

## *Article* **Simple Fabrication of Photodetectors Based on MoS<sup>2</sup> Nanoflakes and Ag Nanoparticles**

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**Abstract:** Low-dimensional transition-metal dichalcogenides (TMDs) have recently emerged as promising materials for electronics and optoelectronics. In particular, photodetectors based on mono- and multilayered molybdenum disulfide (MoS<sub>2</sub>) have received much attention owing to their outstanding properties, such as high sensitivity and responsivity. In this study, photodetectors based on dispersed MoS<sub>2</sub> nanoflakes (NFs) are demonstrated. MoS<sub>2</sub> NFs interact with Ag nanoparticles (NPs) via low-temperature annealing, which plays a crucial role in determining device characteristics such as good sensitivity and short response time. The fabricated devices exhibited a rapid response and recovery, good photo-responsivity, and a high on-to-off photocurrent ratio under visible light illumination with an intensity lower than  $0.5\:\rm{mW/cm^2}.$ 

Keywords: transition-metal dichalcogenides (TMDs); MoS<sub>2</sub> nanoflakes; MoS<sub>2</sub> photodetectors; visible light sensor



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### **1. Introduction**

Low-dimensional transition-metal dichalcogenides (TMDs) have received considerable attention as promising materials for high-performance semiconductors in several fields such as electronics, optoelectronics, and energy conversion and storage  $[1-8]$  $[1-8]$ . In particular, extensive research has been conducted to explore molybdenum disulfide (MoS<sub>2</sub>), which has a direct bandgap structure contributing to its excellent electrical and optical properties  $[9,10]$  $[9,10]$ . The fundamental properties of MoS<sub>2</sub>, such as quantum confinement effects and the functions of chalcogen vacancies and photoexcited carriers, have been extensively studied for their practical and potential applications [\[11–](#page-10-3)[15\]](#page-10-4). Several electronic and optoelectronic devices, including field-effect transistors, charge-trap memories, and photodetectors based on mono- and multilayered  $MoS<sub>2</sub>$ , have been realized  $[16–19]$  $[16–19]$ . Interestingly, thin layers of  $MoS<sub>2</sub>$  with structural integrity exhibit high light-absorption coefficients, enabling sensitive photon detection via photoexcited carriers. These thin layers are conventionally fabricated using chemical vapor deposition (CVD) growth methods [\[20](#page-10-7)[–22\]](#page-10-8). Recently, solution-phase exfoliation and stabilization of TMDs have been proposed as alternative methods that facilitate facile and rapid fabrication [\[23–](#page-10-9)[26\]](#page-10-10). These methods enable synthesis of  $MoS<sub>2</sub>$  with small dimensions, such as nanoflakes (NFs), in a size-controlled manner, demonstrating their significant advantages such as low-temperature and solutionbased processing. However, in the context of photodetecting, connectivity between  $M$ nanostructures with high light-absorption coefficients is required during film formation to provide conducting pathways for the collecting photoexcited carriers generated in  $MoS<sub>2</sub>$ through electrodes. Thus, considerable research is underway to achieve high electrical conductivity and environmental stability in nanostructured  $MoS<sub>2</sub>$  films. For example, band-selective photodetection has been successfully demonstrated using TMD nanosheets exfoliated with amine-terminated polymers in solution [\[27\]](#page-10-11).

In this study, thin photodetectors based on dispersed MoS<sub>2</sub> NFs are presented, and the optoelectronic properties for high absorption coefficients of photons are discussed in relation to experimental and theoretical studies. Initially,  $MoS<sub>2</sub>$  NFs are synthesized in the solution phase with planar dimensions of  $\sim$ 20 nm for thin film formation via the drop-coating method, using Ag nanoparticles (NPs) formed from Ag nanofilms to ensure electrical connectivity between the  $MoS<sub>2</sub>$  NFs. The Ag contacts to bulk  $MoS<sub>2</sub>$  layers are known to become ohmic, and the resistivity of the  $MOS<sub>2</sub>$  layers decreases after annealing at 400–600 ◦C [\[28\]](#page-10-12). Furthermore, Ag NPs and islands can enhance light absorption in photoresponsive devices via plasmonic  $[29,30]$  $[29,30]$ . Thus, the photoexcited carriers in MoS<sub>2</sub> can be efficiently collected even under low-intensity illumination (<0.5 mW/cm<sup>2</sup>) with rapid response and recovery times. Photodetectors based on MoS<sub>2</sub> NFs and Ag NPs have exhibited good photodetection abilities under low-intensity illumination and ambient conditions. This study provides a novel and simple route to achieve good performance thin photodetectors with desirable photodetection abilities for practical applications, particularly under low-intensity illumination conditions. These results demonstrate great potential for the development of advanced light-sensing systems, and other TMD-based applications such as transistors, memories, and energy conversion and storage devices.

#### **2. Materials and Methods**

#### *2.1. Preparation of MoS<sup>2</sup> NFs Solution*

MoS<sup>2</sup> NFs were prepared using a simple liquid exfoliation technique; 500 mg of MoS<sup>2</sup> micro-crystals (Sigma Aldrich, St. Louis, MO, USA) were dispersed in 250 mL of a deionized (DI) water:ethyl alcohol (1:1) solution. The mixture was sonicated using a probe sonic tip (19 mm in diameter) at a power of 500 W using 10 s ON and 10 s OFF pulses for 10 h. DI water:ethyl alcohol solution (1:1, 50 mL) was added into the beaker every 2 h to maintain the volume of the  $MOS<sub>2</sub>$  solution (250 mL) because the solution easily evaporated during ultrasonication owing to the high temperature. Additionally, the continuous feeding of the solution prevented a steep increase in temperature during the ultrasonication process. Subsequently, the solution was diluted to 1000 mL and centrifuged for 5 min at 5000 rpm to separate and remove the unexfoliated  $MoS<sub>2</sub>$ . The supernatant solution was further centrifuged at 8000 rpm for 30 min to remove large  $MoS<sub>2</sub>$  particles. Approximately 90% of the supernatant solution was filtered under vacuum onto a membrane paper with a pore size of 100 nm. The filtered solution was dried in an oven to concentrate the MoS<sub>2</sub> NF solution, until the volume of the solution reached 500 mL.

#### *2.2. Photodetector Fabrication*

Photodetectors were fabricated based on the schemes shown in Figure [1a](#page-2-0). For example, the photodetector (20 nm Ag, 400  $^{\circ}$ C, vacuum, 24 h) exhibited high performance. In the typical procedure for the bottom-mode photodetector, a rectangular  $SiO<sub>2</sub>$  (300 nm)/Si substrate with dimensions of  $1 \times 1$  cm<sup>2</sup> was cleaned using oxygen plasma equipment. The substrate was drop coated with the  $MoS<sub>2</sub>$  NF solution at a solution/substrate ratio of  $\sim$ 0.3 mL/cm<sup>2</sup>. Subsequently, the solution was dried on the substrate in an oven at 80  $\degree$ C for 30 min. The top Ag thin film was evaporated onto the sample under vacuum ( $2 \times 10^{-6}$  Torr) using a thermal evaporation system. The prepared sample was then annealed at 400 °C for 24 h in a muffle furnace at 1 atm, using a heating rate of 50 °C/min. After cooling to room temperature, the Au electrodes (50 nm) were evaporated onto the thin annealed film under vacuum using a patterned shadow mask. For the middle-mode photodetector, a 10 nm Ag layer was deposited on the  $SiO<sub>2</sub>$  substrate and annealed at  $400\degree$ C for 24 h at atmospheric pressure. The MoS<sub>2</sub> solution was then drop coated and dried in an oven at 80  $\degree$ C for 30 min. A second 10 nm thick Ag film was deposited on the dried sample and annealed under the same conditions. Subsequently, the Au electrodes (50 nm) were evaporated onto the thin annealed film, as described above. An optical image of the fabricated device is shown in Figure [1c](#page-2-0).

<span id="page-2-0"></span>

Figure 1. (a) Illustration of the fabrication of photodetecting devices. (b) Schematic of the bottomand middle-mode structures. (**c**) Optical image of the fabricated device and magnified image of Ag and middle-mode structures. (**c**) Optical image of the fabricated device and magnified image of Ag islands on the MoS<sub>2</sub> layer. (**d**) SEM image of MoS<sub>2</sub> film and magnified AFM image of boxed area (e) Size distribution of the MoS<sub>2</sub> NFs. (f) Raman spectra of MoS<sub>2</sub> film on silver film.

# *2.3. Process and Measurements 2.3. Process and Measurements*

The following equipment was used: ultrasonicactor (SONICS-VCX500, SONICS, town, CT, USA), centrifuge (UNIVERSAL 320R, Hettich, Beverly, MA, USA), field emission scanning electron microscope (FESEM, JSM-7500F, JEOL, Tokyo, Japan), vacuum muffle furnace (Neytech Qex, DEGUSSA-NEY DENTAL, INC., Bloomfield, CT, USA), light source (FOK-100W, Fiber Optic Korea, Cheonan, Korea), photodetectivity measurement system (4200-SCS, Keithley, Beaverton, OR, USA), thermal evaporation system, and solar simulator for the on/off test (XES-301S, SAN-EI ELECTRIC CO., Ltd., Osaka, Japan). The following equipment was used: ultrasonicactor (SONICS-VCX500, SONICS, New-

#### **3. Results and Discussions**

As the solvent of the  $MOS<sub>2</sub>$  NFs solution was slowly evaporated, the  $MOS<sub>2</sub>$  NFs were aggregated in a thin film form on the substrate. The surface morphology of the  $M_2$ film after solvent evaporation was examined as shown in Figure [1d](#page-2-0). Scanning electron microscope (SEM) and atomic force microscopy (AFM) images clearly revealed that the  $M$ oS<sub>2</sub> NFs were agglomerated, forming continuous domains. The thickness of the  $M$ oS<sub>2</sub> film was measured to be  $\sim$ 20 nm, indicating the multilayered MoS<sub>2</sub> domains. Size distribution of the  $MoS<sub>2</sub>$  NFs in the solution is also shown in Figure [1e](#page-2-0). Diameters of the NFs were mostly smaller than 300 nm, and it was also found that the most probable diameter of the NFs was 150 nm. In addition, Raman spectroscopy was employed to clarify the existence of the MoS<sup>2</sup> NFs in the film without significant changes in chemical composition. Two prominent peaks were observed around 381 cm<sup>-1</sup> and 409 cm<sup>-1</sup>, as shown in Figure [1f](#page-2-0). These peaks can be assigned to the multilayered  $MoS<sub>2</sub>$  in consideration of the peak shifts, which are typically observed in the multilayered  $MoS<sub>2</sub>$ . It is worth noting that the center of the thin film was not completely covered with the  $MoS<sub>2</sub>$  NFs, due to the coffee-ring effect that occurred in the drop-casting process, and thus the substrate was partially exposed to air.

Figure [2](#page-4-0) shows the SEM micrographs of the annealed Ag nanofilm on  $MoS<sub>2</sub>$  layers at various temperatures (without annealing and annealed at 200, 400, 450, 500, and 550 °C). All samples were annealed for 24 h at atmospheric pressure. The surface of the Ag nanofilm  $(20 \text{ nm thick})$  on the MoS<sub>2</sub> layer before the annealing process was flat, and some dark spots appeared on the surface, as shown in Figure [2a](#page-4-0). The dark spots are slightly dented and considered to be an uncovered region of the MoS<sub>2</sub> film. After annealing, the Ag film on MoS<sup>2</sup> was dewetted and formed Ag islands on the surfaces, as shown in Figure [2b](#page-4-0)–f. Exfoliated MoS<sub>2</sub> nanosheets are known to be electrically conductive [\[31\]](#page-10-15); however, the electrical conductivity of  $MoS<sub>2</sub>$  films after the drop-coating process was low because there are many inter-nanosheet junctions between the  $MoS<sub>2</sub>$  nanosheets, which complicates electron conduction between them at low voltages [\[32\]](#page-10-16). By annealing the Ag film, Ag diffused into the MoS<sub>2</sub> layer, increasing the MoS<sub>2</sub> conductivity. Furthermore, the contact between the metal and the  $MoS<sub>2</sub>$  layer is known to become ohmic after diffusion, reducing the resistivity [\[33\]](#page-10-17). Thus, annealing of the Ag film improved the electrical contact between the MoS<sub>2</sub> layers. In particular, the device, which was solely based on MoS<sub>2</sub> without Ag, did not show any photo response. As mentioned above, this result is possibly originating from the inter-nanosheet junctions reducing the electrical conductivity. The  $M$ oS<sub>2</sub> NFs were also concentrated at the edge of the thin film due to the coffee-ring effect in the drop-casting process, causing domain discontinuities near the center. Such disconnection between  $MoS<sub>2</sub>$  disrupts the electron transportation and the photo response. However, when the Ag nanofilm was formed and annealed on the sample, the  $MoS<sub>2</sub>$  domains were well connected to each other through the Ag islands consisting of the Ag NPs. The radii of the Ag islands were measured to be in the range of 10–600 nm, and the particle size increased with the annealing temperature (See Figure [2\)](#page-4-0). It was also observed that small Ag NPs  $\left($  <10 nm) were attached to the MoS<sub>2</sub> surface, leading to connection between Ag and MoS<sub>2</sub> after annealing. These results are consistent with the previous studies reporting that Ag can be easily attached to the  $MoS<sub>2</sub>$  NFs. It has been reported that the Ag NPs can be attached to the MoS<sub>2</sub> surface via the formation of the Ag ions in the solution [\[34\]](#page-10-18), and the MoS<sub>2</sub> layer can play a role as a photocatalyst with the Ag NPs [\[15\]](#page-10-4). Notably, the surface plasmon resonance effect of metal NPs can increase visible light absorption [\[35,](#page-11-0)[36\]](#page-11-1). Surface plasmons can be localized by Ag NPs, and the excitation of localized surface plasmon resonance can occur. This leads to an enhanced electric field, which increases the photocurrent of the MoS<sub>2</sub> layer.

<span id="page-4-0"></span>

Figure 2. FESEM micrographs of annealed Ag nanofilms on the MoS<sub>2</sub> layers at various temper-The thickness of the deposited Ag film was 20 nm. Samples were annealed at (**a**) room temperature atures. The thickness of the deposited Ag film was 20 nm. Samples were annealed at (a) room temperature (without annealing), (b) 200 °C, (c) 400 °C, (d) 450 °C, (e) 500 °C, and (f) 550 °C. The  $\mathbf r$  represent the 100 nm. solid white bars represent the 1  $\mu$ m length scale and the sold white bars in the inset of the  $(c,d)$ 

Thin photodetectors based on  $MoS<sub>2</sub>$  NFs and Ag NPs were fabricated as shown in Figure [1a](#page-2-0). The two types of device structures, bottom-mode and middle-mode devices, are also described in Figure [1b](#page-2-0). Prior to measuring performance of the Ag-coated  $MoS<sub>2</sub>$  devices, a device with only the  $MoS<sub>2</sub>$  film on the  $SiO<sub>2</sub>/Si$  substrate was fabricated that was annealed at various temperatures from 200 to 1000  $\degree$ C in a muffle furnace. However, no photo response was observed in the device. Subsequently, two bottom-mode devices were fabricated with 20 and 110 nm thick Ag films. The Ag nanofilm on the MoS<sub>2</sub> layer was annealed at 400 °C. The characteristic curves of the devices are shown in Figure [3a](#page-5-0),b. Additionally, a device with a 200 nm Ag film was fabricated. However, the results for this device are not presented because the Ag layer was too thick, and Ag did not form islands after annealing. Thus, the device with a 200 nm Ag film short circuited and exhibited a maximum current of 1  $\times$  10 $^{-2}$  A at all voltages. The characteristic curve  $\alpha$  and  $\alpha$  the annealed de-

Subsequently, the channel width of the Au electrodes was varied from 90 to 1000 μm, as shown in [Fi](#page-5-0)gure 3a,b. The characteristic current vs. voltage curves of the annealed device with the 20 nm Ag film are shown in Figure 3a, and those of the annealed devi[ce](#page-5-0) with the 110 nm Ag film are shown in Figure 3b. The devices were exposed under illumination using a visible light source (OSRAM, Munich, Germany, 64637) with a power density of 14.1 mW/cm<sup>2</sup>. All the devices were photoresponsive, and the devices were not strongly dependent on the channel width. As shown in Figure 3c, both devices with 20 and 110 nm Ag films show dark currents below  $1 \times 10^{-6}$  A and on-currents at 10 V over  $1 \times 10^{-4}$  A. Moreover, the on/off current ratios of the de[vice](#page-5-0)s with 20 and 110 nm Ag films are shown in Figure 3c. The fabrication conditions (20 nm Ag film thickness and 500  $\mu$ m channel width) showed the best perform[an](#page-5-0)ce and were adopted for further experiments. As shown in Figure 3d, the on/off ratio was affected the performance of the devices based on the annealing temperature conditions. The highest on-current at 10 V was observed for the device

<span id="page-5-0"></span>annealed at 450 ◦C. However, the off-current was also relatively higher than those of the devices annealed at 300 and 400 °C. Among them, the device annealed at 400 °C, which had the highest on/off ratio  $(1.66 \times 10^3)$ , was selected for the fabrication process for better results in this study.



**Figure 3.** Output characteristics (output current vs. sample bias voltage) of the bottom−mode pho-**Figure 3.** Output characteristics (output current vs. sample bias voltage) of the bottom−mode photodetecting devices under various fabricating conditions: (a) 20 nm and (b) 110 nm Ag films annealed at 400 °C with various electrode channel widths (90, 500, and 1000 μm). Output currents were measured under visible light illumination with an intensity of 14.1 mW/cm<sup>2</sup> (on) and 0.0 mW/cm<sup>2</sup> (off). (c) Output currents and on/off ratios of bottom-mode devices in  $(a,b)$  at a bias voltage of 10 V. of 10 V. (**d**) Output currents and on/off ratios at a bias voltage of 10 V of the bottom−mode devices (**d**) Output currents and on/off ratios at a bias voltage of 10 V of the bottom−mode devices with a  $500 \ \mu$ m electrode channel width and 20 nm Ag film thickness annealed at various temperatures (300, 400, 450, and 500  $^{\circ}$ C).

output characteristics and photoresponsivity were measured under visible light illumination with various intensities, as shown in Figure 4a. For the photoresponsive measurements, two sharp probes were brought into contact with the Au electrodes of the device. As mentioned previously, the device with 20 nm of Ag film and annealed  $\frac{1}{20}$ at 400 °C showed the highest performance allong the habiteated devices. Its photote-<br>sponsivity was  $4.37 \times 10^{1}$  AW<sup>-1</sup> under low-intensity illumination (~0.5 mW/cm<sup>2</sup>) and decreased to 1.53 × 10<sup>1</sup> AW<sup>-1</sup> at a light intensity of 14.1 mW/cm<sup>2</sup>. The photocurrent gradually increased as the light intensity increased, and the photoresponsivity remained constant at ~1.5 × 10<sup>1</sup> AW<sup>-1</sup>. It is noteworthy that the photocurrent increased to ~11 mA at a sample bias voltage of 10 V under high-intensity illumination The photocurrent of the device rapidly changed from  $1.7 \times 10^{-5}$  to  $\sim 2.5 \times 10^{-3}$  A in high-intensity is intensity in the time-resolved photo response of the de-resolved photo response of the de-To evaluate the photodetection properties of the device annealed at 400  $^{\circ}$ C, the at 400 ◦C showed the highest performance among the fabricated devices. Its photore- $(14.1 \text{ mW/cm}^2)$ . The time-resolved photo response of the device is shown in Figure [4b](#page-6-0).

response to the on/off switching of light illumination (126 mW/cm<sup>2</sup>) at a constant sample bias voltage of 10 V. The photo response and recovery times were consistently measured as  $\sim$ 324 and  $\sim$ 262 ms, respectively, because the on- and off-currents instantaneously returned to their initial levels without any losses. It is noteworthy that the shutter speed of the light source (a few milliseconds) was not compensated, and thus, the real response times were probably shorter than the measured values. The reversibility of the photoresponsive device is shown in the inset in Figure [4b](#page-6-0). As the light illumination switches on and off, the initial off-current and on-current values are repeatedly obtained.

<span id="page-6-0"></span>

**Figure 4.** (**a**) Output characteristics of the bottom−mode photodetecting device with 20 nm of Ag **Figure 4.** (**a**) Output characteristics of the bottom−mode photodetecting device with 20 nm of Ag film annealed at 400 °C with a 500  $\mu$ m electrode channel width. Output currents were measured dider visible light indiffusion with various intensities of 0.0 (dark), 0.5, 1.8, 4.8, 8.5, 12.5, and 14.1 mW/cm<sup>2</sup>. (**b**) Real-time characteristics of the output current measured in response to a light intensity of 14.1 mW/cm<sup>2</sup> at a constant sample bias voltage of 10 V. The data clearly show the reversible photoresponsivity of the device. under visible light illumination with various intensities of 0.0 (dark), 0.5, 1.8, 4.8, 8.5, 12.5, and

above the results, it was different of the device with a 10 nm thick Ag film was lower than that  $\frac{1}{2}$ . of the other fabricated devices with thicker Ag films, it exhibited a higher on/off ratio at 10 V compared with the other devices. Based on this result, another device configuration was evaluated to increase the on/off ratio. The iniquie-mode structure of the fight-sensing<br>device was designed, as shown in Figure [1b](#page-2-0). To increase the light absorption of the device while maintaining a high on/off ratio, an Ag nanofilm was deposited and annealed before the MoS<sub>2</sub> drop-coating process. This structure is called a 'middle-mode' structure, and the structure of previously discussed is called a 'bottom-mode' structure, as shown in Figure [1b](#page-2-0).<br>The decimation of the structures vise determined by the position of the MeS, layer on the Ag films. In this study, the thickness of the Ag film below the  $MoS<sub>2</sub>$  layer was 10 nm, and the same Ag film thickness was used for the device with the middle-mode structure. All Ag nanofilms of the devices were annealed immediately after deposition, as described <sub>1b</sub>. The designation of the structure was determined by the position of the most of the MoS2 layer on the devices with thicker Ag films. Thus, the middle-mode structure is suggested for increasing the on/off ratio of the photoresponsive device. Based on the results, it was difficult to increase the on/off ratio above  $2.0 \times 10^3$ using the MoS<sub>2</sub>-Ag photoresponsive materials formed under the investigated conditions. was evaluated to increase the on/off ratio. The middle-mode structure of the light-sensing The designation of the structures was determined by the position of the  $M_0S_2$  layer on previously. Particularly, the off-current of the device with 10 nm of Ag film annealed at

The characteristic curves of the two different devices annealed at 400  $^{\circ}$ C are shown in Figure [5a](#page-8-0). The off-current of the bottom-mode device  $(Ag(20 \text{ nm})/MoS<sub>2</sub>/substrate)$ at a sample bias voltage of 10 V was relatively higher than the middle-mode device (Ag  $(10 \text{ nm})/MoS<sub>2</sub>/Ag (10 \text{ nm})/substrate}$ , which was annealed at the same temperature. The device with the middle-mode structure showed a lower off-current, which resulted in a high on/off current ratio at 10 V. As shown in Figure [5b](#page-8-0), the on-current of the middle-mode device under illumination with a visible light intensity of 14.1 mW/cm<sup>2</sup> and a sample bias voltage of 10 V was 6.88  $\times$  10<sup>-5</sup> A, and the off-current under the same conditions was  $1.25 \times 10^{-9}$  A. Thus, the middle-mode device annealed at 400 °C exhibited low on- and off-current values, and the on/off current ratio was  $5.61 \times 10^4$  at 10 V, which is higher than that of the bottom-mode device with a 20 nm Ag film annealed at the same temperature. As shown in Figure [5b](#page-8-0), the photocurrent of the middle-mode device gradually increased as the light intensity increased from 0 to 14.1 mW/cm<sup>2</sup> at a sample bias voltage of 10 V. The photoresponsivity was 1.17 AW<sup>-1</sup> under low-intensity illumination (~1.8 mW/cm<sup>2</sup>) and decreased to 9.75  $\times$  10<sup>-1</sup> AW<sup>-1</sup> at a light intensity of  $14.1 \text{ mW/cm}^2$ .

Another device was fabricated under different annealing conditions to reduce the annealing temperature. The characteristic curves of the two different devices annealed at 300 ◦C are shown in Figure [5c](#page-8-0). The off-current of the middle-mode device at a sample bias voltage of 10 V was lower than that of the bottom-mode device with a 20 nm Ag film annealed at 300 °C. The middle-mode device exhibited a higher on/off current ratio at a sample bias voltage of 10 V, compared with the bottom-mode device. As shown in Figure [5d](#page-8-0), the on-current at a sample bias voltage of 10 V under illumination with a visible light intensity of 14.1 mW/cm<sup>2</sup> was 1.74  $\times$  10<sup>-4</sup> A, and the off-current under the same conditions was  $1.22 \times 10^{-8}$  A. The middle-mode device annealed at 300 °C showed low on- and off-current values, and the on/off current ratio was  $1.42 \times 10^4$ , which is 82.7 times higher than that of the bottom-mode device with a 20 nm Ag film annealed at 300 °C. The photocurrent of the middle-mode device at a sample bias voltage of 10 V gradually increased as the light intensity increased from 0 to 14.1 mW/cm<sup>2</sup>, as shown in Figure [5d](#page-8-0). The photoresponsivity was  $8.10 \times 10^{-2}$  AW<sup>-1</sup> under lowintensity illumination (~1.8 m $\rm \bar{W}/\rm cm^2)$  and increased to 2.47 AW $^{-1}$  at a light intensity of 14.1 mW/cm<sup>2</sup>. Moreover, switching test was performed using the middle-mode device, of which the  $MoS<sub>2</sub>$  film was sandwiched between the two Ag films (i.e., top and bottom). Each Ag film was 10 nm thick, and annealed at 300 °C. The device was repeatedly exposed to the visible light with an intensity of  $14.1 \text{ mW/cm}^2$  for 60 s. The current rapidly increased and decreased in response to the light as shown in Figure [5e](#page-8-0). The device responded 43 cycles during 60 s, and the on-current was consistently maintained at ~1.6  $\times$  10<sup>-4</sup> A on average.

Based on these results, the on/off current of the device can be increased by fabricating a middle-mode structure and decreasing the annealing temperature to enhance the performance. Although the performance was not very high, the device annealed at 300 ◦C exhibited sufficient performance for application as a photoresponsive device. As reported in a previous study, Ag NPs located below the  $MoS<sub>2</sub>$  layer enhanced the light absorption in the photoresponsive system [\[35\]](#page-11-0). In this study, a dewetted Ag film formed NPs on a MoS<sub>2</sub> layer, which enhanced light absorption in the system. Thus, the dark current value was not significantly changed, and the on-current greatly increased owing to the enhanced light absorption by the Ag NPs below the active layer, resulting in an increase in the on/off ratio of the photoresponsive device.

<span id="page-8-0"></span>

**Figure 5.** (**a**) Output characteristics of the bottom-mode device with 20 nm (top) of Ag film and **Figure 5.** (**a**) Output characteristics of the bottom-mode device with 20 nm (top) of Ag film and middle-mode device with 10 nm (top)/10 nm (bottom) of Ag film, both annealed at 400 °C. (**b**) Output characteristics of the middle-mode device with  $10 \text{ nm}$  (top)/ $10 \text{ nm}$  (bottom) of Ag film annealed characteristics of the middle mode device with variation with (concomp of  $\chi$ ) intensities. at 400 °C under visible light illumination with various intensities. (**c**) Output characteristics of the bottom-mode device with 20 nm (top) of Ag film and middle-mode device with 10 nm (top)/10 nm (bottom) of Ag film, both annealed at 300 °C. (**d**) Output characteristics of the middle-mode device with 10 nm (top)/10 nm (bottom) of Ag film annealed at 300 °C under visible light illumination with various intensities. The on and off-currents of  $(a,c)$  were measured under visible light illumination with an intensity of 14.1 mW/cm<sup>2</sup>. The output currents of (**b**,**d**) were measured under visible light illumination with various intensities of 0.0 (dark), 1.8, 4.8, 8.5, 12.5, and 14.1 mW/cm<sup>2</sup>. (**e**) Switching test curve of the middle-mode device with 10 nm (top)/10 nm (bottom) of Ag film annealed at 300 ℃. The device responded 43 cycles for 60 s under visible light illumination with an intensity of  $14.1 \text{ mW/cm}^2$ .

## **4. Conclusions**

Photodetectors were developed based on MoS<sub>2</sub> NFs as the conversion center to transfer energy from photons to electrons in the thin film. In this study, after annealing, Ag diffused into the  $MoS<sub>2</sub>$  layer, which decreased the resistance of the inter-nanosheet junctions between the  $MoS<sub>2</sub>$  layers. Ag islands connected discontinuous  $MoS<sub>2</sub>$  NFs each other. This increased the conductivity of the  $MOS<sub>2</sub>$  layer. Moreover, the newly formed Ag islands on the  $MoS<sub>2</sub>$  layer enhanced the absorption efficiency of light because the surface plasmon resonance effect of metal NPs increases visible light absorption. Two different device modes were fabricated for the photodetector. First, bottom-mode devices were fabricated to determine the optimal fabrication conditions based on performance. The bottom-mode device with a 20 nm Ag film annealed at 400 ◦C showed the highest performance, with a photoresponsivity of  $4.37 \times 10^1$  AW<sup>-1</sup> under low-intensity illumination (~ $0.5\ \mathrm{mW/cm^2}$ ) at a sample bias voltage of 10 V, and it exhibited the highest on/off ratio (1.66  $\times$  10<sup>3</sup>). Second, a middle-mode device was fabricated to increase the on/off ratio. The middle-mode device annealed at  $400\degree$ C exhibited lower off-current, which caused a high on/off current ratio of  $5.61 \times 10^4$  at a sample bias voltage of 10 V. Therefore, the on/off ratio increased by over an order and was 82.7 times higher than that of the bottom-mode device annealed at 300 °C. In conclusion,  $MoS<sub>2</sub>$  NFs play a major role in transferring newly generated electrons to the Ag film under illumination. Therefore, the developed methodology is proposed as an effective way to capture energy from conversion centers, such as TMD NFs using nano-thick metal films. This is a crucial concept for the utilization of various NFs and TMDs in optoelectronic applications. Thus, these results are expected to contribute to the advancement of high-performance photoresponsive systems for light-sensing applications.

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#### **References**

- <span id="page-9-0"></span>1. Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS<sup>2</sup> transistors. *Nat. Nanotechnol.* **2011**, *6*, 147–150. [\[CrossRef\]](http://doi.org/10.1038/nnano.2010.279) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/21278752)
- 2. Kim, S.; Konar, A.; Hwang, W.-S.; Lee, J.H.; Lee, J.; Yang, J.; Jung, C.; Kim, H.; Yoo, J.-B.; Choi, J.-Y.; et al. High-mobility and low-power thin-film transistors based on multilayer MoS<sub>2</sub> crystals. *Nat. Commun.* 2012, 3, 1011. [\[CrossRef\]](http://doi.org/10.1038/ncomms2018) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/22910357)
- 3. Wang, H.; Yu, L.; Lee, Y.H.; Shi, Y.; Hsu, A.; Chin, M.L.; Li, L.-J.; Dubey, M.; Kong, J.; Palacios, T. Integrated circuits based on bilayer MoS<sub>2</sub> transistors. *Nano Lett.* **2012**, 12, 4674–4680. [\[CrossRef\]](http://doi.org/10.1021/nl302015v) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/22862813)
- 4. Wang, K.; Wang, J.; Fan, J.; Lotya, M.; O'Neill, A.; Fox, D.; Feng, T.; Zhang, X.; Jiang, B.; Zhao, Q.; et al. Ultrafast saturable absorption of two-dimensional MoS<sub>2</sub> nanosheets. *ACS Nano* 2013, 7, 9260–9267. [\[CrossRef\]](http://doi.org/10.1021/nn403886t)
- 5. Ross, J.S.; Klement, P.; Jones, A.M.; Ghimire, N.J.; Yan, J.; Mandrus, D.G.; Taniguchi, T.; Watanabe, K.; Kitamuira, K.; Yao, W.; et al. Electrically tunable excitonic light-emitting diodes based on monolayer WSe<sub>2</sub> p-n junctions. *Nat. Nanotechnol.* **2014**, *9*, 268–272. [\[CrossRef\]](http://doi.org/10.1038/nnano.2014.26)
- 6. Pospischil, A.; Furchi, M.M.; Mueller, T. Solar-energy conversion and light emission in an atomic monolayer p-n diode. *Nat. Nanotechnol.* **2014**, *9*, 257–261. [\[CrossRef\]](http://doi.org/10.1038/nnano.2014.14)
- 7. Stephenson, T.; Li, Z.; Olsen, B.; Mitlin, D. Lithium ion battery applications of molybdenum disulfide (MoS<sub>2</sub>) nanocomposites. *Energy Environ. Sci.* **2014**, *7*, 209–231. [\[CrossRef\]](http://doi.org/10.1039/C3EE42591F)
- <span id="page-10-0"></span>8. Voiry, D.; Yamaguchi, H.; Li, J.; Silva, R.; Alves, D.C.; Fujita, T.; Chen, M.; Asefa, T.; Shenoy, V.B.; Eda, G.; et al. Enhanced catalytic activity in strained chemically exfoliated WS<sub>2</sub> nanosheets for hydrogen evolution. *Nat. Mater.* **2013**, 12, 850–855. [\[CrossRef\]](http://doi.org/10.1038/nmat3700)
- <span id="page-10-1"></span>9. Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.Y.; Galli, G.; Wang, F. Emerging photoluminescence in monolayer MoS<sup>2</sup> . *Nano Lett.* **2010**, *10*, 1271–1275. [\[CrossRef\]](http://doi.org/10.1021/nl903868w)
- <span id="page-10-2"></span>10. Mak, K.F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T.F. Atomically thin MoS<sub>2</sub>: A new direct-gap semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 136805. [\[CrossRef\]](http://doi.org/10.1103/PhysRevLett.105.136805)
- <span id="page-10-3"></span>11. Lebègue, S.; Eriksson, O. Electronic Structure of Two Dimensional Crystals from *ab Initio* Theory. *Phys. Rev. B* **2009**, *79*, 115409. [\[CrossRef\]](http://doi.org/10.1103/PhysRevB.79.115409)
- 12. Kuc, A.; Zibouche, N.; Heine, T. Influence of Quantum Confinement on the Electronic Structure of the Transition Metal Sulfide TS<sup>2</sup> . *Phys. Rev. B* **2011**, *83*, 245213. [\[CrossRef\]](http://doi.org/10.1103/PhysRevB.83.245213)
- 13. Cheiwchanchamnangij, T.; Lambrecht, W.R. Band Structure Calculation of Monolayer, Bilayer, and Bulk MoS<sup>2</sup> . *Phys. Rev. B* **2012**, *85*, 205302. [\[CrossRef\]](http://doi.org/10.1103/PhysRevB.85.205302)
- 14. Zeng, H.; Liu, G.B.; Dai, J.; Yan, Y.; Zhu, B.; He, R.; Xie, L.; Xu, S.; Chen, X.; Yao, W.; et al. Optical Signature of Symmetry Variations and Spin-Valley Coupling in Atomically Thin Tungsten Dichalcogenides. *Sci. Rep.* **2013**, *3*, 1608. [\[CrossRef\]](http://doi.org/10.1038/srep01608)
- <span id="page-10-4"></span>15. Daeneke, T.; Carey, B.J.; Chrimes, A.F.; Ou, J.Z.; Lau, D.W.M.; Gibson, B.C.; Bhaskaran, M.; Kalantar-Zadeh, K. Light driven growth of silver nanoplatelets on 2D MoS<sub>2</sub> nanosheets templates. *J. Mater. Chem. C* 2015, 3, 4471-4478. [\[CrossRef\]](http://doi.org/10.1039/C5TC00288E)
- <span id="page-10-5"></span>16. Mondal, B.; Som, A.; Chakraborty, I.; Baksi, A.; Sarkar, D.; Pradeep, T. Unusual reactivity of MoS<sub>2</sub> nanosheets. *Nanoscale* 2016, 8, 10282–10290. [\[CrossRef\]](http://doi.org/10.1039/C6NR00878J)
- 17. Liu, K.K.; Zhang, W.; Lee, Y.H.; Lin, Y.C.; Chang, M.T.; Su, C.Y.; Chang, C.-S.; Li, H.; Shi, Y.; Zhang, H.; et al. Growth of large-area and highly crystalline MoS<sub>2</sub> thin layers on insulating substrates. *Nano Lett.* **2012**, 12, 1538–1544. [\[CrossRef\]](http://doi.org/10.1021/nl2043612)
- 18. Paur, M.; Molina-Mendoza, A.J.; Bratschitsch, R.; Watanabe, K.; Taniguchi, T.; Mueller, T. Electroluminescence from multi-particle exciton complexes in transition metal dichalcogenide semiconductors. *Nat. Commun.* **2019**, *10*, 1709. [\[CrossRef\]](http://doi.org/10.1038/s41467-019-09781-y)
- <span id="page-10-6"></span>19. Vella, D.; Barbosa, M.B.; Trevisanutto, P.E.; Verzhbitskiy, I.; Zhou, J.Y.; Watanabe, K.; Taniguchi, T.; Kajikawa, K.; Eda, G. In-Plane Field-Driven Excitonic Electro-Optic Modulation in Monolayer Semiconductor. *Adv. Opt. Mater.* **2022**, *10*, 2102132. [\[CrossRef\]](http://doi.org/10.1002/adom.202102132)
- <span id="page-10-7"></span>20. Zhan, Y.; Liu, Z.; Najmaei, S.; Ajayan, P.M.; Lou, J. Large-area vapor phase growth and characterization of MoS<sub>2</sub> atomic layers on a SiO<sup>2</sup> substrate. *Small* **2012**, *8*, 966–971. [\[CrossRef\]](http://doi.org/10.1002/smll.201102654)
- 21. Lim, Y.R.; Song, W.; Han, J.K.; Lee, Y.B.; Kim, S.J.; Myung, S.; Lee, S.S.; An, K.-S.; Choi, C.-J.; Lim, J. Wafer-Scale, Homogeneous MoS<sup>2</sup> layers on Plastic Substrates for Flexible Visible-Light Photodetectors. *Adv. Mater.* **2016**, *28*, 5025–5030. [\[CrossRef\]](http://doi.org/10.1002/adma.201600606) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/27119775)
- <span id="page-10-8"></span>22. Golub, A.S.; Zubavichus, Y.V.; Slovokhotov, Y.L.; Novikov, Y.N. Single-layer dispersions of transition metal dichalcogenides in the synthesis of intercalation compounds. *Russ. Chem. Rev.* **2003**, *72*, 123–141. [\[CrossRef\]](http://doi.org/10.1070/RC2003v072n02ABEH000789)
- <span id="page-10-9"></span>23. Zheng, J.; Zhang, H.; Dong, S.; Liu, Y.; Tai Nai, C.; Suk Shin, H.; Jeong, H.Y.; Liu, B.; Ping Loh, K. High yield exfoliation of two-dimensional chalcogenides using sodium naphthalenide. *Nat. Commun.* **2014**, *5*, 2995. [\[CrossRef\]](http://doi.org/10.1038/ncomms3995) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/24384979)
- 24. Qiao, W.; Yan, S.; He, X.; Song, X.; Li, Z.; Zhang, X.; Zhong, W.; Du, Y. Effects of ultrasonic cavitation intensity on the efficient liquid-exfoliation of MoS<sub>2</sub> nanosheets. *RSC Adv.* 2014, 4, 50981. [\[CrossRef\]](http://doi.org/10.1039/C4RA09001B)
- 25. Coleman, J.N.; Lotya, M.; O'Neill, A.; Bergin, S.D.; King, P.J.; Khan, U.; Young, K.; Gaucher, A.; De, S.; Smith, R.J.; et al. Two-dimensional nanosheets produced by liquid exfoliation of layered materials. *Science* **2011**, *331*, 568–571. [\[CrossRef\]](http://doi.org/10.1126/science.1194975) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/21292974)
- <span id="page-10-10"></span>26. Gan, Z.X.; Liu, L.Z.; Wu, H.Y.; Hao, Y.L.; Shan, Y.; Wu, X.L.; Chu, P.K. Quantum confinement effects across two-dimensional planes in MoS<sup>2</sup> quantum dots. *Appl. Phys. Lett.* **2015**, *106*, 233113. [\[CrossRef\]](http://doi.org/10.1063/1.4922551)
- <span id="page-10-11"></span>27. Velusamy, D.B.; Kim, R.H.; Cha, S.; Huh, J.; Khazaeinezhad, R.; Kassani, S.H.; Song, K.; Cho, S.H.; Hwang, I.; Lee, J.; et al. Flexible transition metal dichalcogenide nanosheets for band-selective photodetection. *Nat. Commun.* **2015**, *6*, 8063. [\[CrossRef\]](http://doi.org/10.1038/ncomms9063)
- <span id="page-10-12"></span>28. Souder, A.; Brodie, D.E. Electrical contacts and conductivity of MoS<sub>2</sub> layer structures. *Can. J. Phys.* 1971, 49, 2565–2571. [\[CrossRef\]](http://doi.org/10.1139/p71-306)
- <span id="page-10-13"></span>29. Quan, J.; Zhang, J.; Qi, X.; Li, J.; Wang, N.; Zhu, Y. A study on the correlation between the dewetting temperature of Ag film and SERS intensity. *Sci. Rep.* **2017**, *7*, 14771. [\[CrossRef\]](http://doi.org/10.1038/s41598-017-15372-y)
- <span id="page-10-14"></span>30. Deng, Y.; Chen, M.; Zhang, J.; Wang, Z.; Huang, W.; Zhao, Y.; Nshimiyimana, J.P.; Hu, X.; Chi, X.; Hou, G.; et al. Thicknessdependent morphologies of Ag on n-layer MoS<sub>2</sub> and its surface-enhanced Raman scattering. *Nano Res.* **2016**, 9, 1682–1688. [\[CrossRef\]](http://doi.org/10.1007/s12274-016-1062-5)
- <span id="page-10-15"></span>31. Ogilvie, S.P.; Large, M.J.; Wood, H.J.; Graf, A.A.; Lee, F.; Salvage, J.P.; King, A.A.K.; Dalton, A.B. Size selection and thin-film assembly of MoS<sub>2</sub> elucidates thousandfold conductivity enhancement in few-layer nanosheet networks. *Nanoscale* 2022, 14, 320–324. [\[CrossRef\]](http://doi.org/10.1039/D1NR05815K) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/34932055)
- <span id="page-10-16"></span>32. Abraham, M.; Mohney, S.E. Annealed Ag contacts to MoS<sup>2</sup> field-effect transistors. *J. Appl. Phys.* **2017**, *122*, 115306. [\[CrossRef\]](http://doi.org/10.1063/1.4991961)
- <span id="page-10-17"></span>33. Schuller, J.A.; Barnard, E.S.; Cai, W.; Jun, Y.C.; White, J.S.; Brongersma, M.L. Plasmonics for extreme light concentration and manipulation. *Nat. Mater.* **2010**, *9*, 193–204. [\[CrossRef\]](http://doi.org/10.1038/nmat2630) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/20168343)
- <span id="page-10-18"></span>34. Xiao, P.; Mencarelli, D.; Chavez-Angel, E.; Joseph, C.H.; Cataldo, A.; Pierantoni, L.; Torres, C.M.S.; Sledzinska, M. Reversing the Humidity Response of MoS<sub>2</sub>-and WS<sub>2</sub>-Based Sensors Using Transition-Metal Salts. *ACS Appl. Mater. Interfaces* **2021**, 13, 23201–23209. [\[CrossRef\]](http://doi.org/10.1021/acsami.1c03691) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/33950679)
- <span id="page-11-0"></span>35. Ferry, V.E.; Verschuuren, M.A.; Li, H.B.; Verhagen, E.; Walters, R.J.; Schropp, R.E.; Atwater, H.A.; Polman, A. Light trapping in ultrathin plasmonic solar cells. *Opt. Express* **2010**, *18*, A237–A245. [\[CrossRef\]](http://doi.org/10.1364/OE.18.00A237)
- <span id="page-11-1"></span>36. Pan, R.; Kang, J.; Li, Y.; Zhang, Z.; Li, R.; Yang, Y. Highly Enhanced Photoluminescence of Monolayer MoS<sub>2</sub> in Plasmonic Hybrids with Double-Layer Stacked Ag Nanoparticles. *ACS Appl. Mater. Interfaces* **2022**, *14*, 12495–12503. [\[CrossRef\]](http://doi.org/10.1021/acsami.1c21960)