and annealed samples were observed in the STEM. Annealing was conducted in Ar at various temperatures for 1 h. HAADF: STEM imaging was performed using JEOL JEM-2100F TEM/STEM with double spherical aberration (Cs) correctors (CEOS GmbH, Heidelberg, Germany). The collecting angle was between 100 and 267 mrad. The lens aberrations were optimized by evaluating the Zemlin tableau of amorphous carbon. The residual spherical aberration was almost zero (C$_s$ = −0.8 ± 1.2 nm with 95% certification). The acceleration voltage was set to 120 kV which is the lowest voltage with effective C$_s$ correctors in the system. SL-MoS$_2$ was identified by observing the STEM signal intensity of individual lattice sites as described in the previous reports. Occasionally, beam-induced damage occurred during observation resulting in the formation of point defects and vacancy clusters. Thus the observation time was minimized to avoid beam-induced changes. The HAADF STEM simulations were performed using the xHREM software (HREM Research). The algorithm of the code has been verified to be reliable for simulating C$_s$-corrected STEM images.\textsuperscript{20} In the calculations, the probe convergence angle is 25 mrad and the HAADF detector inner and outer angles are 100 and 267 mrad, respectively.

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgment. G.E. acknowledges the Singapore National Research Foundation for funding the research under the NRF Research Fellowship. G.E. also acknowledges the Royal Society for the Newton International Fellowship and financial support from the Centre for Advanced Structural Ceramics (CASC) at Imperial College London. M.C. and D.V. acknowledge support from NSF ECCS Award 1128335. H.Y. acknowledges the Japan Society for the Promotion of Science (JSPS) for financial support through Postdoctoral Fellowship for Research Abroad. This research was partly supported by JST, PRESTO, and JSPS, Grant-in-Aid for challenging Exploratory Research (24656028).

REFERENCES AND NOTES


