Optical characterization of MoS\textsubscript{2} sputtered thin films

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Abstract. We studied on the crystallinity of as-sputtered and annealed MoS\textsubscript{2} thin films by Raman scattering. The samples were prepared by RF magnetron sputtering, and the thermal annealing was carried out under sulfurous atmosphere. Although as-sputtered MoS\textsubscript{2} thin films clearly showed the deterioration of the lattice ordering, it was drastically improved by the thermal annealing due to the sulfurization of the sample. And since the sulfurization occurred remarkably on the top surface of MoS\textsubscript{2} sputtered thin films, it was expected to be an effective method to realize a few-layer MoS\textsubscript{2} sputtered thin films with high crystallinity.

1. Introduction
After the discovery of graphene, two-dimensional layered materials have played a major role in materials science. Members of two-dimensional materials are still growing from insulators, topological insulators, semiconductors, semimetals, to superconductors. Among them, transition metal dichalcogenides (TMDs) such as molybdenum disulfides (MoS\textsubscript{2}) demonstrated unexpected photoluminescence [1-4] and other favorable physical properties over those of the bulk toward real devices when they were thinned to monolayers [5-11]. Therefore, family of TMDs has been expected to substitute for silicon as new electronic devices. To realize such devices based on MoS\textsubscript{2} and other TMDs, appropriate synthetic methods must be established. In this study, we studied on MoS\textsubscript{2} thin films fabricated by sputtering technique, which has been expected as a new method to produce the large area MoS\textsubscript{2} thin films.

2. Experimental
MoS\textsubscript{2} thin films were prepared on SiO\textsubscript{2}/Si substrates by RF magnetron sputtering method. MoS\textsubscript{2} ceramics target with purity of 99 % was used, and the growth temperature was varied from 100 °C to 520 °C. The samples were prepared by following procedures. First, the chamber was evacuated to the order of 10\textsuperscript{-3} Pa by using the combination of diffusion and rotary pumps. And then, Ar gas was introduced to the chamber and the pressure was adjusted to be about 0.5 Pa. The substrate was heated to desired temperature and RF electric field with the power of 100 W was applied to the target for the excitation of Ar ion plasma. To clean the surface of the target, sputtering was carried out for several seconds with the shutter closed. After that, the shutter was opened and MoS\textsubscript{2} thin film was deposited for 5 minutes. Furthermore, we carried out the thermal annealing for the samples under sulfurous
atmosphere with different duration. For the process, we newly prepared the hand-made annealing equipment as shown in figure 1. It was consisted of two electric furnaces connected in series and the quartz tube was installed through furnaces. Sulfur powder was placed on the upstream side and vaporized by heating at 80°C, and the sulfur vapor was carried to the downstream side by flowing N₂ carrier gas of 200 sccm. As-sputtered MoS₂ thin films were placed on the downstream side and annealed at 600°C. The crystallinity of the samples was evaluated by Raman scattering technique. Hexagonal MoS₂ belongs to the space group D₆h (P6₃/mmc), and a group theoretical analysis gives 3 Raman-active modes of E₁g, E₂g and A₁g at the Γ-point in the Brillouin zone [12-16]. Raman spectra were obtained by using an Ar-ion laser at 514.5 nm with incident laser power of a few milliwatt.

3. Results and discussion

3.1. Growth temperature dependence

The film thicknesses were evaluated by cross-sectional scanning electron microscopy. All the samples had the thickness of several tens of nano-meters or more. Figure 2(a) shows Raman spectra of as-sputtered samples prepared with different growth temperature. For comparison, the spectrum taken from the bulk MoS₂ is shown in the bottom of the figure. No Raman signals were observed in the sample grown at room temperature, indicating that MoS₂ lattice could not be structured well and it might be amorphous. On the other hand, broad Raman peaks were appeared at 376 and 411 cm⁻¹ in samples grown above 100°C. Although they could be assigned as E₂g and A₁g mode in terms of their frequencies, they appeared at different peak positions compared to those of bulk. It is well-known that the peak frequency depends on the number of MoS₂ layer up to a few layers[17]. However, the samples could be regarded as bulk MoS₂ from the viewpoint of Raman scattering, because they have the thickness which corresponds to several tens of MoS₂ layers. Therefore, the observed peak shift is not due to the thickness of MoS₂ film. In addition, observed peaks showed an extremely broad shape compared to that of bulk, which suggests that the observed spectra showed a shape similar to the phonon density of states (p-DOS)

![Figure 1. Schematic diagram of the equipment for the thermal annealing under sulfurous atmosphere.](image)

![Figure 2. Raman spectra of the samples grown at different temperature (a), and the plot of the peak widths as a function of the growth temperature (b).](image)
of MoS₂[15]. It is also well-known that the Raman spectrum taken from defective materials shows a spectral shape which well-reflects the shape of p-DOS due to the breaking of Raman selection rule. In our samples, it is obvious that the samples contain a lot of defects due to its broad Raman features. And then, these peaks slightly narrowed with the increase in growth temperature as shown in figure 2(b). This shows that the crystallinity could be improved slightly by growing with higher temperature. However, it was not significant, because both peaks show still broad features compared with those of bulk. This might be caused by sulfur vacancies in MoS₂ lattice, which could not be suppressed by its high vapor pressure at higher temperature.

3.2. The effect of the thermal annealing under sulfurous atmosphere

We carried out the thermal annealing for MoS₂ sputtered thin films under sulfurous atmosphere by using the annealing equipment shown in fig. 1. The thermal annealing was performed at 600 °C for 2 hours for the samples grown at 100 °C, 300 °C and 520°C. Figure 3 shows Raman spectra of the annealed samples, and both spectra taken from the sample before/after annealing were shown to compare the effect of thermal annealing. Raman signals of MoS₂ become obviously sharp in all samples after the thermal annealing, indicating the thermal annealing has remarkable effect on the improvement of the crystallinity due to the sulfurization of the sample. Furthermore, it was also observed the difference in the peak shapes between each annealed sample. Among them, the sample grown at 300 °C showed the sharpest peaks of 3.0 and 3.3 cm⁻¹ for E₂g and A₁g modes with high symmetry shape, respectively. These values were close to those of bulk MoS₂ (E₂g: 1.6 cm⁻¹ and A₁g: 2.0 cm⁻¹). On the other hand, the annealed samples grown at 100 °C and 520 °C showed the broader peaks and asymmetric shape. E₂g and A₁g peaks of the sample grown at 100 °C had the widths of 10 and 7.2 cm⁻¹ and showed asymmetry shape tailed to lower and higher frequency side, respectively. And, both peaks became narrower to 4.4 and 5.8 cm⁻¹ in the annealed sample grown at 520 °C, but these were broader than those of the annealed sample grown at 300 °C. This suggests that the annealing effect depends on the sputtering condition of the samples, that is, it is necessary to prepare the as-sputtered samples fabricated by optimal growth temperature.

3.3. The thermal annealing time dependence

We prepared the samples annealed for different duration. The duration was varied from 30 minutes to 120 minutes. Raman spectra of the samples were shown in figure 4, and it contains the spectra of as-sputtered and bulk MoS₂ for comparison. Although all the spectra showed very similar shapes and almost overlapped, the spectrum taken from the sample annealed for 30 minutes had slight broader peaks in both peaks of E₂g and A₁g mode than others. From the result, the sulfurization process occurs at the initial stage of the annealing and sufficient effect can not be obtained even if the duration of the thermal annealing is prolonged. And, it was found that the broad bands tailed to lower and higher frequency side of E₂g and A₁g peaks correspond to those of as-sputtered sample. Roughly speaking, the annealed
samples may consist of the two components, in which the one has the MoS$_2$ lattice with comparatively long-range lattice ordering and the other does not. Here, we consider the process of sulfurization. Since sulfurization occurs from the top surface toward to the inside, sulfur atoms need to diffuse into the inside of the films to be sulfurized for entire the film. However, the top surface become covered with high-quality two-dimensional MoS$_2$ layer in the initial stage of sulfurization process, and it might make the incorporation of sulfur atoms from the atmosphere more difficult. And, this becomes one of the reasons why sufficient improvement could not be obtained even if the annealing is carried out for long time. Therefore, the thermal annealing under sulfurous atmosphere will become effective method to improve the crystallinity for a few-layer MoS$_2$ thin films.

4. Conclusion

We investigated the influence of the thermal annealing for MoS$_2$ sputtered thin films by Raman scattering. As-sputtered MoS$_2$ thin films showed broad Raman signals due to the deterioration of the crystallinity in MoS$_2$ lattice. And in MoS$_2$ sputtered thin films after thermal annealing under sulfurous atmosphere, Raman signals became sharp drastically because the crystallinity was improved by the incorporation of sulfur atoms from the atmosphere and the formation of the long-range lattice ordering by thermal annealing. Since these phenomena occurred remarkably on the top surface of MoS$_2$ sputtered thin films, the thermal annealing under sulfurous atmosphere has a great effect on the improvement of the crystallinity for a few-layer MoS$_2$ thin films.

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