Controlled Synthesis of ZrS₂ Monolayer and Few Layers on Hexagonal Boron Nitride

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Supporting Information

ABSTRACT: Group IVB transition metal (Zr and Hf) dichalcogenide (TMD) monolayers can have higher carrier mobility and higher tunneling current density than group VIB (Mo and W) TMD monolayers. Here we report the synthesis of hexagonal ZrS₂ monolayer and few layers on hexagonal boron nitride (BN) using ZrCl₄ and S as precursors. The domain size of ZrS₂ hexagons is around 1−3 µm. The number of layers of ZrS₂ was controlled by tuning the evaporation temperature of ZrCl₄. The stacking angle between ZrS₂ and BN characterized by transmission electron microscopy shows a preferred stacking angle of near 0°. Field-effect transistors (FETs) fabricated on ZrS₂ flakes showed n-type transport behavior with an estimated mobility of 0.1−1.1 cm² V⁻¹ s⁻¹.

Figure 1. Illustrations of synthesis and crystal structure of layered ZrS₂. (a) Schematic of the low-pressure chemical vapor deposition (LPCVD) synthesis of ZrS₂ on a BN/SiO₂/Si substrate. (b) Chemical structure of 1T ZrS₂.

A new complementary material to zero-band-gap graphene, two-dimensional (2D) transition-metal dichalcogenides (TMDs) with sizable band gaps have attracted broad interest.¹−³ Whereas Group VIB TMD monolayers and few layers, such as MoX₂ and WX₂ (X = S, Se, Te), have been extensively studied, including their synthesis, optical properties, and electrical properties,⁶−¹⁸ Group IVB TMD monolayers and few layers, such as ZrX₂ and HX₂ (X = S, Se, Te), have rarely been studied but can have superior electrical properties.¹⁹−²⁸ The calculated room-temperature mobilities limited by acoustic phonons can be ≈1200 and ≈2300 cm² V⁻¹ s⁻¹ for ZrS₂ and ZrSe₂ monolayers, respectively, which are much higher than that of MoS₂ (∼400 cm² V⁻¹ s⁻¹).²⁴ Theoretical calculations also showed that ZrS₂-based and ZrSe₂-based tunneling field-effect transistors (TFETs) can have sheet current densities of up to 800 and 8000 µA/µm (∼10⁻⁵ and ∼10⁻¹⁰ times higher than that of MoS₂), respectively, which are favored in low-power devices.²³ However, the synthesis of ZrX₂ (X = S, Se, Te) monolayers is challenging and has not been reported. The difficulties may arise from multiple Zr−X (X = S, Se) phases, including layered ZrX₂ as well as nonlayered Zr₃X₄ and ZrX₄.²⁹−³³ Here, by using hexagonal boron nitride (BN) as a deposition template, we successfully synthesized high-quality ZrS₂ monolayer and few layers.

The strategy for the synthesis of ZrS₂ flakes is schematically illustrated in Figure 1a. Briefly, ZrCl₄ and S powders were placed in the upstream of the furnace at temperatures of ∼170 and 130 °C, respectively. The center of the furnace was heated to 950 °C. BN flakes on SiO₂/Si substrates were put in different positions in the downstream portion of the furnace, where the temperature was around 600−900 °C. The growth was done at a pressure of 0.6 Torr with an Ar and H₂ flow. ZrS₂ crystals have the 1T structure, as shown in Figure 1b. The crystal constants are a = b = 3.66 Å and c = 5.82 Å.³⁵,³⁶ Zr atoms are octahedrally coordinated by six sulfur atoms. In the S−Zr−S sandwich structure, the second S atomic layer is rotated by 60° with respect to the first S layer. A typical scanning electron microscopy (SEM) image of ZrS₂ flakes on a BN substrate is shown in Figure 2a. ZrS₂ hexagonal flakes with sizes of 1−3 µm were selectively deposited only on BN flakes, while there were no ZrS₂ flakes on the bare SiO₂ regions. The reason could be that BN is an atomically flat substrate with a potentially lower nucleation rate, which is more favored in large-crystal growth. The low-magnification transmission electron microscopy (TEM) image in Figure 2b shows a ZrS₂ flake that was transferred onto a carbon grid. A
Additionally, the total pressure and H₂ flow rate also affected the deposition (Figure S2). At lower total pressures, the ZrS₂ flakes were larger and thinner. At higher H₂ flow rates, the ZrS₂ flakes were thinner but more rounded. When the growth time was increased, the flakes became thicker and inhomogeneous (Figure S3).

The number of layers of ZrS₂ flakes can be controlled by tuning the evaporation temperature of ZrCl₄ (Figure 3). ZrS₂ flakes with different ZrCl₄ evaporation temperatures: (a) 170 °C, (b) 175 °C, (c) 180 °C. (d) Vapor pressure and thickness with different ZrCl₄ evaporation.

Figure 2. Characterizations of as-prepared ZrS₂ flakes. (a) SEM image of ZrS₂ deposited on BN/SiO₂/Si. (b) TEM and (inset) HRTEM images of hexagonal ZrS₂. (c) SAED pattern and (inset) schematic illustration of the atomic arrangement of the hexagonal ZrS₂ shown in (b). (d−f) AFM images of ZrS₂ monolayers and few layers. (g, h) XPS spectra of as-synthesized ZrS₂. (i) Raman spectra of as-synthesized ZrS₂ with different vapor pressure of ZrCl₄ (Figure 3; also see the SI).

Further, X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition of the as-prepared ZrS₂ flakes (Figure 2g). The Zr 3d₅/₂ and Zr 3d₇/₂ peaks at 181.7 and 184.1 eV and the S 2p₁/₂ and S 2p₃/₂ peaks at 160.8 and 162.0 eV (Figure 2h) are consistent with the reported peak positions for ZrS₂.³² Raman spectra of the ZrS₂ flakes are shown in Figure 2i. The E₁g mode at 247 cm⁻¹, the A₁g mode at 314 cm⁻¹, and the A₄g mode at 331 cm⁻¹ were observed from thick ZrS₂ flakes (four layer and 10 nm flakes).³⁶,³⁷ No peaks were observed for the ZrS₂ monolayer and bilayers, possibly because of the weak signal and easy oxidation of the ZrS₂ monolayer and bilayer under laser irradiation in atmosphere.

The position of the BN/SiO₂/Si substrates (corresponding to different deposition temperatures) played an important role in the ZrS₂ deposition. The optimized deposition temperature was ~800 °C (Figure S1 in the Supporting Information (SI)), in which isolated large hexagonal ZrS₂ flakes were obtained. Higher deposition temperatures (i.e., substrates closer to the furnace center) gave thick inhomogeneous films. Lower deposition temperatures (i.e., substrates further from the furnace center) gave less dense and smaller ZrS₂ hexagons. Additionally, the total pressure and H₂ flow rate also affected the deposition (Figure S2). At lower total pressures, the ZrS₂ flakes were larger and thinner. At higher H₂ flow rates, the ZrS₂ flakes were thinner but more rounded.

Figure 3. Controlling the layer number of ZrS₂ by tuning the ZrCl₄ evaporation temperature. (a−c) AFM analysis of ZrS₂ with different ZrCl₄ evaporation temperature: (a) 170 °C, (b) 175 °C, (c) 180 °C. (d) Vapor pressure and thickness with different ZrCl₄ evaporation.
Different ZrS₂ flakes under TEM yielded the stacking angle distribution (Figure 4f), which revealed a preferred stacking angle of near 0°.

An FET was fabricated on ZrS₂ multilayers (Figure 5) using 50 nm Pt/5 nm Ti as contact electrodes. The channel length of the FET was ∼2 μm (Figure 5a inset). The ZrS₂ devices exhibited n-type transport behavior (Figure 5b). The field-effect mobility \( \mu_{\text{FET}} \) was estimated to be ∼0.1–1.1 cm² V⁻¹ s⁻¹, which is much lower than the theoretical mobility. More effort is needed to engineer the contacts as well as the device structure.

In summary, we have presented an approach for synthesizing ZrS₂ atomic layers with a controlled number of layers by the LPCVD method on hexagonal BN. This method can also be used to synthesize ZrSe₂ monolayer and few layers (Figure S4). The obtained ZrS₂ layers exhibited a hexagonal shape with sizes of a few micrometers. The stacking angle between ZrS₂ and the BN substrate spans several degrees but is mostly near 0°. FET devices based on ZrS₂ flakes exhibited n-type transport behavior with an estimated mobility of ∼0.1–1.1 cm² V⁻¹ s⁻¹ (Figure S5). This simple and controllable approach opens up a new way to produce highly crystalline ZrS₂ and ZrSe₂ atomic layers and the potential for HfX₂ (X = S, Se), which are promising materials for nanoelectronics.

**ASSOCIATED CONTENT**

Supporting information

Experimental details; effects of deposition temperature, Ar/H₂ flow rate, and growth time on ZrS₂ synthesis; relationship between ZrCl₄ evaporation temperature and vapor pressure; estimation of ZrS₂ mobility; characterization of as-synthesized ZrSe₂ monolayer and few layers; and more electrical measurements on ZrS₂ FETs. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03807.

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

L.X. acknowledges support from the National Natural Science Foundation of China (NNSFC) (21373066 and 11304052), the Beijing Nova Program (2015B049), and the China Postdoctoral Science Foundation (2013MS540900). J.Z. acknowledges support from the NNSFC (21233001, 21129001, 51272006, and 51121091).

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