Research Paper

Preparation of MoS₂ Nanopetals by RF Magnetron Sputtering and Electron-Beam Irradiation

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Abstract

We demonstrate the preparation of molybdenum disulfide (MoS₂) nanopetals by RF magnetron sputtering and electron-beam irradiation (EBI). To investigate the structure and the surface morphology of MoS₂ films, atomic force microscopy (AFM), Raman spectroscopy, and scanning electron microscopy (SEM) were carried out. AFM results reveal that the surface roughness of MoS₂ increases with increase in deposition. After EBI process, the surface roughness decreases except for MoS₂ deposited for 5 min. In addition, EBI process increases the crystallinity of MoS₂ films, which is confirmed by Raman spectroscopy. The increase of crystallinity and the change of surface morphology are induced by inelastic scattering, which is the interaction between incident electrons and target material. SEM images display nanopetal structure of EBI-treated MoS₂ and we expect EBI-treated MoS₂ to be a potential candidate for applications such as gas sensors and hydrogen evolution reactions due to its vertically exposed edge sites.

Keywords: 2D material, Molybdenum disulfide, Nanopetal, Electron beam irradiation, Sputtering

I. Introduction

A single-layer graphene presented the advantages of two-dimensional (2D) materials [1], however, the absence of bandgap in graphene restricts its application in electronic and optoelectronic devices. Recently, other 2D materials with a bandgap, such as transition metal dichalcogenide (TMD), generated interest as an analogous structure of graphene. Molybdenum disulfide (MoS₂), which is the most researched TMD, has direct bandgap of 1.8 eV [2] in single-layer and indirect bandgap of 1.2 eV in bulk [3]. Furthermore, MoS₂ exhibits a high carrier mobility of $\sim 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in top-gate field-effect transistor (FET) [4]. These unique and outstanding optical and electrical properties make MoS₂ a promising material for high performance of electronic and optoelectronic devices.

To utilize the exceptional properties of MoS₂ films, mechanical exfoliation, which is the most familiar method previously used for obtaining graphene, was carried out [4]. However, mechanical exfoliation has several disadvantages such as small area, low uniformity, low yield, and difficult thickness control of the film. To overcome this challenge, chemical vapor deposition [5] and physical vapor deposition [6] were investigated. Until

now, using these methods to single-layer and few-layer (less than 7 atomic layers) of MoS₂ films were obtained. However, obtaining multilayer (more than 7 atomic layers) of MoS₂ was rarely attempted. Most of the preparation and device application of MoS₂ were focused on ultra-thin films. However, a few previous reports of multilayer MoS₂ have suggested the potential for its device applications [7-9] since multilayer structure of MoS₂ is insensitive to the extrinsic factors [10] and enhances the current flow of FET [11].

In this work, we report the preparation of MoS₂ nanopetals prepared by RF magnetron sputtering and electron-beam irradiation (EBI) process. EBI process was introduced as an effective method of MoS₂ preparation [12]. However, since earlier reports only explored few-layer MoS₂ films, various thicknesses of MoS₂ films were prepared and the surface morphology change and Raman spectroscopy with EBI process were investigated in this work. For EBI-treated MoS₂ films, we observed an increase in crystallinity and decrease in surface roughness when compared to as-deposited MoS₂ films. We believe that our results will contribute to broadening the understanding of MoS₂ film preparation.

II. Experimental details

RF magnetron sputtering system (Infovion Inc.) was used for synthesizing MoS₂ films of different thicknesses.

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The purity and diameter of MoS₂ target were 99% and 50.8 mm, respectively. The sputtering parameters were as follows: RF power of 20 W, Ar flow rate of 10 sccm, working pressure of 5 mTorr, and a working distance of 135 mm. The sputtering time was varied from 5 to 120 min. There was no substrate heating. The SiO₂ (100 nm)/Si wafer was used as the substrate and was cleaned by ethanol, acetone, and isopropyl alcohol prior to MoS₂ sputtering. After deposition of MoS₂, EBI process, the equipment for which was housed in the same chamber as RF magnetron sputtering system, was conducted. The EBI parameters were as follows: RF power of 300 W, DC power of 1000 V, Ar flow rate of 10 sccm, working pressure of 0.8 mTorr, and a working distance of 75 mm. The process time was 1 min. There was no additional heating and the substrate temperature heated of about 100°C was a result of 1 min of EBI.

To determine the thickness of MoS₂ films, atomic force microscopy (AFM; WITec, Alpha 300 S) was performed. In addition, the surface roughness of various thicknesses of MoS₂ was measured and compared before and after EBI process. Raman spectroscopy (WITec, Alpha 300 S) was carried out to investigate the structural differences between a given film, before and after EBI process, for different thicknesses of MoS₂. Laser wavelength with 532 nm and a grating with 1800 grooves × mm⁻¹ were used. Scanning electron microscopy (SEM; Jeol, JSM-6700F) was performed to investigate the change of surface morphology of MoS₂.

III. Results and discussion

Figure 1(a) shows the height profile for MoS₂ films, obtained by AFM. The thicknesses of MoS₂ films deposited for 5, 30, 60, and 120 min were 4.5, 7.5, 22, and 34 nm, respectively. Figure 1(b) shows a correlation of the thickness to the deposition time. The trend line for deposition rate is linear and has a coefficient of determination (R^2) as

Figure 1. (a) Height profile of MoS₂ films of various thicknesses, estimated by AFM. (b) Correlation between deposition time and height of MoS₂ film.

Figure 2. Raman spectra of MoS₂ films of various thicknesses before and after EBI.

0.9679, which indicates a high reliability of the trend.

Raman spectroscopy is an effective method for determining the crystallinity of MoS₂ because crystalline MoS₂ exhibits two Raman peaks of E_{2g} (~380 cm⁻¹) and A_{1g} (~408 cm⁻¹) while amorphous MoS₂ exhibits no peaks. Figure 2 shows the Raman spectra of MoS₂ films of different thicknesses before and after the EBI process. DC power and process time of EBI process were 1000 V and 1 min, respectively. After EBI process, the intensities of the two typical Raman peaks increased regardless of the

Figure 3. Surface morphology of MoS₂ films of various thicknesses (a)-(d) before and (e)-(h) after EBI. Deposition times of the MoS₂ films were (a), (e) 5 min, (b), (f) 30 min, (c), (g) 60 min, and (d), (h) 120 min.

Figure 4. SEM images of MoS₂ nanopetals. MoS₂ films were deposited for 120 min. (a), (b) Before EBI and (c), (d) after EBI. Magnifications were (a), (c) $\times 50,000$ and (b), (d) $\times 100,000$.

thickness, which indicates the increase of crystallinity. However, the appearance of Raman peaks was observed for the as-deposited MoS₂ films even before the EBI process. With increase in deposition time, the initially deposited MoS₂ became the seed layer for MoS₂ deposited thereafter. As a result, MoS₂ films with longer deposition time (60 min and 120 min) could grow as crystalline structures while MoS₂ films with shorter deposition time (5 min and 30 min) grew as amorphous structure.

Figures 3(a)-(d) shows AFM images for the surface morphology and roughness value of the as-deposited MoS₂ films for different thicknesses. Those of EBI-treated MoS₂ films are depicted in Figs. 3(e)-(h). The measured area was $5 \times 5 \mu\text{m}^2$. The surface roughness of the as-deposited MoS₂ films deposited for 5 min was 0.565 nm, which indicates that the surface morphology is very flat. It was similar to the surface roughness of the SiO₂/Si substrate of 0.524 nm. However, the surface roughness of MoS₂ films increased as the thickness of MoS₂ films increased, and as-deposited MoS₂ deposited for 120 min showed the surface roughness of 1.506 nm. Interestingly, the surface roughness of MoS₂ increased after EBI process only in case of MoS₂ deposited for 5 min. Other samples showed a decrease in the surface roughness after the EBI process. The surface roughness change is due to the interaction between incident electrons of EBI and the target material of MoS₂. In this experiment, owing to the large mass difference between atomic nuclei and electron and energy of electrons as low as 1000 V, inelastic scattering is more dominant than elastic scattering [13]. Inelastic scattering induces local excitation, bond breaking, and atomic rearrangement. A sequence of processes transforms amorphous as-deposited MoS₂ into crystalline MoS₂ and changes the surface roughness.

To verify the surface morphology change of EBI-treated MoS₂ films, SEM was performed. Figure 4 shows the

SEM images of as-deposited and EBI-treated MoS₂ films, which were deposited for 120 min. The scale bar is 100 nm. Both as-deposited and EBI-treated MoS₂ displayed nanopetal shape similar to other sputtered MoS₂ films [14, 15]. The nanopetal structure of as-deposited MoS₂ was densely compacted, however, after EBI process, the density of nanopetal structure decreased because of the sharper morphology of nanopetals. As illustrated by Figs. 4(c) and 4(d), EBI-treated MoS₂ grew uniformly with exposed edge sites. Since these vertically exposed edge sites of MoS₂ play an important role in improving catalytic activity and sensing property [16], we expected EBI-treated MoS₂ to be a potential candidate for gas sensor and hydrogen evolution reaction (HER). Furthermore, because morphology of MoS₂ is significantly affected by fabrication parameters [14,15], optimized sputtering and EBI parameters for more dense and uniform morphology would be required to application of EBI-treated MoS₂ in gas sensor and HER.

IV. Conclusions

The MoS₂ films were synthesized by RF magnetron sputtering and EBI process. Deposition rate of MoS₂ was derived and the effect of EBI on MoS₂ films was investigated by Raman spectroscopy, AFM, and SEM. After undergoing EBI process, MoS₂ films exhibited higher intensities of Raman peaks, thus indicating higher crystallinity. For MoS₂ for longer deposition time (60 and 120 min), even the as-deposited MoS₂ exhibited two typical Raman peaks while MoS₂ with shorter deposition time (5 and 30 min) exhibited none. Surface roughness of MoS₂ films increased with increasing deposition time. EBI-treated MoS₂ films showed decreased surface roughness except for MoS₂ film deposited for 5 min. SEM images displayed sharp nanopetal structure of EBI-treated MoS₂ films, which is expected to be a potential candidate for sensing and catalytic applications.

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