Highly Flexible and Transparent Multilayer MoS$_2$ Transistors with Graphene Electrodes

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A highly flexible and transparent transistor is developed based on an exfoliated MoS$_2$ channel and CVD-grown graphene source/drain electrodes. Introducing the 2D nanomaterials provides a high mechanical flexibility, optical transmittance ($\sim$97.4%), and current on/off ratio ($>10^4$) with an average field effect mobility of $\sim$4.7 cm$^2$ V$^{-1}$ s$^{-1}$, all of which cannot be achieved by other transistors consisting of a MoS$_2$ active channel/metal electrodes or graphene channel/graphene electrodes. In particular, a low Schottky barrier ($\sim$22 meV) forms at the MoS$_2$/graphene interface, which is comparable to the MoS$_2$/metal interface. The high stability in electronic performance of the devices upon bending up to $\pm$2.2 mm in compressive and tensile modes, and the ability to recover electrical properties after degradation upon annealing, reveal the efficacy of using 2D materials for creating highly flexible and transparent devices.
Flexible and transparent electronics have not only added aesthetic value but allow for more versatility in the design and use of devices. Because a thinner material structure induces high values of mechanical flexibility and optical transparency, graphene and MoS2 should be excellent candidates for flexible and transparent electronics. For a switching device, a demonstration of the promising electrical properties of the 2D materials for an active channel and electrodes would be appealing. This paper demonstrates an example of using exfoliated MoS2 and graphene grown by chemical vapor deposition (CVD) to generate highly flexible and transparent transistors on a polyethylene terephthalate (PET) substrate. Here, we will discuss the versatility of using 2D materials to achieve the mechanical, optical, and electrical properties required for this type of device as studied by an electrical analysis and stability tests upon mechanical bending. In particular, because the interfacial barrier height between the active channel and electrodes should play an important role in the device performance, a detailed study on the contact between MoS2 and graphene is also provided.

2. Results and Discussion

Figure 1 illustrates the schematic flow for the fabrication of highly flexible and transparent transistors based on MoS2 and graphene. The process begins by exfoliating the multilayer MoS2 mechanically from the bulk using an adhesive tape and then placing the printing onto a highly doped n-type silicon substrate with a 100-nm-thick silicon dioxide (SiO2) layer (Figure 1a,b). Then, a patterned multilayer graphene is transferred on the MoS2 layer (Figure 1c). After coating a poly(methyl methacrylate) (PMMA) supporting layer (Figure 1d), etching the sacrificial SiO2 in buffered oxide etchant (BOE), J. T. Baker, Center Valley, Pa, USA) delaminates the PMMA layer together with the MoS2 channel and graphene electrodes without losing the alignment of the pattern array (Figure 1e). Finally, the PMMA layer is transferred onto various substrates containing gate and dielectric layers (Figure 1f). The detailed fabrication process is described in the Experimental Section.

Because the number of layers in the 2D materials is dependent on the conditions of the CVD (graphene) and exfoliation (MoS2), the thickness distribution of samples used in this study was confirmed by optical microscopy (OM) and Raman spectroscopy prior to device fabrication (see Supporting Information). In the case of graphene, the color distribution and corresponding ratio of 2D and G peaks indicate that the multilayers are randomly distributed as islands with a full factor of 46% in the sea of a small number of layers. For MoS2, judging from the OM image and the difference in the Raman shift between the E2g and A1g peaks, the average full factor was estimated to be 7% with the combination of a few layers and thick multiple layers on the substrate. Due to the nature of the exfoliation method, the number of films aligned between the source/drain as well as the dimensions of the films should be varied. From the OM images of the two sets of 14 × 7 transistor arrays used in this study, the range of the number of multilayer MoS2 films between the graphene electrodes was estimated to be from zero to 10, including a single flake with an occupancy of ∼22% (see Supporting Information). Although the representative MoS2 film shown in Figure 2a,b was diagonally aligned with some variations for thickness (58 ± 14.5 nm), width (1 to 3.9 μm), and length (5.5 to 7 μm), constant values for the length (4 μm) and width (3 μm) of the active channel were used for further device characterization. Figure 2c,d presents the electrical properties of the representative MoS2 transistor with a back gate configuration. Depletion type nMOS characteristics are typical behaviors of undoped MoS2, MOSFETs. The average field effect mobility (μFE), threshold voltage (Vth), and Ion/Ioff were estimated from 10 devices to be 5.9 ± 3.2 cm2 V−1s−1, −27.1 ± 1.7 V, and 3 ± 4.5 × 104, respectively. According to the literature, we believe that the mobility can be improved by optimizing the thickness (6–10 nm) of multilayer MoS2 film and using high-k dielectric layer such as Al2O3.

To understand the efficiency of charge injection at the interface of MoS2 (electron affinity of −4.3 eV) and graphene (work function of −4.6 eV), the change in the drain current versus drain voltage curves was monitored as a function of temperature from 140 to 300 K at VGS = −30 V (Figure 3a,b). To avoid the effects of a thermally assisted tunneling current resulting from the short tunneling distance of MoS2, the VGS near the turn-on voltage was selected for monitoring. Because the alignment of energy levels forms the Schottky contact, the injection barrier was estimated from><tex>\text{I} = AA^*T^2 \exp \left( - \frac{(\phi_B - q^4\sqrt{4\pi\varepsilon_0\varepsilon_r}\frac{V}{k_BT})}{k_B T} \right) \quad (1)</text>where A is the contact area, A* is the effective Richardson constant, \(\phi_B\) is the Schottky barrier height, q is the electron charge, V is the applied forward bias, \(\varepsilon_0\) and \(\varepsilon_r\) are the dielectric constant and relative permittivity, respectively, and kB is the Boltzmann constant. The Richardson-Schottky equation can provide a theoretical explanation of the thermal emission current as a function of temperature for a given barrier height. The experimental Richardson-Schottky plots for MoS2 and graphene are shown in Figure 3c,d. The Richardson-Schottky plots for MoS2 and graphene are shown in Figure 3c,d. The solid lines represent a fitting analysis of the experimental data reported in Figure 3a,b. The fitting results show the agreement between the experimental data and the theoretical model, indicating that the Schottky contact between MoS2 and graphene can be explained by the Richardson-Schottky equation.
permittivities of the vacuum and MoS$_2$, respectively, $d$ is the width of the interface barrier, $k_B$ is the Boltzmann constant, and $T$ is the temperature. From the slope of $\ln(I_0/T^2)$ versus $1/T$ in the simplified equation $^4$ $I = A^*T^2 \exp(-\Phi_B/k_B T)$ at $V = 0$, an average $\Phi_B$ was estimated to be $22 \pm 7$ meV at $V_{GS} = -30$ V for four different devices (Figure 3c). Here, $I_0$ values

Figure 2. a) Scanning electron microscopy (SEM) images of a multilayer MoS$_2$ transistor with the graphene source/drain electrodes on an SiO$_2$/Si substrate. a-inset) Magnified SEM image of the selected area. b-top) Atomic force microscopy (AFM) image of the selected region, including the multilayer MoS$_2$ active channel of the device. b-bottom) height profile of the selected line of the AFM image. c) $I_{DS-V_{GS}}$ and (d) $I_{DS-V_{DS}}$ characteristics of a representative MoS$_2$ transistor.

Figure 3. a,b) Temperature-dependent (a) $I_{DS-V_{GS}}$ (b) $I_{DS-V_{DS}}$ characteristics of a multilayer MoS$_2$ transistor with graphene source/drain electrodes. c) Arrhenius plots [ln($I_0/T^2$) versus 1000/T] from the $I_{DS-V_{GS}}$ curves in (a), where the Schottky barrier height ($\Phi_B$) was extracted from the slope of the dotted red line. d) Temperature-dependent normalized field effect mobility ($\mu_{FE}$) calculated from the $I_{DS-V_{DS}}$ curves in (b).
were extracted from the linear regions at low voltage range (i.e. 0.2–1 V) in the \( I_n \) versus \( V_{DS} \) curves. \[^{40}\] Compared to the barrier height of 300 meV by simple calculation, the lower \( \Phi_B \) presumably originates not only from a good adhesion, which arises from the small interlayer spacing, low binding energy, and few lattice mismatches, as expected from the computational simulation, \[^{41}\] but also from electrical doping by the gate bias or interface trap states. \[^{42–44}\] Judging from the comparable temperature were also examined by extracting the normalized mobility reaches its highest value (\( \mu = \frac{\text{FE}}{L} \)) and by the solid red oval line) and by \( \Phi_B \) values for Ni, \[^{42}\] Cr, \[^{43}\] Sc, \[^{37}\] and Ti, \[^{44}\] graphene should also be a good candidate for the electrode of an MoS\(_2\) transistor. 

Next, the charge transport characteristics as a function of temperature were also examined by extracting the normalized \( \mu_{FE} \) from Figure 3b at the gate voltages corresponding to the same electron concentration of \( n = C_{eq}(V_G-V_F) = -10^{12} \text{cm}^{-2} \). The mobility reaches its highest value (\( -1.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \)) at 200 K and decreases by \(-4\%\) from 180 to 140 K (marked by the solid red oval line) and by \(-10\%\) from 200 to 300 K (marked by the dashed blue oval line), as shown in Figure 3d. According to the literature \[^{24,45}\] it is believed that the former is due to ionized impurity scattering, while the latter is due to optical and acoustic phonon scattering.

Figure 4a displays highly flexible MoS\(_2\) transistors fabricated on a PET substrate coated with indium tin oxide (ITO) (see Supporting Information for other MoS\(_2\) transistors on a glass substrate). After patterning the bottom gate electrode, spin-coating and annealing a cross-linkable poly (4-vinyl phenol) (c-PVP, 400 nm) forms a gate dielectric layer. Next, placing the sample prepared in the step shown in Figure 1e on a PET film and removing PMMA using acetone generates the final device with 23 sets of graphene source/drain electrodes. The final device has an average optical transmittance of 74\% in the wavelength range between 400 and 800 nm, whereas PET in the same range exhibits \(-86\%\) average optical transmittance (Figure 4b). Figure 4c includes representative transfer curves (\( I_{DS}-V_{GS} \)) of the fabricated device. Based on the testing of ten different devices, the \( \mu_{FE} \), \( V_{th} \), and \( I_{ds}/I_{off} \) are found to be \( 4.7 \pm 3.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \), \(-12.2 \pm 3 \text{ V} \), and \( 4.8 \pm 4.9 \times 10^4 \) at \( V_{DS} = 0.5 \text{ V} \), respectively. The \( I_{DS}-V_{GS} \) curves have linear (see Supporting Information) and saturation regions in low and high \( V_{GS} \) ranges, respectively (Figure 4d). The former is attributed to the quasi-ohmic contact at the MoS\(_2\)/graphene interface, and the latter is from the channel pinch-off.

To investigate the mechanical stability of the MoS\(_2\) transistors, the changes in the relative values of \( \mu_{FE} \) and \( V_{th} \) were monitored as a function of the bending radius (\( r \)) and number of bending cycles from eight different devices, as shown in Figure 4e (see Supporting Information). Upon bending up to \(-2.2\) and \( 2.2 \text{ mm} \) (minus and plus signs denote compressive and tensile modes, respectively), the electronic performance was stable with only slight variations of \( \mu_{FE} \) (less than \( 6\% \)) and \( V_{th} \) (\( \pm 1.7 \text{ V} \)). Although we observed some changes in \( \mu_{FE} \) (30\% decrease) and \( V_{th} \) (difference: \(-8.9 \text{ V} \)) after bending cycles of up to 10,000 between \( r = \infty \) and 2.7 mm, such degradation was recovered by annealing at 200 °C for 2 h. We believe that the electrical degradation originates from water or oxygen molecules adsorbed onto the surface of the MoS\(_2\) film rather than from an irreversible reaction; a similar behavior in other MoS\(_2\) transistors with metal electrodes has also been reported. \[^{44,46}\]

### 3. Conclusion

We successfully developed ultrathin transistors on a PET substrate with \( \mu_{FE} = 4.7 \pm 3.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \), \( V_{th} = -12.2 \pm 3 \text{ V} \), \( I_{ds}/I_{off} = 4.8 \pm 4.9 \times 10^4 \), and transmittance = \(-74\%\) by using exfoliated MoS\(_2\) channel and CVD-grown graphene source/drain. The low Schottky barrier height at the MoS\(_2\)/graphene interface makes graphene an appealing candidate for the replacement of opaque and rigid metals. The high stability of electrical properties at bending radii of \( \pm 2.2 \text{ mm} \) and the ability to recover electrical properties after degradation upon annealing reveal the efficacy of using 2D materials for creating highly flexible and transparent devices.

### 4. Experimental Section

The detailed growth and pattern processes of multilayer graphene films to form source/drain electrodes are shown in the Supporting Information. We used growing methods similar to those reported elsewhere in the literature. \[^{47}\]

**Fabrication of Multilayer MoS\(_2\) Transistors on SiO\(_2\)/Si:** A channel layer was formed by exfoliating multilayer MoS\(_2\) films from the bulk (SPI Supplies) using adhesive 3M tape and transferring the films onto a highly doped n-type silicon substrate of thermally oxidized SiO\(_2\) (thickness: 100 nm). Next, placing the patterned graphene with the PMMA supporting layer and drying at 50 °C for 30 min laminated the different 2D materials. After removing the PMMA by a cleaning process in acetone, methanol, and deionized (DI) water, annealing at 200 °C for 2 h in a flow of N\(_2)/H\(_2\) (4%) finished the fabrication of the bottom gate MoS\(_2\) transistors (see Supporting Information).

**Fabrication of Multilayer MoS\(_2\) Transistors on a PET Substrate:** After spin-coating PMMA onto the bottom gate MoS\(_2\) transistors, etching the SiO\(_2\) sacrificial layer in a BOE solution delaminated the PMMA layer with the MoS\(_2\) channel and graphene electrodes. Placing the PMMA layer onto the PET substrate contained a patterned ITO gate electrode and c-PVP gate dielectric layer (400 nm, \( \varepsilon_r = 3.6 \)), followed by a cleaning process in acetone, methanol, and DI water, generated highly flexible and transparent MoS\(_2\) transistors. The patterned gate electrode was prepared by photolithography and wet etching in an ITO etchant. The gate dielectric layer was formed by spin-coating the mixture solution of PVP powder (10 wt\%) and poly(melamine-co-formaldehyde) methylated (5 wt\%) in propylene glycol monomethyl ether acetate (PGMEA) and annealing at 180 °C for 2 h. After all device fabrication, the final MoS\(_2\) transistors on a PET substrate were annealed at 200 °C for 2 h in a flow of N\(_2)/H\(_2\) (4%).

**Measurement of the Devices:** The electronic characteristics of all fabricated MoS\(_2\) devices were evaluated using a semiconductor parameter analyzer (Agilent B1500A, Agilent Technologies, Santa Clara, CA, USA, and Keithley 4200, Keithley Instruments, Inc., Cleveland, OH, USA). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images were obtained with a Hitachi S-4700 microscope (Hitachi, Ltd., Tokyo, Japan) and a Park Systems XE-100 (Park Systems Corp., Suwon, Korea), respectively. The optical transmittance was measured by an absorption spectrophotometer (Lambda 750, Perkin Elmer Inc., Waltham, MA, USA).

**Calculation for Field-Effect Mobility:** The field effect mobility (\( \mu_{FE} \)) was determined using the following equation. \[^{19}\]

\[
\mu_{FE} = \frac{\text{FE}}{W \cdot L \cdot V_{DS}}
\]
where $L$ is the channel length, $g_m$ is the transconductance ($dI_{DS}/dV_{GS}$), $W$ is the channel width, $C_{ox}$ is the gate oxide capacitance, and $V_{DS}$ is the drain voltage.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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