Surface Plasmon-Enhanced Photodetection in Few Layer MoS$_2$ Phototransistors with Au Nanostructure Arrays


1. Introduction

Graphene and related 2D materials have emerged as potential building blocks for a variety of fundamental optical and electronic components, including field-effect transistors (FETs), nonvolatile memory devices, photonics devices, and phototransistors.\[1\] Graphene exhibits an ultrahigh carrier mobility of $\approx 100,000$ cm$^2$ V$^{-1}$ s$^{-1}$, but it reveals a considerable limitation in regard to real device applications due to its zero bandgap nature.\[14\] Therefore, it is very difficult for graphene to be used for digital circuits or optoelectronic devices, which need clearly defined on/off states. Very recently, MoS$_2$ appears to be an alternative 2D nanoflake, due to its optical sensitivity, mechanical flexibility, extraordinary on/off ratio ($\approx 10^8$), absence of dangling bonds and compatibility to silicon complementary metal oxide semiconductor (CMOS) processes,\[15-18\] which may overcome the drawbacks of graphene. More importantly, in great contrast to the zero bandgap issue of graphene, MoS$_2$ has a large semiconducting bandgap of 1.8 eV for a monolayer and 1.2 eV for bulk layer, which can enable many fascinating nanoelectronics and optoelectronics applications.\[19-22\] Monolayer and few-layer MoS$_2$
FETs with high current on/off ratios and steep subthreshold swings (65 mV decade⁻¹) have already been demonstrated in a top-gated FETs.[23] High performance flexible MoS₂ transistors can be achieved on Al₂O₃ or HfO₂ substrates.[24,25] MoS₂-based gas sensors exhibit excellent sensitivity to NO₂, NH₃, and humidity.[26–28] Logic transistors, memory devices, and complementary inverters can be fabricated from vertically stacked graphene/MoS₂ multiheterostructures.[29,30] MoS₂ has piezoelectric properties and can be used for sensitive nanomechanical transducers and resonators.[31–33] Moreover, monolayer and few-layer MoS₂ also display light absorption, photoluminescence (PL), and electroluminescence capabilities, enabling phototransistor operation.[34–37] Previous studies demonstrated that single-layered MoS₂ phototransistors have good stability and photoswitching time of ≈50 ms.[38,39] However, the performance of previously reports for MoS₂ phototransistors is limited by the low photoresponsivity, which is largely due to its poor light absorption properties.[38,39] To overcome this limitation, we demonstrate a large plasmonic resonance enhancement of photocurrent response in few-layer MoS₂ phototransistors by utilizing Au nanoparticles or periodic Au nanoarrays. For the first time, we achieved a threefold enhancement of photocurrent response in few-layer MoS₂ phototransistors with a periodic Au nanoarray. The photocurrent enhancement can be mainly attributed to both the enhanced near-field oscillation and scattering effect of metal nanoparticles.[4,40,41] The localized surface plasmon (LSP) in metal nanoparticles leads to oscillation of conduction electrons in metal nanoparticles. Due to the oscillation, light is trapped around the surface of Au nanoplate, leading to an enhanced local electrical field effectively improving the light absorption of MoS₂.[4] Moreover, the scattering effect can also enhance the photocurrent response. The optical energy scattered by one Au nanoparticle can be collected by nearby Au nanoparticles as plasmons instead of decaying as free-space light.[4,42,43] Our findings provide a possibility to realize high photoresponsivity and wavelength selectable MoS₂-based optoelectronic devices.

In this work, the single or few-layer MoS₂ was mechanically exfoliated from molybdenite crystals and transferred onto p+Si/SiO₂ (300 nm) substrates. The metal Cr/Au (10 nm/40 nm) source/drain (S/D) electrodes were defined by electron beam lithography (EBL), metallization, and lift-off processes. The 4 nm thick Au nanoparticles were directly deposited onto few-layer MoS₂ phototransistors using thermal evaporation technique. The well-defined Au nanoarrays were created by EBL and thermal evaporation processes. Prior to the deposition of periodic Au nanoarrays, 1 nm HfO₂ passivation layer was deposited onto MoS₂ by atomic layer deposition (ALD).

2. Results and Discussion

In a typical experiment, the MoS₂ nanoflake was exfoliated from bulk MoS₂ and transferred onto p+Si/SiO₂ substrates using the Scotch tape. Figure 1a shows the schematic and optical microscope image of a typical few-layer MoS₂-based phototransistor. It is found out that the channel length and width are approximately 3 and 4 µm, respectively. Figure 1b,c depicts the optical microscope image of a representative MoS₂ nanoflake and its AFM image. The height of the MoS₂ nanoflake is ≈4.5 nm, as shown in Figure S1 (Supporting Information). Figure 1d displays the optical microscope image of single- and few-layer MoS₂ nanoflake and its PL mapping image. The optical contrast indicates that the MoS₂ on the right (region B) is a single layer. The PL mapping image of the same MoS₂ nanoflake
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Figure 2. a) Logarithmic $I_{ds}/I_{off}$ ratio versus $V_{gs}$ transfer characteristics of few-layer MoS$_2$ phototransistors under illumination. The laser wavelength is 532 nm with intensity ~200 μW. b) Linear $I_{ds}$ versus $V_{gs}$ output characteristics of the same device. c) Photocurrent ($I_{photo}$) and $I_{on}/I_{off}$ ratio as a function of back-gated voltages. d) Linear $I_{ds}$ versus $V_{gs}$ curves under illumination with different intensities (80, 100, 120, 160, and 200 μW). e) Photoswitching behavior of the same phototransistor at different $V_{gs}$ (~−20, −10, and 0 V). f) Threshold voltage ($V_T$) as a function of illumination power (0, 120, and 200 μW).

Further demonstrates its single-layer nature. As has been demonstrated by the previous report, bulk MoS$_2$ has an indirect bandgap of $\approx$1.2 eV, but the single-layer MoS$_2$ has been reported to exhibit a direct bandgap of $\approx$1.8 eV.$^{[9-22]}$ Therefore, the PL peak around 680 nm is mainly attributed to the direct interband recombination of the photogenerated electron-hole pairs in the single-layer MoS$_2$ nanoflake as shown in Figure 1e. Figure 1f presents the Raman spectra of single-layer and few-layer MoS$_2$ nanoflake. Two peaks around 380 and 400 cm$^{-1}$ are attributed to the in-plane opposite vibration of two S atoms with respect to the Mo atom between them ($E_{2g}^{1}$ mode) and out-of-plane opposite vibration of two S atoms ($A_{1g}$ mode), respectively. In addition, from single-layer to few-layer MoS$_2$, the $E_{2g}^{1}$ mode undergoes a red shift while the $A_{1g}$ mode undergoes a blue shift, as shown in Figure 1f (red line).

Figure 2 displays the optoelectronic performance of few-layer MoS$_2$ phototransistors. The $I_{ds}$ versus $V_{gs}$ transfer characteristics (Figure 2a) show that the device had a respectable $I_{on}/I_{off}$ ratio of $\approx$10$^8$ and on-current of $\approx$20 μA. Figure 2b shows the $I_{ds}$ versus $V_{ds}$ output characteristics of the same MoS$_2$ phototransistor. The linear behavior demonstrates that the electrodes are Ohmic contacts and the back-gated biases could fully control the carrier density of the devices. Despite the single or few-layer, MoS$_2$ can absorb photons of energy ranging from ultraviolet to near-infrared region.$^{[38,39,45]}$ Under illumination, the few-layer MoS$_2$ phototransistor has a distinct photocurrent response with maximum net photocurrent ($I_{photo}$) of $\approx$4.6 μA at $V_{gs}$ = 80 V, as shown in Figure 2a. Figure 2c presents the photocurrent ($I_{photo}$) and $I_{Light}/I_{Dark}$ ratio as a function of back-gated biases. It is found that the output photocurrent increased when the back-gated biases changed from ~80 to 80 V (blue line). However, the $I_{Light}/I_{Dark}$ ratio decreased with the increased back-gated voltage (red line). To further illustrate the physical mechanism in Figure 2c, Figure S2 (Supporting Information) presents the schematic energy band diagram of MoS$_2$ FETs. In the on-state ($V_{gs}>V_T$), increasing the back-gated voltage can lower the Schottky barriers at the contacts (top image, Figure S2 (Supporting Information)), resulting in a more efficient photocarrier extraction and injection. In addition to the photogenerated electron-hole pairs, thermionic and tunneling current also contribute to the detector current. In the off-state ($V_{gs}<V_T$), the device has a relatively higher Schottky barrier, resulting in the less photocurrent extraction (downward image, Figure S2 (Supporting Information)). However, operating the MoS$_2$ phototransistors in the off-state brings the advantage of high signal-to-noise ratio (SNR), since the devices have a reduced dark current, as shown in Figure 2c (red line). Figure 2d shows the output characteristics of few-layer MoS$_2$ phototransistors under different illumination power levels. The photocurrent increases gradually when the optical power increases from 80 to 200 μW. The increased photocurrent is mainly attributed to the increased number of photogenerated electron–hole pairs as the incident optical power increases. Figure 2e shows the stability and photoswitching characteristic of few-layer MoS$_2$ phototransistors. The photocurrent as a function of time was measured under alternating dark and illumination conditions at different back-gated voltages. The on–off photoswitching behavior is well retained even after 60 repeated cycles. Figure 2f shows the device threshold voltage ($V_T$) changing as a function of illumination power. In MoS$_2$ phototransistors, both the photovoltaic (PV) and photoconductive (PC) effects show strong photogain.$^{[45]}$ The PV effect in MoS$_2$ phototransistors is referred as “phototagging” effect, resulting in a change in $V_T$.$^{[45]}$ The $I_{photo}$ induced by PV effect is $\approx$4 μA, as shown in “Supporting Information”. The PV effect dominates the photocurrent response in MoS$_2$ phototransistors, because the total photocurrent $I_{photo}$ is $\approx$4.6 μA. Figure S3 (Supporting Information) shows the photocurrent response of MoS$_2$ phototransistors with periodic...
Au nanoarrays, indicating that the PV effect still dominates the photocurrent response.

The performance of MoS$_2$ phototransistors reported to date is limited to low photoresponsivity due to small light absorption intensity. To overcome the limitation, here we report a new strategy to integrate few-layer MoS$_2$ with Au plasmonic nanostructures. The Au nanoparticles can be directly deposited onto few-layer MoS$_2$ phototransistors using the thermal evaporation system, as shown in Figure 3a. The Au nanoparticles act as subwavelength scattering sources and nanoantennas to simultaneously improve both light absorption and photocarrier collection in multi-layer MoS$_2$ transistors, because the Au nanoparticles can concentrate free space light into deep-subwavelength antenna gaps, where MoS$_2$ light interaction is greatly enhanced.$^{[46,47]}$

Moreover, the photoresponsive charge-transfer effect can also enhance the photocurrent, because Au nanostructures were directly contacted with MoS$_2$ layer.$^{[46,47]}$ The scanning electron microscope (SEM) images of Au nanoparticles with different thicknesses (from 1 to 4 nm) present a high-density array of Au nanoparticles as depicted in Figure 3b. The statistics of Au nanoparticles (Figure 3c) in the SEM image shows that the number of Au nanoparticles decreases from 360 to 140, when the thickness increases from 1 to 4 nm. To study the plasmonic resonance effect of Au nanoparticles, ultraviolet to visible spectral analysis is used to characterize the micro-region light absorption spectrum. Figure 3d exhibits maximum plasmon resonance enhanced absorption of $\approx 24\%$ with an obvious resonance peak around 680 nm (black line). The plasmon resonance peak displays a red shift as the thickness of Au nanoparticles increases from 1 to 4 nm. Additionally, the plasmon resonance intensity becomes much stronger with the increasing Au nanoparticles thickness and size. Figure 3e shows the output characteristics of device photocurrent. The incident laser wavelength is 632 nm. It is can be seen that the few-layer MoS$_2$ phototransistor with Au nanoparticles has an overall 2× higher photocurrent than that of original one. The illumination power dependence studies show that the output photocurrent increases linearly with the illumination power, as indicated in Figure 3f.

To further understand the plasmonic resonance-enhanced photodetection, we have synthetized well-defined periodic Au nanoarrays on few-layer MoS$_2$ phototransistors using the EBL approach. Figure 4a shows the 3D schematic of few-layer MoS$_2$ phototransistors with periodic Au nanoarrays. To avoid being damaged by the Au nanoarrays deposition and negative effects of ambient moisture, a 1 nm HfO$_2$ dielectric layer was deposited on few-layer MoS$_2$ as a passivation layer using the ALD technique.$^{[38,48]}$ Figure 4b displays the SEM image of a representative Au nanoarrays deposited onto the MoS$_2$ phototransistors. It is determined that the Au nanoarrays were quite uniform. The inset of Figure 4b shows the well-defined Au nanoarrays with 160 nm width, 180 nm length, 50 nm height, and 300 nm period. To study the plasmonic resonance effect of well-defined Au nanoarrays, we employed scanning photocurrent microscopy (SPM) to characterize the micro-region light absorption spectrum. Figure 4c shows the plasmon resonance absorption spectrum of the Au nanoarrays/HfO$_2$/MoS$_2$ hybrid structure, which indicates a plasmonic resonance peak around 630 nm. Comparing the output photocurrent as shown in Figure 4d, it is seen that the MoS$_2$ phototransistors with Au nanoarrays have an overall 3× higher photocurrent than those without Au nanoarrays. The incident wavelength is 632 nm. Figure 4e presents the photocurrent generation as a function of laser power. The red and black lines indicate the device photocurrent with/without Au nanoarrays, respectively. The photocurrent scales linearly with the illumination power. Figure 4f exhibits the photocurrent as a function of laser wavelength, demonstrating that the phototransistors with Au nanoarrays have the largest photocurrent at a
wavelength of 632 nm. However, the photocurrent response of MoS$_2$ phototransistors without the Au nanoarrays does not change significantly with the changing of illumination wavelength. The photocurrent enhancement is consistent with the LSP-enhanced light absorption of the periodic Au nanoarrays, as shown in Figure 4c.

To better understand the LSP effect of periodic Au nanoarrays, a COMSOL Multiphysics simulator was employed to calculate the electrical field distribution near a single Au nanoplate. Figure 5a shows the plasmonic resonance intensity as a function of incident light wavelength, demonstrating a plasmonic resonance peak around 630 nm. We further achieved the average enhanced light intensity as a function of distance from bottom of Au nanoplate, as shown in Figure 5b. The initial point is taken at −1 nm from the bottom of Au nanoplate. It shows that the average optical energy decays rapidly with increasing distance from the Au nanoplate. Figure 5c exhibits a dark-filed optical image of MoS$_2$ phototransistor with periodic Au nanoarrays. It can be seen that a MoS$_2$ layer with Au nanoarrays (region A) has an enhanced optical field in contrast to the one (region B) without the Au nanoarrays. Figure 5d (lift image)
shows electrical field distribution in a cross section of Au nanoplate. The XY plane field image is taken at ~3 nm from the bottom of Au nanoplate. The field image indicates that the light is enhanced and trapped in close proximity of the Au nanoplate. Figure 5d (right image) shows the dark-field optical image of 10 x 10 μm² periodic Au nanoarrays on p-Si/SiO₂ substrate. It is found out that the region with periodic Au nanoarrays exhibited a bright spot. The enhancement of light absorption in MoS₂ phototransistors with Au nanoarrays originates from the energy transfer effect in the LSP coupling and/or the strong local field enhancement of nanoscale gaps between Au nanoplates.[46,47] In this manner, the MoS₂ light interaction is largely enhanced because of high electrical field intensity inside the nanoscale gaps.[47]

3. Conclusion

In summary, this paper offers an avenue to improve the photocurrent response of few-layer MoS₂ phototransistors by integrating MoS₂ with Au plasmonic nanostructures. Coupling Au nanoparticles or nanoarrays with atomically thin MoS₂ can result in an enhanced local optical field near the MoS₂ layer. We obtained a twofold increase in the photocurrent by depositing 4 nm thick Au nanoparticles sparsely onto MoS₂ phototransistors. Moreover, the photocurrent of few-layer MoS₂ phototransistors exhibits a threefold increase with periodic Au nanoarrays (300 nm period, 160 nm wide, 180 nm length, and 50 nm height). The optical simulation shows that plasmon resonance effect is mainly attributed to the near-field oscillation and scattering effect of the periodic Au nanoarrays. Coupling the atomically thin few-layer MoS₂ with plasmonic nanostructures can effectively convert the local plasmonic enhancement effect into an electrical signal, and thus has the potential to enable the design of next-generation plasmon resonance-based devices for image sensors or multiplexed bio-sensor arrays.

4. Experimental Section

Phototransistors Fabrication and Measurements: Few-layer MoS₂ nanoflakes are mechanically exfoliated from bulk MoS₂ crystals and transferred onto p-Si/SiO₂ (300 nm) substrates. Then the substrates are spin-coated with methyl methacrylate (MMA) and poly methyl methacrylate (PMMA). The S/D electrodes are defined by EBL (JEOL 6510 with NPGS), metallization, and lift-off processes. The Cr/Au (10 nm/40 nm) electrodes are deposited by thermal evaporation technique. The 4 nm thick Au nanoparticles are directly deposited onto few-layer MoS₂ phototransistors by the thermal evaporation process. The periodic Au nanoray is fabricated in the same way as for S/D electrodes preparation. The electrical characteristics are implemented with the Lakeshore TTPX Probe Station and Agilent 4155C Semiconductor Parameter Analyzer.

Numerical Simulation: To simulate the LSP resonance effect, COMSOL Multiphysics was used in this work. In this mode, a semi-infinite Si layer (n_Si = 4), 300 nm SiO₂ layer (n_SiO₂ = 4), 3 nm MoS₂ layer, 2 nm HfO₂ layer, and a Au nanoplate (300 nm period, 160 nm wide, 180 nm length, and 50 nm height) were defined from bottom to up, where n_Au was provided by ref[44]. The X, Y-axis boundary condition was set to periodic, and the Z-axis boundary condition was set to scattering boundary condition, where an interior port boundary was provided as the excitation light source. A stationary solver was built to solve different frequency light coupling effect with plasmonic nanostructures.

Supporting Information

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

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