

## MOCVD of Monolayer MoS<sub>2</sub> using Novel Molybdenum Precursor *i*-Pr<sub>2</sub>DADMo(CO)<sub>3</sub>

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### ABSTRACT

*Metal organic precursor has a sufficiently high vapor pressure at low temperature, contributing high-speed low-temperature MOCVD-MoS<sub>2</sub> film formation. We fabricated monolayer MoS<sub>2</sub> by 1 step cold-wall MOCVD using di-isopropyl-diazadiene-molybdenum tricarbonyl [*i*-Pr<sub>2</sub>DADMo(CO)<sub>3</sub>] and di-tertiary-butyl disulfide [(*t*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>S<sub>2</sub>]. These precursors are able to be vaporized using bubbling system and deposited at low temperature. From the XPS investigations, Mo-S bonding peaks were observed and S:Mo ratio was calculated as 2:1, suggesting formation of MoS<sub>2</sub>. Moreover, molybdenum carbides and nitrogen impurities were not observed which was confirmed by XPS and EDX. From the results of Raman spectroscopy, AFM height distribution, and spectroscopic ellipsometry, it was determined that the film thickness is 0.64 nm which is corresponding to monolayer MoS<sub>2</sub>, the lateral grain size is approximately 100 nm, and the bandgap energy is 1.8 eV.*

### INTRODUCTION

Two-dimensional layered molybdenum disulfide has superior device performances even in a thin region [1]. Single-layer (1L) MoS<sub>2</sub>, in particular, shows novel properties, which are significantly different from bulk MoS<sub>2</sub>. Accordingly, it is desired to establish a fabrication technique of the high quality MoS<sub>2</sub> thin film with superior mass productivity. Various fabrication techniques have been previously introduced, and especially chemical vapor deposition (CVD) can produce high-quality thin film [2]. CVD is mainly classified into two types [3]. The first is regarded as a two-step CVD, in which metal Mo precursor is initially deposited by e-beam evaporation and then sulfurized to form MoS<sub>2</sub> [4]. The second is regarded as a one-step CVD, wherein gaseous of Mo and S precursors are simultaneously introduced and react to form

MoS<sub>2</sub> [5]. Among them, 1 step CVD is suitable for fabrication of large grain size MoS<sub>2</sub> thin film. In general, solid powder precursors, such as MoO<sub>3</sub> and elemental S, are mainly used for CVD; however, their low vapor pressure largely limit the reaction rate. Contrastingly, metal organic precursor has a sufficiently high vapor pressure at low temperature, contributing high-speed low-temperature MoS<sub>2</sub> film formation. In our previous studies, we exploited di-tertiary-butyl disulfide [(t-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>S<sub>2</sub>] as for the sulfur precursor used in two-step CVD [6-9]. In this study, we exploited di-isopropyl-diazadiene-molybdenum tricarbonyl [i-Pr<sub>2</sub>DADMo(CO)<sub>3</sub>] as for the novel molybdenum precursor used in one-step CVD. This organic compound is able to be vaporized using bubbling system and deposited at low temperature compared with MoO<sub>3</sub>, and is hence carried into the reaction chamber more easily and safely. In addition, i-Pr<sub>2</sub>DADMo(CO)<sub>3</sub> has high absorptivity organic group diazadiene; therefore, there is a possibility that the surface reaction can be more dominant compared to Mo(CO)<sub>6</sub>. Thanks to this property of i-Pr<sub>2</sub>DADMo(CO)<sub>3</sub>, it is possible to fabricate MoS<sub>2</sub> films higher purity than MOCVD using Mo(CO)<sub>6</sub> because particles produced by gas-phase reaction were suppressed. Moreover, it is also expected to improve the reproducibility; therefore, MOCVD using i-Pr<sub>2</sub>DADMo(CO)<sub>3</sub> have higher productivity than Mo(CO)<sub>6</sub>. In this study, we investigated thermal decomposition and chemical state of i-Pr<sub>2</sub>DADMo(CO)<sub>3</sub> by hot-wall CVD and grown monolayer (1L) MoS<sub>2</sub> by cold-wall 1-step MOCVD using i-Pr<sub>2</sub>DADMo(CO)<sub>3</sub> and (t-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>S<sub>2</sub>.

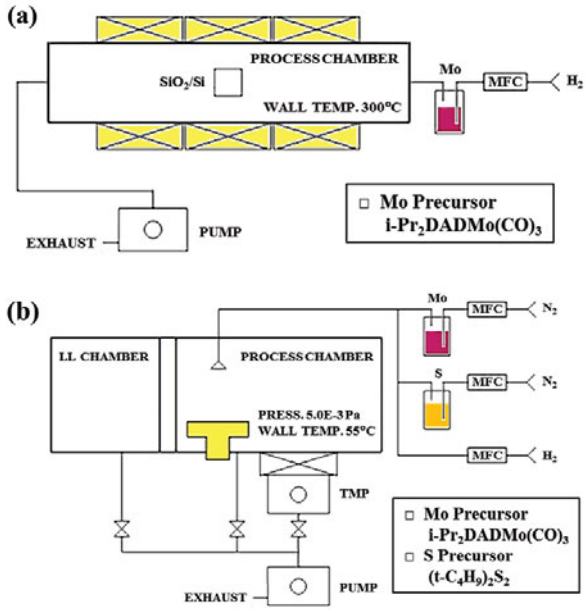


Figure 1(a) Hot wall MOCVD system for investigating thermal decomposition of i-Pr<sub>2</sub>DADMo(CO)<sub>3</sub>. (b) Cold-wall MOCVD system for growth of 1L MoS<sub>2</sub>.

## EXPERIMENT

Figure 1(a) shows the hot wall MOCVD system for investigating thermal decomposition of  $i\text{-Pr}_2\text{DADM}(\text{CO})_3$ . Gas phase molybdenum precursor was carried into the reaction chamber by  $\text{H}_2$  bubbling and deposited on the  $\text{SiO}_2/\text{Si}$  substrate. The growth conditions were a substrate temperature of  $300^\circ\text{C}$ , a chamber pressure of 1 Torr, and a deposition time of 30 min. Figure 1(b) shows cold-wall MOCVD system for growth of 1L  $\text{MoS}_2$ . Gas phase molybdenum and sulfur precursors were carried into the reaction chamber by  $\text{N}_2$  bubbling and deposited on the  $\text{SiO}_2/\text{Si}$  substrate. Growth conditions were a substrate temperature of  $250^\circ\text{C}$ , a chamber pressure of 0.3 Torr, S-precursor to Mo-precursor partial pressure ratio of 314, and a deposition time of 30 min.

## RESULTS AND DISCUSSION

### Thermal decomposition of $i\text{-Pr}_2\text{DADM}(\text{CO})_3$

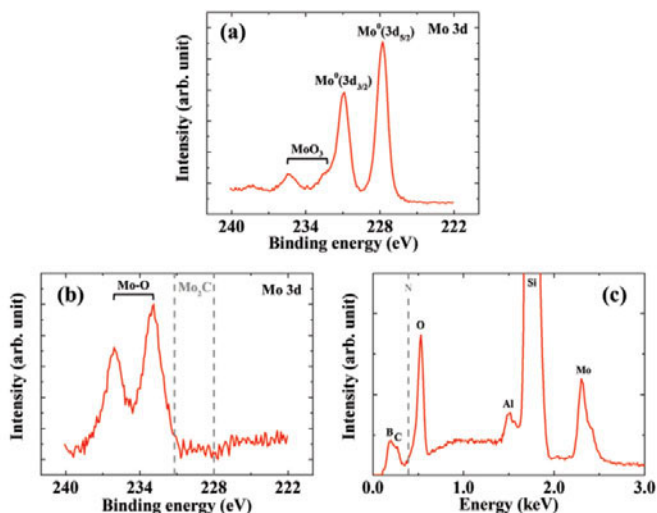


Figure 2(a) Mo 3d XPS spectrum of  $i\text{-Pr}_2\text{DADM}(\text{CO})_3$ . (b) Mo 3d XPS spectrum of the film deposited at  $300^\circ\text{C}$ . (c) EDX spectrum of the deposited film.

Figure 2(a) shows Mo 3d XPS spectrum of  $i\text{-Pr}_2\text{DADM}(\text{CO})_3$ . It was confirmed that central Mo atom in the molecule was Mo(0). Owing to this property, it is considered that the bond with the ligand is easily broken, contributing to suppression of carbon and nitrogen contamination. It is also expected to work effectively to reduce the growth temperature. Figure 2(b) shows Mo 3d XPS spectrum of the film deposited at  $300^\circ\text{C}$ . The intensity of Mo-O bonding peak, which corresponds to  $\text{MoO}_3$ , increased after the thermal decomposition, while the Mo(0) peak disappeared. It suggests that the molybdenum precursor is decomposed into metal molybdenum at  $300^\circ\text{C}$  and then reacted with residual oxygen content in the processing chamber. Molybdenum corbides ( $\text{Mo}_2\text{C}$ )

were not confirmed from the results of XPS investigation and N impurities were not observed in EDX spectrum as shown in Figure 2(c). The C peak observed in Figure 2(c) is due to carbon contamination on the substrate surface prior to the deposition.

**Growth of 1L MoS<sub>2</sub> by Cold-wall 1-step MOCVD**

Figure 3 shows Mo3d and S2p XPS spectra of the MoS<sub>2</sub> film. From the XPS investigations, Mo-S bonding peaks were observed and S:Mo ratio was calculated as 2:1, suggesting formation of MoS<sub>2</sub>. Moreover, molybdenum carbides and nitrogen impurities were not observed which was confirmed by XPS and EDX. Figure 4(a) shows Raman spectrum of the MoS<sub>2</sub> film. From the results of Raman spectroscopy, Raman characteristic peaks, E<sub>12g</sub><sup>1</sup> and A<sub>1g</sub>, were observed, indicating formation of MoS<sub>2</sub> crystal. The frequency difference between the E<sub>12g</sub><sup>1</sup> and A<sub>1g</sub> peaks was 22.2 cm<sup>-1</sup>, which is corresponding to the monolayer MoS<sub>2</sub> fabricated by MOCVD at 250°C [10]. The reason why the frequency difference between E<sub>12g</sub><sup>1</sup> and A<sub>1g</sub> peaks increased in contradiction to the previous studies of MoS<sub>2</sub> films is because the growth temperature in our study (250°C) is lower than the previous studies, indicating our fabricated MoS<sub>2</sub> film has crystal disorders. Therefore, it is considered that the increase of the frequency difference was caused by the breakdown of the k = 0 Raman selection rule due to disorders in crystal structures [9]. Figure 4(b) shows AFM image of the film surface and its height distribution. It was confirmed that the film thickness was 0.64 nm and the lateral grain size is approximately 100 nm. Figure 5(a) shows optical constants of the film investigated by spectroscopic ellipsometry. From the results of the spectroscopic ellipsometry, it was determined that the film thickness is 0.6 nm which is also supporting the monolayer MoS<sub>2</sub> growth lead by the Raman and AFM results. As shown in figure 5(a), the A, B, and C exciton peaks were observed which suggests high-crystallinity of the film. Using the extinction coefficient, we determined bandgap value E<sub>g</sub> of the film by Tauc plot method [11] as shown in Figure 5(b). The absorption coefficient of the 1L MoS<sub>2</sub> was calculated using the equation  $\alpha=4k\pi/\lambda$ ; the obtained value was used in the Tauc plot equation expressed by  $(\alpha hv)^m = A(hv-E_g)$ , where *A* is a constant and *m* characterizes the transition process. 1L MoS<sub>2</sub> was expected to undergo a direct transition; hence, *m* is 2 [12]. As a result, it was confirmed that the bandgap energy is 1.8 eV which also proof the monolayer MoS<sub>2</sub>.

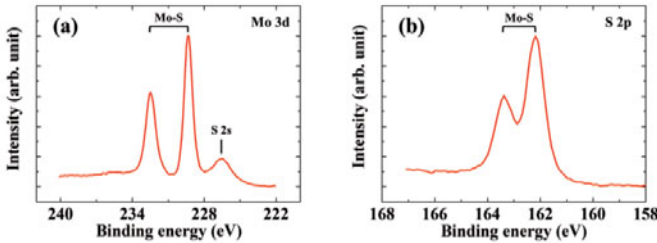


Figure 3(a) Mo3d and (b) S2p XPS spectra of the MoS<sub>2</sub> film.

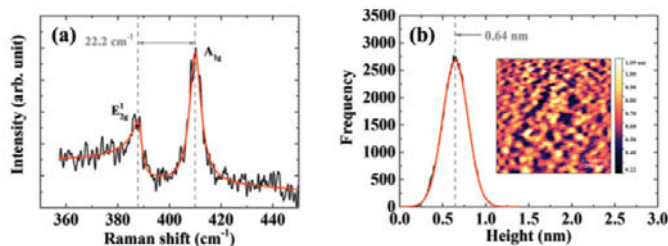


Figure 4(a) Raman spectrum of the MoS<sub>2</sub> film. (b) AFM image of the film surface and its height distribution.

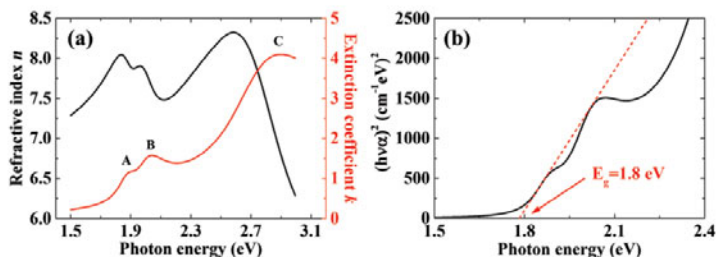


Figure 5(a) Optical constants of the MoS<sub>2</sub> film investigated by spectroscopic ellipsometry (b) Tauc plot of the MoS<sub>2</sub> film.

## CONCLUSIONS

In conclusion, we exploited di-isopropyl-diazadiene-molybdenum tricarbonyl [i-Pr<sub>2</sub>DADMo(CO)<sub>3</sub>] as for the novel molybdenum precursor used in 1-step cold-wall MOCVD. From the results of hot-wall CVD using i-Pr<sub>2</sub>DADMo(CO)<sub>3</sub>, it was confirmed that the organic molybdenum precursor decomposed at <300°C. From the results of cold-wall 1-step MOCVD using i-Pr<sub>2</sub>DADMo(CO)<sub>3</sub> and (t-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>S<sub>2</sub>, we fabricated 1L MoS<sub>2</sub> on SiO<sub>2</sub>/Si substrate at 250°C. From the results of Raman spectroscopy, AFM height distribution, and spectroscopic ellipsometry, it was determined that the film thickness is 0.64 nm, the lateral grain size is approximately 100 nm, and the bandgap energy is 1.8 eV.

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