2D transition metal dichalcogenides are promising channel materials for the next-generation electronic device. Here, vertically 2D heterostructures, so called van der Waals solids, are constructed using inorganic molybdenum sulfide (MoS$_2$) few layers and organic crystal – 5,6,11,12-tetrphenylnaphthacene (rubrene). In this work, ambipolar field-effect transistors are successfully achieved based on MoS$_2$ and rubrene crystals with the well balanced electron and hole mobilities of 1.27 and 0.36 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. The ambipolar behavior is explained based on the band alignment of MoS$_2$ and rubrene. Furthermore, being a building block, the MoS$_2$/rubrene ambipolar transistors are used to fabricate CMOS (complementary metal oxide semiconductor) inverters that show good performance with a gain of 2.3 at a switching threshold voltage of $-26$ V. This work paves a way to the novel organic/inorganic ultrathin heterostructure based flexible electronics and optoelectronic devices.

1. Introduction

2D materials such as graphene, hexagonal boron nitride (h-BN), and molybdenum disulfide (MoS$_2$) have gained comprehensive interests in the past decade because of their unique electronic, chemical, and physical properties.$^{[1,2]}$ Although graphene has ultrahigh mobility,$^{[3]}$ the zero band-gap and poor switching characteristics make it difficult to be used as a channel material.$^{[2,4]}$ On the other hand, metal chalcogenides, especially for 2H phase transition metal dichalcogenides (TMDs), due to the sizable band gap, have been regarded as favorable candidates for electronic devices such as field-effect transistors (FETs) and as an essential component in modern electronic products, such as computers, cell phones, and flat panel displays.$^{[5]}$ Using FETs as the building block, the ambipolar operation has been intensively adapted in logic circuits to overcome the limitations of the integrated circuits that use only unipolar logic.$^{[6,7]}$ To achieve ambipolar FETs, it is crucial to provide channel semiconductors that allow dual operation of both p and n types.$^{[8]}$ However, until now, reported FETs based on TMDs mainly show unipolar (n-type) characteristic,$^{[9,10]}$ and very few of p-type characteristics have been reported.$^{[11]}$

2D heterostructure is a promising direction artificial structure to realize ambipolar nature because the order, thickness, and the materials themselves can be optimized for specific functionality. Typical heterostructures include core–shell sphere, vertical and lateral films, etc.$^{[12,13]}$ Also, traditional bulk heterostructures typically require the epitaxial growth of an n-type semiconductor onto a p-type semiconductor and vice versa using costly and sophisticated systems such as metal-organic chemical vapor deposition. Moreover, for bulk materials, several other factors, such as the lattice mismatch between the different materials make it difficult to find a candidate to realize conventional heterostructures.
2D materials provide an alternative solution to overcome this limitation. Since 2D materials can be thinned down to a monolayer, they can also be restacked with others to form the so-called van der Waals heterostructures. This method offers complete freedom in the choice of materials and also allows no interdiffusion of atoms at the interface, since each layer can exist in freestanding form, e.g., Gong et al. synthesized vertical and in-plane WS2-MoS2 heterostructures. Rath et al. reported Bi2Se3-PbS for application in solar cells. Beside 2D materials, organic materials have also caught eyes due to their flexibility, reasonable mobility, low temperature synthesis, and low cost, making them complementary to the 2D materials. Although inorganic–organic hybrid ambipolar FETs have been reported in some work, studies on 2D based inorganic–organic heterostructures are still not well explored. In addition, some of the ambipolar FETs do not exhibit well-balanced hole and electron mobility at the same time due to the poor compatibility between the organic and inorganic components. This will also result in the further application for flexible and ultrathin inverter circuits.

MoS2 is a typical TMD in 2D family, and its extremely low leaking current makes it a great candidate for ultralow power-consuming devices, not mentioning its excited optical properties. Heterostructures combining both 2D materials and organic materials will be of great interest in flexible electronics. Organic crystals can also make a surface modification to tailor the nature of the 2D few layers due to the band energy match. More importantly, our recent work demonstrated the MoS2/rubrene p–n junction. MoS2 has a layered structure and the thickness of monolayer MoS2 is around 6–7 Å, which consists of a hexagonally packed layer of Mo atoms sandwiched between two layers of chalcogen atoms. The intralayer Mo–S bonds are predominantly covalent in nature. While rubrene (C22H18) is an aromatic hydrocarbon consisting of a backbone of four fused benzene rings (tetracene) with four substituted phenyl groups. It has an orthorhombic structure and D18 point group symmetry as well. It is regarded one of the most promising organic materials with high carrier mobility.

In this work, by combining MoS2 and rubrene, novel organic–inorganic MoS2/rubrene FETs were successfully synthesized. High-performance ambipolar behavior with well-balanced hole and electron mobilities were achieved in these devices. Furthermore, CMOS inverter circuits also show good performance with a gain of 2.3 at a switching threshold voltage of −26 V. Our work suggests that, by integrating organic and inorganic 2D materials, novel nanoelectronic and optoelectronic devices are possible.

2. Fabrication of MoS2/Rubrene Heterostructures FET and Inverter Devices

MoS2 and rubrene were used to make inorganic/organic heterostructures. Rubrene powder was purchased from Sigma-Aldrich with 99% purity. The rubrene single crystals were grown by physical vapor transport method which was normally used for growth of organic single crystals. About 200 nm thickness of rubrene was controlled synthesized in this work. MoS2 crystals were synthesized by chemical vapor deposition method which was reported somewhere. MoS2 thin flakes were exfoliated from single crystal by using scotch tape method.

Figure 1a–f shows the fabrication procedures for MoS2/rubrene heterostructures. By varying the stacking configuration of the 2D materials and the organic crystals, various electric transport behaviors may be achieved. To fabricate an ambipolar FET (Figure 1a–c), thin MoS2 flakes were exfoliated onto doped Si with 300 nm SiO2 substrate. Photolithography was used to pattern the source and drain electrodes. The thermal evaporator was used to deposit the contact (5 nm Cr and 50 nm Au) electrode. After evaporation, the samples were soaked in acetone overnight to remove photoresist, followed by cleaning with Isopropyl alcohol (IPA) and deionized (DI) water (Figure 1b). Subsequently, the rubrene was deliberately aligned to bridge across the source and drain electrode in order to contact MoS2 (Figure 1c). To laminate the rubrene, the crystals were carefully picked up and manually aligned under optical microscopy with a 5x objective lens. To make a CMOS inverter circuit, isolated MoS2 FET and rubrene FET were fabricated on the same substrate and connected in parallel. Finally, one ends of the electrodes of the MoS2 and the rubrene were interconnected together by wire bonding, while the other ends were tied to VDD and ground (GND), respectively.

3. Results and Discussion

Figure 2a,b shows the schematic of the device and the false-colored scanning electron microscope (SEM) image of a typical device, respectively. To fabricate the ambipolar FET, rubrene is laminated over the MoS2 layer to contact with both the source and drain electrodes (Figure 2a). It should be noted that the schematic picture does not reflect the actual size of the device. Compared to the thickness of Au electrode (50 nm), channel length (7 μm) are much larger than the Au electrodes.

Figure 2c,d shows the transfer and output curves of the fabricated MoS2-rubrene FET recorded at room temperature, respectively. Distinct ambipolar FET characteristics are observed in these two panels. Similarly, the mobility of both electrons and holes are estimated from the linear region in the transfer curve based on equation: where W is the channel length, C is the capacitance between the channel and the back gate per unit area (C = εε0/d), ε0 is the vacuum permittivity, εr is the relative permittivity, and d is the thickness of SiO2 layer. At drain bias of 0.5 V, the ambipolar FET exhibits well-balanced electron and hole mobility, μe = 0.36 cm2V−1s−1 and μh = 1.27 cm2V−1s−1, respectively, with an on/off ratio of 104 (Figure 2c). The highly linear parts of current output in I=−V at low negative voltage indicate the low resistance between the metal contact to both MoS2 and rubrene, allowing efficient injection of both electron and hole carriers (Figure 2d).
It is worth to highlight that the obtained hole mobility of 1.27 cm² V⁻¹ s⁻¹ in our inorganic–organic ambipolar FET is several magnitudes higher compared to previous reports on organic ambipolar FETs.[6,8] Most MoS₂ FETs display n-type transport, the difficulty in fabricating high-performance p-type MoS₂ FET is largely caused by the difficulty of hole injection from the source/drain contacts due to large Schottky barrier heights to the valence band[28] (a small Schottky barrier height to the conduction or valence band leads to n- or p-type FETs, respectively). However, in both cases, the mechanism of the ambipolar behavior in these MoS₂ devices is still unclear.[29]

Figure 1. a–c) Fabrication of MoS₂-rubrene ambipolar FET: the rubrene was laminated directly on the top of the as-fabricated MoS₂ FET with electrodes. d–f) Fabrication of MoS₂-rubrene inverter: two separate MoS₂/rubrene based FETs were first fabricated and then connected in serials.

Figure 2. a) Schematic representation of the ambipolar FET based on the MoS₂-rubrene heterostructure. b) False-colored SEM image of the actual fabricated ambipolar FET. c) The transfer and d) output curve of the MoS₂-rubrene ambipolar FET.
Based on the qualitative band diagram shown in Figure 3a, we proposed a possible mechanism for the ambipolar behavior in the MoS$_2$-rubrene heterostructure. In a typical FET, the carrier transport behaviors are highly dependent on the alignment of the metal work function ($\Phi$) of the source and drain electrodes with the Fermi energy levels of the channel material.$^{[30,31]}$ In this work, the electrode metals Cr/Au has a work function $\Phi_{\text{Cr/Au}} = 4.8$ eV.$^{[32]}$ For rubrene, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are estimated to be $\approx 5.36$ and 3.15 eV, respectively. This LUMO value is $\approx 3.15$ eV below the vacuum level.$^{[33]}$ For few layer MoS$_2$, the conduction band and valence bands are located at about 4.0 and 5.2 eV, respectively.$^{[34,35]}$ (Figure 3a). Once rubrene and MoS$_2$ was connected and the gate voltage was applied onto both, the band diagram was aligned as shown in Figure 3b. The alignment of the HOMO level of rubrene with $\Phi_{\text{Cr/Au}}$ results in a small Schottky barrier for efficient hole injection from Cr/Au to rubrene. Similarly, the alignment of the conduction band of MoS$_2$ with $\Phi_{\text{Cr/Au}}$ allows efficient electron injection. In other words, the source/drain electrodes work function (4.8 eV) provides electron injection into the conduction band (4.28 eV).$^{[36]}$ When forming the organic/inorganic heterostructure, HOMO and LUMO level for rubrene and MoS$_2$ FETs are tied to $V_{\text{DD}}$ and GND, respectively. The voltage input is applied to the back gate terminal, while the output voltage is measured at the interconnected MoS$_2$-rubrene drain terminal. The working mechanism of the CMOS inverter can be explained based on the circuit diagram depicted in Figure 4b. When a HIGH voltage is applied at the input gate terminal, p-type rubrene FET switches to OFF state while n-type MoS$_2$ FET switches to ON state. Since the source terminal of MoS$_2$ FET is connected to GND, the measured output voltage is LOW. This effectively changes the logic HIGH to LOW, giving rise to an inverting behavior. Similarly, the ON/OFF states of the FETs can be reversible when a LOW voltage is applied at the input gate terminal. Figure 4c shows the voltage transfer curve of the CMOS inverter with $V_{\text{DD}}$ tied to 2.0, 3.3, and 5.0 V, respectively. Under these three bias, the inverter is able to switch fully from the specific $V_{\text{DD}}$ to 0 V. The threshold voltage that is required to switch the inverter is $\approx -26$ V. It is well known that the conductivity of MoS$_2$ FETs is typically higher than rubrene FETs. Hence, the gate voltage at which both MoS$_2$ and rubrene FETs are turned ON at the same current level is in the negative gate bias regime. Figure 4d shows that the maximum voltage gain achievable for the inverter is about 2.3. It is worth to mention that this value is much higher than previous works based on MoS$_2$-carbon nanotube (CNT)$^{[37]}$ MoS$_2$-black phosphorus (BP)$^{[38]}$ and MoS$_2$-Bi$_2$Sr$_2$Co$_2$O$_8$ (BSCO).$^{[13]}$ The performance of the inverter can be further improved by dielectric engineering.
In conclusion, we have fabricated an inorganic–organic heterostructure consisting of inorganic MoS$_2$ and organic crystal rubrene. Based on them, an ambipolar FET was successfully obtained and showed the hole mobility and electron mobility of 0.36 and 1.27 cm$^2$ V$^{-1}$ s$^{-1}$, respectively. Such ambipolar behaviors can be explained by the band alignment of the work function and Femi level. In addition, The CMOS inverter of MoS$_2$/rubrene displayed a good voltage gain of 2.3 at a switching threshold voltage of $-26$ V. This work shows great potentials for the fabrication of novel devices by integrating inorganic and organic materials, and further facilitates the design of flexible nanoelectronic and optoelectronic devices.

3.1. Material Characterization and Electrical Characterization

Optical microscopy (Olympus) was used to identify suitable MoS$_2$ flakes as well as to assist in the alignment of rubrene flakes onto the as-fabricated MoS$_2$ FETs, in order to achieve suitable configurations in this work. The thickness of the MoS$_2$ and rubrene flakes was measured by noncontact atomic force microscope (AFM) (Cypher S – Asylum Research). Electrical measurements were carried in ambient air at room temperature using a semiconductor parameter analyzer (Agilent, B1500A) and Lakeshore probe station.

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