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Surface Modification of Two-Dimensional Layered Molybdenum Disulfide Thin Film Using MW Hydrogen Plasma

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1. Introduction

It is known that molybdenum disulfide (MoS_2) shows different physical properties depending on the number of layers. Since the single layer film is a semiconductor having a band gap of about 1.8 eV, it is expected to be applied as a flexible optoelectronic device. In addition, since MoS_2 shows hydrogen evolution reaction (HER), it is expected to be used as an electrode catalyst of a fuel cell. The active site which is mainly defects formed within MoS_2 layers contributes to HER[1)]. However, since the basal-plane occupying most of the surface area of MoS_2 monolayer is inert[2)]. Therefore, we irradiated 2.4 GHz microwave (MW) excited hydrogen plasma to the MoS_2 films synthesized by chemical vapor deposition (CVD) method. We investigated the effect of plasma treatment by measuring the change in the properties of the MoS_2 films.

2. Experimental Methods

The MoS_2 films were deposited on the SiO_2/Si substrates heated to 600-700 °C. In this method, molybdenum (VI) MoO_3 and sulfur were used as precursors in the reaction furnace filled with argon gas. The film quality of MoS_2 depends on gas pressure, substrate temperature and so on. The synthesized MoS_2 films were treated with 2.4 GHz microwave (MW) excited hydrogen plasma to modify the film characteristics, such as the atomic ratio of sulfur and molybdenum S/Mo. The MoS_2 films before and after plasma treatments were characterized with X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD).

3. Results and discussion

Figure 1 shows the S/Mo atomic ratio dependent on H_2 plasma treatment time. The S/Mo ratio was estimated from XPS surface analysis. The S/Mo ratio decreased from 2.73 to 1.8 with plasma treatment time. The stoichiometric value of S/Mo= 2 was obtained for plasma treatment for 10 min. It is speculated that sulfur atoms in

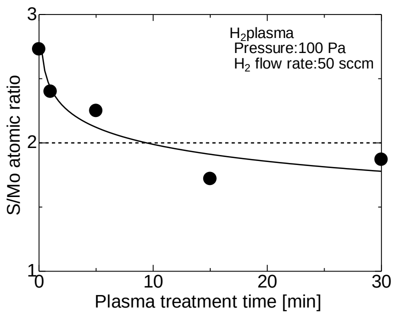

Fig. 1. S/Mo atomic ratio of H_2 plasma treated MoS_2 surface.

MoS_2 film were etched by hydrogen ions and radicals in the plasma.

Figure 2 shows the results of XRD analysis of the MoS_2 film treated without and with hydrogen plasma for different treatment time. The intrinsic peak of MoS_2 is (002) plane ($2\theta = 14.5°$), (004) plane ($2\theta = 29.2°$), (006) plane ($2\theta = 44.4°$) and (008) plane ($2\theta = 60.4°$). These peaks indicate that the synthesized MoS_2 film had two-dimensional layered structure. After plasma treatment, these peaks did not change. Therefore, it is suggested that crystallinity of the film is maintained in the measurement depth region of XRD after plasma treatment.

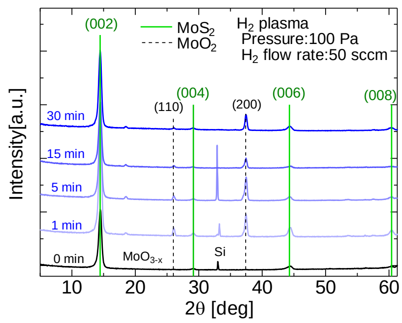

Fig. 2. XRD patterns of H_2 plasma treated MoS_2 surfaces.

The MoS_2 films treated with hydrogen plasma were also analyzed with Raman spectroscopy. Two main characteristic peaks of MoS_2 films corresponded to the E^1_{2g} mode (~376.7 cm^{-1}, in-plane vibration of S atoms) and A_{1g} mode (~402.7 cm^{-1}, out-of-plane vibration) of the pristine MoS_2[3)]. It is known that the frequency difference between the A_{1g} mode and the E^1_{2g} mode of monolayer MoS_2 is 20.4 cm^{-1}. The frequency difference of the MoS_2 film synthesized by our method was 25.0 cm^{-1}, the film is considered to be multilayer film. The peak difference was not changed after hydrogen plasma treatment.

4. Conclusion

MoS_2 films synthesized by CVD method was treated with MW hydrogen plasma. According to the experimental results, sulfur vacancies were successfully formed on only basal-plane of MoS_2 film using hydrogen plasma. In this plasma treatment, sulfur atoms are referentially etched from MoS_2 film.

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