Two-Terminal Multibit Optical Memory via van der Waals Heterostructure

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2D van der Waals (vdWs) heterostructures exhibit intriguing optoelectronic properties in photodetectors, solar cells, and light-emitting diodes. In addition, these materials have the potential to be further extended to optical memories with promising broadband applications for image sensing, logic gates, and synaptic devices for neuromorphic computing. In particular, high programming voltage, high off-power consumption, and circuit complexity in integration are primary concerns in the development of three-terminal optical memory devices. This study describes a multilevel nonvolatile optical memory device with a two-terminal floating-gate field-effect transistor with a MoS$_2$/hexagonal boron nitride/graphene heterostructure. The device exhibits an extremely low off-current of $\approx 10^{-14}$ A and high optical switching on/off current ratio of over $=10^6$, allowing 18 distinct current levels corresponding to more than four-bit information storage. Furthermore, it demonstrates an extended endurance of over $=10^4$ program–erase cycles and a long retention time exceeding $3.6 \times 10^4$ s with a low programming voltage of $-10$ V. This device paves the way for miniaturization and high-density integration of future optical memories with vdWs heterostructures.

Artificially stacked individual 2D van der Waals (2D vdWs) materials adopting heterostructures for specific functions is of growing interest. This assembly can be used to create an almost unlimited number of combinations and extraordinary properties[1–3] for novel multifunctional electronic and optoelectronic devices.[4–6] These devices include field-effect transistors (FETs),[7] photodetectors,[8,9] light-emitting diodes,[10] solar cells,[11] and memory.[12,13] Recently, vdWs heterostructure-based nonvolatile optical memory have been investigated for broad potential applications in imaging sensors,[14] logic gates,[15] optoelectronic demodulators,[16] and synaptic devices for neuromorphic systems.[17–18]

These 2D vdWs materials and their hybrids are considered to be an ideal platform for nonvolatile optical memory owing to their strong light-matter interactions[19–21] and significant photogenerated charge trapping derived from their very large surface-to-volume ratio.[22–24] In addition, the mechanical strength and atomic thickness of 2D vdWs materials allow for device miniaturization in flexible and wearable optoelectronics.[25–27] The demonstration of 2D vdWs materials-based optical memory in the FETs of few-layer copper indium selenide (CuIn$_7$Se$_{11}$) has been reported[14] along with hybrids of graphene/MoS$_2$[5] on a silicon substrate. These devices exhibit low optical switching on/off ratios ($<1[5]$ and $\approx 10^{14}$), high off-currents ($=400$ µA[3] and 20 pA[14]), and short retention times (50 s[14]), preventing their use in high quality image sensors and multilevel storage devices.

Using oxygen plasma treatments to create more charge trap sites at SiO$_2$ surface, monolayer MoS$_2$-FET-based optical memory on silicon substrate has exhibited a long retention time of $=10^4$ s.[28] However, the data storage capacity of eight levels of the material remains limited for practical applications due to moderate switching on/off ratio of $=4700$. Importantly, the memory function of these devices relies on charge trapping of photoexcited carriers in defects and impurities on either the surface or material/SiO$_2$ interface.[15,28] This results in short retention times and sensitivity to environmental factors. A charge trapping layer acting as a floating gate, instead of charge trapping at the materials/SiO$_2$ interface, can be introduced via gold nanoparticle/crosslinked poly(4-vinylphenol)/MoS$_2$ heterojunction-FETs, which significantly increase both the switching on/off ratio ($=10^6$) and retention time ($>10^4$ s).[29] Similarly, by storing charge in the hexagonal boron nitride (h-BN) dielectric layer, the WSe$_2$/h-BN-FET-based optical memory on silicon also exhibited a high on/off ratio of $1.1 \times 10^6$, realizing a data storage capability of up to 128 distinct states.[30]

Despite the long retention time and high on/off ratios of the recently developed vdWs heterostructure-based optical memory...
devices, high off-current, programming voltage, and off-power consumption hinder their application. More importantly, all of the optical memory devices rely on the three-terminal architecture of the gate, source, and drain electrodes. This limits the capacity for device miniaturization and increases circuit complexity in terms of scalability and integration functionality, which represent significant challenges in the field of three-terminal memory devices.

Herein, we propose a two-terminal multibit nonvolatile optical memory in the floating-gate FET via MoS$_2$/h-BN/graphene heterostructure. In this device, the top monolayer MoS$_2$ is used as both a conducting channel and light absorption layer, while the bottom graphene layer serves as a floating gate and the thin h-BN flake sandwiched between them acts as a dielectric tunneling layer. Application of an appropriate negative source–drain voltage ($V_{DS}$) pulse can induce electron tunneling through the h-BN layer for storage in the bottom graphene floating gate, eventually exerting an effective negative gate bias for an extremely low off-current. Subsequently, upon light pulse exposure, the photogenerated holes in MoS$_2$ can easily tunnel through the small triangular hole-barrier of MoS$_2$/h-BN to neutralize the stored electron in the bottom graphene layer. These processes lead to an ultrahigh on/off ratio of $>$10$^9$ and 16 distinct storage levels (four-bit storage).

Figure 1a shows a schematic of the two-terminal optical memory device based on the floating gate FET of MoS$_2$/h-BN/graphene heterostructure on a silicon substrate. The device was fabricated through sequential transfer and stacking of the monolayer graphene, h-BN flake, and monolayer MoS$_2$. This was followed by electron-beam lithography and metal deposition on MoS$_2$ to form the electrodes. The thickness and crystalline quality of the h-BN flake, monolayer MoS$_2$, and graphene in the device were characterized by atomic force microscopy (AFM), photoluminescence, and Raman spectroscopy measurements, respectively (Sections S1 and S2, Supporting Information). More details regarding device fabrication and characterization are described in the Experimental Section.

Figure 1b shows the hysteresis in the current–voltage ($I_{DS}$–$V_{DS}$) characteristics of the 7 nm thick h-BN device with a sweeping $V_{DS}$ voltage of $-10$ V to $3$ V and floating graphene without illumination. In the forward sweep from $-10$ to 3 V, all $I_{DS}$ curves progressively drop to an ultralow current of $\approx 10^{-14}$ A at $V_{DS} = -0.5$ V, remaining at a similar level until the $V_{DS}$ reaches 3 V. This originates from two successive processes: i) under the initially high negative $V_{DS}$ bias, electrons tunnel from the drain through the h-BN barrier to be confined in the floating graphene, and ii) when $V_{DS}$ sweeps to a low voltage, the tunneling process is inhibited and the confined electrons in the floating graphene induce an effective negative gate to switch off the MoS$_2$ channel current.[$^{13}$] In the backward sweep until $V_{DS} = 0$ V from 3 V, the off-state of the MoS$_2$ channel ($\approx 10^{-14}$ A) remains unchanged, and gradually recovers its initial on-state with a slight hysteresis as $V_{DS}$ reaches $-10$ V (black curve).

When the electrons are confined in the floating graphene at an off-state of 3 V, a 458 nm light pulse can be illuminated on the device for 1 s, and the photogenerated holes in the MoS$_2$ channel tunnel through the h-BN layer to neutralize the confined electrons in the graphene. Consequently, the current in the MoS$_2$ channel sharply increases from $10^{-14}$ to $10^{-8}$ A (10$^{-10}$ A) for a light power of 160 nW (16 nW) and the high current level remains during the entire backward sweep, resulting in the large hysteresis of the illuminated $I_{DS}$–$V_{DS}$ curves (orange and olive curves). The electrons in the floating graphene can be modulated by light illumination at a positive $V_{DS}$ to reduce the MoS$_2$ channel resistance. This feature can be used for nonvolatile optical memory applications. The aforementioned optical switching behavior with light illumination at 3 V is also valid in the off-state range (from 0 to 3 V) (see Section S3, Supporting Information). Furthermore, it is worth noting that our device can be operated as three-terminal FET optical memory with silicon gate bias and MoS$_2$ channel (see Section S4, Supporting Information).

To examine the reliability of MoS$_2$/h-BN/graphene heterostructure for optical memory, the device was subjected to several resistance-switching cycles by successive $V_{DS}$ pulses for programming ($V_{DS-pro}$) at $-10$ V and readout current at 0.5 V, with light pulses for erasing (Figure 1c). Each cycle includes 1) programming, 2) off-current reading, 3) erasing, and 4) on-current reading processes. Each process is highlighted by the corresponding lateral and vertical energy band diagrams in Figure 1d. Owing to the intrinsically n-doped MoS$_2$ (see Section S5, Supporting Information), the channel exhibited reasonably high conductance, $I_{DS} = 5 \times 10^{-10}$ A with $V_{DS-read} = 0.5$ V in the dark. To program the memory device, a $V_{DS-pro}$ pulse of $-10$ V for 1 s was utilized, which is much smaller than the programming gate bias of three-terminal optical memory devices.$^{[14,28–31]}$ Under this $V_{DS-pro}$ pulse bias, the $I_{DS}$ abruptly increased to $\approx 10^{-9}$ A ($I_{1}$ in Figure 1c). Simultaneously, electrons from the drain can tunnel through the h-BN barrier to the floating graphene via the Fowler–Nordheim mechanism$^{[11,32]}$ due to the large potential difference (Figure 1d—(1) Programming, bottom). However, these electrons become confined and spread out in the floating graphene since they cannot tunnel to the source (or MoS$_2$) due to the negligible potential drop between the two materials.$^{[13]}$

When the $V_{DS-pro}$ is switched to $V_{DS-read} = 0.5$ V for current reading, electron tunneling between the drain and floating graphene is prohibited. The confined electrons in the graphene synchronously induce an effective negative gate bias of $\approx -2.5$ V to the MoS$_2$ channel,$^{[18]}$ which enlarges the effective Schottky barrier for electrons between the metal contacts and MoS$_2$ channel.$^{[33]}$ This enlarged effective Schottky barrier impedes electron injection from the metal contacts to MoS$_2$ channel (Figure 1d—(2) Off-current reading, center). Accordingly, the $I_{DS}$ sharply decreases to $8 \times 10^{-12}$ A (off-current), $\approx 100$ times smaller than that of the initial current ($5 \times 10^{-10}$ A) and subsequently retains the off-current level for a prolonged period ($I_{2}$ in Figure 1c). This sharp decrease of $I_{DS}$ also refers to the gradual decrease in $I_{DS}$ to off-current ($\approx 10^{-14}$ A) upon forward sweeping from $-10$ to 3 V in Figure 1b. Owing to the limit in terms of minimum measurable current of the Agilent B2900 system used for the operating sequence measurement, the off-current level cannot reach an ultralow $\approx 10^{-14}$ A compared to that of the $I_{DS}$–$V_{DS}$ measurements using the Keithley 4200 semiconductor characterization system (SCS), as shown in Figure 1b.

For erasing, a light pulse with a power of 160 nW for 1 s was illuminated on the device to excite electron–hole pairs in the MoS$_2$ during $V_{DS-read} = 0.5$ V. Owing to the large electron-barrier...
of MoS$_2$/h-BN, the photogenerated electrons are trapped in the MoS$_2$. Meanwhile, the photogenerated holes most likely tunnel through the small triangular hole-barrier of the MoS$_2$/h-BN to the floating graphene, driven by the confined electrons in the graphene (Figure 1d—(3) Erasing, bottom). These tunneling holes neutralize the confined electrons in the graphene, removing the effective negative gate to the MoS$_2$ channel. Consequently, the Schottky barrier of the MoS$_2$ and metal
contacts is reduced and narrowed, facilitating electron injection from the metal contacts to MoS$_2$ channel (Figure 1d—(4) On-current reading). In addition, the free electron density in MoS$_2$ is increased by the blocked photoexcited electrons. Thus, the device is switched to the on-state, as indicated by a sharp increase in readout current, followed by stabilization at $\approx 25 \times 10^{-9}$ A, $\approx 50$ times higher than that of the initial current $\approx 5 \times 10^{-10}$ A ((3) and (4) in Figure 1c).

Excellent retention time and cyclic programming/erasing (P/E) endurance are essential for the reliability of a nonvolatile memory device for data storage. Figure 2a shows the highly reliable retention characteristics over $3.6 \times 10^4$ s for the 9 nm thick h-BN device. The off- and on-state retention times were independently measured by monitoring the time-dependent $I_{DS}$ at $V_{DS\text{-read}} = 0.1$ V after programming and erasing, respectively. The device was programmed with an applied negative $V_{DS\text{-pro}}$ pulse ($-12$ V, 2 s) and erased by illumination with a 458 nm light pulse (400 nW, 0.4 s), and read by $V_{DS\text{-read}} = 0.5$ V. c) $I_{DS}$–time curve under with light pulses ($P = 160$ nW, $t_{\text{exp}} = 0.1$ s, $\lambda = 458$ nm) every 25 s, exhibiting the capability of multilevel memory.

Figure 2b shows the off- and on-current of $10^4$ P/E cycles with an interval of 100 cycles. Each P/E cycle includes programming by a negative $V_{DS\text{-pro}}$ pulse ($-12$ V, 0.2 s), off-current reading for 0.5 s, erasing by a 458 nm light pulse (400 nW, 0.4 s), and on-current reading for 0.5 s. The current was measured at $V_{DS} = 0.5$ V. The largely unchanged on- and off-current after $10^4$ P/E cycles indicates the high durability and stability of the MoS$_2$/h-BN/graphene memory. This reliability of the device is attributed to its extreme stability against voltage stress imparted by the h-BN dielectric layer.$^{[34,35]}$ The high P/E current ratio and long retention time of the MoS$_2$/h-BN/graphene optical memory could be used to achieve multilevel optical data storage. Figure 2c shows the multilevel $I_{DS}$ under periodic illumination of 18 light pulses (160 nW and 0.1 s exposure time) at $V_{DS\text{-read}} = 0.5$ V. The stepwise $I_{DS}$ was clearly distinct with increasing pulse numbers. We clearly observed 18 levels in six orders of current for 18 light pulses with clear gaps between successive levels compared to the background noise (inset of Figure 2c), justifying the reliability and validity of all data storage levels for the MoS$_2$/h-BN/graphene optical memory. Although we successfully demonstrated 18 current
levels, it is noticed that the number of levels is significantly
relies on bias condition, pulse light intensity, and instrument
accuracy we used.

Figure 3a shows the photoresponse memory of the 7 nm
thick h-BN device with different excitation wavelengths at a reading voltage \( V_{DS-read} = 0.5 \) V. b) Time-dependent \( I_{DS} \) at different light pulse powers under 458 nm illumination, exposure time \( t_{exp} = 1 \) s, reading voltage \( V_{DS-read} = 0.5 \) V. Time-dependent \( I_{DS} \) was recorded for 20 s for each pulse power and separately
plotted, regardless of the initial time. c) Variation of \( I_{DS} \) as a function of light pulse power \( P \) in semi-log (left axis) and linear (right axis) scales. The dashed line represents a linear fit between \( I_{DS} \) and \( P \). The inset is a log–log plot of \( I_{DS} \) versus \( P \) for \( P \) of <40 nW and the dashed line was fitted using a power-law function \( I_{DS} \sim P^\alpha \), \( \alpha = 3.7 \).

Figure 3 shows the wavelength- and power-dependent photoresponse memory characteristics. a) Photoresponse memory characteristics of the 7 nm thick h-BN device under illumination at wavelengths of 811, 725, 638, and 458 nm. The device was programmed by \( V_{DS-pro} = -10 \) V for 1 s to switch to the off-state prior to illumination. The photoresponse memory was subsequently evaluated by reading the time-dependent \( I_{DS} \) with \( V_{DS-read} = 0.5 \) V for 40 s both pre- and post-light pulse for each wavelength. The power and duration of the light pulse were fixed at 80 nW and 1 s, respectively, for all wavelengths. During the preillumination period, all reading \( I_{DS} \) were at the same level of \( 10^{-14} \) A in the off-state, ensuring identical initial states for each independent measurement. After application of a 638 or 458 nm light pulse (1.94 or 2.7 eV, respectively), whose energies are higher than that of the bandgap of monolayer MoS\(_2\) (1.86 eV, Section S2, Supporting Information), the \( I_{DS} \) increased steeply from \( 10^{-14} \) A to \( 10^{-8} \) A and remained stable for a long period. On other hand, \( I_{DS} \) remained largely unchanged after application of the 811 or 725 nm light pulse (1.53 or 1.71 eV, respectively), since the photon energies are smaller than that of the MoS\(_2\) bandgap. Thus, the photogenerated carriers in MoS\(_2\) are responsible for the optical memory of the MoS\(_2\)/h-BN/graphene, as

opposed to the photoactivated mid-gap states in the h-BN layer, as suggested in previous reports.[30,36]

We further investigated the pulse power-dependent photoresponse memory at 458 nm with a fixed exposure time of 1 s, as shown in Figure 3b (638 nm in Figure S6a, Supporting Information). The optical memory can be accessed even with a small light pulse power of 2 nW, corresponding to a light energy of 2 nJ (light power multiplied by exposure time). This highlights the high optical sensitivity of the fabricated device, similar to that of WSe\(_2\)/h-BN optical memory.[10] Figure 3c shows the variation of the on-state \( I_{DS} \) as a function of pulse power \( P \) at 458 nm in semi-log (left axis) and linear (right axis) scales. Variation of \( I_{DS} \) shows two distinct operating regions: sub-threshold and above a threshold power of 40 nW. Above the threshold power, the on-state \( I_{DS} \) exhibits a linear relationship with \( P \) (right axis), while it follows a power-law dependence on \( P \) (\( I_{DS} \sim P^\alpha \)) in the sub-threshold region (inset of Figure 3c). A similar trend of on-state \( I_{DS} \) versus pulse power was also observed for 638 nm illumination (Figure S6b,c, Supporting Information). Noticeably, the pulse-power-dependent \( I_{DS} \) is similar to the \( I_{DS-V_{GS}} \) characteristic of FET (Figure S5, Supporting Information), further indicating that the optical memory feature is driven by the recombination of photoexcitation in MoS\(_2\) with confined electrons in the floating graphene.
Furthermore, we examined the exposure time-controlled photoresponse memory of the prepared devices. The device was programmed at $V_{DS-pro} = -10 \text{ V}$ for 1 s at the same off-current level to guarantee similar starting points for every measurement. Figure 4a shows the $I_{DS}$ variation for a duration of 20 s during the off-current and light illumination at different exposure times (light power of 80 nW). The photoresponse memory functionality was obtained even with a short exposure time of 0.01 s, corresponding to 0.8 nJ. The exposure-time-dependent on-state $I_{DS}$ is plotted as a function of exposure time at a given power and is identical to that of the pulse power dependence for a set exposure time, as shown in Figure 4b. This strongly suggests that the optical memory device can operate in response to exposure time or light power.

We next investigated the effect of $V_{DS-pro}$ pulse on the photoresponse memory characteristics of the device (Section S7, Supporting Information). Figure 4c shows the variation of the off-current (black), on-current (red), and on/off ratio (blue) as a function of the $V_{DS-pro}$ voltage. The $V_{DS-pro}$ pulse duration was fixed at a programming time of 1 s for different voltages. With $V_{DS-pro} \leq -8 \text{ V}$, the device is completely off with $I_{DS} \approx 10^{-14} \text{ A}$, corresponding to an on/off current ratio of $\approx 10^4$. However, the on/off current ratio drops rapidly to 10 when $V_{DS-pro} > -8 \text{ V}$ due to the increased off-current, as the voltage is insufficient to induce electron tunneling from the drain to floating graphene. It should be noted that the programming voltage of the optical memory device can be further reduced by using thinner h-BN flakes. The photoresponse memory characteristics were also investigated with $V_{DS-read}$ (Figure S3a, Supporting Information). The device was programmed using a $V_{DS-pro}$ pulse ($-10 \text{ V}, 1 \text{ s}$) and erased by a light pulse (50 nW, 1 s). Figure 4d shows the dependence of $V_{DS-pro}$ on the photoresponse memory of the fabricated optical memory device.

In conclusion, we successfully demonstrated the floating gate FET of MoS$_2$/h-BN/graphene heterostructure logic circuits such as “AND” and “OR,” can be simply realized (Section S8, Supporting Information). This represents a significant improvement in terms of integration compared to conventional complementary metal-oxide-semiconductor logic circuits with n- and p-type FETs.

In conclusion, we successfully demonstrated the floating gate FET of MoS$_2$/h-BN/graphene heterostructure as a two-terminal, nonvolatile optical memory device. Using $V_{DS}$ voltage and light illumination, the fabricated optical memory device could control electron tunneling to the floating graphene to modulate resistance of the MoS$_2$ channel, enabling programmable functions for optical memory. Optical memory operation originates from the photogenerated carriers in MoS$_2$, rather than the photoexcited carriers from the mid-gap states in the h-BN flake. The resulting two-terminal optical memory can operate with a small programming voltage of $-10 \text{ V}$ and...
minimal light pulse energy of 2 nJ. The device exhibits an ultralow off-current of $\approx 10^{-14}$ A and high programming/erasing current ratio of $\approx 10^6$, allowing for $> 18$ distinct storage states per cell. The device also exhibits high reliability with a prolonged retention time of $\approx 3.6 \times 10^4$ s and $> 10^4$ consecutive P/E cycles of cyclic endurance. Moreover, the two-terminal optical memory strategy developed herein may be applied to other 2D vdWs semiconductors. The excellent mechanical flexibility of 2D vdWs materials (graphene, few-layer h-BN, and MoS$_2$) without the gate electrode and rigid oxide insulator will be advantageous in future flexible and stretchable optoelectronic technology. In addition, the two-terminal architecture can facilitate the scalability and functionality of novel multifunctional optoelectronic devices.

Experimental Section

Device Fabrication Process: The MoS$_2$/h-BN/graphene heterostructure was fabricated on a SiO$_2$/Si substrate as follows. First, monolayer graphene flakes grown by chemical vapor deposition (CVD) were transferred onto the SiO$_2$/Si substrate using the poly(methyl methacrylate) (PMMA)-mediated bubbling transfer method.[10] Next, the h-BN flake was obtained from mechanical exfoliation on a dual-layer of PMMA/poly(vinyl alcohol) (PVA) coated SiO$_2$/Si substrate. The few-layer h-BN flake was transferred to the top of a graphene flake using dry transfer. By dissolving the bottom PVA layer, the h-BN flake/PMMA layer was floated on water and picked up on the arm of a manipulator in the dry transfer system for aligning and stacking onto the target graphene flake with the aid of a video microscope. To place the MoS$_2$ on the top of the h-BN/graphene, the CVD-grown monolayer of MoS$_2$ on a SiO$_2$/Si wafer was spin coated with PMMA film as a supporting layer. The PMMA-supported MoS$_2$ film was subsequently detached from the SiO$_2$/Si wafer in dilute hydrofluoric (HF) acid. The film was cleaned three times in deionized water baths to remove the remaining HF. It was then flipped over and picked up on the arm of the manipulator for aligning and stacking onto the h-BN/graphene stack, in a similar manner as the transfer of h-BN. Finally, chromium/gold (5 nm/50 nm thickness) electrodes were deposited using electron beam evaporation, followed by patterning via electron-beam lithography. 

Characterizations (AFM, Raman, and Electrical Measurements): AFM images were obtained using the E-sweep/NanoNavi Station scanning probe microscopy (SII NanoTechnology, Inc). The Raman spectra were obtained under ambient conditions using commercial equipment (NT MDT, NTEGRA Spectra PNL) with an excitation wavelength of 532 nm (2.33 eV). All optoelectronic measurements were conducted in a vacuum of $10^{-6}$ Torr at room temperature. The I–V characteristics, photoresponse, and retention time of the prepared devices were measured using a Keithley 4200-SCS Parameter Analyzer and transistor–transistor logic (TTL) modulation laser sources. The operating sequence and endurance performance of the devices were measured using an Agilent B2902A Precision Source/Measure Unit and TTL laser.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

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