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Fabrication of Molybdenum disulfide (MoS_2) with environmental-friendly by atmospheric-pressure solution-based mist CVD

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Abstract

Molybdenum disulfide (MoS_2), a typical transition metal dichalcogenide layered material is expected to be one of the next-generation electron and semiconductor materials. In this study, we fabricated MoS_2 thin films on large area substrates by atmospheric-pressure solution-based mist chemical vapor deposition (CVD) - one of the functional thin film fabrication technologies. Hexaammonium heptamolybdate tetrahydrate ($(NH_3)_6$ Mo_7O_{24}・$4H_2O$) and thiourea (CH_4N_2S) were used as Mo and S sources respectively, and methanol was used as a solvent. The Raman spectroscopy and GIXD analysis confirmed formation of MoS_2 at 400 °C. In addition, the optical constants of MoS_2 were evaluated by spectroscopic ellipsometry using the thickness value obtained by TEM.

1. Introduction

In our laboratory, we have developed mist CVD method, which is one of the functional thin film fabrication technologies under atmospheric pressure with precursor solutions. Several kinds of functional thin films and devices have been fabricated by mist CVD and evaluated up to now. Through the development, mist CVD has been established as the technology for fabricating the high-quality and uniform thin films on large-area substrates under atmospheric pressure despite solution-based atmospheric-pressure nature of the process.

Recently, layered transitional metal dichalcogenide (TMD) materials, whose inter-layere bonding is vdW force, have received much attention owing to their excellent properties [1]. In this study, we focused on layered MoS_2, which is a promising TMDs for future device because of the close band gap with a-Si:H and easy integration into conventional electronic device technology. Generally, the layered MoS_2 thin films have been fabricated by mechanical exfoliation (ME) [2], chemical vapor deposition (CVD) [3], and molecular beam epitaxy (MBE) [4]. However, there are some problems to be solved for scaling up those processes to industrial level. In ME, size of layered MoS_2 thin films is smaller than 200 µm [5]. In CVD and MBE, a large amount of energy is consumed by the heater set at 700 °C [6] and the vacuum pump keeping the low pressure of 3×10^{-10} Torr ($\approx4\times10^{-8}$ Pa).[7] Therefore, the development of a new method suitable for industrial scale is very important. Thus, in this study, we optimized the experimental conditions in order to fabricate high-quality and uniform MoS_2 thin films on large area substrates by mist CVD.

2. Experiment

In the experiment, MoS_2 was fabricated by a homemade fine-channel type mist CVD system, which was designed to achieve the uniform flow and homogeneous temperature in the reactor. The details of mist CVD were reported elsewhere [8]. The Si substrates covered by thermal SiO_2 were selected. Prior to the thin-film growth, substrates were cleaned at growth temperature for 2minutes by O_3 generated from O_2. Thin films were fabricated by using a precursor solution containing a mixture of Hexaammonium Heptamolybdate Tetrahydrate ($(NH_4)_6Mo_7O_{24}$・$4H_2O$) and thiourea (CH_4N_2S) dissolved in methanol. The growth temperature was 400 °C.

Next, bonding state and crystal structure were evaluated by Raman spectroscopy and grazing incident x-ray diffraction (GIXD). The cross-section of the sample was observed by TEM (JEOL JEM-2100F). The focused ion beam (FIB; FEI QUANTA 3D 200i) system was used for preparation of the cross-sectional sample. Additionally, optical constants of the layered MoS_2 were analyzed by spectroscopic ellipsometry (JA Woollam, M-2000D) using the thickness obtained by TEM measurement.

3. Results and Discussions

Figure 1 shows photo images of substrate surface before and after fabrication of MoS_2. The color of the substrate clearly changed after the deposition. The result of Raman spectroscopy is shown in Figure 2. Two raman peaks around 380 cm^{-1} (E^1_{2g}) and 410 cm^{-1} (A_{1g}) were observed from the samples prepared by mist CVD. These peaks were observed at several points on the substrate. Similer peak intensity suggested high uniformity of the thin film. In the GIXD spectrum, the peak corresponding to the MoS_2 (0002) plane is observed at 14.4° (Fig.3) [9]. It is evident that MoS_2 thin film covered the entire surface of the substrate. Figure 4 depicts the cross-sectional TEM images. From the figure, it can be seen that dark stripes repeated 7 or 8 times indicating that 7 or 8 MoS_2 layers were fabricated by mist CVD. The interlayer distance of MoS_2 is reported as 0.615nm [10]. From this result, it is estimated that the film thickness is 4.55 nm.

4. Conclusions

In this study, MoS_2 thin film has been successfully fabricated at low temperature of 400 °C and atmospheric pressure using mist CVD. The fabrication of MoS_2 thin film on entire substrate was confirmed by Raman spectroscopy and GIXD. The TEM image, clearly showed that the layered MoS_2 can be prepared by mist CVD. The optical properties were also analyzed by ellipsometry. We believe these results may create a bright future. The details of experiments and results will be discussed in the conference. From this study, we found the direction of uniform MoS_2 thin films on entire substrates. We would like to fabricate and evaluate it until conference.

References

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Table Experimental Condition

Solute	: $(NH_4)_6Mo_7O_{24}$, $4H_2O$: CH_4N_2S
Solvent	: Methanol
Concentration	: $(NH_4)_6Mo_7O_{24}$ ・ $4H_2O$: CH_4N_2S = 0.00357 : 0.05 [mol/L]
Growth time	: 10 min
Substrate Temp.	: 400 °C
Substrate	: SiO_2/Si (30× 30 mm^2 SiO_2 : 100 nm, p^+-Si 0.02 Ωcm)
Growth system	: Fine Channel type mist CVD system
Gas	: N_2 (c.g. : 2.0 L/min, d.g. : 1.0 L/min)
Ultrasonic transducer	: 2.4 MHz, 24 V 0.625 A, 3

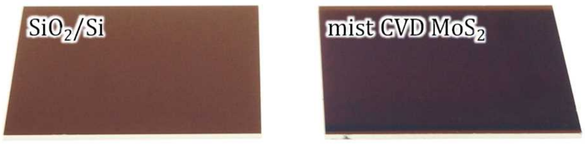

Fig.1 photo images of substrate surface before and after fabrication of MoS_2.

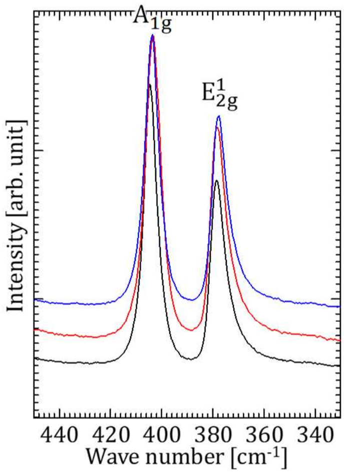

Fig.2 Raman spectra of samples fabricated at 400 °C.

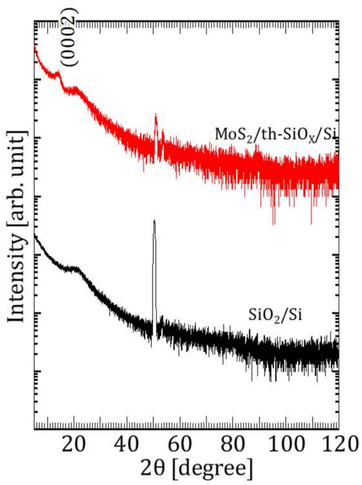

Fig.3 GIXD spectra of SiO_2/Si substrate and MoS_2.

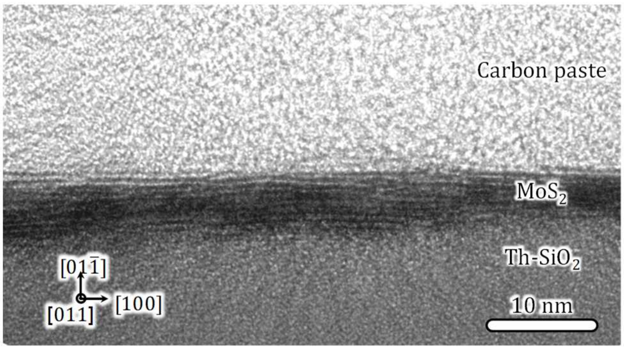

Fig.4 Cross-sectional TEM image of the MoS_2 fabricated by mist CVD on SiO_2/Si substrate.