Phase conversion of chemically exfoliated molybdenum disulfide

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ABSTRACT

Multilayer MoS_2 is exfoliated by Li treatment. A thin film of Li-treated MoS_2 contains a large portion of 1T phases. This is attributed to the atomic structural change caused by Li insertion, which is investigated using X-ray photoelectron spectroscopy (XPS). In a phase recovery via thermal annealing at 523 K in air, we observe another phase, referred to as the relaxed 1T phase, with a slightly larger binding energy than the 1T phase. After annealing at 523 K in air, the peak intensity of the relaxed 1T phase is reduced, accompanying a strong MoO_x peak and weak S $2s$ peak, according to XPS. This indicates that the annealing of Li-treated MoS_2 in air yields sulfur vacancies that induce the oxidation of Mo. However, after annealing at 523 K in vacuum, no MoO_x is observed, and the considerable peak intensity of the relaxed 1T phase remains, which starkly contrasts Raman-spectroscopy results supporting a full recovery from the 1T phase to the 2H phase. The absence of a gating effect of the Li-treated MoS_2 device supports the possibility of an incomplete phase change of Li-treated MoS_2 annealed in a vacuum.

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1. Introduction

In the past decade, various two-dimensional layered materials have been introduced in the search for a new semiconductor to replace Si, whose carrier mobility is severely degraded by increased surface scattering as the device size is scaled down to the nanometer range [1–3]. Graphene, which has a single-atom-thick honeycomb carbon structure, has no dangling bonds on the surface and a linear band structure that enables the carrier to move like a massless particle. However, because of its zero bandgap, the realization of logic circuits using graphene is difficult [4]. For this reason, transition-metal dichalcogenides (TMDs) with no dangling bonds and a sizeable bandgap of 1−2 eV [5–8] have attracted worldwide attention. Among TMDs, MoS_2 has received the most attention owing to its high mobility and stability. Thus, numerous studies on MoS_2 have been undertaken for the characterization of field-effect transistors (FETs) and the realization of logic gates and sensors [9–11].

Monolayer MoS_2 exhibits n-type behaviors with a large contact resistance, reducing the device performance [10]. To reduce the

Schottky barrier height of MoS_2, various metals have been deposited as electrodes [12–16]. However, the metal-MoS_2 barrier height exhibits Fermi-level pinning [14], implying that the Fermi-level mismatch between the metal and MoS_2 cannot be reduced by choosing a metal with a work function comparable to that of MoS_2. Recently, this technical difficulty was circumvented by using the polymorphic phase of MoS_2 [17]. A new phase of MoS_2 that differs from semiconducting 2H-phase MoS_2 (2H-MoS_2) can be synthesized by intercalating Li ions [18–20] or using an electron beam [21]. In the case of chemical doping with Li ions, Li-treated MoS_2 exhibits a metallic trait that is induced by the structural modification resulting from chemical doping. This simple chemical approach for the synthesis of metallic 1T-phase MoS_2 (1T-MoS_2) introduces the possibility for reverse-phase engineering of MoS_2 if the intercalated Li ions can be successfully removed from the interlayer of MoS_2. Eda et al. showed that 1T-MoS_2 is fully converted into 2H-MoS_2 via annealing at 573 K in an Ar-filled glovebox [19]. Thus, supposing that the phase engineering can be implemented into the device fabrication, larger-area 1T-MoS_2 can be lithographically patterned using a high-power laser that can selectively define a channel of 2H-MoS_2. Then, the ohmic polymorphic junction of MoS_2 can be realized, which is not yet available in Si industries.

In this study, we doped 2H-MoS_2 with Li ions using a wet-

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chemistry approach. Li intercalation triggered the formation of the 1T phase and thus the metallic property of MoS_2. The Li-treated MoS_2 was annealed in air and vacuum conditions at temperatures up to 523 K. However, in contrast to Raman spectroscopy, which indicated revived characteristics of 2H-MoS_2, X-ray photoemission spectroscopy (XPS) demonstrated the existence of seemingly metallic 1T phases with a slightly higher binding energy of Mo $3d$. In addition, the absence of a gating effect in electrical measurements indicated the dominance of the 1T phase in the transport behavior. The results imply that the change from 1T-to 2H-MoS_2 may involve another phase with a narrow bandgap. In light of the discrepancy between the optical and electrical characterizations, further studies are needed to reveal the nature of the contact in polymorphic MoS_2.

2. Experiments

Fig. 1 shows schematics of the preparation of the chemically exfoliated MoS_2 film. For the Li intercalation, 5 g of bulk MoS_2 crystals (two-dimensional (2D) semiconductors) was immersed in 10 mL of a 1.6 M n-butyllithium solution in hexane (Sigma-Aldrich) for 36 h in a circular flask filled with Ar gas (Fig. 1(a)). The Li-intercalated MoS_2 was washed with hexane to remove the excess Li and organic residues on the MoS_2 film. Then, chemical exfoliation of the MoS_2 was performed immediately by ultrasonicating the Li-intercalated MoS_2 in water for 10 min. Because of the insertion of Li atoms into the interlayer of MoS_2, which weakened the layer-to-layer interaction, the layers of MoS_2 were easily separated by sonic agitation. The aqueous solution in which chemically exfoliated MoS_2 was dispersed was centrifuged several times to remove the residual bulk MoS_2 and thick MoS_2 flakes (Fig. 1(b)). The dispersed MoS_2 flakes were filtered several times through an anodic aluminum oxide (AAO) membrane with pores having a diameter of 200 nm (Whatman) to rinse out the excess Li and organic residues by acetone, methanol, water (Fig. 1(c)). The AAO membrane was chemically dissolved using a 1 M NaOH solution,

and free-standing Li-treated MoS_2 films were obtained (Fig. 1(d)). Again, the film was washed in water several times to remove the organic residues. Then, it was transferred onto a Si/SiO_2 substrate. The transferred sample was divided into 1 cm × 1 cm pieces (Fig. 1(e)). These samples were annealed in air and high-vacuum (5×10^{-6} Torr) conditions at 323, 423, and 523 K in order to study the phase changes of the Li-treated MoS_2 (Fig. 1(f)).

Multimodal approaches were implemented to characterize the polymorph of the Li-treated MoS_2. The phase change of the chemically exfoliated MoS_2 film was characterized by an InVia Raman spectrometer (Renishaw) at an excitation laser wavelength of 532 nm. A surface elemental analysis of the chemically exfoliated MoS_2 samples was performed by XPS (K-Alpha, Thermo Fisher).

3. Results and discussion

The structural modifications of the 2H-MoS_2 resulting from the Li treatment were examined using Raman spectra. The Raman spectra of the pristine 2H-MoS_2 shown in Fig. 2(a)—measured before the Li treatment—exhibit two prominent peaks: E_{2g}^1 (383.8 cm^{-1}) and A_{1g} (406 cm^{-1}). E_{2g}^1 is an in-plane vibration mode of Mo and S atoms, where the A_{1g} mode is an out-of-plane vibration of S atoms [22,23]. After the Li treatment, the intensities of these two fingerprint-like MoS_2 peaks were significantly reduced, as shown in Fig. 2(b), and new peaks emerged, signifying structural changes. These new peaks are referred to as J_1 (153 cm^{-1}), J_2 (224 cm^{-1}), and J_3 (329 cm^{-1}). The J_1 and J_3 peaks arose from the formation of Mo atoms in zigzag chains. The vibrations of S atoms in new phases gave rise to the J_2 peak [24,25]. The exact Raman peak positions of J_1, J_2, and J_3 and the corresponding atomic phase of Li-treated MoS_2 remain under debate.

The Li-treated MoS_2 was annealed in an air system at various temperatures: 323, 423, and 523 K. All the J-series peaks faded gradually by an annealing above room temperature, in contrast to the E_{2g}^1 and A_{1g} peaks, whose intensity was increased after the annealing. According to the Raman intensity of the E_{2g}^1 and A_{1g}
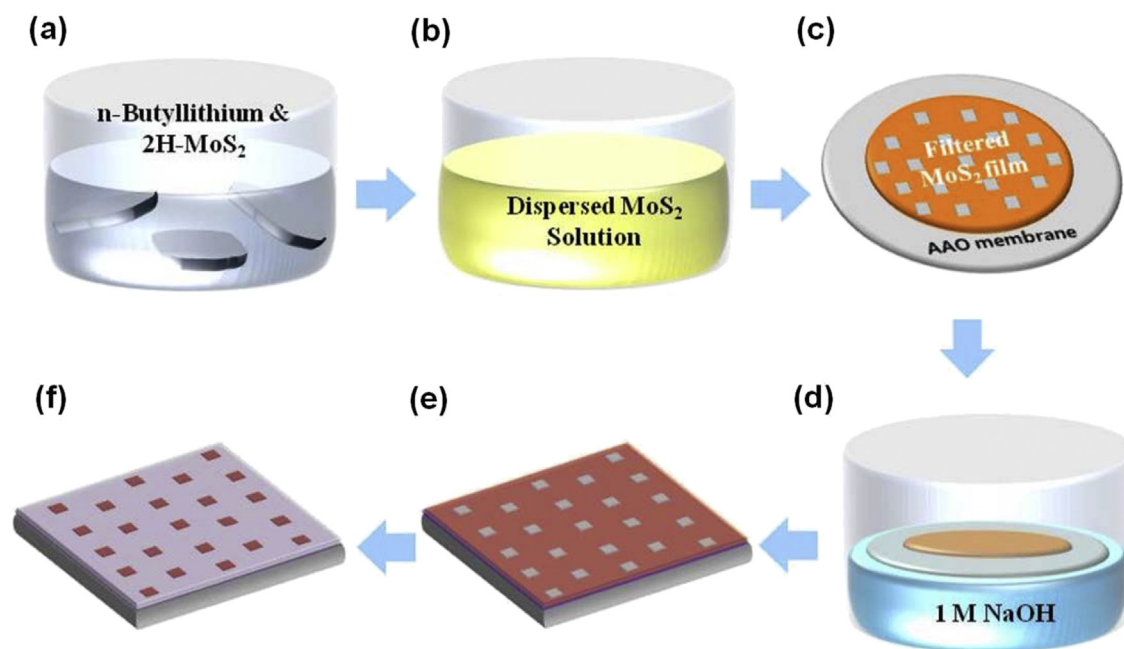

Fig. 1. Schematics for the synthesis of Li-treated MoS_2 film for Raman and X-ray photoelectron spectroscopy. (a) Li intercalation of MoS_2 in 1.6 mol n–Butyllithium solution, (b) uniformly dispersed Li-treated MoS_2 solution after sonication and centrifugation, (c) rinsing and filtering of Li-treated MoS_2 on anodic aluminum oxide (AAO) template, (d) a removal of the AAO template using 1 mol NaOH, (e) wet transfer of the MoS_2 film, and (f) drying of Li-treated MoS_2 film on SiO_2 substrate.