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Improvement of the stability and optoelectronic characteristics of molybdenum disulfide thin-film transistors by applying a nitrocellulose passivation layer

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1. Introduction

Transition metal dichalcogenides (TMDs) have received considerable attention as one of the most promising semiconductor materials for the fundamental driving or sensing unit device of the next-generation nanoelectronics. Among the various TMDs, molybdenum disulfide (MoS₂) is one of the most investigated until now due to its outstanding characteristics, such as its high field effect mobility, high current on/off ratio, desirable bandgap (1.2–1.9 eV), and possibility of visible-light detection [1–3]. Therefore, MoS₂ is evaluated to be a potential material applied to various applications like the backplane of active-matrix displays, integrated circuits, solar cells, photosensors, and optoelectronic devices [4–6].

MoS₂ and other TMDs have some limitations, however, with regard to commercialization as electronic devices. The fabrication process of monolayer, bilayer, and trilayer MoS₂ requires a complex technique, elaborate bonding and crystal control, and uniformity over a large area. Considering these points, multilayer MoS₂ can resolve such issues due to its relatively simple fabrication process, higher density of states, wider spectral response in light detection, and higher electrical characteristics when applied to thin-film transistors (TFTs) [2,7]. Although multilayer MoS₂ can be adopted as the channel of the TFT, there are still unresolved issues with regard to commercialization. The multilayer-MoS₂-based TFT has disadvantages, such as low stability derived from the inherent defects, which are hard to control and are non-uniform; vulnerability against water (H₂O) and oxygen (O₂) from the atmosphere, which degrade the conductivity and field effect mobility; and the hysteresis effects among the transfer characteristics [8,9].

To minimize the aforementioned severe obstacles in the device reliability, a number of studies regarding passivation or encapsulation layers that can protect the surface of the MoS₂ channel layer have been reported [1,9–11]. A representative fabrication method of the passivation layer is the deposition of inorganic materials like Si₃N₄, Al₂O₃, and HfO₂ by vacuum equipment at a high temperature.

In this research, a novel nitrocellulose passivation layer is suggested for improving the stability of MoS₂ TFTs. Nitrocellulose is an organic material conventionally used as a bandage to protect wounds on the skin, as a lacquer, as nail polish, and as a material for protecting other materials due to its high waterproof characteristic,
high flexibility, and biocompatibility [12]. Unlike the previous studies, the proposed passivation layer does not need vacuum equipment, high-temperature deposition, and a complex fabrication process. Furthermore, improvements in the electrical characteristics and photodetection originating from the interaction between nitrocellulose and MoS2 are also expected. Therefore, this facile and multifunctional passivation technology has a strong potential to be applied for unstable multilayer MoS2 TFTs.

2. Experiment

2.1. Preparation of nitrocellulose solution for the passivation layer

Generally, nitrocellulose is fabricated through a nitration process that exchanges hydroxyl groups (–OH) with nitro ester groups (–ONO2–), which improve the water resistance characteristics. In this study, to prepare nitrocellulose solution, a viscous collodion solution composed of nitrocellulose powder and two solvents of ethanol and diethyl ether was diluted by adding more ethanol solvent. To optimize the viscosity of the nitrocellulose solution for uniform spin coating, the ratio of diluted collodion was adjusted. With reference to the previous research, the finalized volumetric ratio of the nitrocellulose solution was 1:5 (collodion:ethanol) [13,14].

2.2. Fabrication process of nitrocellulose-passivated multilayer MoS2 TFTs

First, multilayer MoS2 flakes were mechanically exfoliated from bulk MoS2 crystals (SPI crystals) using Scotch tape. The exfoliated multilayer MoS2 flakes were then transferred onto cleaned heavily-boron-doped silicon (p+-Si) wafers with a 300-nm-thick thermally grown silicon dioxide (SiO2) layer. The width, length, and thickness of the deposited multilayer MoS2 channel layer were 15, 10, and 40 nm, respectively, as shown in Figure 1(b). Then 20-nm-thick Ti and 100-nm-thick Au layers were sequentially stacked as source/drain electrodes through electron beam evaporation. Such electrodes were patterned through conventional photolithography. To achieve the appropriate semiconducting electrical performance of the multilayer MoS2 TFTs, the device was annealed in a furnace at 300°C, in N2 ambient. Additionally, a 25-nm-thick nitrocellulose passivation layer was deposited on the MoS2 TFT by spin-coating nitrocellulose solution with 3000 revolutions per minute (rpm) for 30 s. This spin-coating speed was the optimized condition based on the electrical characteristics of MoS2 TFTs with different nitrocellulose passivation layers, which were spin-coated at 1000–5000 rpm, as shown in Figure 1(c). Finally, the bottom-gate staggered MoS2 TFT with a nitrocellulose passivation layer was fabricated, and the post-annealing process was conducted in air at 120°C for 5 min to form a uniform nitrocellulose thin film, as shown in Figure 1(a).

2.3. Measurements

The electrical characteristics of multilayer MoS2 TFTs were measured by a semiconductor parameter analyzer (model HP 4156C, Agilent Technologies) at room temperature, in dark and ambient conditions. All the transfer characteristics in this study were measured at a 1 V drain voltage (VDS). Additionally, for the purpose of measuring the optoelectrical characteristics, red, green, and blue diode laser sources with 635, 532, and 405 nm wavelengths at 1, 2, 3, and 4 mW/mm² power intensities were used for illumination. The time-dependent photoresponse of a MoS2 TFT was measured by applying a 0.025 Hz red laser pulse (635 nm, 1 mW/mm²). The applied positive-bias temperature stress (PBTS) conditions for measuring the electrical stability of the MoS2 TFTs were a 40 V gate voltage (VGS) and a 50°C temperature for 120 min.

3. Results and discussion

The static contact angle between the deionized (DI) water and the surfaces of the MoS2 and nitrocellulose layers was measured to demonstrate the physical blocking effect
Figure 2. Results of the contact angle measurement with 2 μL deionized water on (a) the MoS2 layer and (b) the nitrocellulose layer.

of the nitrocellulose layer in Figure 2. In the case of the MoS2 layer, the contact angle was 45.7°, indicating relative hydrophilicity. With the surface of the nitrocellulose layer, however, the contact angle was 77.2°, which shows improved waterproof characteristics. Therefore, the devised passivation layer acted as a protection layer against H2O.

In Figure 3(a,b), the MoS2 TFTs without and with a nitrocellulose passivation layer were subjected to harsh PBTS conditions to evaluate the device stability. The threshold voltage (Vth) shifts of the MoS2 TFTs without and with a passivation layer were 11.43 and 4.80 V, respectively, in ambient atmosphere. The reliability of the MoS2 TFT was improved by about 58% compared to a pristine device, by simply stacking the nitrocellulose layer. Additionally, the transfer characteristics of the MoS2 TFT without a nitrocellulose passivation layer were measured under the PBTS condition in a H2O- and O2-free atmosphere (in vacuum). The threshold voltage shift of the device was 5.79 V. These results indicate that the nitrocellulose thin film has outstanding barrier effects to prevent the adsorption of H2O and O2 at the surface of the MoS2 active layer, which act as acceptor-like states [10,13]. Moreover, the PBTS test results have considerable significance from the viewpoint of the unconventional method for verifying the device stability and the unprecedented harsh condition (the gate voltage bias of 40 V for 120 min). The PBTS test is a rare method and is even rarer in the case of the MoS2 TFT stability measurements.

To further evaluate the device stability, the hysteresis values of the pristine and nitrocellulose-passivated MoS2 TFTs, among their transfer characteristics, were compared. The forward sweep of the gate voltage from −50 to 50 V was biased at first, and then the reverse sweep of the gate voltage from 50 to −50 V was biased with a 1 V constant drain voltage. There was clockwise hysteresis in both devices, which indicates that a number of
Figure 4. Transfer characteristics of the MoS$_2$ TFTs without nitrocellulose passivation under (a) red-, (b) green-, and (c) blue-light illumination at different intensities, and with nitrocellulose passivation under (d) red-, (e) green-, and (f) blue-light illumination at different intensities.

Figure 4(a–c) show the transfer curves of the MoS$_2$ TFTs without nitrocellulose passivation under red (635 nm), green (532 nm), and blue (405 nm) laser illumination, respectively, at a 1 V drain voltage. They showed little change in the transfer characteristics under visible-light illumination. The MoS$_2$ TFTs with a nitrocellulose passivation layer, however, exhibited drastic changes between the drain current in a dark state ($I_{\text{dark}}$) and that under illumination ($I_{\text{illuminated}}$) in the off-current region, as shown in Figure 4(c–e). From these results, it was confirmed that the nitrocellulose passivation layer helps improve visible-light absorption and detection. There are figures of merit that can be extensively used to evaluate the photodetection performances: photoresponsivity ($R$), photosensitivity ($PS$), and detectivity ($D^*$).

$$R = \frac{I_{\text{photo}}}{P}$$  \hspace{1cm} (1)

$$PS = \frac{I_{\text{photo}}}{I_{\text{dark}}}$$  \hspace{1cm} (2)

$$D^* = \frac{R}{(2q)^{1/2}}$$  \hspace{1cm} (3)

It was assumed that the shot noise from the dark current is the main contribution when calculating $D^*$. $I_{\text{photo}}$ is the photocurrent density, $P$ is the incident light power density, photocurrent ($I_{\text{photo}}$) = $I_{\text{illuminated}}$–$I_{\text{dark}}$, $q$ is the absolute value of the electron charge ($1.6 \times 10^{-19}$ C), and $I_{\text{dark}}$ is the current density in a dark state [15–17].

To compare the optoelectronic characteristics of the fabricated TFTs, the $R$, $PS$, and $D^*$ of each device were calculated as a function of the gate voltage in Figure 5(a–c). Especially, the photosensitivity increased much compared to the other figures of merit when the nitrocellulose layer was passivated on the MoS$_2$ TFT. The reason for
Figure 5. (a) Photoresponsivity, (b) photosensitivity, and (c) detectivity of the MoS$_2$ TFT with a nitrocellulose passivation layer under red-light (635 nm) illumination at 1 mW/mm$^2$, as a function of the gate voltage. (d) Time-dependent photoresponse characteristics of the MoS$_2$ TFT with a nitrocellulose passivation layer under periodic dark and light illumination conditions.

this was that the distinguished current difference between $I_{dark}$ and $I_{illuminated}$ mainly existed in the depleted condition (negative gate voltage region). The maximum values of $R$, $PS$, and $D^*$ under red light increased 1.51, 6.08, and 1.95 times, respectively, according to the nitrocellulose passivation (Table 1). In Figure 5(d), the time-dependent photoresponse characteristics were measured according to specific illumination conditions. The red light was periodically switched on and off for 20 s, respectively, at 1 mW/mm$^2$ intensity. The drain current was measured at $V_{GS} = -10$ V and $V_{DS} = 1$ V. The nitrocellulose-passivated MoS$_2$ TFT exhibited an instant response to the light stress, with a fast rising time and a fast falling time as well as a higher drain current under the same conditions. As a result, the proposed device had reversible and immediate characteristics between the light-on and light-off states, which are appropriate performances for the use of the proposed device as a photodetector.

The mechanism of enhanced photodetection ability in the nitrocellulose-passivated MoS$_2$ TFTs is shown in Figure 6. Nitrogen atoms from the nitro ester groups in nitrocellulose diffuse into the MoS$_2$ film, and then the lone pair electron of nitrogen leads to form bonds with the Mo atoms that have lost their bond with the S atoms. It was already confirmed that Mo-N bonds generate subgap states (trap sites) into the bandgap, which are mainly distributed near the valence band maximum energy level, the deep-level states, in the authors’ previous studies [5,18]. If the Mo-N bonds mainly generated shallow-level states, the PBTS stability of the device could be severely degraded. The PBTS test results of the MoS$_2$ TFT with nitrocellulose passivation in ambient atmosphere, however, exhibited greater stability than the MoS$_2$ TFT without passivation in a H$_2$O- and O$_2$-free atmosphere. This result demonstrates that the Mo-N bonds from nitrocellulose rarely generate shallow-level states. The newly formed subgap states can provide more photoexcitation routes for the electrons in the valence band. The higher probability of photoexcitation leads to the generation of more electrons in the MoS$_2$ active layer under illumination stress [17,19]. As a result, in this study, a number of photoexcited carriers amplified the optoelectronic characteristics.

From the electrical characteristics summarized in Table 1, the field effect mobility and on/off current ratio in the dark state were heightened 1.13 and 3.05 times, respectively. The aforementioned increase in drain current and the improved field effect mobility were due to the
Table 1. Optoelectronic characteristics of the MoS$_2$ TFTs without and with a nitrocellulose passivation layer.

<table>
<thead>
<tr>
<th>MoS$_2$ TFT</th>
<th>In the dark</th>
<th>Under red light (635 nm, 10 mW/mm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu$E (cm$^2$ V$^{-1}$ s$^{-1}$)</td>
<td>$V_{TH}$ (V)</td>
</tr>
<tr>
<td>W/o NC PVX</td>
<td>3.84</td>
<td>$8.81 \times 10^2$</td>
</tr>
<tr>
<td>W/ NC PVX</td>
<td>4.33</td>
<td>$2.69 \times 10^3$</td>
</tr>
</tbody>
</table>

comprehensive factors. Firstly, preventing the adsorption of the external molecules on the channel and oxidation in the channel made the MoS$_2$ channel sustain higher conductivity compared to the non-passivated MoS$_2$ channel [11]. Secondly, the non-patterned nitrocellulose layer on the channel may lead to a slight increase in the on current. Although nitrocellulose is not a conductive material, it can provide an electron path, such as a leakage current, in a narrow area between the electrodes when a thin-film state exists. Finally, the lowered contact resistance from the narrowed Schottky barrier between the metal electrode and the MoS$_2$ active layer was affected. The Schottky barrier between the metal electrode and the multilayer TMD layer leads to a high contact resistance, and this is one of the representative inherent drawbacks in TMD-based TFTs [20]. In the case of nitrocellulose-passivated multilayer MoS$_2$ TFTs, the nitrocellulose layer, which has inherent electrical polarity and relatively high polarizability, exists as positive interface dipoles at the surface of n-type MoS$_2$ channel [15]. It is acceptable that the positive dipoles at the interface between the nitrocellulose and the MoS$_2$ induced a quasi-Fermi level move towards the conduction band [19]. This energy level formation could thus reduce the Schottky barrier width, and thereafter, the electrons could tunnel through the narrowed barrier, as shown in Figure 6.

4. Conclusion

The nitrocellulose material was suggested as a passivation layer to improve the electrical stability of multilayer molybdenum disulfide (MoS$_2$) thin-film transistors (TFTs). This novel passivation layer effectively blocked the adsorption of H$_2$O and O$_2$ at the surface of the MoS$_2$ active layer, which led to a reduced $V_{TH}$ shift under the positive-bias temperature stress (PBTS) tests, and hysteresis. In addition to the improved reliability, the nitrocellulose passivation layer provided more functions: (1) improving the performance of photodetection in the visible-light region by the generated subgap states; and (2) decreasing the contact resistance by the narrowed Schottky barrier from the positive dipoles at the interface between the nitrocellulose and MoS$_2$ layers. As a consequence, the multifunctional nitrocellulose passivation layer can be applied to MoS$_2$ TFTs, which have a potential to be used for the next-generation electronics, such as a backplane of flexible displays and a photosensor of an Internet of Things (IoT) device.
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