

Electrical Properties and Photo-response of FETs based on Few-layer WS₂ Nanoflakes

Hang YANG^{1,a}, Shi-Qiao QIN^{2,b}, Fei WANG^{1,c}, Jin-Yue FANG^{1,d} and Xue-Ao ZHANG^{1,e*}

¹College of Science, National University of Defense Technology, Changsha 410073, China

²College of Optoelectronic Science and Engineering, National University of Defense Technology, Changsha 410073, China

^ayanghangNUDT@163.com, ^bsqqin@nudt.edu.cn, ^cwangfei_815@163.com, ^dfjy_nudt@yahoo.com,

^exazhang@nudt.edu.cn

*Corresponding author

Keywords: Few-layer WS₂ nanoflakes, Field effect transistor (FET), Electrical properties, Photo-response

Abstract. The photo-electrical properties of few-layer WS₂ nanoflakes, fabricated by mechanical exfoliation, were systematically studied in this paper. The few-layer WS₂ FETs are n-type and possess a high gate modulation (On/Off ratio is larger than 10⁴) and a relatively high carrier mobility ($7.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The photo-electrical properties of the device shows sensitive photo response, high photoresponsivity ($R_{\lambda} = 3.5 \text{ mA/W}$), quick response time ($t < 20 \text{ ms}$), high external quantum efficiency ($\eta = 0.68\%$), and high detection rate ($D = 1.7 \times 10^9 \text{ W}^{-1}$) to red light(638nm). These results showed that the extraordinary performance of the device based on few-layer WS₂, which might open a new way to develop few-layer WS₂-based material in the application of FETs and optoelectronics.

Introduction

Since graphene has been discovered by Geim and Novoselov in 2004[1], this two-dimensional (2D) material with typically extraordinary properties has attracted extensive research in the last few years[2-5]. Disappointingly, low On/Off ratio and low photoreponsivity has immensely restricted the application of this star material in logic transistor field and optoelectronics[6, 7].

Fortunately, atomically thin WS₂, a new 2D material (transition-metal Dichalcogenide, TMD), has exhibited a remarkable On/Off ratio and a high mobility[8, 9]. Compared to graphene, it may be more promising for the practical application in logical device. Besides the outstanding electrical properties, WS₂ is a direct-bandgap semiconductor when exfoliated to monolayer state, which allow a high absorption coefficient under photoexcitation[10].

Although single-layer WS₂ has been studied before[8, 11], to our knowledge, few has investigated the photo-electrical properties of few-layer WS₂(<5 layers). Just as Geim said[12], even though monolayer graphene has plenty of excellent properties, bilayer and few-layer deserve carefully studying as well. Therefore, electrical properties and photo-response of FETs based on few-layer WS₂ nanoflakes were systematically investigated in this paper.

Results indicate that few-layer has a relatively better photo-response than single-layer and multi-layer. More importantly, the complexity of the fabrication process of monolayer 2D material-based devices, such as thin-film transistors, limits their use[13]. Moreover, a further advantage of few-layer 2D material is its nearly degenerate direct and indirect bandgaps and high anti-photocorrosion stability[14, 15]. Accordingly, few-layer WS₂ may possibly be more promising in the application of FETs and optoelectronics.

Experimental Details

Device fabrication: The transistors based on few-layer WS_2 were fabricated by standard micro-nano technology (EBL and EBE). Firstly, WS_2 nanoflakes were exfoliated from the WS_2 crystals (HQ graphene company) onto 300 nm SiO_2/Si substrates (doped p++, conductivity: $0.01\text{--}0.02\ \Omega\cdot\text{cm}$) using mechanical exfoliation technique [1]. Once WS_2 nanoflakes were obtained, contacts were drawn using standard electron-beam lithography, and metallization was carried out with Ti/Au (20 nm/70 nm). Ti was chosen for the strong adhesion force with SiO_2/Si substrate, however, may causing poor semi-metal contact. In devices, the layout of the electrical leads was designed to measure two-probe current–voltage characteristics.

Characterization and photo-electrical properties measurement: The WS_2 nanoflakes were characterized by AFM to comprehend the thickness. The output and transfer electrical properties were measured by Keithley 4200 probe system (company: Cascade Microtech, model: Summit 11000B-M) in atmospheric environment and room temperature (300K). The photo-response of the device to different wavelengths and power density and its response time could be measured by introducing the fiber laser into the 4200 probe system. Photoresponsivity, external quantum efficiency and detection rate can be calculated based on these original data. The power of fiber laser can be modulated continuously from 0 to 28 mW, and the spot diameter is 1 mm.

Results and Discussion

Characterization of few-layer WS_2 Nanoflakes and FETs: Figure 1(a) shows the AFM scanning image of our device, and the thickness of WS_2 is approximately 3 nm, confirmed by AFM (figure 1(b)). As known to all, the interlayer spacing of WS_2 is 0.7 nm, thus we judged that the sample used in the experiment was approximately 4 layer. Figure 1(c) demonstrates the optical image of the device. As shown in the figure, the channel length is 3.979 μm and channel width is 1.957 μm . Figure 1(d) and figure 1(c) illustrates the schematic diagram of back-gated few-layer WS_2 FET, wherein the electrodes are composed of 20 nm Ti and 70 nm Au. By applying the Si/SiO_2 substrate as back-gate, the I_{ds} of the device could be regulated through changing the magnitude of base voltage.

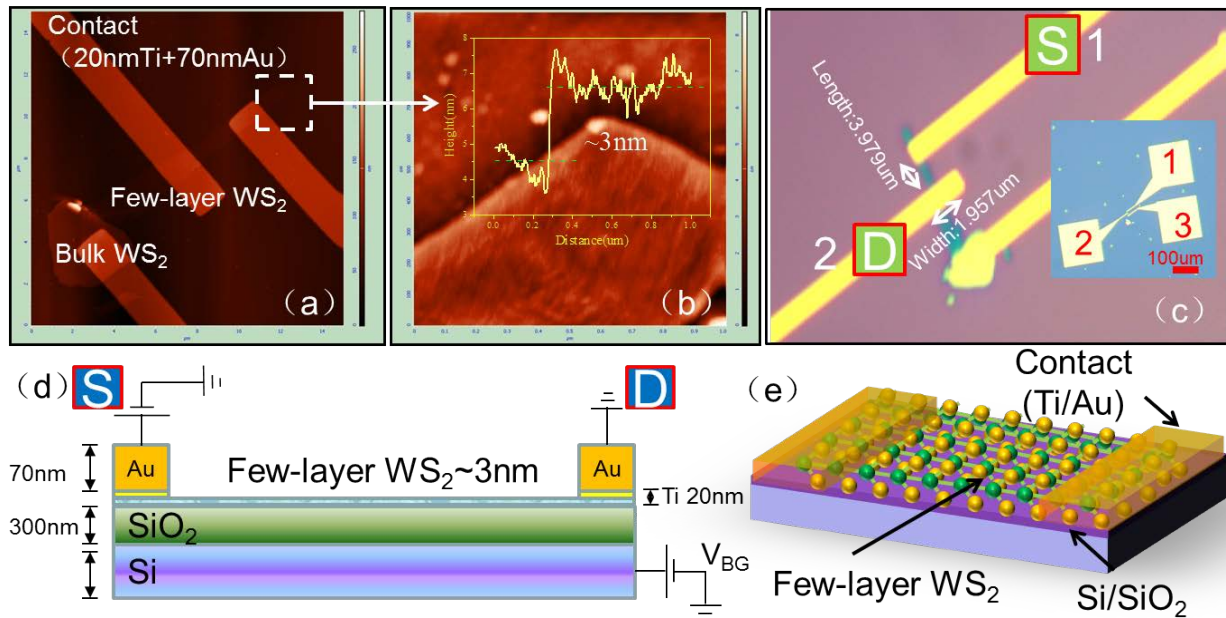


Figure 1. Characterization of few-layer WS_2 Nanoflakes and FETs. (a) AFM scanning image of few-layer WS_2 nanoflakes FET (b) Terrace height of WS_2 nanoflakes (c) Optic image of fabricated few-layer WS_2 FET. The inset shows the image observed by microscope in a lower magnification. (d) Side elevation of fabricated back-gated few-layer WS_2 FET, highly p-doped silicon serves as back gate. (e) Three-dimensional schematic of the typical device structure.

Fundamental Electrical Properties: Figure 2 illustrates the I-V characteristics of few-layer WS₂ nanoflakes FET in high bias voltage(a) and low bias voltage(b). As shown in figure 2(a), the I_{ds} increases when applied a higher backgate voltage. This is because the Fermi level of WS₂ is improved by electron doping from Si/SiO₂ backgate structure. Apparently, the current in negative bias is different from the current in positive bias, which indicates an asymmetrical semi-contact. Linear region exists when applied low bias voltage. Figure 2(b) shows the output characteristics when bias voltage sweeps from -0.1V to +0.1V. It is clear that the current is linearly dependent on bias voltage, which means the semi-contact barrier does not have a significant influence on device in low bias. Noticeably, the dark resistance of few-layer WS₂ nanoflakes is extremely high, amazingly reaching hundreds G Ω (when $V_{bg}=0V$). The high resistance mainly results from the low carrier density of this typical material[16, 17].

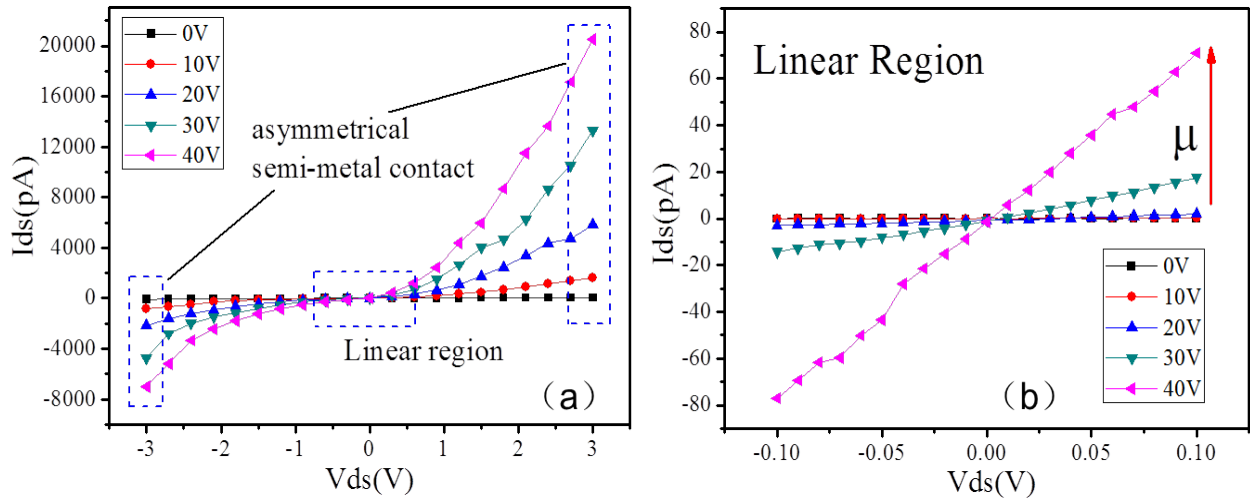


Figure 2. I-V characteristics of few-layer WS₂ nanoflakes FET. (a)The output characteristics of the device when applied different backgate voltage (0V to 40V), bias voltage sweeps from -3V to +3V.(b)Linear region of the device when applied low bias voltage (-0.1V to +0.1V).

The transfer characteristic curves are shown in figure 3(a) and figure 3(b). The electron mobility μ can be obtained from the equation[10]:

$$\mu = \frac{\partial I_{DS}}{\partial V_G} \left(\frac{L}{WC_i V_{DS}} \right) \quad (1)$$

where L is the channel length (3.979 μ m), W is the channel width (1.957 μ m), and C_i is the gate capacitance which can be given by the equation $C_i = \epsilon_0 \epsilon_r / d$. ϵ_0 (8.85 10^{-12} F/m) is vacuum dielectric constant, and ϵ_r (3.9) and d (300nm) are dielectric constant and thickness of SiO₂ respectively.

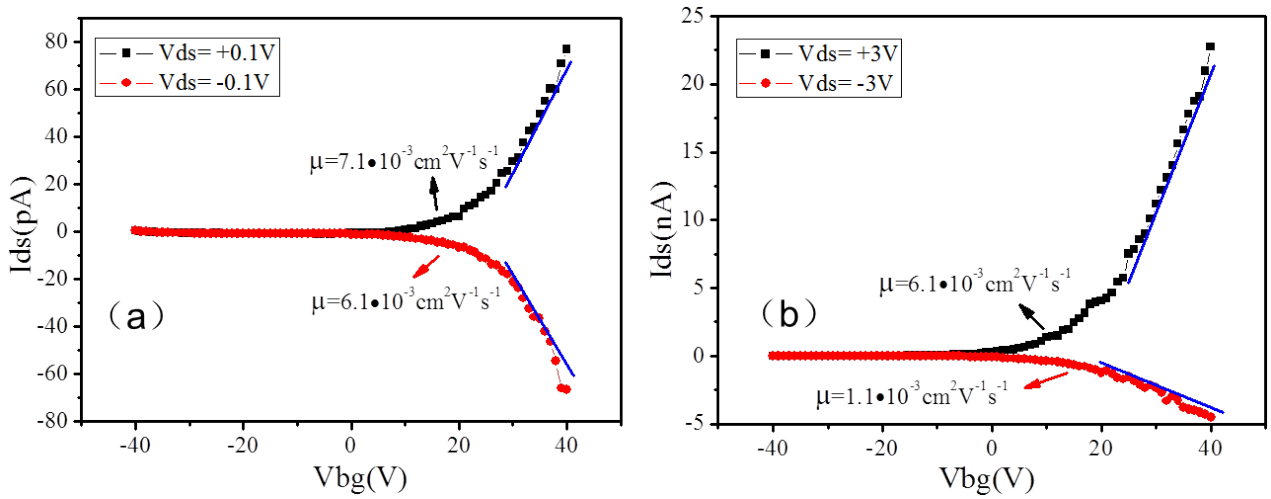


Figure 3. Transfer characteristics of few-layer WS₂ nanoflakes FET. The gate voltage varies from -40V to +40V when bias voltage is a fixed alue .(a)Vds=-0.1V and +0.1V. (b)Vds=-3V and +3V.

According to calculation, the electron mobility is $7.1 \cdot 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($V_{ds}=+0.1\text{V}$) and $6.1 \cdot 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($V_{ds}=-0.1\text{V}$). However, when applied high bias voltage, the electron mobility has a signifancant difference in positive bias ($6.1 \cdot 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and negative bias ($1.1 \cdot 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). This is mainly because the asymmertrical semi-contact, which is in accordance with the previous measurement data(figure 2(a)). Besides, the On/Off ratio may reaches amazingly 10^4 in few-layer WS₂ nannoflakes FET calculated by the experimental data. Accordingly, although the mobility of few-layer WS₂ is lower than graphene, however, it possesses extrodinary On/Off ratio, thus WS₂ is more promising to be applied in the logic operation device compared to the graphene.

As previous research reported[9], WS₂ generally exhibit an n-type conductivity type. Similayerly, the WS₂ device we prepared also demonstrated an n-type property. This phenomenon is owing to Se vacancies in the process of synthesis.

Photo-electrical properties: Bulk WS₂ is an indirect-bandgap (1.4eV) semiconductor, but can turn into a direct-bandgap (2.1eV) material when exfoliated into the monolayer state[9]. Unlike bulk or multi-layer WS₂, few-layer still demonstrates an intense optical excitation. According to the theoretical analysis[9], the few-layer WS₂ nanoflakes can respond to the visible light. Thus, 638nm laser light was exerted to investigate the photo-electrical properties of WS₂. For convenience, the laser power showed in figure measured by photo-power meter (THORLABS PM100A) is total power of incident laser rather than the light on the device.

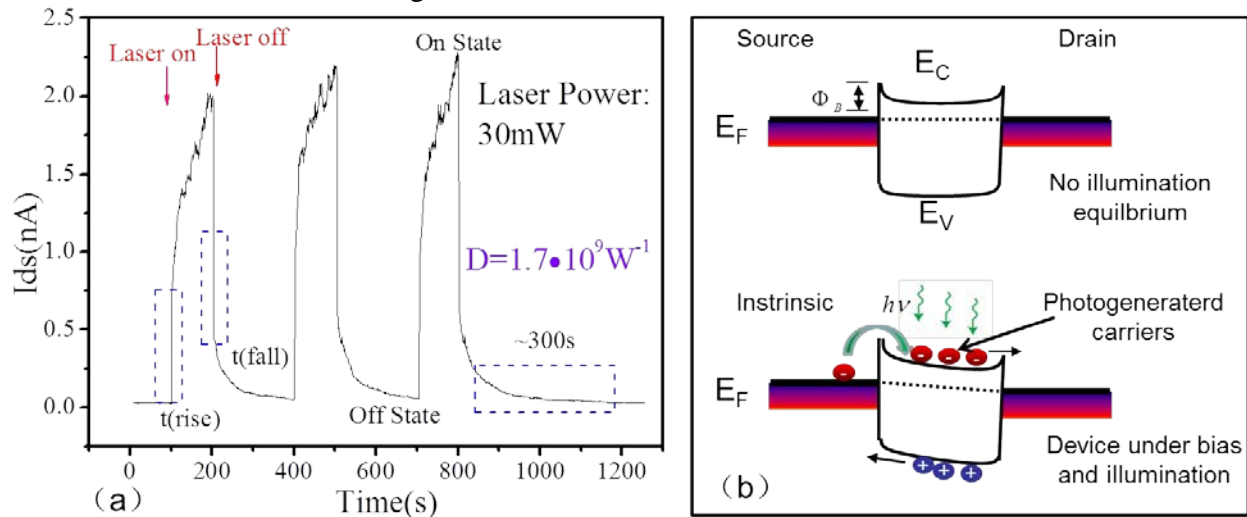


Figure 4. Photo-response of few-layer WS₂ optoelectrical device.(a) Time-resolved photoresponse of the device, during the light switching on/off at source drain voltage of +3V($V_{bg}=0\text{V}$). (b) Band

diagram of the few-layer WS₂ photo-detector taking into consideration Schottky barriers at the contacts. E_F is the Fermi level energy, E_C the minimum conduction band energy, E_V the maximum valence band energy and ϕ_B the Schottky barrier height.

The device exhibits fast dynamic response for both rise and decay process (figure 5(a)), the response and recovery time (blue dotted line frame) is shorter than the detection limit of our measurement setup (20ms). Disappointedly, owing to the existing of defect state, the electron-hole pairs can not be separated and recombined at its intrinsic property. As seen in the figure, the photocurrent continuously grows up when exerted laser irradiation. Besides, when laser is turned off, the device needs approximately 300s to recombine all the electron-hole pairs in defect state. However, it is of no significant influence on detecting light. Here, we introduce the detection rate, defined as:

$$D = \frac{I_{on}/I_{off}}{P_{in}} \quad (2)$$

This parameter can well characterize the S/N (signal to noise) ratio of photoresponse of the device. Owing to the dark resistance of device is particularly large, the device based on WS₂ showed excellent performance in detection. By calculation, the detection rate of the device reaches up to highly $1.7 \cdot 10^9 W^{-1}$, showing its good switching performance, which could be effectively applied in measuring the photo-electric signal.

The behavior of photo-generated charge-carriers of photodetector can be explained by a simple energy band diagram (figure 4(b)). With no illumination and without applying gate or drain bias, the device is in its equilibrium state, characterized by Schottky barriers at the contacts[18]. Illuminating the device with laser light, resulting in light absorption and excitation of electron-hole pairs, which can be extracted by applying a drain-source bias[13, 18, 19].

Figure 5(a) demonstrates the I_{ds} - V_{ds} characteristics under different laser power, where the drain current increased when the laser power was enhanced at a fixed drain-source voltage (-3V and +3V) due to the growth in the photogenerated current with the increased laser power.

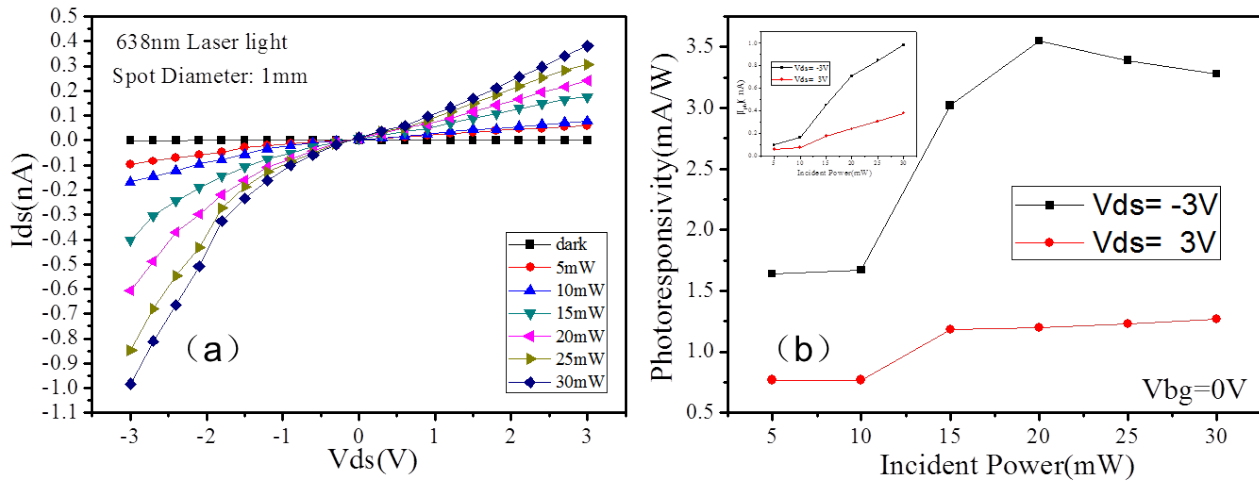


Figure 5. Photo-response of few-layer WS₂ optoelectronic device. (a) Drain-source (I_{ds} - V_{ds}) characteristic of the device under different illumination intensities. (b) The dependence of photo-current upon the laser power when $V_{DS} = -3V$ and $+3V$. The inset is the photo-responsivity obtained by calculating.

Photoresponsivity is defined by the equation $R_\lambda = I_{ph}/P_{in}$, where $I_{ph} = I_{on} - I_{off}$ (I_{on} and I_{off} represent photo current and dark current respectively), and $P_{in} = P_{laser} \cdot (S_{area}/S_{spot})$. Therefore, we applied the equation to calculate the photoresponsivity.

$$R_\lambda = \frac{I_{on} - I_{off}}{P_{laser} \cdot (S_{area}/S_{spot})} \quad (3)$$

According to the data in optic image (figure 1(c)), the photosensitive area of the device $S_{area} = L \cdot d$, where $L=3.979\mu m$, $d=1.957\mu m$, meaning that the actual working area to be $7.787\mu m^2$. Furthermore, $S_{spot} = 0.785mm^2$ owing to the spot diameter is 1mm.

Figure 4(b) shows the photoreponsivity of various laser power when $V_{ds}=-3V$ and $V_{ds}=+3V$. The inset shows the photogenerated current was proportional to the drain-source voltage at a fixed laser power. The photoreponsivity of positive area is continuously larger than which in negative area due to asymmetrical semi-contact. In general, the lower limit of the photo responsivity is determined by the dark resistance and the responsivity will be maintained at a constant value as photocurrent increase until the light saturation[20]. The photorponsivity of the fabricated device in experiment can surprisingly attain $3.5mA/W$ ($V_{ds}=+3V$, laser power= $20mW$), which means a potential in the practical application.

As for the practical application of the photo-detector, a highly significant parameter is the external quantum efficiency (EQE) $\eta(\lambda)$. When photo-response lies in linear region, external quantum efficiency can be obtained by the equation:

$$\eta(\lambda) = \frac{R_{\lambda} hc}{q \lambda} \quad (4)$$

where R_{λ} is photoresponsivity, h on behalf of Planck constant ($6.62 \cdot 10^{-34} J \cdot s$), c the velocity of light ($3 \cdot 10^8 m/s$), q the elementary charge of electricity ($1.6 \cdot 10^{-19} C$) and λ the wavelength of the incident light. According to the experimental data, the $\eta(\lambda)$ of fabricated device could reach as high as 0.68% ($V_{ds}=+3V$, $V_{bg}=0V$) when responding to red light.

Summary

To summarize, we have fabricated phototransistors based on few-layer WS_2 . Due to the unique structural properties of two-dimensional material, devices based on it exhibit a high photo-electrical properties. The device demonstrate a high On/Off ratio ($\sim 10^4$) and relatively high carrier mobility ($7.1 \cdot 10^{-3} cm^2 V^{-1} s^{-1}$). In our experiment, 638 nm laser light was systematically investigated. Performance parameters, such as photoresponsivity ($R_{\lambda} = 3.5 mA/W$), response time ($t < 20ms$), external quantum efficiency ($\eta = 0.68\%$), detection rate ($D = 1.7 \times 10^9 W^{-1}$) and the photocurrent as a function of incident power were studied. Combining our results with large-area material preparation methods such as liquid scale exfoliation or CVD growth, together with the simplicity of the device presented here, could also result in the fabrication of inexpensive, high-sensitivity and flexible few-layer WS_2 optoelectronic devices. Possible fields of applications could include consumer imaging sensors suitable for low-light photography, for example in cell-phone cameras, which currently suffer from poor low-light performance, or in sensors for fluprescence imaging.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (No. 11574395), the Research Programme of National University of Defense Technology (No. JC15-02-01), the open foundation of State Key Laboratory of high Performance Computing (No. 201301-02), and the open foundation based on the innovation platform of Hunan key laboratories (No. 13K022).

References

- [1] Novoselov KS, Geim AK, Morozov S, Jiang D, Zhang Y, Dubonos Sa, et al. Electric field effect in atomically thin carbon films. science. 2004;306(5696):666-9.
- [2] Abajo FJGD, Koppens FHL, Chang DE, Thongrattanasiri S, editors. Graphene Plasmonics. Fourth International Workshop on Theoretica; 2011.

- [3] Bertolazzi S, Krasnozhon D, Kis A. Nonvolatile memory cells based on MoS₂/graphene heterostructures. *ACS nano*. 2013;7(4):3246-52.
- [4] Novoselov KS, Jiang Z, ., Zhang Y, ., Morozov SV, Stormer HL, Zeitler U, ., et al. Room-temperature quantum Hall effect in graphene. *Science*. 2007;315(5817):1379-.
- [5] Xia F, Mueller T, Lin Y-m, Valdes-Garcia A, Avouris P. Ultrafast graphene photodetector. *Nature nanotechnology*. 2009;4(12):839-43.
- [6] Geim AK, Novoselov KS. The rise of graphene. *Nature materials*. 2007;6(3):183-91.
- [7] Geim AK. Graphene: status and prospects. *Science*. 2009;324(5934):1530-4.
- [8] Gutiérrez HR, Perea-López N, Elías AL, Berkdemir A, Wang B, Lv R, et al. Extraordinary room-temperature photoluminescence in triangular WS₂ monolayers. *Nano letters*. 2012;13(8):3447-54.
- [9] Cong C, Shang J, Wu X, Cao B, Peimyoo N, Qiu C, et al. Synthesis and Optical Properties of Large - Area Single - Crystalline 2D Semiconductor WS₂ Monolayer from Chemical Vapor Deposition. *Advanced Optical Materials*. 2014;2(2):131-6.
- [10] Huo N, Yang S, Wei Z, Li S-S, Xia J-B, Li J. Photoresponsive and gas sensing field-effect transistors based on multilayer WS₂ nanoflakes. *Scientific reports*. 2014;4.
- [11] Zhang Y, Zhang Y, Ji Q, Ju J, Yuan H, Shi J, et al. Controlled growth of high-quality monolayer WS₂ layers on sapphire and imaging its grain boundary. *ACS nano*. 2013;7(10):8963-71.
- [12] Geim A, Novoselov K. The rise of graphene. *naturematerials*, 6: 183–191. March; 2007.
- [13] Radisavljevic B, Radenovic A, Brivio J, Giacometti V, Kis A. Single-layer MoS₂ transistors. *Nature nanotechnology*. 2011;6(3):147-50.
- [14] Yu JH, Lee HR, Hong SS, Kong D, Lee H-W, Wang H, et al. Vertical Heterostructure of Two-Dimensional MoS₂ and WSe₂ with Vertically Aligned Layers. *Nano letters*. 2015;15(2):1031-5.
- [15] Tonndorf P, Schmidt R, Böttger P, Zhang X, Börner J, Liebig A, et al., editors. Photoluminescence Emission and Raman Response of MoS₂, MoSe₂, and WSe₂ Nanolayers. *CLEO: QELS_Fundamental Science*; 2013: Optical Society of America.
- [16] Allain A, Kang J, Banerjee K, Kis A. Electrical contacts to two-dimensional semiconductors. *Nature Materials*. 2015;14(12):1195-205.
- [17] Liu W, Kang J, Sarkar D, Khatami Y, Jena D, Banerjee K. Role of metal contacts in designing high-performance monolayer n-type WSe₂ field effect transistors. *Nano letters*. 2013;13(5):1983-90.
- [18] Lopez-Sanchez O, Lembke D, Kayci M, Radenovic A, Kis A. Ultrasensitive photodetectors based on monolayer MoS₂. *Nature nanotechnology*. 2013;8(7):497-501.
- [19] Tsai D-S, Liu K-K, Lien D-H, Tsai M-L, Kang C-F, Lin C-A, et al. Few-layer MoS₂ with high broadband photogain and fast optical switching for use in harsh environments. *Acs Nano*. 2013;7(5):3905-11.
- [20] Ross JS, Klement P, Jones AM, Ghimire NJ, Yan J, Mandrus D, et al. Electrically tunable excitonic light-emitting diodes based on monolayer WSe₂ pn junctions. *Nature nanotechnology*. 2014;9(4):268-72.