Extended Abstracts of the 2015 International Conference on Solid State Devices and Materials, Sapporo, 2015, pp294-295

Improving Crystalline Quality of Sputtering Deposited MoS_2 Thin Film by Post-Sulfurization Annealing Using $(t\text{-}C_4H_9)_2S_2$

S. Ishihara[1], K. Suda[1], Y. Hibino[1], N. Sawamoto[1], T. Ohashi[2], S. Yamaguchi[2], K. Matsuura[2], H. Machida[3], M. Ishikawa[3], H. Sudoh[3], H. Wakabayashi[2] and A. Ogura[1]

[1]Meiji University, School of Science and Technology
1-1-1 Higashi-Mita, Tama-ku, Kawasaki, Kanagawa, 214-8571, Japan
Phone: +81-44-934-7352, E-mail: ce41007@meiji.ac.jp
[2]Tokyo Institute of Technology
4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8502, Japan
[3]Gas-phase Growth Ltd,
#301 Nokodai-Tamakoganei Venture Port, 2-24-16 Naka, Koganei, Tokyo 184-0012, Japan

Abstract

Disorders such as sulfur vacancies in sputtering deposited MoS_2 thin film may reduce the field-effect mobility. In order to complement sulfur vacancies, we performed post-sulfurization annealing on the sputtered-MoS_2 thin film. As the result, sulfur vacancies in the sputtered-MoS_2 film were filled up with sulfur atoms, and large-scale high-quality MoS_2 thin film was obtained.

1. Introduction

Molybdenum disulfide (MoS_2), which is a kind of the transition-metal dichalcogenides, has a layered structure. It is reported that MoS_2 shows excellent optical and electrical properties even in thin regions, such as the band gap shift from indirect to direct [1] or a comparably high mobility [2]. In most of the previous studies, MoS_2 thin film has been prepared by mechanical exfoliation from bulk MoS_2. However, there are several problems that the mechanical exfoliation method presents limited flake sizes and depletion-mode MOSFETs due to impurities [3, 4].

In order to solve these problems, we fabricated MoS_2 thin film by sputtering deposition under high vacuum conditions. We have achieved to form a large-scale five-layer sputtered-MoS_2 film on SiO_2/Si substrate and to decrease its carrier density dramatically compared to an exfoliated MoS_2 [5, 6]. However, there are some sulfur vacancies in the sputtered-MoS_2 thin film which may reduce the mobility. Therefore, in this study, we performed post-sulfurization annealing on the MoS_2 thin film in order to complement sulfur vacancies, and investigated the physical, chemical and optical properties of sulfurized-MoS_2 film.

2. Results and Discussion

MoS_2 thin film was fabricated by RF magnetron sputtering on SiO_2/Si substrates. The sputtering conditions were as follows: substrate temperature (400°C), RF power (150 W), sputtering duration (155 s) and Ar partial pressure (0.55 Pa). The chamber was evacuated to a pressure of 10^{-6} Pa before the sputtering. The MoS_2 target is 99.79% pure and an effective diameter of 80mm. Post-sulfurization annealing was performed in a quartz tube reactor at atmospheric pressure. During the post-sulfurization annealing, the sputtered-MoS_2 temperature was kept at 600°C. We used di-tertiary-butyl disulfide [$(t\text{-}C_4H_9)_2S_2$] as a sulfur precursor.

Fig. 1 shows (a) Mo 3d and (b) S 2p XPS spectra of as-deposited and sulfurized MoS_2 films. From the MoS_2 peak area ratio (S/Mo), sulfurized MoS_2 film ($MoS_{1.9}$) approached to stoichiometric composition compared to as-deposited MoS_2 film ($MoS_{1.8}$). Therefore, it was confirmed that sulfur vacancies in sputtered-MoS_2 film were complemented with sulfur atoms. Moreover, the MoO_3 peak decreased after the sulfurization compared to the large peak detected in as-deposited MoS_2 film, as shown in Fig. 1 (a). It suggests that the oxygen which combined with sulfur vacancies were substituted with sulfurs by the sulfurization.

Fig. 2 shows a cross sectional TEM image of sulfurized film. From the TEM observation, it was confirmed that the layered MoS_2 film was uniformly fabricated on the SiO_2/Si substrate with the thickness of 5.85 nm (9 layers). Furthermore, from the XRD investigation as shown in Fig. 3, only the MoS_2(002) diffraction peak was detected. This indicated that the MoS_2 film remained parallel to the substrate surface even after the sulfurization.

The optical properties of sulfurized film was investigated using spectroscopic ellipsometry. The optical constants n and k were obtained from fitting of the ellipsometric parameters, Psi and Delta, by fixing the film thickness of 5.85 nm and an incident angle of 75.14°. Then, we calculated the absorption coefficient of sulfurized film using the relation of $\alpha=4\pi k/\lambda$, and taking that value into account for the Tauc plot [7], it was determined that the sulfurized film has an indirect band gap of 1.34 eV (Fig. 4).

Fig. 5 shows Raman spectra of as-deposited and sulfurized films. Raman shifts and intensities were calibrated by a bulk Si peak (Si=520 cm^{-1}). Two Raman modes, E^1_{2g} and A_{1g}, were observed and the peak intensities increased after the sulfurization. Therefore, it was confirmed that crystalline quality of the sputtered-MoS_2 was improved due to the post-sulfurization annealing. Moreover, a frequency difference between E^1_{2g} and A_{1g} peaks of sulfurized film approached to bulk while that of as-deposited film is larger than bulk owing to the k = 0 Raman selection rule breaks caused by sulfur vacancies.

3. Conclusions

From the investigations by Raman and XPS, the sputtered-MoS_2 thin film after sulfurization improved crystalline quality since sulfur vacancies were complemented with sulfur atoms. From the results of TEM, and XRD, it was confirmed that large-scale layered MoS_2 thin film can be obtained by sulfurization of sputtered-MoS_2 thin film. By investigating with spectroscopic ellipsometry, the optical band gap of sulfurized film was determined as 1.34 eV.

References

[1] K.F. Mak, *et al.*, Phys. Rev. Lett., **105** (2010) 136805.
[2] S. Das, *et al.*, Nano Lett., **13** (2012) 100–105.
[3] B. Radisavljevic, *et al.*, Nature Nanotech., **6** (2011) 147-150.
[4] K. Dolui, *et al.*, Phys. Rev. B, **87** (2013) 165402.
[5] T. Ohashi, *et al.*, Jpn. J. Appl. Phys., **54** (2015) 04DN08.
[6] B. Radisavljevic and A. Kis, Nature Mater., **12** (2013) 815-82.
[7] C. Yim, *et al.*, Appl. Phys. Lett., **104** (2014) 103114.

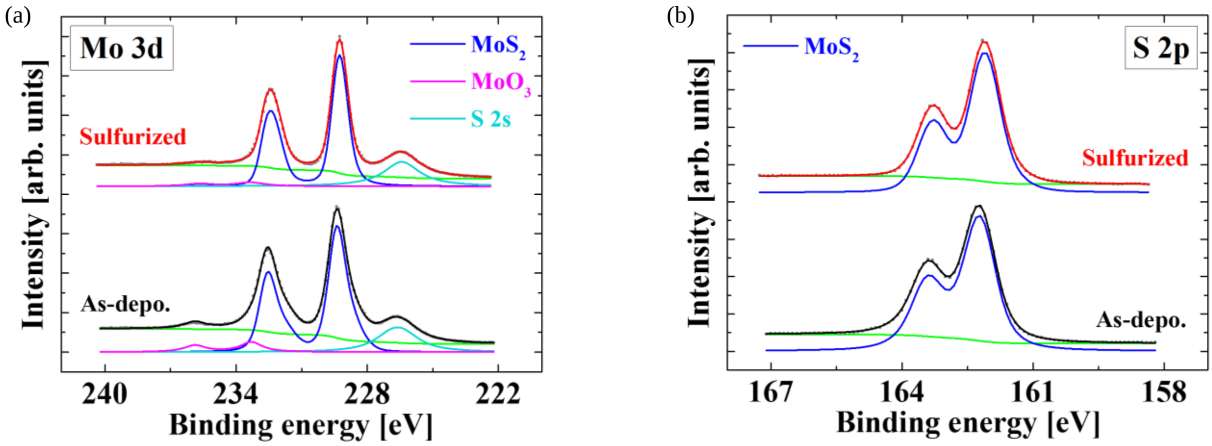

Fig. 1 (a) Mo 3d and (b) S 2p XPS spectra of as-deposited and sulfurized MoS_2 films.

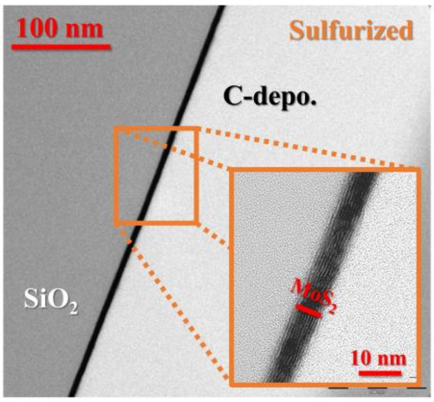

Fig. 2 Cross sectional TEM image of sulfurized film.

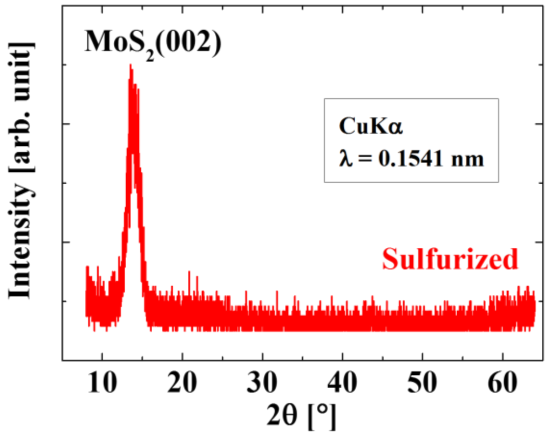

Fig. 3 XRD patterns of sulfurized film.

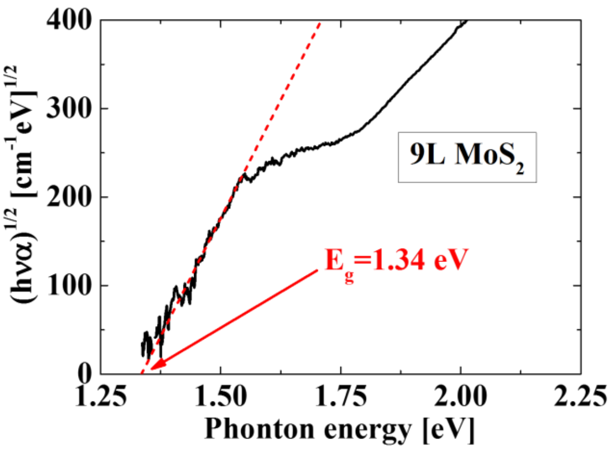

Fig. 4 Tauc plot of sulfurized film.

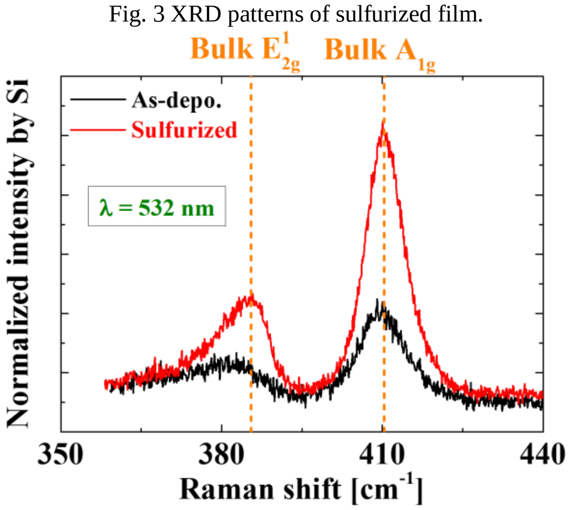

Fig. 5 Raman spectra of as-deposited and sulfurized films.