Chemical Doping Effects on CVD-Grown Multilayer MoSe₂ Transistor

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Multilayer transition metal dichalcogenides (TMDs) potentially provide opportunities for large-area electronics, including flexible displays and wearable sensors. However, most TMDs suffer from a Schottky barrier (SB) and nonuniform defects, which severely limit their electrical performances. Here, a novel chemical doping scheme is presented using poly-(diketopyrrolopyrrole-thiophene) (PDPP3T) to compensate the defects and SB of multilayer molybdenum diselenide (MoSe₂), exhibiting greatly enhanced electrical characteristics, including on-current (≈2000-fold higher) and photoresponsivity (≈10-fold larger) over the baseline MoSe₂ device. Based on comprehensive analysis using X-ray photoelectron spectroscopy, grazing incidence wide-angle X-ray diffraction, atomic force microscopy, and near-edge X-ray absorption of fine structure, it is shown that two mechanisms (dipole-induced and charge-transfer doping effects) account for such enhancements in the multilayer MoSe₂ device. The methodical generality of the strong n-doping behavior of multilayer MoSe₂ is further demonstrated by applying thiophene instead of PDPP3T.

1. Introduction

Over the last few decades, active matrix (AM) organic lighting-emitting diodes (OLEDs) have been extensively developed in preparation for future conformable products and commercial OLED displays.[1] The flexible organic layers in self-illuminating OLEDs offer many advantages over conventional liquid crystal displays (LCDs), such as a superior viewing angle, high brightness and contrast, fast response time, and flexibility.[2] OLEDs are composed of individual image elements called pixels and are driven by an electric current (≈1–5 μA pixel⁻¹) from an AM backplane (AMB). An AMB containing at least one switching transistor, at least one driving transistor, and a capacitor can turn on a selective pixel without scanning an entire array, which provides superiority for moving images.[3] Therefore, thin-film transistors (TFTs) for the AMB are required to have a minimum mobility of >20 cm² V⁻¹ s⁻¹ to satisfy charging rate and driving current specifications. Thus, searching for thin-film semiconducting materials with high carrier mobilities and mechanical flexibilities is the major pursuit toward the realization of next-generation displays.

During the past decade, 2D layered materials from natural bulk materials have been the subject of intensive research due to their high carrier mobilities (μeff), low subthreshold slopes, and robust mechanical flexibilities against mechanical stress, such as cyclic or static bending.[4–9] However, significant challenges still exist to achieve reproducible large-area growth to realize high-yield integrated circuitry. Recently, several research groups have reported transition metal dichalcogenides (TMDs), such as molybdenum disulfide (MoS₂) or molybdenum diselenide (MoSe₂), synthesized by various methods, including thermal chemical vapor deposition (CVD) with subsequent sulfurization of MoO₃ microbelts,[10] the sulfurization of substrates precoated with MoO₃ or Mo films,[11,12] the reaction of MoO₃ and H₂S gas (instead of S[13] or Se powders[14]), a modified method using a vertical tube furnace,[8] and the reaction of MoO₃ powder and Se pellets under atmospheric pressure,[15,16] which allow for the synthesis of high-quality monolayer MoSe₂ with large-scale dimensions.[17,18] However, the reported CVD-grown MoSe₂ transistors have shown poor device performances with relatively low μeff (typically < 20 cm² V⁻¹ s⁻¹)[19–22] and nonuniform doping concentrations with respect to Se vacancies[8,20,23] compared with pristine MoS₂ bulk single crystals. The characteristics are mostly due to large number of defects in the multilayer MoSe₂.[20] Thus, there is a pressing need to develop a scheme to compensate defects and improve the electrical properties of multilayer MoSe₂ for practical electronic applications.

Many research groups have adopted chemical doping techniques using substitution and/or charge transfer.[24,25] Compared with substitutional doping techniques using a metal or inorganic element under high temperature, charge-transfer doping using organic materials exhibits several advantages,
including low-cost processing and large-area coverage, which can be easily applied to not only as-synthesized materials but also as-fabricated devices. Joo and co-workers reported the optical property variations in mechanically exfoliated or CVD-grown single-layer MoS$_2$ hybridized with $\pi$-conjugated organic small molecules (i.e., rubrene and tris(8-hydroxyquinoline) aluminium)$^{[26,27]}$. Park and co-workers reported that the opto-electronic characteristics of mechanically exfoliated tungsten diselenide-, MoS$_2$-, and rhenium diselenide-based semiconductor devices can be enhanced by chemical doping with octadecyltrichlorosilane$^{[28]}$, 3-aminopropyl triethoxysilane$^{[29]}$, or triphenylphosphine$^{[30]}$.

Here, we present a doping technique for CVD-grown multilayer MoSe$_2$ TFTs via spin coating of poly-(diketopyrrolopyrrole-terthiophene) (PDPP3T) followed by thermal annealing. This technique results in strong n-type multilayer MoSe$_2$ with high device performances ($\mu_{\text{eff}} > 75$ cm$^2$ V$^{-1}$ s$^{-1}$, $I_{\text{on}}/I_{\text{off}} > 10^5$) and superb photoresponsive characteristics (photoresponsivity $> 91.2$ AW$^{-1}$). Comprehensive analysis based on X-ray photoelectron spectroscopy (XPS), 2D grazing incidence wide-angle X-ray diffraction (2D GIWAXD), and other supporting spectroscopy techniques reveals that PDPP3T induces strong n-doping phenomena based on molecular dipole and charge-transfer effects at an annealing temperature ($T_A$) of 300 °C. These features lead to considerable improvements in the on-current ($\approx 2000 \times$ higher) and photoresponsivity ($\approx 10 \times$ larger) over the baseline (i.e., as-synthesized) multilayer MoSe$_2$ TFTs.

2. Results and Discussion

2.1. Synthesis of Multilayer MoSe$_2$

As a prestep for the implementation of the PDPP3T doping scheme, we first synthesized multilayer MoSe$_2$ using high-pressure CVD growth. Figure 1a shows a schematic illustration of the multilayer MoSe$_2$ synthesis. During the chemical reaction of MoO$_3$ and Se radicals, hexagonal MoSe$_2$ is layer-by-layer synthesized. High-pressure CVD growth (>760 torr) in the reaction chamber results in a higher nucleation rate and allows MoSe$_2$ to form more than 20 unit crystal layers.$^{[8,20]}$ The synthesis details are given in the Experimental Section. A top-view image of the hexagonal MoSe$_2$ crystal is shown in Figure 1b. Based on the hexagonal crystal structure, tens of MoSe$_2$ layers (>50 L) can be formed. A transmission electron microscopy (TEM) image of the cross-section of an as-synthesized MoSe$_2$ crystal clearly confirms the stacked multilayers of MoSe$_2$ (Figure 1c). The energy-dispersive X-ray spectroscopy (EDS) mapping (Figure 1d) shows a uniform distribution of Mo and Se in the cross-section view, which is also supported by the binding energy peaks of

\[ \text{Mo Ka1} \quad \text{Se Ka1} \]

Figure 1. Synthesis of hexagonal multilayer MoSe$_2$. a) Schematic process for the preparation of hexagonal multilayer MoSe$_2$. b) Top-view optical microscopy image of as-synthesized multilayer MoSe$_2$. c) Cross-sectional TEM image of as-synthesized multilayer MoSe$_2$. d) Cross-sectional EDS mapping of the Mo and Se distributions for as-synthesized multilayer MoSe$_2$. 
Mo 3d and Se 3d in multilayer MoSe₂ XPS spectra (Figure S1, Supporting Information). Further material characterizations of the multilayer MoSe₂ are given in Figure S2 in the Supporting Information.

2.2. Fabrication of the Hybrid PDPP3T-Multilayer MoSe₂

Next, we prepared the hybrid PDPP3T-multilayer MoSe₂ sample by spin coating PDPP3T in an o-dichlorobenzene (ODCB) solution on top of the as-synthesized multilayer MoSe₂. Figure 2a shows an illustration of the fabrication process for the hybrid PDPP3T-multilayer MoSe₂. PDPP3T is a donor–acceptor conjugated polymer and has strong planarity resulting from the unsubstituted terthiophene and diketopyrrolopyrrole units, which enables high molecular packing and edge-on crystallinity. Additionally, the extended 2-hexyldecyl alkyl side chains allow good solubility, as shown in the molecular structure in Figure S3a in the Supporting Information. Therefore, we expect that solution-processed PDPP3T with the π-rich terthiophene unit and edge-on planarity will result in both charge-transfer and dipole-induced doping effects on the multilayer MoSe₂. Our experimental material characterizations of PDPP3T are given in Figure S3 in the Supporting Information. Notably, the molecular morphology of PDPP3T considerably changes depending on its annealing temperature (Tₐ). For verification, we prepared the hybrid PDPP3T-multilayer MoSe₂ samples at three different annealing temperatures (Tₐ = 100, 200, and 300 °C). Figure 2b shows the wide-scan XPS spectra of the prepared samples, indicating the coexistence of multilayer MoSe₂ and PDPP3T in the hybrid structures.

2.3. Chemical Composition of the Hybrid PDPP3T-Multilayer MoSe₂

To investigate the chemical composition of the hybrid PDPP3T-multilayer MoSe₂ in depth, further XPS analysis was performed. Since the major effects of PDPP3T on multilayer MoSe₂ occur at the interface between the two materials, we first removed the top surface of the coated PDPP3T in the prepared samples with argon (Ar) sputtering to gain insight into the interface (Figure 3a,b). Then, XPS was performed to observe the elemental composition changes from preparation at Tₐ = 100, 200, and 300 °C. Figure 3c,d compares the N 1s and S 2p XPS spectra of the PDPP3T films on multilayer MoSe₂. At qz = 164 eV, two pairs of S 2p subpeaks were observed, which match the characteristic peaks of a thiophene group. The XPS results also showed that the atomic intensities of both the N 1s and S 2p peaks gradually increased as Tₐ increased. For Tₐ = 100 °C, lower-intensity N 1s and S 2p peaks were observed. The increased N and S concentration at higher Tₐ = 200 and 300 °C suggests that molecular rearrangement of PDPP3T occurs, and hence, the physical distance between the two materials decreases. Further analysis will be given in the “Microstructures of PDPP3T on multilayer MoSe₂” and “Morphological analysis of PDPP3T on multilayer MoSe₂” sections.

2.4. Microstructures of PDPP3T on Multilayer MoSe₂

Next, we conducted 2D GIWAXD to verify the thermal annealing effects of PDPP3T on the microstructure of the hybrid PDPP3T-multilayer MoSe₂. As shown in Figure 4a, the 2D diffraction image acquired from the GIWAXD results of the as-synthesized multilayer MoSe₂ exhibited strong (002) and (004) diffraction peaks along the qz (out-of-plane) axes, consistent with the X-ray diffraction pattern of the MoSe₂ layers (Figure S2a, Supporting Information). The lattice structure is estimated to be the 2H phase with parameters a = 3.288 Å and c = 13.1 Å, which are consistent with the results from previous reports. The multilayer structure of MoSe₂ was also identified in the low qz space region, depicted by the yellow-dashed box, in which the (002'), (003'), (004'), and (005') reflections were periodically observed.

Figure 4b–d compares the 2D GIWAXD patterns of the hybrid PDPP3T-multilayer MoSe₂ prepared with Tₐ = 100, 200, and 300 °C. All the diffraction patterns show both PDPP3T and MoSe₂ crystalline peaks, indicating the coexistence of MoSe₂ and PDPP3T in the hybrid structures. Among the three Tₐ, two major differences were observed. First, the distinct (00h') diffractions in the low qz space region disappeared in the 2D GIWAXD pattern for the hybrid PDPP3T-multilayer MoSe₂ at higher Tₐ (≥200 °C). The absence of the (00h') diffractions suggests that PDPP3T moved closer to the MoSe₂ interfacial surface, thereby obscuring the (00h') diffractions. This result is
consistent with the aforementioned XPS results, which indicate that the molecular rearrangement of PDPP3T reduces the physical distance between PDPP3T and MoSe2. Second, the molecular orientation of PDPP3T located on top of MoSe2 is affected by the different T_A. At a lower T_A of 200 °C, a weak (100) peak along the out-of-plane direction was observed. Furthermore, at higher T_A (300 °C), three diffraction peaks ((100), (200), and (400)) of PDPP3T were clearly observed, and the intensity of the (100) peak increased. We also investigated the average orientation of the PDPP3T π-conjugated planes on the substrate using near-edge X-ray absorption of fine structure (NEXAFS) spectroscopy (Figure S4, Supporting Information). The tilting angle (α) increased when the film was annealed at a higher T_A (300 °C), three diffraction peaks (100), (200), and (400) of PDPP3T were clearly observed, and the intensity of the (100) peak increased. We also investigated the average orientation of the PDPP3T π-conjugated planes on the substrate using near-edge X-ray absorption of fine structure (NEXAFS) spectroscopy (Figure S4, Supporting Information). The tilting angle (α) increased when the film was annealed at a higher T_A (α = 57.82° (as-coated) → α = 61.78° (T_A = 350 °C)). The details of the NEXAFS measurements and analysis results are given in Note S1 in the Supporting Information. Both the GIWAXD and NEXAFS results indicate that the PDPP3T films have a predominantly edge-on molecular orientation at higher T_A. Koch and co-workers reported that an intrinsic in-plane dipole moment was a dominant component in the total surface dipole moment for edge-on polymer chains. In the molecular dipole of PDPP3T, the unsubstituted thiophene unit has a negative pole toward the sulfur atom, and hence, the dipole of the stronger edge-on PDPP3T molecules can be induced on MoSe2. Therefore, a more perpendicular orientation of the polymeric chains is formed by increasing T_A, where “standing upright” PDPP3T can induce the linear superposition of the molecular dipole moments at the multilayer MoSe2 interface. Further experiment results using GIWAXD are given in Figures S5 and S6, and Note S2 in the Supporting Information.

2.5. Morphological Analysis of PDPP3T on Multilayer MoSe2

To further investigate the crystalline features of PDPP3T in the hybrid structure, the surface morphologies were characterized using atomic force microscopy (AFM), as shown in Figure 5. For the as-coated sample, relatively small domains with irregular shapes and sizes were randomly distributed (Figure 5a), which became more deteriorated at T_A = 100 °C (Figure 5b). However, an obvious change of the surface morphology, in terms of domain size and shape as well as their periodic distribution, was observed in the hybrid structure prepared at T_A = 200 °C (Figure 5c). The domain size increased when T_A = 300 °C (Figure 5d). These results support the increase of the linear superposition of the molecular dipole moments originating from the perpendicularly oriented polymeric chains at high T_A (>200 °C), as stated in the previous “Microstructures of PDPP3T on multilayer MoSe2” section.

2.6. Electrical Characteristics

Next, we fabricated and characterized TFT devices using the hybrid PDPP3T-multilayer MoSe2 to electrically confirm the
doping effect. We first prepared a baseline multilayer MoSe₂ TFT with a bottom gate and top contacted source/drain (S/D) architecture. In addition, the hybrid PDPP3T-multilayer MoSe₂ TFT was fabricated by simply coating PDPP3T on top of the baseline MoSe₂ TFT (Figure 6a). Details of the device fabrication are given in the Experimental Section. For a quantitative comparison, we characterized the single device to obtain four \( I_{DS} - V_{GS} \) (transfer) characteristics. After measuring the transfer curve of the baseline MoSe₂ device, PDPP3T was coated on that device and annealed at \( T_A = 100, 200, \) or \( 300 \) °C to sequentially measure the transfer curves again. Using this investigation, the dependency of the electrical characteristic changes on the PDPP3T doping effect was investigated.

Figure 6b compares the transfer curves of the baseline MoSe₂ TFT and the hybrid PDPP3T-multilayer MoSe₂ TFTs prepared at \( T_A = 100, 200, \) and \( 300 \) °C. The transfer curve of the baseline MoSe₂ TFT (grey) exhibited p-type-dominant ambipolar behavior with an on/off current ratio (\( I_{on}/I_{off} \)) of \( \approx 10^4 \) and on-current of \( \approx 5 \times 10^{-8} \) A (\( \approx 7 \times 10^{-10} \) A) at \( V_{GS} = -50 \) V (\( +50 \) V). These characteristics are attributed to defects resulting from the high-temperature MoSe₂ growth conditions. After coating PDPP3T on top of the MoSe₂ TFT at \( T_A = 100 \) °C, both p- and n-type current were increased by one order of magnitude (green-dashed curve). We believe that the increase of the p-type current resulted from hole carrier transport through PDPP3T, which has p-type semiconducting behavior. This conclusion is supported by the electrical characteristics of the PDPP3T-only TFT, as shown in Figure S7 in the Supporting Information. However, the increase of n-type current resulted from a different source. Since PDPP3T cannot conduct electrons in ambient atmosphere, the enhancement of the n-type current does not originate from PDPP3T charge transport but from the PDPP3T doping effect into multilayer MoSe₂. At \( T_A = 200 \) °C, a larger enhancement of the n-type current was observed. The most pronounced change in the transfer curve was observed at \( T_A = 300 \) °C. As shown in the blue solid curve in Figure 6b, the electron current (\( I_{DS} = 1.5 \times 10^{-6} \) A) at \( V_{GS} = 50 \) V increased by a factor of \( \approx 2000 \) compared to that (\( I_{DS} = 7 \times 10^{-10} \) A) for the baseline MoSe₂ device.

Figure 6c,d shows the \( I_{DS} - V_{DS} \) (output) characteristics of the baseline MoSe₂ TFT and the hybrid PDPP3T-multilayer MoSe₂ TFTs prepared at \( T_A = 300 \) °C. The other output curves of the hybrid PDPP3T-multilayer MoSe₂ TFTs prepared at \( T_A = 100 \) and \( 200 \) °C are given in Figure S8 in the Supporting Information. In the baseline MoSe₂ TFT, the opposite charge carrier (hole current) with a super linear drain current behavior was observed, which is consistent with the results from previous reports for conventional ambipolar TFT characteristics. In contrast, the hybrid PDPP3T-multilayer MoSe₂ TFT prepared at \( T_A = 300 \) °C exhibited unipolar n-type behavior with clear current saturation in the large \( V_{DS} \) region. In addition, the linear region in the output curves implies that the contact between the active component and the S/D electrodes was also improved at \( T_A = 300 \) °C, as shown in Figure S9 in the Supporting Information.
To study the statistical variation of the PDPP3T doping effect on multilayer MoSe₂, we characterized 14 baseline MoSe₂ TFTs and 14 hybrid PDPP3T-multilayer MoSe₂ devices annealed at each \( T_A \) (100, 200, and 300 °C). Figure 6e,f shows the device number histograms with respect to \( \mu_{\text{eff}} \) and \( I_{\text{on}}/I_{\text{off}} \). The histograms were divided by increments of 10. The graphs clearly show that the PDPP3T doping effect led to higher \( \mu_{\text{eff}} \) and \( I_{\text{on}}/I_{\text{off}} \). Figure S10 in the Supporting Information shows the maximum \( \mu_{\text{eff}} \) values of the baseline MoSe₂ TFTs and hybrid MoSe₂-PDPP3T TFTs at each of the three \( T_A \) (3.44, 8.38, 36.14, and 75.6 cm² V⁻¹ s⁻¹, respectively). More details of the TFT performances are listed in Table S1 in the Supporting Information.

### 2.7. Photoresponsive Characteristics

We expected that the PDPP3T doping effects could also enhance the degree of the photoactivation of multilayer MoSe₂. To observe the optoelectronic property changes from the PDPP3T
doping effects, we investigated the transfer characteristics of the multilayer MoSe$_2$ phototransistor before (w/o PDPP3T) and after (w/ PDPP3T) doping under various irradiances ($P_{\text{inc}} = 20–640$ mW cm$^{-2}$). The measurement details of the phototransistors are given in the Experimental Section. Figure 7a,b compares the photoresponsive transfer characteristics of the baseline multilayer MoSe$_2$ TFT and hybrid PDPP3T-multilayer MoSe$_2$ phototransistor prepared at $T_A = 300 ^\circ$C using an applied excitation wavelength ($\lambda_{\text{exc}}$) of 638 nm and applied $V_{\text{DS}}$ of 1 V. Over the entire applied $V_{\text{GS}}$ range, the photoinduced $I_{\text{DS}}$ change is much higher in the hybrid PDPP3T-multilayer MoSe$_2$ TFT than in the baseline multilayer MoSe$_2$ phototransistor. The photoresponsivity was calculated using the equation $R = \frac{I_{\text{ph}}}{P_{\text{inc}}}$, where $I_{\text{ph}}$ is the photoresponse current and $P_{\text{inc}}$ is the incident power. Figure 7c, the extracted photoresponsivity values ($R$) of both the baseline multilayer MoSe$_2$ and hybrid PDPP3T-multilayer MoSe$_2$ phototransistor...
were plotted as a function of $P_{\text{inc}}$ for three different excitation wavelengths ($\lambda_{\text{ex}} = 405, 638, \text{and} 852 \text{ nm}$). A maximum $R$ of 91.2 $\text{A W}^{-1}$ was obtained for the hybrid PDPP3T-multilayer MoSe$_2$ TFT, which is $\approx 6$ times higher than that of the baseline MoSe$_2$ phototransistor at $P_{\text{inc}} = 20 \text{ mW cm}^{-2} \text{ and } \lambda_{\text{ex}} = 638 \text{ nm}$. Figure 7d compares the time-resolved photoswitching behavior of each phototransistor. The photoresponse remains almost identical during light-on and light-off conditions at an interval of 5 s for multiple cycles. The hybrid PDPP3T-multilayer MoSe$_2$ phototransistor showed an enhanced output swing ($|I_{DS}|$ at light-on $- |I_{DS}|$ at light-off) compared with that of the baseline multilayer MoSe$_2$ phototransistor. Further details of the photoresponsive characteristics are listed in Table S2 in the Supporting Information.

**2.8. Mechanism Analysis**

The measured carrier mobility and photoresponsivity of the hybrid PDPP3T-multilayer MoSe$_2$ are considerably higher than those for the as-fabricated multilayer MoSe$_2$. We believe that the following two mechanisms induced by PDPP3T account for such improvements in the hybrid PDPP3T-multilayer MoSe$_2$: (1) the dipole effect in multilayer MoSe$_2$ and (2) charge-transfer doping effects.

First, we will discuss the dipole effect. A common feature of TMD (such as MoSe$_2$)-based TFTs is a Schottky barrier (SB) at the TMD–metal junction,[39] which severely limits carrier injection in the “ON” state—a key device performance parameter to aid carrier mobility and the subthreshold slope. The on-current of the multilayer MoSe$_2$ TFT, which is $\approx 6$ times higher than that of the baseline MoSe$_2$ phototransistor at $P_{\text{inc}} = 20 \text{ mW cm}^{-2} \text{ and } \lambda_{\text{ex}} = 638 \text{ nm}$. Figure 7d compares the time-resolved photoswitching behavior of each phototransistor. The photoresponse remains almost identical during light-on and light-off conditions at an interval of 5 s for multiple cycles. The hybrid PDPP3T-multilayer MoSe$_2$ phototransistor showed an enhanced output swing ($|I_{DS}|$ at light-on $- |I_{DS}|$ at light-off) compared with that of the baseline multilayer MoSe$_2$ phototransistor. Further details of the photoresponsive characteristics are listed in Table S2 in the Supporting Information.
in PDPP3T absorbed on the MoSe2 surface leads to the creation of negatively charged interface dipoles. In this case, the dipole effect at the MoSe2 interface can create excess carriers (Δn) in a channel, which forms a quasi-Fermi level (E_{Fq}) near the conduction band (E_c) under nonequilibrium conditions. Under thermal equilibrium, the electron and hole concentrations are defined as

\[ n_0 = n_i \exp \left( \frac{E_v - E_F}{kT} \right) \quad p_0 = n_i \exp \left( \frac{E_F - E_v}{kT} \right) \]

where \( n_i \) is the intrinsic carrier concentration, and \( E_F \) is intrinsic Fermi energy. As excess carriers under PDPP3T doping are created in the MoSe2 channel, a new quasi-Fermi level for electrons can form at a shallow width in the SB, and thus, electrons can more effectively tunnel through the thin SB by the equation as follows

\[ n = n_0 + \Delta n = n_i \exp \left( \frac{E_F - E_v}{kT} \right) \]

Therefore, the SB width at MoSe2-Ti/Au can be modulated by the dipole moment of PDPP3T.

The second mechanism induced by PDPP3T doping is a charge-transfer effect. PDPP3T has three unsubstituted thiophene rings along the π-conjugation pathway.\textsuperscript{[40]} The lone electron pair of sulfur in thiophene are greatly delocalized over the π-conjugated system.\textsuperscript{[31]} As the distance between MoSe2 and PDPP3T decreases at high \( T_A \), these lone pair electrons are expected to induce negative charge transfer from PDPP3T to multilayer MoSe2, which leads to a higher \( \Delta n \).\textsuperscript{[30,39]} Accordingly, both the dipole and charge-transfer doping effects result in a thinner SB. We extracted the contact potential required for injection (\( V_{\text{inj}} \)) from each output curve (Figure S9, Supporting Information). The \( V_{\text{inj}} \) values of the hybrid PDPP3T-multilayer MoSe2 TFTs were lower than that of the as-fabricated MoSe2 TFT. When \( T_A \) was increased, \( V_{\text{inj}} \) decreased from 1.27 to 0.06 V. We also investigated the contact resistance, \( R_C \) of MoSe2 TFTs before and after PDPP3T doping using the transfer line method (Figure S11, Supporting Information). The baseline MoSe2 TFT without PDPP3T doping exhibited a large \( R_C \) (2\( R_C \approx 4.5 \times 10^{5} \ \Omega \cdot \text{mm} \)). After PDPP3T doping at \( T_A = 300^\circ \text{C} \), however, \( R_C \) was significantly reduced (2\( R_C \approx 1.4 \times 10^{3} \ \Omega \cdot \text{mm} \)). The reduced \( R_C \) and \( V_{\text{inj}} \) supports the modulation of the SB width.

3. Conclusion

In summary, we demonstrated PDPP3T doping in multilayer MoSe2. Comprehensive analysis using XPS, GIWAXD, AFM, and NEXAFS showed that two mechanisms (i.e., dipole and electron charge-transfer effects) accounted for the n-doping effect in the hybrid PDPP3T-multilayer MoSe2 at high \( T_A \). These features led to the fabrication of a TFT and photoresponsible device with better characteristics: high mobility and on-current, large current on/off ratio, and high photoresponsivity. Without the need for other materials or process optimizations, the proposed doping scheme easily provides higher electron modulation by coating a conjugated planar polymer (such as PDPP3T) or heterocyclic compound (such as thiophene) on the as-fabricated multilayer MoSe2.

4. Experimental Section

Synthesis of Multilayer MoSe2 by CVD: Molybdenum trioxide and Se powders (Sigma Aldrich, each 99.5% purity) were placed in the vaporization zone of a quartz tube within a 2 inch diameter furnace. A p-type-doped Si wafer with a 300 nm thick SiO2 layer was cleaned using acetone and isopropyl alcohol. The p-Si/SiO2 substrate was vertically inserted into the deposition zone, and the vaporization and deposition zones of the quartz tube were heated to 800 and 750 °C, respectively, with a temperature gradient of 25 °C min\(^{-1}\), and the temperatures were held for 30 min. During the entire processing, Ar (120 sccm) and H\(_2\) (20 sccm) gases were used as the carrier gas and to maintain the pressure.

Device Fabrication: SiO2 with a thickness of 300 nm was used as a gate dielectric layer. The thickness of the multilayer MoSe2 in Figure 6b–d was \( \approx 38 \text{ nm} \) (Figure S13, Supporting Information). Ti/Au (20/200 nm) was deposited on the SiO2/Si substrate containing the MoSe2 channel layer by E-beam evaporator. To fabricate the S/D electrodes, a Ti/Au layer was patterned by conventional photolithography and an etching procedure. The channel length and width of the device in Figure 6b–d were estimated to be 7.89 and 8.15 \( \mu \text{m} \), respectively. PDPP3T (purchased from Solamer) was dissolved in ODCB at a concentration of 7 mg mL\(^{-1}\). For the hybrid PDPP3T-multilayer MoSe2, the solution was spin coated on top of the MoSe2 channel containing the S/D electrodes. The samples were annealed at \( T_A = 100, 200, \) and 300 °C. The PDPP3T coating and annealing procedures were conducted inside a nitrogen-purged glove box.

Spectroscopic Characterization: XPS with Ar\(^+\) ion sputtering was performed at the Pohang Light Source II (PLS-II) 4D beamline of the Pohang Accelerator Laboratory in Korea. Before the XPS measurements with synchrotron radiation, Ar\(^+\) ion sputtering with 2.5 keV etched the PDPP3T surface. 2D GIWAXD measurements were performed at PLS-II 9A beamline of the Pohang Accelerator Laboratory in Korea. A photon energy of 11.075 keV was used. The incidence angle was equal to 0.08–0.15°. A 2D charge coupled device detector (Rayonix SX165) was used to record GIWAXD patterns.

Device Performances Characterization: Electrical characteristics of the baseline MoSe2 and the hybrid PDPP3T-multilayer MoSe2 TFTs were measured using an Agilent 4156C instrument in ambient air under dark conditions. The photoresponsible behaviors were investigated using a semiconductor characterization system (4200-SCS, Keithley) connected to a probe station at room temperature in ambient air. Radiations with various wavelengths were generated with a Multichannel Fibre-Coupled Laser Source (MCLS, Thorlabs) and guided perpendicular to the phototransistor active channel using Single Mode Fiber Optic Patch Cables (S405-HP for 405 nm, SM600 for 638 nm, and SM800 for 852 nm, Thorlabs). \( P_{\text{in}} \) was measured by a Standard Photodiode Power Sensor (S120VC, Thorlabs) and Meter Console (PM100A, Thorlabs).

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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