Few-Layer MoS$_2$ with High Broadband Photogain and Fast Optical Switching for Use in Harsh Environments

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ABSTRACT Few-layered MoS$_2$ as Schottky metal–semiconductor–metal photodetectors (MSM PDs) for use in harsh environments makes its debut as two-dimensional (2D) optoelectronics with high broadband gain (up to 13.3), high detectivity (up to $\sim 10^{10}$ cm Hz$^{1/2}$/W), fast photoresponse (rise time of $\sim 70$ $\mu$s and fall time of $\sim 110$ $\mu$s), and high thermal stability (at a working temperature of up to 200 °C). Ultrahigh responsivity (0.57 A/W) of few-layer MoS$_2$ at 532 nm is due to the high optical absorption ($\sim 10$% despite being less than 2 nm in thickness) and a high photogain, which sets up a new record that was not achievable in 2D nanomaterials previously. This study opens avenues to develop 2D nanomaterial-based optoelectronics for harsh environments in imaging techniques and light-wave communications as well as in future memory storage and optoelectronic circuits.

KEYWORDS: graphene · MoS$_2$ · photodetector · high-temperature detection · harsh environment
photogating effect, which is not achievable for pristine graphene.

Atomic layered molybdenum disulfide (MoS2), a newly emerging 2D nanomaterial with a direct and finite band gap, may provide a possible solution to surpass the shortages belonging to graphene. Recently, gigantic photoluminescence (PL) enhancement of monolayer MoS2 has been observed experimentally and theoretically (4-fold higher than its bulk counterpart). This is due to a quantum confinement effect that expands the band gap from 1.2 eV (bulk) to 1.9 eV (monolayer) with a transition from "indirect band gap" to "direct band gap". This strong PL of ultrathin MoS2 implies possible applications in optoelectronics, such as PDs, biomedical markers, and sensors. Very recently, as compared to that obtained from pristine graphene (~1 × 10^{-3} A/W), the high photoresponsivity (7.5 × 10^{-3} A/W) from MoS2 phototransistors has been obtained due to direct band gap absorption.

The capability of high-temperature operation would offer great advantages for future smart sensors working under harsh environmental conditions. Some group III–V and IV materials, especially diamond, SiC, and AlN, can fulfill the demands for high-temperature electronics and optoelectronics, exceeding the capabilities of Si devices. For example, for high-temperature photodetection, SiC metal–semiconductor–metal (MSM) PDs have been demonstrated to work at 350 °C. Although those PDs can be operated at a high temperature, all of them are wide-band-gap materials and thus capable of limited detection in only UV/deep UV regions rather than broadband photodetection.

In this study, we report few-layer MoS2 Schottky PDs with back-to-back MSM geometry, capable of broadband photodetection from visible to UV regions with working temperatures up to 200 °C for use in harsh environments. Until few-layer MoS2 was demonstrated here, the broadband responsivity feature was not previously achievable for harsh environment use since all of the photodetection materials for harsh environments are wide-band-gap semiconductors. As a new record, the very high responsivity of 0.57 A/W and detectivity (over 10^{10} cm Hz^{1/2}/W) are due to high optical absorption of ~10% (very high absorption coefficient of up to 7.5 × 10^{7} cm^{-1}) of the few-layer MoS2 and a high photogain of ~13.3. In addition, temporal measurements reveal fast response times (~70 μs) and recovery times (~110 μs). The excellent optical properties of few-layer MoS2 promise a new generation of fast, broadband PDs based on 2D nanomaterials for applications in harsh environments, such as sensing, imaging, and intrachip optical interconnects at high temperatures.

RESULTS AND DISCUSSION

Syntheses of high-quality few-layer MoS2 by chemical vapor deposition have been reported recently. The optimized process used here is able to produce very homogeneous MoS2 trilayers across the whole sample. In general, the more diluted precursor solution and faster dip-coating result in a thinner MoS2 layer. Here, we aim at large-area and superior-quality...
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electron orbit coupling. The splitting of valence bands and the minimum of the conduction band at the K point of the Brillouin zone. The PL spectrum in Figure 1e, consisting of one major peak at 670 nm and one minor peak at 610 nm, further confirms the band gap of our few-layer MoS2.

The two feature peaks indicate the direct band transitions of excitons between the maximum of the split valence bands and the minimum of the conduction band at the K point of the Brillouin zone. The splitting of valence bands is due to the combined effect of interlayer coupling and spin–orbit coupling. The 610 nm emission can be observed only in few-layer MoS2, while 670 nm emission is monolayer-related luminescence, which is decreased with the thickness of the few-layer MoS2. The optical absorption spectrum of three-layer MoS2 in Figure 1f reveals that the absorption coefficient of few-layer MoS2 is up to 7.5 × 10^5 cm^-1 in the visible wavelength region, indicating that three-layer MoS2 can absorb ~10% of incident light. In addition, the two optical absorption peaks also match the direct excitonic transition peaks of MoS2 at around 610 and 670 nm observed in the PL spectrum, as shown in Figure 1e.

Figure 2a–b show the schematic and the optical microscopic top-view image of the few-layer MoS2 MSM PDs, respectively. To boost the photosensitivity of the few-layer MoS2, the devices were fabricated in MSM geometry with Schottky contacts to MoS2, effectively lowering the dark current. Accordingly, 100 nm thick Au layers as Schottky contacts were deposited on few-layer MoS2 using electron beam deposition. Figure 2c presents the photocurrent as a function of time under 532 nm laser illumination (light intensity \( I_{\text{light}} = 2.0 \times 10^4 \text{ W/m}^2 \)) with a reverse bias Schottky barrier. The transition between OFF and ON states reveals the response/recovery speed of the MoS2 PDs. The results are shown in Figure 2d, from which the rise time (from 10% to 90% of the maximum photocurrent as switching light from OFF to ON) and the fall time (from 90% to 10% of the maximum photocurrent as switching light from ON to OFF) of MoS2 MSM PDs can be estimated to be 70 and 110 \( \mu \text{s} \), respectively. The photoresponse times of MoS2 MSM PDs measured in this study are 3 orders of magnitude shorter than those reported previously (~50 ms). The difference of the response speed between the work done in ref 26 and our work could be explained from three aspects. First of all, the contact electrode to MoS2 in our work is pure Au with a high work function of 5.47 eV. The two back-to-back Schottky contacts to MoS2 formed by the high-work-function metal lead to low dark current (due to the presence of two back-to-back Schottky barriers) and fast photoresponse speed (due to fast carrier sweeping in the depletion regions under the electric fields of the reverse bias Schottky barrier). We further estimated the electric fields of the reverse bias Schottky barrier under 5 V bias to be more than 6 × 10^5 V/m by \( E = V/L \), where \( E \) is the electrical field, \( V \) is the applied voltage, and \( L \) is the contact spacing. As the bias voltage increases, the electric fields of the reverse bias Schottky barrier will increase. Second, we employed the MSM structure with the “interdigital” electrode pattern, which can facilitate the efficient collection of photocarriers and contribute to faster response speed. Third, the difference between two works (ref 26 and ours) may not merely come from the device, but the improvement of the measurement system. The time resolution of our measurement system is 10 \( \mu \text{s} \), which is apparently higher than that of ref 26 (~tens of milliseconds). Moreover, we do note that the photoresponse times could be further improved via increasing the Schottky barrier height between contact metal and MoS2 as well as reducing surface defects and metal contact spacing.

To demonstrate the feasibility of few-layer MoS2 PDs in practical uses, the following investigations were performed, including (i) spectral responsivity, (ii) light intensity-dependent photocurrent, and (iii) light modulation frequency-dependent photogain measurements, as shown in Figure 3a–c, respectively. In Figure 3a, spectral responsivity and photogain of the MoS2 MSM PDs were measured under a bias of 10 V. Within the visible wavelength region the responsivity is ~660 nm agrees with the direct band gap of the MoS2 films (~1.9 eV). Note that ultrahigh responsivity up to 0.57 A/W obtained here is 3 orders of
Figure 3. (a) Photogain and responsivity as a function of wavelength measured under a bias of 10 V. (b) Light intensity-dependent photocurrent of the MoS2 PDs at 10 V. (c) Frequency dependence of the photogain measured under a bias of 10 V and 532 nm laser illumination ($I_{\text{light}} = 2.0 \times 10^4 \text{W/m}^2$).

Moreover, the noise equivalent power (NEP) is an important parameter of a PD that is frequently quoted, i.e., the optical signal power required to generate a photocurrent signal ($I_{\text{ph}}$) that is equal to the total noise current ($I_n$) in the PD at a given wavelength and within a bandwidth of 1 Hz. The NEP represents the required optical power to achieve a signal-to-noise ratio (SNR) of 1 with a bandwidth of 1 Hz. The detectivity ($D^*$), the reciprocal of NEP, is a figure of merit used to characterize the performance of a photodetector. Under a 10 V bias, the calculated NEP of the MoS2 MSM PDs in this study is $1.1 \times 10^{-10}$ W/cm Hz$^{1/2}$ by $\text{NEP} = P/f^{1/2} = (2eJ_0)^{1/2}/R$, where $P$ is incident optical power, $f$ is frequency bandwidth of the photodetector, $R$ is responsivity, $e$ is electronic charge, and $J_0$ is dark current density, leading to a $D^* \sim 10^{10}$ cm Hz$^{1/2}$/W. To compare with commercially available AlGaN-based PDs ($2.65 \times 10^{10}$ cm Hz$^{1/2}$/W) and Si-based PDs ($\sim 10^{12}$ cm Hz$^{1/2}$/W) reported previously, the detectivity of few-layer MoS2 MSM PDs should be further improved via reducing the dark current and increasing the responsivity.

To quantitatively analyze the relationship of the photocurrent to the light intensity, the photocurrent was measured under a bias of 10 V with $I_{\text{light}}$, as shown in Figure 3b. Measurements were performed from low to high light intensity to prevent artifacts caused by persistence or temperature transients. The photocurrent ($I_{\text{ph}}$) versus $I_{\text{light}}$ is fitted by a power-law relationship ($I_{\text{ph}} \propto I_{\text{light}}^n$) with $n = 0.71$, by which a near-linear relationship can be obtained. The generation rate of photocarriers is proportional to the amount of photon absorption, implying that the defects in the few-layer MoS2 contribute little to the photocurrent.

The dynamics of the photogenerated carriers can be further manifested based on the high-frequency measurement of the MoS2 PDs. The measurement was carried out under a bias of 10 V with a mechanical chopper to modulate the frequency of light sources. As shown in Figure 3c, the photocurrent gradually reduces with the modulation frequency due to the limitation of response rates. One can see that even in the sub-millisecond domain the photocurrent values are still larger than unity. We note that the defects in the MoS2 limit the performance of MoS2 PDs; carrier mobility, photoresponse time, and responsivity can be further improved via reducing the defects in the MoS2 layers. We envision that once the defect can be eliminated significantly, the performance of superior crystalline MSM PDs is boosted further with an appropriate device design.
PDCR of MoS2 PDs as a function of temperature measured under a bias of 5 V and 532 nm laser illumination ($I_{light} = 2.0 \times 10^3 \text{ W/m}^2$).

To demonstrate photodetection applications under harsh conditions, the thermal stability of the MoS2 PDs is evaluated by measuring the photocurrent/dark current ratio (PDCR = ($I_{ph} - I_{d}$)/$I_{d}$, where $I_{ph}$ is the photocurrent under illumination and $I_{d}$ is the dark current) from room temperature to 250°C.28,50 The PDCR curve in Figure 4 shows that the few-layer MoS2 PDs are capable of photodetection even at 200°C, mainly due to small levels of current leakage and high thermal stability of MoS2 at high temperatures. A further increase in temperature lowers the PDCR of MoS2 PDs. When the temperature increases to 250°C, the PDCR value decreases to unity, indicating that the MoS2 PDs cannot work properly. The noticeable deterioration in PD performance may be due to the oxidation of few-layer MoS2 and the generation of the thermal carriers, which cannot be eliminated at high temperatures.51 It should be noted that the oxidation of MoS2 to MoO3 in a dry O2 environment could occur at 375 K.52 Moreover, Mikhene et al. have also reported that the degradation of the nanographite film PD sensitivity is caused by the oxidation of the nanographite at high temperature.53 Therefore, we envision that further improvements including the passivation layers for preventing oxidation, reducing surface defects, and reinforcing the Au/MoS2 interface might be able to extend the working temperatures of MoS2 PDs.28,54

CONCLUSION

In summary, for the first time, 2D nanomaterials using few-layer MoS2 as MSM PDs with broadband high responsivity/photogain and fast photoresponse for applications in harsh environments are demonstrated. The broadband absorption feature of few-layer MoS2 was not achievable previously for harsh environment use since all materials for harsh environments are wide-band-gap semiconductors. At 10 V bias, the photogain of up to 13.3 leads to ultrahigh responsivity and detectivity of MoS2 up to 0.57 A/W and ~1010 cm Hz1/2/W, respectively, which was not obtainable in pristine graphene and MoS2-based PDs before. The MoS2 MSM PDs exhibit a very fast and stable photoresponse, i.e., ~70 μs of rise time and ~110 μs of fall time. Although the thickness of few-layer MoS2 is only ~1.9 nm, the optical absorption of MoS2 is as high as ~10% over the visible region. Furthermore, few-layer MoS2 shows an excellent sensitivity factor (PDCR) that is up to ~10 even at 200°C. Few-layer MoS2, a new class of 2D nanomaterials with broadband high photogain and fast optical switching, holds promise for the next-generation optical devices in harsh conditions.

METHODS

For the preparation of few-layer MoS2, 0.25 g of (NH4)2MoS4 (Alfa Aesar, purity of 99.99%) was added to 20 mL of DMF to form a 1.25 wt% solution. It was sonicated for 20 min to achieve a homogeneous (NH4)2MoS4 solution. The sapphire substrates were first cleaned with a piranha solution ($H_2SO_4/H_2O_2$, 7:3) to remove the surface contaminants. The cleaned substrates were immersed into the (NH4)2MoS4 solution, followed by slow pulling-up (0.5 mm/s). After that, the substrates were baked on a hot plate at 120°C for 30 min until the majority of solvent molecules were evaporated. The substrate was then placed on the edge of a quartz tube with a flow of H2 (20 sccm) and Ar (80 sccm). When the temperature in the center of the furnace reached 300°C, the substrate was moved to the center of the furnace. Sixty minutes later, the sample was cooled to room temperature under H2/Ar ambient by putting the sample back to the tube edge. The sample was moved to the furnace center again for the second postannealing when the center of the furnace reached 1000°C in an Ar sulfur environment at 500 Torr. After the process of growing MoS2 layers on sapphire, we transferred the MoS2 layers onto freshly cleaned SiO2/Si substrates for fabricating MSM PDs.

The MSM PDs were defined using photolithography with active areas of 500 × 158 μm², and 8 μm wide, 150 μm long, and 100 nm thick interdigitated Au electrodes with 8 μm wide spacing to serve as Schottky contacts on MoS2/SiO2/Si substrates were utilized for the MSM PDs. The MoS2 MSM PDs were measured under 532 nm laser (beam diameter is ~1 mm) illumination in air. After the fabrication process of MoS2, MSM Schottky PDs, surface morphology and thickness of the atomically thin MoS2 were revealed by atomic force microscopy (Veeco Dimension Icon system), Raman and PL spectra were obtained by confocal Raman microscopic systems (NT-MDT) with a 473 nm laser (spot size of laser is ~0.5 μm in diameter). The Si peak at 520 cm⁻1 was used for calibration in the experiments. Field-emission transmission electron microscopy (JEOL JEM-2100F, operated at 200 kV with a point-to-point resolution of 0.19 nm) was used to investigate the microstructures. The samples for HRTEM were prepared using a lacy-carbon Cu grid to scratch the surface of MoS2 samples. The absorbance spectra were measured with a JASCO V-670 UV–visible spectrometer in the spectral range from 380 to 800 nm. The Keithley 4200-SCS semiconductor characterization system and the EQE-R3011 spectral response system (Enli Technology Co., Ltd.) were used to measure I–V characteristics and responsivity of the few-layer MoS2 PDs.

Conflict of Interest: The authors declare no competing financial interest.

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REFERENCES AND NOTES


