Mo2C/MoS2 Lateral Heterostructure formed by Chemical Conversion of Molybdenum Disulfide

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Abstract

The metallic molybdenum carbide (Mo₂C) which is one of the MXene was synthesized through the chemical conversion of semiconducting molybdenum disulfide (MoS₂). The conversion area of Mo₂C was controlled by that adjusting the thermal annealing time under the CH₄ and H₂ atmosphere. The metallic Mo₂C film was synthesized with a sheet resistance of 123.6 Ω sq⁻¹. Atomically sharp Mo₂C/MoS₂ lateral junction were formed with low contact resistance (1.2 k Ω ·µm) and low Schottky barrier height (26 meV). This work provides a manufacturable synthesis method of Mo₂C from MoS₂ and the formation of a metal/semiconductor in-plane junction structure. This brand-new synthesis strategy of MXene will be a greatly important for future 2D heterojunction structures and feasible device applications.

1. Introduction

Mxenes, which are one of the group of two-dimensional (2D) materials, have attracted great interest in recent years as part of efforts to investigate 2D materials beyond graphene. The attractive properties of MXenes have been reported such as an ultrahigh electrical conductivity (Mo₂C) [1], an excellent thermal conductivity (Ti₂CO₂) [2], and unique optoelectronic activities (Ti_2CT_x) [3,4], which overcome several fundamental limits of other 2D Materials. In spite of the demonstrated excellent properties of MXenes, applications of MXenes have been limited by a lack of scalable synthesis methods that yield stable MXene films. In this work, we demonstrated that the synthesis of the fully converted 2D metallic Mo₂C layers through the chemical conversion process of 2D MoS₂ crystals with the thermal annealing under CH₄ and H₂, using Cu foil as a catalyst. The converted Mo₂C region was determined by thermal annealing time period. The electronic properties of the synthesized Mo₂C were investigated through the four-probe and Hall measurements. Fully converted Mo₂C nanosheets measured an excellent sheet resistance (123.6 Ω sq⁻¹) and carrier concentration (5.84×10⁻¹³ cm⁻²). Partial conversion of MoS₂ by controlling the annealing period provided the formation of metallic/semiconducting (Mo₂C/MoS₂) junction with an atomically sharp interface and a low contact resistance (1.2 k Ω ·µm) and Schottky barrier height (SBH) (26 meV).

2. Results and discussion

Synthesis of Mo_2C nanosheets via chemical conversion process of MoS_2 .

Fig. 1 (a) describes the process by which Mo₂C nanosheets were converted from MoS₂ crystals under CH₄ and H₂ under 820 °C thermal heating. The chemical conversion of Mo₂C started, where hydrodesulfurization and carburization occurred. S atoms at the edge were separated by a reaction with H• radicals, and CH₃• radicals combined with the Mo-terminated edge (red dotted line in Fig. 1a) after decomposition of CH₄ in the existence of the Cu catalyst. The reduction of S atoms occurred proximally to the CH₃-terminated Mo, followed by the formation and lateral extension of Mo-C-Mo bonds, yielding H_2S as a byproduct. Fig. 1 (b), (c), and (d) show OM images of a single flake before (upper images) and after (bottom images) annealing under different annealing time conditions. The red dotted lines represent the area in which MoS₂ was converted into Mo₂C. The converted regions were increased as the increasing of annealing time. The Mo₂C converted region was found to increase as the thermal annealing time increased. X-ray photoelectron spectroscopy (XPS) was used to measure the chemical composition of the converted Mo₂C and the pristine and unconverted MoS₂ depending on thermal annealing time conditions. Fig. 1 (e) shows the Mo²⁺ oxidation state contributed 0% to the intensity prior to annealing, and the portion of Mo²⁺ increased to 18.27%, 37.96%, and 72.03% at 1, 2, and 3 h annealing times. This trend in the Mo 3d spectra supported the substitutional conversion from MoS₂ to Mo₂C. The atomic structure of synthesized Mo₂C/MoS₂ junction and Mo₂C nanosheets were characterized by high-resolution transmission electron microscopy (HRTEM) in Fig. 1 (f) and (g) respectively. Fig. 1 (f) shows the cross-sectional HRTEM images of the Mo₂C/ MoS₂ junction. In the MoS₂ region, the layer-by-layer distance was estimated to be 6.2 Å, whereas the region in Mo₂C displayed different crystalline structures with a 1.8 Å d-spacing value along the Mo₂C (102) direction. The Mo₂C/MoS₂ heterostructure was epitaxially formed with atomically sharp interface. From Fig. 1 (g), HRTEM image with the corresponding side-view FFT pattern (inset in Fig. 1 (g)), identifying the layered structure of the synthesized Mo₂C with an atomic spacing of 4.8 Å which is correspond to the lattice parameter reported for Mo_2C in the *c* direction[5].

Electrical properties of the synthesized Mo₂C nanosheet and the Mo₂C/MoS₂ junction

The carrier transport properties of the synthesized Mo₂C nanosheets were measured using four-probe and Hall measurements, as shown Fig. 2 (a) and (b). Fig. 2 (a) shows the I -V characteristics obtained from 4-probe measurement. The Sheet resistance of Mo₂C (R_{Mo2C}) was calculated as 123.6 Ω sq⁻¹ through the expression of $R_{Mo2C} = (V_{23}/I_{14}) \times (W/L)$. Fig. 2 (b) shows the carrier concentration of the synthesized Mo₂C nanosheet was extracted to be 5.84×10^{13} cm⁻² by the Hall measurement, which value was extracted from the slope of the V_H (Hall voltage) – B (magnetic field) curve. Fig. 3 (a) compares the I_D - V_G transfer curves of MoS₂ FET. Case A (red curves) shows electrons injected from Mo₂C electrode into MoS₂ channel and black curves were measured injected from Ti electrode to the MoS₂. The on-state-current from the lateral contacted Mo₂C electrode was 4 times higher than vertical contacted Ti electrode. The SBH in the lateral Mo₂C/MoS₂ junction was calculated to be 26 meV in Fig. 3 (b). From the Fig. 3 (c), We estimated the contact resistance (R_c) in the lateral MoS₂/Mo₂C junction using gate bias-induced four-probe measurements. Extremely low Rc values (20 to 1.2 k Ω ·µm with R_{channel} from 10⁶ to 10⁵ Ω sq⁻¹) were obtained from the Mo₂C/MoS₂ lateral junctions, about 2 orders of magnitude lower than the values extracted from the vertical Ti/MoS₂ junction.

3. Conclusions

In this report, we demonstrate the manufacturable synthesis method of metallic 2D Mo₂C nanosheets through the chemical conversion of semiconducting 2D MoS₂ films. Our results showed that Mo₂C nanosheets with controllable thickness (3-100 nm) and size of lateral dimension (100 μ m). The synthesized Mo₂C showed an outstanding sheet resistance of 123.6 Ω sq⁻¹ and the carrier concentration of 5.84×10¹³ cm⁻². Partial conversion of MoS₂ by controlling annealing time provided a lateral metallic/semiconducting junction that showed atomically sharp interface, excellent contact resistance(1.2 k Ω ·µm) and low Schottky barrier height(26 meV) for future electronic device applications.

References

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Fig. 1 (a) Schematic illustration of the Mo₂C synthesis via thermal annealing under CH₄ and H₂. (b)-(d) OM images before (upper images) and after (bottom images) annealing over different annealing times: (b) 1 h annealing, (c) 2 h annealing, and (d) 3 h annealing (Scale bars: 10 μ m), (e) Statistical analysis of the Mo₂C/MoS₂ XPS data to obtain the Mo⁴⁺ 3d and Mo²⁺ 3d XPS peak integrated intensity percentages of the Mo 3d total intensity (f) Cross-sectional view HRTEM image of the Mo₂C/MoS₂ junction (g) Cross-sectional view HRTEM image of the fully converted Mo₂C.

Fig. 2 (a) Voltage-current curves obtained from the four-terminal



Mo₂C device and inset figure of the device structure used in each measurement (b) Hall voltage measurements under various magnetic fields and OM images of the fully converted Mo₂C device with four-terminal electrodes (inset).



Fig. 3 (a) I_{DS} - V_G curves obtained from electrons injected from Mo_2C into MoS_2 (case A) and electrons injected from Ti into MoS_2 (case B) (b) Electron barrier heights extracted from $ln(I_{DS}^2/T)-q/K_bT$ for a lateral Mo_2C/MoS_2 contact (c) R_c obtained using the four-probe measurement method for vertical Ti/MoS₂ contact (black rectangles) and lateral Mo_2C/MoS_2 contact (red circles).