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

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ABSTRACT

Nitrocellulose is proposed as a passivation layer for multilayer molybdenum disulfide (MoS2) thin-film transistors (TFTs) to improve the stability of the devices. After the devised passivation layer was stacked, the threshold voltage shift of the nitrocellulose-passivated MoS2 TFT after the positive-bias temperature stress tests decreased from 11.43 to 4.80 V. This enhanced stability was the result of the protection of the MoS2 channel from external reactive molecules like H2O, O2, and others in the atmosphere. Not only the stability was improved; the electrical performance was also enhanced. The field effect mobility and on/off ratio increased 1.13 and 3.05 times, respectively, due to the narrowed width of the Schottky barrier from the interfacial dipoles between the nitrocellulose and the MoS2 layers. Additionally, the formation of Mo-N bonding generated deep-level subgap states into the bandgap, which led to a higher probability of photoexitation. Therefore, the MoS2 TFT with a nitrocellulose passivation layer exhibited 202.35 A/W enhanced photoresponsivity, $1.83 \times 10^3$ photosensitivity, and $9.94 \times 10^9$ Jones detectivity under 635 nm light at 10 mW/mm2.

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 MoS$_2$ are also expected. Therefore, this facile and multifunctional passivation technology has a strong potential to be applied for unstable multilayer MoS$_2$ 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 (–ONO$_2$–), 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 MoS$_2$ TFTs

First, multilayer MoS$_2$ flakes were mechanically exfoliated from bulk MoS$_2$ crystals (SPI crystals) using Scotch tape. The exfoliated multilayer MoS$_2$ flakes were then transferred onto cleaned heavily-boron-doped silicon (p$^+$-Si) wafers with a 300-nm-thick thermally grown silicon dioxide (SiO$_2$) layer. The width, length, and thickness of the deposited multilayer MoS$_2$ 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 MoS$_2$ TFTs, the device was annealed in a furnace at 300°C, in N$_2$ ambient. Additionally, a 25-nm-thick nitrocellulose passivation layer was deposited on the MoS$_2$ 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 MoS$_2$ 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 MoS$_2$ 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 MoS$_2$ 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 (V$_{DS}$). 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/mm$^2$ power intensities were used for illumination. The time-dependent photoresponse of a MoS$_2$ TFT was measured by applying a 0.025 Hz red laser pulse (635 nm, 1 mW/mm$^2$). The applied positive-bias temperature stress (PBTS) conditions for measuring the electrical stability of the MoS$_2$ TFTs were a 40 V gate voltage (V$_{GS}$) 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 MoS$_2$ 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 MoS\textsubscript{2} layer and (b) the nitrocellulose layer.

The contact angle measurement with 2 μL deionized water on the MoS\textsubscript{2} layer and the nitrocellulose layer is shown in Figure 2. In the case of the MoS\textsubscript{2} 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 H\textsubscript{2}O.

In Figure 3(a,b), the MoS\textsubscript{2} TFTs without and with a nitrocellulose passivation layer were subjected to harsh PBTS conditions to evaluate the device stability. The threshold voltage (V\textsubscript{th}) shifts of the MoS\textsubscript{2} TFTs without and with a passivation layer were 11.43 and 4.80 V, respectively, in ambient atmosphere. The reliability of the MoS\textsubscript{2} TFT was improved by about 58% compared to a pristine device, by simply stacking the nitrocellulose layer. Additionally, the transfer characteristics of the MoS\textsubscript{2} TFT without a nitrocellulose passivation layer were measured under the PBTS condition in a H\textsubscript{2}O- and O\textsubscript{2}-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 H\textsubscript{2}O and O\textsubscript{2} at the surface of the MoS\textsubscript{2} 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 MoS\textsubscript{2} TFT stability measurements.

To further evaluate the device stability, the hysteresis values of the pristine and nitrocellulose-passivated MoS\textsubscript{2} TFTs, among their transfer characteristics, were compared. The forward sweep of the gate voltage from −50 to 50 V was biased 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
electrons are trapped in multilayer MoS2 TFTs. As it is widely known that H2O and O2 adsorption onto the surface of the MoS2 channel leads to a large hysteresis, it was assumed that the trapping of electrons in the devices was mainly due to the above-mentioned acceptor-like states from the H2O and O2. In Figure 3(c,d), the hysteresis was slightly reduced when the device was passivated by nitrocellulose. As a result, H2O and O2 could be efficiently prevented from adsorption at the surface of the MoS2 layer. The reason for the slight decrease in hysteresis, however, may be the difficulty of reducing the trap sites in the front channel region of multilayer MoS2 by passivating the backchannel region. Furthermore, it was found that the drain current was increased after the passivation of nitrocellulose; this phenomenon will be discussed later.

Figure 4(a–c) show the transfer curves of the MoS2 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 MoS2 TFTs with a nitrocellulose passivation layer, however, exhibited drastic changes between the drain current in a dark state (Idark) and that under illumination (Iilluminated) 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*).

\[
R = \frac{J_{\text{photo}}}{P} \\
PS = \frac{I_{\text{photo}}}{I_{\text{dark}}} \\
D^* = \frac{R}{(2qI_{\text{dark}})^{1/2}}
\]

It was assumed that the shot noise from the dark current is the main contribution when calculating D*. \(J_{\text{photo}}\) 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 \((1.6 \times 10^{-19} \text{ C})\), 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 MoS2 TFT. The reason for
Figure 5. (a) Photoresponsivity, (b) photosensitivity, and (c) detectivity of the MoS2 TFT with a nitrocellulose passivation layer under red-light (635 nm) illumination at 1 mW/mm², as a function of the gate voltage. (d) Time-dependent photoresponse characteristics of the MoS2 TFT with a nitrocellulose passivation layer under periodic dark and light illumination conditions.

this was that the distinguished current difference between $I_{\text{dark}}$ and $I_{\text{illuminated}}$ 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/mm² intensity. The drain current was measured at $V_{GS} = -10$ V and $V_{DS} = 1$ V. The nitrocellulose-passivated MoS2 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 MoS2 TFTs is shown in Figure 6. Nitrogen atoms from the nitro ester groups in nitrocellulose diffuse into the MoS2 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 MoS2 TFT with nitrocellulose passivation in ambient atmosphere, however, exhibited greater stability than the MoS2 TFT without passivation in a H2O- and O2-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 MoS2 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.

|                | In the dark | Under red light (635 nm, 10 mW/mm$^2$) |
|----------------|-------------|---------------------------------------|
|                | $\mu_{FE}$ (cm$^2$ V$^{-1}$ s$^{-1}$) | On/off ratio | $V_{TH}$ (V) | Max. $R$ (A/W) | Max. $PS$ | Max. $D^*$ (Jones) |
| W/o NC PVX     | 3.84        | $8.81 \times 10^2$ | −6.08 | 133.63 | 3.01 $\times 10^2$ | 5.09 $\times 10^9$ |
| W/ NC PVX      | 4.33        | $2.69 \times 10^6$ | −6.30 | 202.35 | 1.83 $\times 10^3$ | 9.94 $\times 10^9$ |

Figure 6. Mechanism of improved stability, photodetection ability, and electrical characteristics in the nitrocellulose-passivated multilayer MoS$_2$ TFTs.

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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