H-2-01 (Invited) Extended Abstracts of the 2020 International Conference on Solid State Devices and Materials, VIRTUAL conference, 2020, pp499-500

Growth of transition-metal-dichalcogenide in-plane heterostructures

Yasumitsu Miyata[1]

[1]Tokyo Metropolitan Univ.
1-1, Minami-Osawa, Hachioji 192-0397, Japan
Phone: + 81-42-677-2508 E-mail: ymiyata@tmu.ac.jp

Abstract

We report on our recent progresses of chemical vapor deposition (CVD) growth and device applications of two-dimensional heterostructures based on transition metal dichalcogenide (TMDC) atomic layers. In particular, the use of organic liquid precursors enables the formation of in-plane heterostructures with atomically-sharp interface and nanometer-width quantum wires. Similar high quality heterostructures with large grain size can be obtained by improved solid-precursor CVD. We fabricated electric double layer light-emitting diodes (EDLEDs) of large-area in-plane heterostructures and observed unique interface-derived electroluminescence (EL).

1. Introduction

Conventional semiconductor heterojunctions with two-dimensional (2D) interfaces have been an important topic, both in modern solid state physics and in electronics and optoelectronics applications. Recently, Atomic layers of transition metal dichalcogenides (TMDCs, Fig.1a) are expected as an ideal component for atomically-thin 2D semiconductor heterojunction with one-dimensional (1D) interface because of their superior electronic properties. Even though there have been many reports on the growth and device studies [1-4], it still remains necessary to develop a sophisticated technique for forming 2D heterostructures with atomically-straight interface and to characterize their interface properties.

For this purpose, we have developed the chemical vapor deposition (CVD) processes of TMDC-based heterostructures [5-9]. For example, using metal organic liquid precursors with high supply controllability, we were able to grow four different types of TMDCs, consisting of WS_2, WSe_2, MoS_2, and $MoSe_2$ monolayers [9]. This process enables the successive formation of in-plane heterostructures of such monolayers with clean atomically sharp and zigzag-edge straight junctions without defects or alloy formation. Furthermore, we have also improved CVD process with solid precursors to obtain large-area heterostructures, and have investigated their interface optical properties by using electroluminescence (EL) imaging and spectroscopy.

2. Experimental

TMDC-based in-plane heterostructures were prepared through the growth of second monolayers from the edges of firstly-grown monolayers as illustrated in Fig. 1b using CVD with various precursors. For metal organic CVD, we have used the CVD system with four liquid precursors: $(t\text{-}BuN{=})_2W(NMe_2)_2$, $(t\text{-}BuN{=})_2Mo(NMe_2)_2$, $(t\text{-}C_4H_9)_2S_2$ and $(C_2H_5)_2Se_2$ (Fig.1c) [9]. When the substrate temperature was at the set point (600~650 °C), the precursors were supplied by bubbling N_2 through precursor reservoirs to the substrate under atmospheric pressure. In-plane heterostructures were obtained by conducting a second CVD after the first growth.

To prepare large-area samples, we have also conducted CVD with solid precursors including WO_3, MoO_2, S, and Se as shown in Fig.1d. For these precursors, the growth temperature can be raised to 800~1100 °C. In-plane heterostructures were grown by introducing a moving mechanism of multiple transition metals and chalcogen precursors during the CVD process. The optical images of samples grown from the liquid and solid precursors are presented in Fig.1e,f.

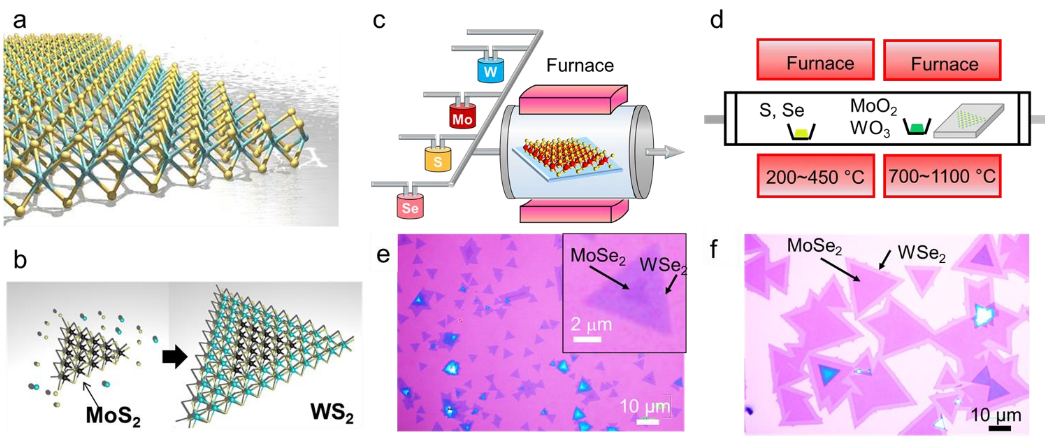

Fig.1 Schematic illustrations of (a) monolayer TMDC and (b) the heteroepitaxial growth of a WS_2/MoS_2 in-plane heterostructure. (c) Schematic illustrations of CVD systems with (c) liquid precursors and (d) solid precursors. (e) Optical images of $WSe_2/MoSe_2$ in-plane heterostructures grown from (e) liquid and (f) solid precursors.

Results and Discussion

The metal organic precursors used in this work were found to permit the growth of high-quality TMDC monolayer single crystals at low temperature under atmospheric pressure. The contentious CVD process of these monolayers produced six different in-plane heterostructures including MoS_2/WS_2, WSe_2/WS_2, $MoS_2/MoSe_2$, $WSe_2/MoSe_2$, $WS_2/MoSe_2$ and MoS_2/WSe_2 monolayers. Fig.2a-c displays the optical image and photoluminescence (PL) intensity maps of MoS_2/WS_2 in-plane heterostructure grown on graphite. In Fig.2b,c, PL peaks attributable to the inner WS_2 and outer MoS_2 can be clearly seen. This indicates that the initially-grown grains were able to maintain their structure and composition during the second growth step. In every sample, the second-growth TMDCs were preferentially formed around the edges of the first-growth grains rather than on the surface. Furthermore, the scanning tunneling microscope (STM) images demonstrate that the heterointerface junction consisted of atomically-straight zigzag edges of Mo and W atoms, and that the MoS_2 and WS_2 honeycomb lattices were smoothly connected with one another (Fig.2d). Using such high-quality sample, the spatial variations in the local density of state of MoS_2/WS_2 interfaces were visualized by scanning tunneling spectroscopy (STS) analyses. As shown in Fig.2e, the valence and conduction band edges were smoothly connected within 2~3 nm zone around the interface. The conduction band minimum (CBM) and valence band maximum (VBM) of the MoS_2 monolayer were located below the CBM and VBM of the WS_2 monolayer, respectively, indicating the formation of a type II staggered gap at the heterointerface, as predicted by theoretical calculations.

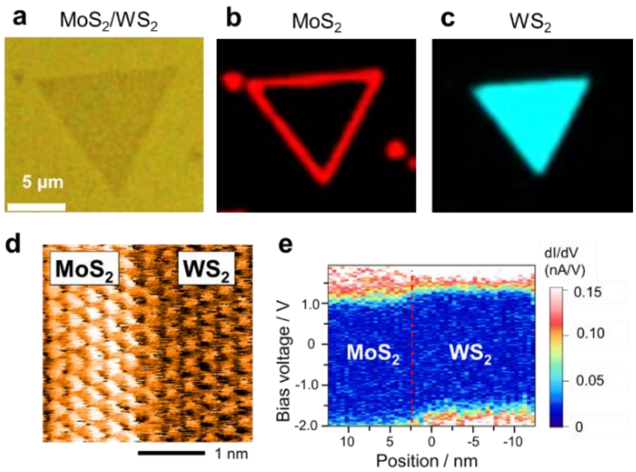

Fig.2 (a) Optical microscopy image, PL intensity maps for (b) 1.77 to 1.94 eV and (c) 1.94 to 2.07 eV, (d) STM image, and (e) color scale map of the dI/dV spectra of a MoS_2/WS_2 heterostructure.

To prepare larger-area samples, we have also improved the CVD growth with the solid precursors. As shown in Fig.1f, the present growth process can produce triangle grains with 20~60 µm in size. Such large grains enable us to observe spatially-resolved EL from the interface. For EL observation, we have fabricated the electric double layer light-emitting diodes (EDLEDs) with ion gel (Fig.3a) [10]. For WS_2/WSe_2 in-plane heterostructure, the devices show linear light emission from the interface by applying voltage (Fig.3b,c). Interestingly, the EL peaks are shifted compared with the PL peaks of WS_2 and WSe_2. The shift can be explained by lattice strain in WS_2/WSe_2 lattice mismatched interface. Furthermore, circularly-polarized EL was also observed for WS_2 exciton peak even at room temperature. This is probably due to strain-assisted valley magnetoelectric effect. The present results indicate that TMDC-based heterointerfaces provide a unique system to control their electrical and optical properties.

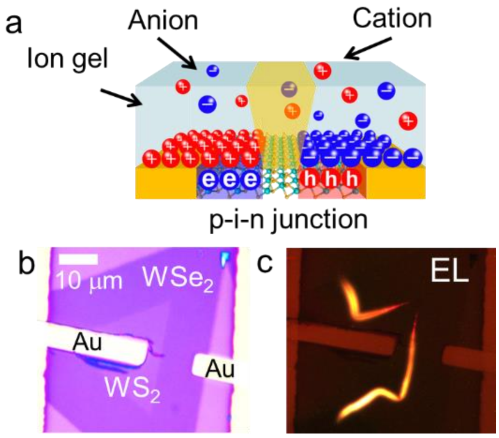

Fig.3 (a) Schematic illustration of the TMDC-based in-plane heterostructure EDLED. (b) Optical and (c) EL images of WS_2/WSe_2 EDLED device.

4. Conclusion

In summary, we have demonstrated the continuous growth of TMDC-based in-plane heterostructures with atomically straight interfaces by liquid precursors. The edge-initiated heteroepitaxial growth would provide a means of fabricating a wide variety of in-plane and vertical superlattices, nanoribbons and nanowires based on layered chalcogenides. We have also presented the interface emission by using EDLEDs based on high-quality in-plane heterostructures.

Acknowledgements

This work was supported by JST CREST (grant no. JPMJCR16F3) and Grants-in-Aid for Scientific Research (B) (no. JP18H01832).

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