Hall-effect mobility enhancement of sputtered MoS$_2$ film by sulfurization even through Al$_2$O$_3$ passivation film simultaneously preventing oxidation

Masaya Hamada, Kentaro Matsuura, Takuro Sakamoto, Haruki Tanigawa, Iriya Muneta, Takuya Hoshii, Kuniyuki Kakushima, Kazuo Tsutsui, and Hitoshi Wakabayashi

Tokyo Institute of Technology, Yokohama, Kanagawa 226-8502, Japan

E-mail: hamada.m.af@m.titech.ac.jp

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An aluminum oxide (Al$_2$O$_3$) passivation film that prevents the oxidation of a sputtered and sulfurized molybdenum disulfide (MoS$_2$) film was investigated for an enhancement of the Hall-effect mobility. A remarkably high Hall-effect electron mobility value of 100 cm$^2$ V$^{-1}$ s$^{-1}$ was achieved using 3 nm passivation film, as compared to 25 cm$^2$ V$^{-1}$ s$^{-1}$ for an as-deposited MoS$_2$ film, because sulfurization is able to be yielded even through the Al$_2$O$_3$ film into the MoS$_2$ film. © 2020 The Japan Society of Applied Physics

1. Introduction

Transition metal di-chalcogenide films are atomically thin semiconductors, in which the molybdenum disulfide (MoS$_2$) has a relatively high mobility (300 cm$^2$ V$^{-1}$ s$^{-1}$), flexibility, and visible light transparency. Moreover, moderate band gaps of 1.8 and 1.2 eV are calculated for single and multi-layers, respectively. 5 Owing to unique properties, various applications have been extensively investigated. For such applications, it is necessary to obtain a large area with uniform characteristics using appropriate deposition methods. Layered MoS$_2$ films have been frequently prepared using mechanical exfoliation and chemical vapor deposition (CVD) methods. In the exfoliation method, it is difficult to control the number of layers, minimize the amount of contaminations and enlarge the film area. In contrast for the CVD method, the MoS$_2$ film has larger area than that for exfoliation method. However, to deposit a continuous MoS$_2$ film, it is necessary to apply perylene-3,4,9,10 tetracarboxylic acid tetrapotassium salt to the surface of the substrate, that influences the intrinsic properties of the MoS$_2$ film. On the other hand, there have been various attempts at using a sputtering method synthesizing layered MoS$_2$ film. A sputtering method is one of the most widely used vapor deposition technique and has been widely used to deposit thin films onto various substrates. Through this approach, it is possible to deposit a uniform film with a large area without any special pre-treatment. Because the deposition is conducted in a high vacuum, contaminations can be eliminated. It has been confirmed that a layered MoS$_2$ film on a SiO$_2$ film can be successfully formed through sputtering. Furthermore, the fabrication of a top gate metal–insulator–semiconductor field-effect transistor using a sputtered MoS$_2$ film has been performed. Although sulfur atoms are easily out-diffused from the MoS$_2$ film during ultra-high vacuum (UHV) sputtering, we have found that sulfur annealing compensates for sulfur defects, resulting in a mobility enhancement. However, during the cooling in the sulfur annealing process, a direct sulfur deposition and unintentional molecular adsorption are concerned, and which could lead to contaminations in following process steps and degradation of interfacial properties. In addition, a sputtered MoS$_2$ film easily oxidizes owing to its lattice defects, and it has been speculated that a passivation film is important to prevent such defects. For such a film, it is desirable to adapt materials which can be deposited with a damage-free and a high quality. An aluminum oxide (Al$_2$O$_3$) is one of the candidate materials owing to a high quality deposition with atomic layer deposition (ALD) and low influence on the carrier transport in a MoS$_2$ film with the suppression of the Coulomb scattering.

In this study, we originally propose and investigate a new method suppressing unexpected sulfur deposition and pollutants from the ambient through an Al$_2$O$_3$ passivation film deposited by the ALD for improving a crystallinity and electrical properties of a sputtered MoS$_2$ film, as shown in Fig. 1.

2. Experimental methods

A base substrate of silicon dioxide/silicon (SiO$_2$/Si) was cleaned using a mixture of sulfuric acid and hydrogen peroxide (H$_2$SO$_4$:H$_2$O$_2$ = 4:1) to remove any particles and organic substances from the SiO$_2$ surface. The MoS$_2$ films were formed using an UHV radio frequency (RF) magnetron sputtering, as shown in Fig. 2(a). As the sputtering conditions, a substrate temperature of 450 °C, an argon (Ar) pressure of 0.55 Pa, an Ar flow rate of 7 sccm, and an RF power of 50 W were applied and, a distance of 180 mm was maintained between the MoS$_2$ target and the substrate. The purity of the MoS$_2$ target was 99.79%. An Al$_2$O$_3$ passivation film was deposited at 300 °C using trimethylaluminium (TMA) gas and H$_2$O vapor on the MoS$_2$ film through the ALD method as an ex situ process, in which an Al$_2$O$_3$ film could be uniformly formed because of dangling bonds at the surface of a poly-crystalline sputtered MoS$_2$ film. A quality that tends to be high because it has high insulation properties and the field effect of the FETs works well. For sulfur compensation in a MoS$_2$ film through an Al$_2$O$_3$ passivation film, sulfur annealing was conducted using the setup shown in Fig. 2(b). The sulfur powder source was placed in the first zone, which was heated at 250 °C, and the sample wafer was placed in the second zone heated at a
temperature of 400 °C–700 °C for 40–60 min in an Ar flow under 100 Pa. Sulfur atoms diffuse into the MoS2 film even through an Al2O3 passivation film. After annealing, the Raman spectroscopy was conducted using a laser wavelength of 532 nm. The Hall-effect was measured using the Van der Pauw method with annealed samples divided into coupons of 1 cm × 1 cm, with silver paste contacts placed at their four corners.

3. Results and discussion

To evaluate the crystallinity of the MoS2 film, the Raman spectra were measured after Al2O3 film deposition and the following sulfur annealing. Figures 3(a) and 3(b) show the full width at half maximum (FWHM) values of A1g and E1g2 modes as a function of the sulfurization temperature for the stacked structure of the sputtered MoS2 film underneath the Al2O3 passivation film. The crystallinity of the MoS2 film is improved by the sulfurization even through the Al2O3 passivation film at various thicknesses. The bottom dashed lines correspond to the measured FWHM values of the bulk-MoS2 film. The FWHW of E1g2 mode has been reported to be more sensitive to crystal defects than A1g one, and our results are also in good agreement with that. For both the plots for A1g and E1g2, the FWHM values decrease with an increase in the sulfurization temperature. This is because the sulfur defects in the sputtered MoS2 film were compensated by the diffused sulfur atoms through the Al2O3 film.

To confirm the sulfur compensation in the MoS2 film through the Al2O3 film, the Raman shifts of the A1g and E1g2 peaks in the sputtered MoS2 films as a function of the sulfurization temperature are shown in Figs. 4(a) and 4(b), respectively. In both A1g and E1g2 modes, the Raman peak positions approach that of the bulk MoS2 film as the sulfurization temperature increases and the Al2O3 film thickness decreases, except at 700 °C with the Al2O3 film. A reduction in sulfur vacancies shifts the Raman peaks of the MoS2 film to a higher wavenumber side, and the E1g2 mode is strongly improved rather than the A1g one. Therefore, the shifts of the both A1g and E1g2 peaks to a higher wavenumber side in our results indicate the sulfur compensation was successfully performed through the Al2O3 film. Since the Raman shifts are also affected by a strain, the shifts to a lower wavenumber side at a higher temperature of 700 °C are considered to be caused by the thermal coefficient difference between the MoS2 and the Al2O3 films connected by covalent bonds at the grain boundary of the MoS2 surface, but no serious influence on the electrical properties is speculated.

For further improvements in sulfurization even through the Al2O3 film, the sulfurization time was extended up to 60 min at a sulfurization temperature of 700 °C, as shown in Figs. 5(a) and 5(b). In both A1g and E1g2 modes, the FWHM values saturate with an increase in the sulfurization time for more than 40 min. This confirms that a sulfurization time of even 40 min is adequate.

To confirm the distribution of sulfur diffusion into the MoS2 films through the Al2O3 film, the Auger electron spectroscopy (AES) depth profile from a surface side is measured for a 3 nm Al2O3/MoS2 sample annealed at 700 °C for 40 min, as shown in Fig. 6. We assumed that the interface
between the Al₂O₃ and MoS₂ films is located around 15 cycles at half of the Mo and Al intensities. Because a sulfur concentration increases with an increase in the cycle in the Al₂O₃ film, it is understood that sulfur atoms were diffused toward the MoS₂ film through the Al₂O₃ film. Moreover, because no significant increase in oxygen intensity is observed in the MoS₂ film, a large portion of the MoS₂ film is not affected by the oxidation during the following processes. These suggest that the Al₂O₃ film ensures a stability of the MoS₂ film without overly suppressing sulfurization.

To confirm electrical properties of the MoS₂ film, the Hall-effect mobilities of the electrons depending on the Al₂O₃ film thickness are shown in Fig. 7, in which the Al₂O₃ deposition at 300 °C and sulfur annealing at 700 °C were conducted for 40 min just after the MoS₂ deposition. The Hall-effect mobility increases with a decrease in the Al₂O₃ film thickness. Although the mobility of the MoS₂ film without the Al₂O₃ film has the highest value, the degradation of the MoS₂ film itself and the interface characteristics between the semiconductor and insulator are serious concern owing to the oxidation of the MoS₂.

Fig. 4. The Raman shifts for sputtered 3 nm MoS₂ film in (a) A₁₁ and (b) E₂₁ modes as functions of the sulfurization temperature and Al₂O₃ thickness. An improvement in the crystallinity of the MoS₂ film was observed on the sulfurization temperature.

Fig. 5. FWHM values of the Raman spectra for sputtered 3 nm MoS₂ film in (a) A₁₁ and (b) E₂₁ modes as a function of the sulfurization time.

Fig. 6. AES depth profiles of 3 nm Al₂O₃/3 nm MoS₂ sample annealed at 700 °C for 40 min. A MoS₂ film was successfully sulfurized preventing its oxidation during the fabrication processes and evaluation.

Fig. 7. The Hall-effect mobility of 3 nm MoS₂ film sulfur-annealed at 700 °C for 40 min as a function of the Al₂O₃ thickness in which the plots indicate the mean values with the corresponding standard errors.
film upon exposure to air. Even with a 3 nm Al2O3 passivation film, a higher mobility of 100 cm2 V−1 s−1 is achieved compared to 25 cm2 V−1 s−1 for the as-deposited MoS2 film. Since the sulfur compensation considerably improves the mobility of the MoS2 film even through the Al2O3 passivation film, which is necessary to achieve the higher mobility of the MoS2 film, simultaneously protecting the MoS2 film.

Our results will contribute to stabilizing the electrical properties of the sputtered MoS2 film after the crystallinity improvement process with suppression of a sulfur contamination and an unexpected pollution. This sulfurization process is going to be applied to logic devices in IoT edge products.

4. Conclusion

An improvement of the crystallinity of a sputtered MoS2 film was achieved by the sulfurization, even through the Al2O3 film. Eventually, a higher Hall-effect mobility of 100 cm2 V−1 s−1 was achieved with a 3 nm Al2O3 passivation film as compared to 25 cm2 V−1 s−1 for an as-deposited MoS2 film. Our new crystallinity improvement process will contribute to stabilizing the electrical properties of the sputtered MoS2 film. In future study, if the sputtering of a MoS2 film and the deposition of an Al2O3 passivation film are simultaneously executed in a vacuum, further improvements in the electrical characteristics of a sputtered MoS2 film can be expected.

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ORCID iDs

Masaya Hamada https://orcid.org/0000-0002-5830-5283
Takuya Hoshii https://orcid.org/0000-0002-2873-8715

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