Raman imaging studies on perforated MoS$_2$ films prepared by RF sputtering method

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Abstract. We investigated the spatial distribution of the crystallinity for sputtered-MoS$_2$ films by Raman imaging technique. MoS$_2$ lattice could not be structured in as-sputtered sample prepared at room temperature. The crystallinity could be improved by thermal annealing at 630 °C in vacuum condition. However, annealed MoS$_2$ films had two kinds of circular perforated areas on their top surface. In one area, MoS$_2$ film was evaporated and the substrate was exposed. In another area, MoS$_2$ films formed a hillock shape and showed tensile strain. In addition, the crystallinity was deteriorated in hillock formed area, which is due to the generation of sulfur vacancies by thermal annealing.

1. Introduction
Scientific researches on layered materials such as graphene and transition metal dichalcogenides (TMDs) have led to a new understanding of fundamental properties of nanomaterials and suggested the possibilities for the realization of high performance electronic devices. Molybdenum disulfide (MoS$_2$), which is one of TMDs, has unique and tunable electronic properties, and some electronic devices using single or bilayer MoS$_2$ micro-flakes fabricated by mechanical exfoliation have been reported [1-4]. However, it is necessary to establish the fabricating method of a few layer MoS$_2$ films with large area for the integration of devices. A few layer MoS$_2$ films could be grown on a substrate by chemical vapor deposition so far, but they also had micro-flake shapes [5,6]. In this study, we fabricated MoS$_2$ films by RF sputtering method and investigated their crystallinity by Raman imaging technique.

2. Experimental
MoS$_2$ thin film samples were prepared on SiO$_2$/Si substrate at room temperature for 30 minutes by RF sputtering method. The film thickness was estimated at 70 nm by using stylus-type surface profile measurement. After sputtering processes, the samples were annealed at 300 °C and 620 °C for 2 hours in vacuum (~10$^{-6}$ Torr). Raman imaging measurement was carried out by a confocal microscope using 532 nm laser. The incident laser light was expanded linearly by using the cylindrical lens, and it was focused on the sample surface. And then, scattered light was recorded using CCD detector with 400×1340 pixels.
3. Results and discussion

3.1. Surface morphology
Figure 1(a), (b) and (c) show the optical microphotographs of the samples. As-sputtered MoS₂ film had flat surface with no noticeable unique structure as shown in fig.1(a). On the other hand, annealed MoS₂ films showed two kinds of circular structures on their top surface with the size of micro-meter. They could be distinguished as film evaporated area (area 1) and hillock formed area (area 2). The schematic diagram of the surface morphology is shown in fig.1(d). In addition, the density of these areas increased as increase in annealing temperature.

3.2. Scanning auger electron microscopy
We observed Auger electron spectroscopy (AES) to investigate the chemical composition of the sample annealed at 620 °C. Figure 2(a) shows scanning secondary electron microscope (SEM) image of the sample, and figure 2(b), (c), (d) and (e) show AES images obtained for molybdenum, sulfur, oxygen and silicon, respectively. AES images revealed that the MoS₂ thin films were evaporated and SiOₓ/Si substrate was exposed in area 1, because signals come from molybdenum and sulfur were hardly detected but signals from oxygen and silicon were strongly observed in area 1. AES measurement can detect auger electrons escaping from the top surface, and the escaping depth is roughly estimated at several nm from the surface. Therefore, AES images indicate the chemical composition of the top surface. On the other hand, AES images taken from the flat area and area 2 showed the same features, which indicates that they have almost same chemical composition at their top surface.

3.3. Raman imaging measurement
Raman imaging measurement was carried out to investigate the spatial distribution of the crystallinity in MoS₂ thin films. Hexagonal MoS₂ belongs to the space group D₆h (P6₃/mmc), and a group theoretical analysis gives 3 Raman-active modes of E₁₈ (287 cm⁻¹), E₁₁₂g (383 cm⁻¹) and A₁₄ (409 cm⁻¹) at the Γ-point in the Brillouin zone [7]. Figure 3(b), (d) and (f) show CCD detector images of Raman signals for the

![Figure 1](image1.png)  
**Figure 1.** Optical microphotographs of as-sputtered MoS₂ (a) and annealed MoS₂ at 300 °C (b), 620 °C (c). The schematic diagram of the sample surface morphology after annealing is shown in (d).

![Figure 2](image2.png)  
**Figure 2.** SEM image of the annealed sample at 620 °C (a), and AES images of molybdenum (b), sulfur (c), oxygen (d) and silicon (e), respectively.
samples. In the images, the vertical and bottom horizontal axes correspond to those of the CCD detector pixels, respectively. Raman shift and the signal intensity are denoted on the upper horizontal axis and the contrast using grayscale. The incident laser expanded linearly focused on the surface along the line shown in the optical micrographs of figure 3 (a), (c) and (e), respectively. As shown in figure 3 (b), the CCD image of as-sputtered MoS$_2$ showed only the Raman signal derived from SiO$_2$/Si substrate at 520 cm$^{-1}$, and the signal was uniform in all probing area. This indicates that MoS$_2$ lattice could not be structured in as-sputtered sample. On a side note, the broad and weak signal was observed slightly at the range from 900 to 1000 cm$^{-1}$, which is not Raman signal from the sample but the background signal from the equipment. In addition, in the sample annealed at 300 °C, Raman signals derived from MoS$_2$ was not observed yet as shown in figure 3 (d). However, Si signals observed at 300, 520 and 980 cm$^{-1}$ taken from area 1 showed higher signal intensity compared with the flat area [8], because SiO$_2$/Si substrate was exposed in area 1 as revealed by AES measurement. These features are well reflected in the CCD image of the sample annealed at 620 °C as shown in figure 3 (f), but two additional Raman signals

![Optical microphotographs and CCD images of Raman signals](image)

**Figure 3.** Optical microphotographs and CCD images of Raman signals for as-sputtered sample (a)(b), and the samples annealed at 300 °C (b)(c), 620 °C (c)(d), respectively. The incident laser was expanded linearly and focused on the surface along the line shown in the optical micrographs.
were observed at 380 cm\(^{-1}\) and 410 cm\(^{-1}\) at all probing places except area 1. These signals correspond to \(E_{2g}\) and \(A_{1g}\) modes of MoS\(_2\) phonon, indicating that MoS\(_2\) lattice was formed by thermal annealing at 620 °C. Here, we consider about the area 2. Although Si signals taken from area 2 showed higher signal intensity than that of the flat area, Si substrate was not exposed as revealed by AES measurement. These results suggested that MoS\(_2\) film formed a hillock shape with hollowed inside in area 2. In addition, Raman signals shifted to lower frequency side and both peaks were broadened slightly compared with the flat area. These values were plotted in figure 4(c) and (d) so that the detailed values can be compared. The plots showed that both peak shifts and the broadening occurred at the same time in area 2. And then, they gradually became advance from the edge toward the center. The peak shift indicates that MoS\(_2\) lattice had the tensile strain along the both direction of in-plane and perpendicular to the plane in area 2. And, the broadening indicates the deterioration of the crystallinity, which was caused by the generation of sulfur vacancies in MoS\(_2\) lattice by thermal annealing due to its high vapour pressure.

4. Conclusion
In this study, we investigated the spatial distribution of the crystallinity for as-sputtered and annealed MoS\(_2\) thin films by using Raman imaging technique. Although the lattice ordering was not structured in as-sputtered MoS\(_2\) sample, the crystallinity was improved by thermal annealing. However, annealed MoS\(_2\) films showed two kinds of circular structures on their top surface, which were generated by evaporation of the films and forming a hillock shape, respectively. MoS\(_2\) film with hillock shape showed tensile strain along the both direction of in two-dimensional plane and perpendicular to the plane. In addition, the deterioration of the crystallinity was observed in hillock area due to the generation of sulfur vacancies.

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