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Erkiliç, Ufuk

Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Ji, Hyun Goo

Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Matsuda, Kazunari

Institute of Advanced Energy, Kyoto University

Ago, Hiroki

Interdisciplinary Graduate School of Engineering Sciences, Kyushu University / Global Innovation Center (GIC), Kyushu University

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Synthesis and Properties of Perovskite/2D Material Heterostructures

Ufuk Erkişç¹, Hyun Goo Ji¹, Kazunari Matsuda², Hiroki Ago^{1,3,*}

¹ Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Fukuoka 816-8580, Japan

² Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

³ Global Innovation Center (GIC), Kyushu University, Fukuoka 816-8580, Japan.

Corresponding author email: h-ago@gic.kyushu-u.ac.jp

Abstract: Organic-inorganic hybrid perovskites are one of the most extensively studied materials for diverse optoelectronic applications such as, solar cells, photodetectors, and light emitting diodes. Thus, vertically stacked heterostructures of perovskites with various materials provides new routes to achieve better device performance, increase efficiency and, expand the application areas in the perspective of optoelectronic devices. However, most of the studies on perovskites have focused on solution based deposition techniques which gives bulk thin films that are difficult to be implemented into heterostructure by conventional lithography techniques because these perovskites are soluble in most of the common solvents. Here, we show solvent and lithography-free synthesis and optical properties of vertically aligned heterostructures of perovskite and WS₂.

Keywords: Perovskite, TMDC, Heterostructure

1. INTRODUCTION

Over the past decade, organic-inorganic hybrid perovskites have attracted great attention thanks to their exceptional properties, such as long carrier diffusion lengths, high optical absorption, strong luminescence, and bandgap tunability through chemical composition [1]. Methylammonium lead halide perovskite is a subclass of perovskites with the chemical formula CH₃NH₃PbX₃, where CH₃NH₃⁺ and Pb²⁺ are cations, and X (I, Br⁻ or Cl⁻) is anion (Fig. 1) [2]. Meanwhile, monolayer transition metal dichalcogenides (TMDCs) such as WS₂ are considered to be one of most promising materials for electronic and optoelectronic applications because of their superior physical and optical properties. WS₂ shows unique band structure that depends on number of layer; while bulk WS₂ is an indirect semiconductor, monolayer WS₂ is a direct-gap semiconductor with a band gap of ~2.0 eV. WS₂ shows strong photoluminescence (PL) in the visible range and also has excellent device performance with high on/off ratios [3].

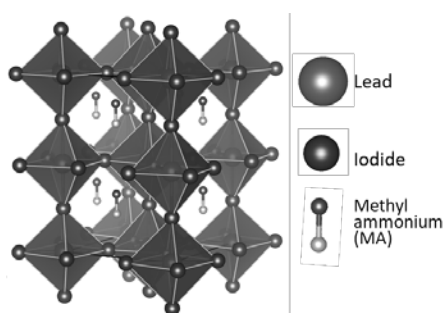


Fig. 1. Crystal model of CH₃NH₃PbI₃.

Considering the advantages of these two classes of materials, integration of the perovskites with TMDC materials offers a new opportunity to obtain unique properties. However, because of the vulnerability of perovskites to common solvents, conventional wet transfer processes are not applicable to create new heterostructures [4].

In this study, we demonstrate preferential vapor deposition of lead iodide (PbI₂) onto monolayer WS₂ and successive vapor-phase conversion to perovskite (methyl ammonium lead iodide (MAPbI₃))/WS₂ heterostructure. Preferential growth of PbI₂ via vapor deposition allowed us to obtain large area and uniform perovskite/WS₂ heterostructures which is unattainable through other methods, such as spin coating, drop casting, or mechanical exfoliation.

2. EXPERIMENTAL PROCESS

Synthesis of the monolayer WS₂ by chemical vapor deposition (CVD) on c-plane sapphire reported by our group earlier [3, 5]. Briefly, WO₃ and sulfur powders were placed in a three-zone furnace. The WO₃, sulfur, and substrates were heated at 1065 °C, 165 °C and 925°C, respectively, while keeping the system under constant Ar flow at ambient pressure. For vapor-deposition of PbI₂ onto WS₂, PbI₂ powder was placed on center of a CVD furnace. As-grown WS₂ on sapphire substrate was put in the downstream. Then quartz tube was evacuated to base pressure and followed by 50 ccm of Ar gas. Temperature was gradually increased to 360°C and deposition was carried out in 15 min. Figure 2 shows a schematic representation of the experimental setup. Afterwards, PbI₂ was converted to perovskite (MAPbI₃) by vapor phase intercalation of methyl ammonium at 130 °C for 4 h under a constant Ar flow. Optical images were taken by optical microscope (Nikon Eclipse ME600). Raman and photoluminescence (PL) spectra were measured with a Raman spectroscope (Tokyo Instruments Nanofinder 30) using a 532 nm excitation laser at low excitation power.

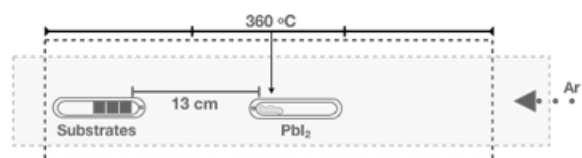


Fig. 2. Schematic representation of vapor-deposition setup.

3. RESULTS AND DISCUSSION

Figure 3a shows a schematic illustration of perovskite/WS₂ heterostructure. The optical image of perovskite with different thicknesses on WS₂ is given in Figure 3b. Layered structure of PbI₂ is noticeable on the optical image.

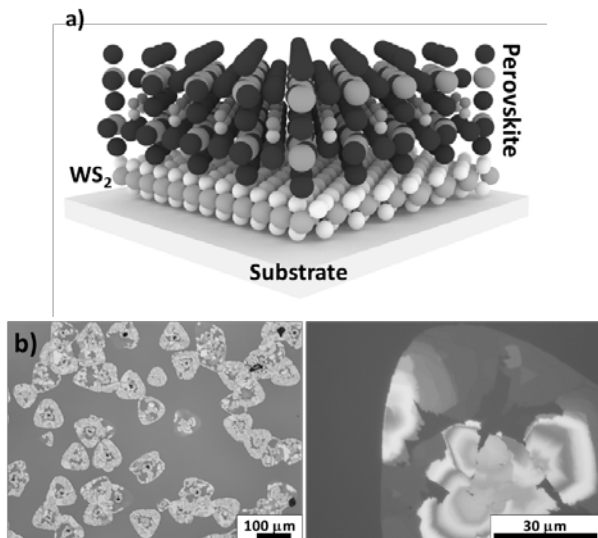


Fig. 3. a) Schematic illustration of perovskite/WS₂ heterostructure. b) Optical image of perovskite with WS₂.

Raman spectra taken from the pristine PbI₂ and perovskite on WS₂ were given in Figure 4. For PbI₂ and perovskite, the Raman peak at 73 cm⁻¹ was assigned to the shearing motion between two iodide layers (E_g). The vibration at 97 cm⁻¹ corresponded to the symmetric stretch (A_{1g}). On the other hand, WS₂ gave in-plane acoustic phonon mode 2LA(M) at 356 cm⁻¹ and A_{1g} mode at 418 cm⁻¹. These results imply that we successfully deposited PbI₂ and converted it perovskite without damaging monolayer WS₂.

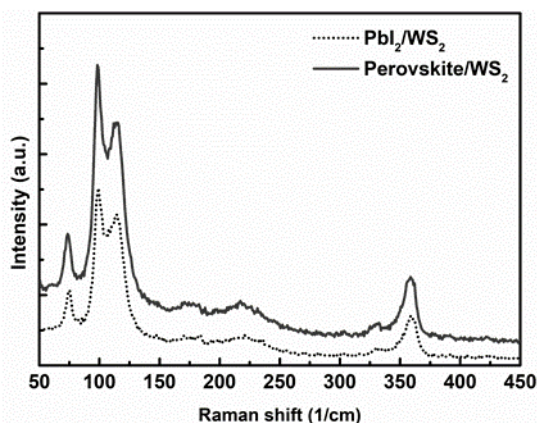


Fig. 4. Raman spectra of pristine PbI₂ and perovskite on WS₂.

Photoluminescence (PL) spectra have been taken from pristine MAPbI₃, pristine WS₂, and the heterostructure (Fig. 5). The thick pristine MAPbI₃ showed an intense PL peak at ~1.65 eV, while WS₂ showed a moderate PL peak at ~2.0 eV. In the case of the heterostructure, PL peaks from both MAPbI₃ and WS₂ were significantly quenched. It is known that MAPbI₃/WS₂ interface exhibits type-II band alignment which is desirable for photonic devices, such as solar cells, photodetectors, and light emitting diodes [6]. Considering the type-II

band alignment, PL quenching can be attributed to charge transfer at the interface.

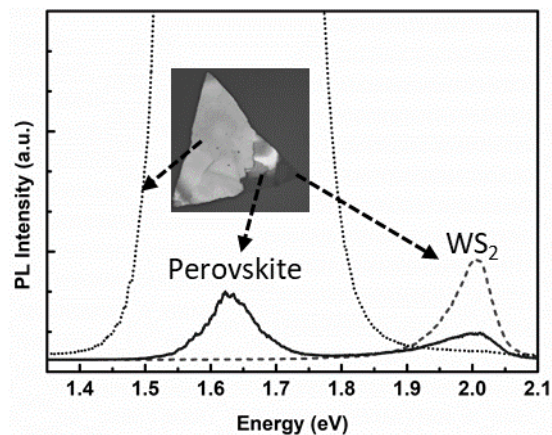


Fig. 5. PL spectra of pristine MAPbI₃, pristine WS₂, and the heterostructure.

Figure 6 depicts a PL mapping for perovskite on WS₂, indicating that WS₂ is fully covered with a uniform perovskite layer.

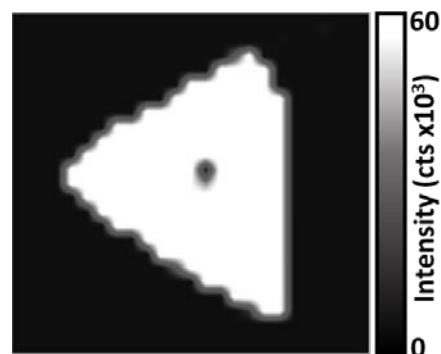


Fig. 6. PL mapping of perovskite deposited on a WS₂ grain.

4. CONCLUSIONS

Vertically stacked heterostructure of perovskite/WS₂ was achieved by vapor-deposition method without causing damage on either of the materials. Therefore, we believe that this solvent-free approach will enable new applications in optoelectronics, especially, for light diodes and photodetectors which require advanced patterning techniques.

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