Self-aligned-TiSi₂ bottom contact with APM cleaning and post-annealing for sputtered-MoS₂ film

Satoshi Igarashi*, Yusuke Mochizuki, Haruki Tanigawa, Masaya Hamada®, Kentaro Matsuura, Iriya Muneta, Kuniyuki Kakushima, Kazuo Tsutsui, and Hitoshi Wakabayashi

Tokyo Institute of Technology, 4259, Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan

E-mail: igarashi.s.ad@m.titech.ac.jp

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1. Introduction

Transition metal dichalcogenides (TMDCs) with atomically thin layered semiconductors have garnered much attention for various device applications, because of their remarkable optical and electrical characteristics.⁹,¹⁴ Among TMDCs, a molybdenum disulfide (MoS₂) film has a tunable bandgap from 1.2 eV for bulk to 2.4 eV for a single layer, and high electron mobility of 200 cm²·V⁻¹·s⁻¹ in a single-layer MoS₂ transistor.⁴,⁵ Therefore, the MoS₂ film is expected to be applied as a MOSFET channel material for large-scale integrations (LSIs). As a practical MoS₂-film synthesis method, chemical vapor deposition (CVD) has been widely investigated.⁶⁻⁸ In order to obtain a large and uniform CVD-MoS₂ film, it is necessary to apply oxygen plasma pretreatment to the substrate surface, however, the roughness of the substrate surface influences the electrical properties.⁹ Although a precoating of an alkali-metal-containing Mo precursor is required followed by sulfurization, alkali-metal contaminations can be concerned with unexpected carrier generation.¹⁰ For these reasons, we focused on RF magnetron sputtering. With this method, large and uniform MoS₂ films have been deposited without any pretreatment on the substrate, and minimal contaminations were ensured via the high-vacuum process.¹¹ Therefore, sputtering is identified as a practical MoS₂-film fabrication method. For improving the MoS₂ device performance, the reduction of the contact resistance is a critical issue.¹² In the case of extremely short-channel MOSFETs, the contact resistance dominates the total resistance between the source and drain regions. In previous studies, various metal contacts were evaluated with the aim of reducing the contact resistance.¹³⁻²⁵ Figure 1 shows the benchmark of the Schottky-barrier height to the MoS₂ film depending on the work function in various metal contacts. Even if the same metal contact is used, the Schottky barrier height for MoS₂ varies due to uncontrolled Fermi level pinning.¹⁴,²² However, this benchmark shows that low-Schottky-barrier-height electron transport has been obtained using metals with low work functions, such as scandium (Sc), aluminum (Al) and titanium (Ti). On the other hand, photoresist residues in the MoS₂ devices influence electrical performances. It has been reported that organic molecules, which adhere to a MoS₂ film, modulated the carrier density, thus intrinsic properties in a MoS₂ film are not able to be obtained.²⁶ Moreover, organic contaminations at the interface between metal/MoS₂ films cause the Fermi level pinning.²⁷ In order to suppress such external influences, the photore sist must be removed. In the case of bottom-contact structures, the MoS₂ film must be immediately deposited just after the removal of the photore sist. Dissolution with organic solvents for the removal of the photore sist is not sufficient due to the existence of residual contaminations.²⁸ Therefore additional cleaning with oxidation is required, e.g. a sulfuric acid and hydrogen peroxide mixture (SPM) or an ammonia and hydrogen peroxide mixture (APM) cleanings, in which, however, it is difficult to perform for metal bottom contact. In contrast, a metal silicide bottom contact with SPM or APM cleaning reliably yields clean interfaces between not only MoS₂/TiSi₂ films but also the MoS₂/SiO₂ underlaying layer. A metal silicide is a compound of a transition metal and silicon (Si), which has simultaneously higher oxidation resistance than that of metals and low resistivity.²⁹ Moreover, a metal silicide film can be easily obtained on the Si bottom contact surface via a self-aligned process and was governed in the current Si-based LSI fabrication process.³⁰ In our previous study, sputtered-MoS₂ n-type MOSFETs with molybdenum silicide (MoSi₂) bottom contacts were evaluated, where the MoS₂ contact surface was pre-cleaned by SPM before MoS₂ deposition.³¹ However, the on/off ratio of the drain current for the MOSFET is as small as approximately 10² due to the high parasitic resistance. Therefore we focused on self-aligned titanium silicide (TiSi₂) as a contact material for MoS₂ bottom-contact devices to reduce the contact resistance. A self-aligned-TiSi₂ film has a lower work function (4.53 eV) than that of MoSi₂ (4.82 eV), and high oxidation resistance during APM cleaning before MoS₂-film deposition.³² Therefore, a self-aligned-TiSi₂ film is a suitable candidate for a practical contact in n-type MoS₂ channel MOSFETs. The TiSi₂ bottom contact for the MoS₂ film with a post-annealing in forming gas (FG) and an APM cleaning was...
briefly reported by just electrical characteristics of transmission line model (TLM) devices. In this study, we deeply investigate the contact characteristics between sputtered-MoS2 and self-aligned-TiSi2 films using additional analyses.

2. Experimental methods

Figure 2 shows the fabrication of a TLM device to extract contact resistance. First, an n-doped poly-Si film on a SiO2/Si substrate was cleaned using SPM with H2SO4:H2O2:H2O = 4:1 at 180 °C for 10 min and diluted HF (DHF) for 1 min. The poly-Si as the bottom contact was patterned by chemical dry etching in CF4 gas flow and cleaned by SPM and DHF in order to remove the photoresist. A self-aligned-TiSi2 film was synthesized by Ti and titanium nitride (TiN) sputtering in ultra-high vacuum and following annealing at 650 °C. The total resistances are shown in Figs. 3(a) and 3(b), respectively. The current–voltage (I–V) characteristics were measured to extract the sheet and contact resistances. Moreover, time-of-flight secondary ion mass spectrometry (TOF-SIMS) depth profiles and cross-sectional transmission electron microscopy (TEM) images were obtained to characterize the TiSi2/MoS2 contact.

3. Results and discussion

Figure 4(a) shows the I–V characteristics of devices at the same contact distance of 10 μm before and after FG annealing at 300 °C–800 °C. Ohmic contacts were observed between 500 °C and 650 °C. Figure 4(b) shows current values at 1 V, depicted in Fig. 4(a), depending on the FG annealing temperature. The highest current was obtained by annealing at 650 °C. The total resistances RF with a contact distance L of 10–35 μm was calculated from the fitting line of the I–V characteristics between −0.5 and 0.5 V. Figure 5 shows the RF depending on L for the TLM devices annealed in FG at 650 °C. The fitted line in Fig. 5 can be expressed by

\[ R_F = 2R_C + R_{CH} = 2R_C + \frac{R_{SH}L}{W}, \]

where \( R_F \), \( R_{CH} \), and \( W \) are the contact resistance, channel resistance, sheet resistance of a channel film, and the contact width of 251 μm, respectively. Therefore, \( R_C \) and \( R_{SH} \) are obtained from the intercept and slope of the fitting line, respectively. Generally, this calculation could not be applied in the case of the Schottky contact, because the contact resistance changes with applied voltage due to the presence of the Schottky barrier. Therefore, the contact resistances are discussed from the total resistances calculated in the same voltage range around 0 V for both Ohmic and even Schottky contacts.

The sheet resistances of the MoS2 films underneath the Al2O3 films depending on FG annealing temperature are shown in Fig. 6. It is confirmed that the sheet resistances decrease with an increase in temperature. Here, the sheet resistance can be expressed by

\[ R_{SH} = \frac{1}{en\mu}, \]

where \( e \), \( \mu \), and \( n \) are the electron charge, carrier mobility and density, respectively. It has been reported that sputtered-MoS2 film has many sulfur defects, which act as n-type dopants. In this study, sulfur defects were compensated by residual sulfur atoms in sputtered-MoS2 film during the FG annealing. Moreover, the compensation resulted in carrier mobility enhancement, because of the suppression in carrier scattering at the defects. Therefore, it is speculated in the FG annealing case that although the carrier mobility and density simultaneously increases and the substrate, 230 mm, and substrate temperature, 400 °C. Then, a 10 nm thick aluminum oxide (Al2O3) film was directly deposited on the MoS2 film by an atomic layer deposition (ALD) at 300 °C using trimethylaluminum and H2O. Optical lithography and reactive ion etching in Ar and BCl3 gases were performed for device isolation. The TLM devices were finally treated by FG annealing with 3% H2 in N2 gas at 300 °C–800 °C in order to reduce the contact resistance. A cross-sectional illustration and the top view of the device obtained by scanning electron microscopy are shown in Figs. 3(a) and 3(b), respectively. The current–voltage (I–V) characteristics were measured to extract the sheet and contact resistances. Moreover, time-of-flight secondary ion mass spectrometry (TOF-SIMS) depth profiles and cross-sectional transmission electron microscopy (TEM) images were obtained to characterize the TiSi2/MoS2 contact.

**Fig. 1.** Schottky-barrier height to n-type MoS2 depending on work function in various metal contacts reported in previous studies.13–20

**Fig. 2.** Fabrication process of TLM devices with sputtered-MoS2 channel and self-aligned-TiSi2 bottom contact.

**Fig. 3(a).** Cross-sectional view of the device obtained by scanning electron microscopy.
decreases, the carrier mobility is dominant as compared to the carrier density, as understood in Eq. (2).

Figure 7 shows the contact resistance depending on the FG annealing temperature. The lowest contact resistance of $1.9 \times 10^7 \ \Omega \cdot \mu m$ was obtained by FG annealing at 650 °C and a two-order reduction in the contact resistance as compared to that before annealing was achieved. Up to 650 °C, the contact resistance decreases with an increase in annealing temperature. On the other hand above 700 °C, the contact resistance increases with an increase in annealing temperature.

Figure 3. (Color online) (a) Cross-sectional illustration and (b) top view of TLM devices obtained by SEM for channel lengths of 10–35 μm with a width of 251 μm.

Figure 4. (Color online) (a) Current–voltage characteristics and (b) currents at 1 V depending on various FG annealing temperatures up to 800 °C. Ohmic contacts were observed at 500 °C–650 °C, and the highest current was obtained at 650 °C.

Figure 5. Total resistance $R_T$ depending on TiSi$_2$ bottom contact distance with FG annealing at 650 °C. $R_T$ was obtained from range of $I$–$V$ characteristics, shown in Fig. 4(a). Sheet resistance, $R_{SH}$, and contact resistance, $R_C$, were calculated from slope and intercept of fitting line, respectively.

Figure 6. Sheet resistances of sputtered-MoS$_2$ channel underneath Al$_2$O$_3$ film, depending on the FG annealing temperature.

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temperature. Here, as mentioned in the Introduction, the APM cleaning was applied before MoS$_2$ deposition for cleaning the interface between MoS$_2$/TiSi$_2$ films and MoS$_2$/SiO$_2$ films, in order to obtain the intrinsic properties of the MoS$_2$ channel and contact performances. However, as shown in Fig. 7, it is confirmed that the contact resistances were dramatically reduced by FG annealing, as compared to the contribution of APM cleaning.

To investigate the contact interface before and after FG annealing, a TOF-SIMS analysis was performed. Figures 8(a) and 8(b) show the TOF-SIMS depth profiles for the special sample structure of Al$_2$O$_3$/MoS$_2$/TiSi$_2$/poly-Si/SiO$_2$/Si stacks. As shown in Fig. 8(a), the peaks of profiles on H and OH were enhanced only in Al$_2$O$_3$ film after FG annealing with H$_2$ gas, in contrast with the $^{34}$S, Si$_4$, and Al$_2$O$_3$ ones. Generally, H and OH-group terminations to dangling bonds in an ALD-Al$_2$O$_3$ film are reduced by the thermal annealing in inactive gases. However, in the case of FG annealing, it is consistent with previous reports which describe that dangling bond terminations with hydrogen were found. Therefore, FG annealing is an effective process for the reduction of fixed charges in the Al$_2$O$_3$ film by introducing not only H but also OH-group. As shown in Fig. 8(b), the Ti diffusion was found after FG annealing, in contrast with the Mo, Si, and Al$_2$O profiles. Here, the TiSi$_2$ film has a metastable state of C$_{49}$-TiSi$_2$ formed at 680 °C in this study. This result is consistent with that of a previous study, according to which a Ti film reacts with a MoS$_2$ film. Therefore, the Ti diffusion easily occurred at the interface between the MoS$_2$ and the metastable C$_{49}$-TiSi$_2$ films. As mentioned above, it is considered that a carrier density of the MoS$_2$ channel was reduced with an increase in the annealing temperature up. In the case of metal/MoS$_2$ interface, the increase in the Schottky barrier width in a MoS$_2$ film was found because of the decrease in carrier density, resulting in the increase in contact resistance. However, due to the Ti diffusion, defects were introduced to the MoS$_2$ film around the TiSi$_2$ contact. The carrier transport effectively enhanced via these defect states, therefore the contact resistance decreased with the increase in annealing temperature up to 650 °C. On the other hand, above 700 °C, as shown in Fig. 7, the Schottky contact was observed and the contact resistance increased. If we assumed in the case of excessive Ti diffusion that the contact interface became MoS$_2$/Ti-contained-MoS$_2$/Si-rich-TiSi$_2$/TiSi$_2$ and the Si-rich-TiSi$_2$ layer act as the Schottky barrier, the thickness of the Si-rich-TiSi$_2$ layer and the width of the Schottky barrier might increase during higher temperature annealing. Therefore, the contact resistance increased when the annealing temperature increased from 700 °C to 800 °C. Eventually, the FG annealing at 650 °C leads the lowest contact resistance in this study.

In order to investigate the contact structure and thickness of each film, cross-sectional TEM images of the TLM device after FG annealing were obtained. As shown in Fig. 9(a), a self-aligned-TiSi$_2$ film synthesized at the poly-Si surface is observed with the thickness about 20–30 nm. In addition, a layered-MoS$_2$ film is observed even at the side of the TiSi$_2$ contact. This result indicates that high coverage of a MoS$_2$ film was obtained on three-dimensional structures by sputtering deposition. Since the observed roughness in fluences the electrical properties of the MoS$_2$ film, such as carrier mobility and density, as shown in Fig. 9(b), the device fabrication process needs to be improved, in order to enhance the device performances.

4. Conclusions
The electrical characteristics of a self-aligned-TiSi$_2$ bottom-contact for sputtered-MoS$_2$ devices with APM cleaning and post-annealing in FG ambient were demonstrated, based on a
lower work function and high oxidation resistance. A two-order reduction in the contact resistance was achieved by FG annealing at 650 °C, because of the Ti diffusion through the interface of the contact. This TiSi2 contact can be practically applicable for n-type MoS2 channel MOSFETs.

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**ORCID iDs**

Masaya Hamada https://orcid.org/0000-0002-5830-5283

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