Control of photocurrent and multi-state memory by polar order engineering in 2H-stacked α - In_2Se_3 ferroelectric

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ABSTRACT Controlling the polar order in ferroelectric materials may enrich the diversity of their property and functionality, offering new opportunities for the design of novel electronic and optoelectronic devices. In this paper, we report a planar multi-state memory device built upon a two-dimensional (2D) van der Waals layered ferroelectric material, 2H α - In_2Se_3 . Three (high, median and low) resistance states are demonstrated to be interconvertible in this device with a fast switching speed, excellent endurance and retention performances *via* the modulation of the polar order of the ferroelectric α - In_2Se_3 layers under an in-plane electric field. Remarkably, reversible switching between the median-resistance state and the low-resistance state can be achieved by an ultralow electric field of 1–2 orders of magnitude smaller than the reported values in other 2D ferroelectric material-based memory devices. Furthermore, the three different polar order states are discovered to exhibit distinctive photo-responses. These results demonstrate great potentials of α - In_2Se_3 in nonvolatile high-density memory and advanced optoelectronic device applications.

Keywords: van der Waals ferroelectric semiconductors, 2H-stacked α - In_2Se_3 , polar order arrangement, photocurrent, multi-state memory

INTRODUCTION

The rapid increase in information in the big-data era has driven the need to develop ultra-high-density information storage and novel multifunctional devices [1,2]. In this endeavor, tremendous efforts on device fabrication have been mainly focusing on either scaling down the feature size of the devices, which however would encounter reliability issues due to the leakage current [3], or stacking conventional components into a three-dimensional (3D) architecture with complex circuit [4]. Alternatively, multilevel storage within one memory cell is also a promising solution for further expanding the storage capability [5]. Ferroelectric materials are such an idea platform to provide multilevel states by controlling the electric polarization with the application of an external electric field [6,7]. In the past decade, organic ferroelectric poly(vinylidene fluoride-co-trifluoro ethyl-

ene) (PVDF-TrFE) insulator has been used to demonstrate a multi-level memory in ferroelectric field-effect transistor (FeFET) by gate voltage modulation [8–10]. More recently, the perovskite ferroelectric $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ was also reported to have multi-state polarization *via* control of the switching pathway [11]. However, these materials suffer from some critical issues, which hinder their integration with the current semiconductor technology and reduce their efficiency in data reading/writing [12]. Besides, the PVDF-TrFE usually requires a large coercivity voltage [8,13] and the synthesis of high-quality perovskite ferroelectrics requires sophisticated preparation processes. Therefore, it is more desirable to achieve multi-state memory in single and easily integrated ferroelectric semiconductor with a small switching voltage for low-power and high-density information storage.

At present, emerging 2D van der Waals (vdW) ferroelectrics may avert the above issues and enable nondestructive data reading and indefatigable data writing, thanks to their clean vdW interfaces and narrow-band-gap nature [12]. Among the known 2D vdW ferroelectric semiconductors, α - In_2Se_3 possesses robust room-temperature ferroelectricity even down to the monolayer limit, and large-area samples can be grown using simple and low-cost preparation methods [14–16]. Moreover, the α - In_2Se_3 ferroelectric has two different stacking constructions, namely hexagonal (2H) and rhombohedral (3R) structures [17–19]. Although both of them have some similar properties such as the interlocked in-plane (IP) and out-of-plane (OOP) ferroelectricity [17,20–23], mechanical flexibility [24,25] and bandgap tunability [2,26], pristine 2H α - In_2Se_3 shows a distinctive polarization arrangement, that is, the interlayer IP polarization is alternately anti-parallelly aligned [16]. This special polar order configuration can bring striking physical properties, such as layer-dependent IP phase contrast and polarization [16,20].

Herein, considering that (1) the polar order of 2H α - In_2Se_3 multilayer (ML) films could be rearranged into diverse forms, and (2) the diverse and easy polar order rearrangement would bring distinctive electronic and optoelectronic properties, we explored polar order engineered resistance state and the corresponding photocurrent in 2H α - In_2Se_3 . We demonstrated a three-state memristive behavior in a 2H α - In_2Se_3 -based planar

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device controllably obtained by applying different IP voltages. This memristor shows relatively fast switching speed (milliseconds), excellent endurance (>300 cycles) and retention (>4500 s) simultaneously. In particular, the reversal switch between the median-resistance state (MRS) and the low-resistance state (LRS) is realized under an ultralow electric field of $\sim 5.7 \times 10^2 \text{ V cm}^{-1}$, being 1–2 orders of magnitude smaller than those currently reported in 2D ferroelectrics. Furthermore, the distinctive photoresponse occurs in these states with the different polar order configurations, due to the varied built-in electric field (E_{bi}) of the different polar orders that separates the photo-generated carriers in different extent. These results suggest that 2H $\alpha\text{-In}_2\text{Se}_3$ is a promising material for the development of nonvolatile multi-state memories and advanced optoelectronic devices.

EXPERIMENTAL SECTION

2H flakes were exfoliated from bulk crystals bought from Nanjing MKNANO Tech. Co., Ltd. (www.mukenano.com). Then the exfoliated $\alpha\text{-In}_2\text{Se}_3$ flakes were transferred onto SiO_2 (285 nm)/Si substrates. Subsequently, the $\alpha\text{-In}_2\text{Se}_3$ planar devices were fabricated by a laser direct-writing (MicroWriter ML 3 Baby Plus) lithography process followed by thermal evaporation of the Cr (10 nm)/Au (60 nm) electrode metals, and lift-off.

The cleaved $\alpha\text{-In}_2\text{Se}_3$ flakes were characterized by the following means: an optical microscope (OM, Aosvi L100-HK830), an X-ray diffractometer (XRD, Ultima IV-185), and Raman spectroscopy (Horiba Labarum HR Evolution, 532 nm). The cross-

sectional high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were acquired using an aberration corrected FEI Titan Themis 200 at 200 kV with spatial resolutions of 0.08 nm. The TEM samples were fabricated by focused ion beam (FIB, FEI Helios 450S) cutting. The $\alpha\text{-In}_2\text{Se}_3$ flakes of different thicknesses were identified by atomic force microscope (AFM, Bruker Dimension Icon). The ferroelectric measurements were conducted on a piezoresponse force microscopy (PFM) under resonance-enhanced mode. All electrical measurements were performed in a vacuum (10^{-6} Torr, 1 Torr = 133.3 Pa) chamber of Lakeshore probe station with a Keithley 4200 semiconductor parameter analyzer. Commercial light-emitting diode (LED) lamps were used to provide light source, and the maximum power intensity was $\sim 10.5 \text{ mW cm}^{-2}$. The light intensities were measured by a FieldMate + PM150X photometer.

RESULTS AND DISCUSSION

High-quality 2H $\alpha\text{-In}_2\text{Se}_3$ flakes were directly exfoliated onto different substrates (SiO_2/Si or Pt/Ti) from bulk $\alpha\text{-In}_2\text{Se}_3$ crystal. The bulk crystal was firstly characterized by X-ray diffraction (XRD). The diffraction pattern only exhibits the *c*-plane peak, which fits well with the hexagonal structure (Fig. S1a) [17,25,27]. To visualize the atomic-scale structure of as-exfoliated flakes, the state-of-the-art aberration-corrected STEM was used to acquire the cross-sectional HAADF images of the samples. Fig. 1a shows a 2H-stacking layered structure of a 180-degree IP rotation with respect to the adjacent layers. The Raman spectrum of the

Figure 1 High-resolution STEM (HR-STEM), Raman, PFM and PL characterizations of the obtained ML 2H $\alpha\text{-In}_2\text{Se}_3$ flakes. (a) Cross sectional HR-STEM image. Scale bar, 1 nm. (b) Typical Raman spectrum. (c) The IP phase image after writing two square patterns being subjected to $\pm 5 \text{ V}$ DC tip bias consecutively. Scale bar, 250 nm. (d) PL spectroscopy with an optical bandgap of $\sim 1.52 \text{ eV}$.

sample (~ 57 nm) shows four typical peaks at ~ 88 , 105, 179 and 194 cm^{-1} (Fig. 1b), which can be assigned to the E_g , $A_1(\text{LO} + \text{TO})$ (LO is longitudinal optical phonon, and TO is transverse optical phonon), $A_1(\text{TO})$ and $A_1(\text{LO})$ phonon modes of 2H $\alpha\text{-In}_2\text{Se}_3$, respectively [17,28,29]. The 2H $\alpha\text{-In}_2\text{Se}_3$ flakes have the same Raman peaks except for the $A_1(\text{LO})$ phonon mode with increasing thickness. When the thickness of $\alpha\text{-In}_2\text{Se}_3$ is less than 38.4 nm, the peak at 194 cm^{-1} undergoes blue shifts (Fig. S1b). This result indicates that the 2H $\alpha\text{-In}_2\text{Se}_3$ flakes have stable Raman peaks when the thickness of $\alpha\text{-In}_2\text{Se}_3$ is equal to or greater than 38.4 nm. The ferroelectric polarization of a ~ 57 -nm-thick 2H $\alpha\text{-In}_2\text{Se}_3$ sample was determined by PFM. Fig. 1c and Fig. S2 show the clear IP and OOP PFM phase contrast after writing two square patterns by applying ± 5 V direct current (DC) tip bias consecutively, indicating the polarization reversal and interlocked ferroelectricity [16,17]. The same results also exist in a 19-nm-thick 2H $\alpha\text{-In}_2\text{Se}_3$ (Fig. S3). The photoluminescence (PL) spectrum shows a narrow bandgap characteristic of 2H $\alpha\text{-In}_2\text{Se}_3$ (~ 57 nm) with an optical bandgap of ~ 1.52 eV, corresponding to a photoresponse in near-infrared and visible bands (Fig. 1d).

Next, we explored the possibility of resistive switching upon the regulation of polar order alignment in a thick (~ 59 nm) 2H $\alpha\text{-In}_2\text{Se}_3$ layer. We measured the current-voltage (I - V) curves of 2H $\alpha\text{-In}_2\text{Se}_3$ -based planar device in different electrical poling states (Fig. S4). The I - V curve of the as-exfoliated device under ± 1.0 V maximum-sweep voltage does not show hysteresis characteristic (Fig. 2a). However, when a $+9.0$ V poling voltage bias is applied to the device, the obvious hysteresis characteristic can be observed under ± 1.0 V (Fig. 2b). This could be attributed to the different polar order configurations. The interlayer anti-

parallel polarization configuration in the initial polarization state of the 2H $\alpha\text{-In}_2\text{Se}_3$ is stable and this polarization configuration needs applying a larger voltage to change. And the polarization directions are difficult to be switched by applying a small voltage; thus the I - V curve of the device does not show hysteresis characteristic under ± 1.0 V maximum-sweep voltage (Fig. 2d①). When a $+9$ V poling voltage bias is applied to the device, the stable interlayer anti-parallel polarization configuration is changed, and the corresponding IP polarizations are partially rearranged (Fig. 2d②). In such case, the partial polarization directions are easily reversed, and the device shows the obvious hysteresis characteristic under applying a small voltage (± 1.0 V) (Fig. 2b). As shown in Fig. 2b, d, when applying a small positive IP electric field (IP- E_+), the partial P_{Left} (polarization to the left, orange) of 2H $\alpha\text{-In}_2\text{Se}_3$ is reversed to the P_{Right} (polarization to the right, blue), the device shows the LRS (SET process, Fig. 2d③). Similarly, when the partial P_{Right} is also reversed to the P_{Left} , the device is switched into an MRS (RESET process, Fig. 2d④). Hence, the device can be repeatedly switched between the LRS and MRS by an applying ultralow electric field of $\sim 5.7 \times 10^2\text{ V cm}^{-1}$, being 1–2 orders of magnitude smaller than those currently reported in 2D ferroelectrics (Table S1). This ultralow switching electric field is desirable and appealing for low-power ferroelectric memristors. Furthermore, it is noted that there are obvious multi-step current jumps during SET (I) and RESET (II) processes (Fig. 2b and Fig. S5a). The enlarged views of I and II processes are shown in Fig. S5b, c, respectively. Four obvious current jumps corresponding to positive voltages of ~ 0.36 , ~ 0.43 , ~ 0.74 and ~ 0.95 V are found in the SET process with the device resistance states switching from the MRS into LRS. Meanwhile, the three obvious current jumps are also

Figure 2 The multi-state memory of ML 2H $\alpha\text{-In}_2\text{Se}_3$ -based planar device induced by engineering configurations of polarization orientation. (a–c) I - V characteristics of the device after applying different poling voltage biases including (a) 0 V, (b) $+9.0$ V and (c) -9.0 V. (d) Schematic illustration of the multi-state memory with different polarization orientation configurations.

observed in the RESET process corresponding to negative voltages of ~ -0.23 , ~ -0.31 and ~ -0.48 V with the device resistance states changing from the LRS to MRS. These results demonstrate a step-by-step switching process of the ferroelectric polarization from P_{Left} to P_{Right} and P_{Left} to P_{Right} in the 2H α - In_2Se_3 film.

The SET voltages ($P_{\text{Left}} \rightarrow P_{\text{Right}}$) are higher than the RESET voltages ($P_{\text{Right}} \rightarrow P_{\text{Left}}$), indicating that the P_{Left} requires larger energy to be reversed, which probably arises from an interface polarization pinning effect [30]. When applying a -9.0 V poling voltage bias, the P_{Right} is easily switched into the P_{Left} in 2H α - In_2Se_3 (Fig. 2d④), and the device enters a high-resistance state (HRS), leading to a decrease in the current (Fig. 2c). However, the I - V curve under ± 1.0 V maximum-sweep voltage does not show hysteresis characteristic. This may be due to that the aligned polarization configuration is relatively stable, which makes it difficult to flip the polarization at low voltages. Moreover, the device has not obvious rectification behavior after -9 V poling, probably owing to the influence of asymmetric source and drain interfaces and/or the deviation between the polarization axis and the direction of the applied electric field. The asymmetric interfaces and the deviation can be caused by the irregularity of the as-exfoliated samples. Furthermore, Raman spectroscopies of the device in LRS, MRS and HRS were conducted to rule out structural phase transitions as a possible switching mechanism [31]. The Raman peaks of the MRS and LRS are similar to those of the initial state (Fig. S6a, b), which may be attributed to the negligible structural changes. When the device is switched into the HRS, the Raman peaks at 90, 181 and 195 cm^{-1} have small blue shift of ~ 1 – 2 cm^{-1} (Fig. S6a, b). These results differ from the α -to- β phase transition causing blue shift

(~ 6 cm^{-1}) of Raman peak at 104 cm^{-1} [32], indicating that the above multi-state memory is not caused by phase change. In addition, considering that defect migration can also induce resistive memories, such as Cu ion migration in the vdW ferroelectric CuInP_2S_6 under the electric field [33]. The ion migration usually forms surface particles and changes the sample morphology [33]. Hence, the AFM topography of 2H α - In_2Se_3 planar device at the HRS and LRS were carried out. As shown in Fig. S7, no obvious surface particles and morphological changes were observed in the channel region, demonstrating the defect migration is not the main reason for resistive switching. Moreover, this multi-value resistive switching behavior is also observed in another 51-nm-thick 2H α - In_2Se_3 -based device (Fig. S8).

As critical factors in evaluating the storage performance, the endurance, retention, and write/erase speed of the 2H α - In_2Se_3 planar device were measured. Fig. 3a shows that the three distinctive memresistive states (HRS, MRS and LRS) reversibly interconverted by different poling voltages show excellent endurance over 300 cycles. The device resistances (R_{HRS} (150.9 ± 7.9 k Ω), R_{MRS} (18.3 ± 1.8 k Ω), R_{LRS} (4.5 ± 0.7 k Ω)) and switching voltages (V_{SET} (0.44 ± 0.02 V), V_{RESET} (-0.36 ± 0.02 V)) are found to be fluctuated in a very narrow range (Fig. 3b, c). The switching voltages between MRS and LRS are noticeably smaller than 0.5 V. The $R_{\text{MRS}}/R_{\text{LRS}}$, $R_{\text{HRS}}/R_{\text{MRS}}$ and $R_{\text{HRS}}/R_{\text{LRS}}$ ratios at a reading voltage of 0.2 V are ~ 4 , 8 and 34 over the continuous electric cycling (Fig. 3d). Moreover, Weibull analysis was conducted to further quantify the uniformity of the switching parameters. The Weibull exponents (κ) of R_{HRS} , R_{MRS} , R_{LRS} , V_{SET} and V_{RESET} are ~ 23.48 , 12.45, 7.56, 59.19 and 66.37, respectively,

Figure 3 Three-state resistive switching performances of 2H α - In_2Se_3 -based ferroelectric planar memristor. (a) Three-state resistive switching characteristics of the device with 300 consecutive cycles. Histograms of the (b) HRS, MRS and LRS resistance values recorded at $V_{\text{ds}} = 0.2$ V and (c) switching voltages for 300 cycles. Orange line: SET voltages (MRS $\rightarrow$ LRS); dark cyan line: RESET voltages (LRS $\rightarrow$ MRS). (d) Retention properties of the LRS, MRS and HRS. The switching speeds between (e) HRS and LRS by applying voltage pulses of $+9.0$ V/0.5 ms (upper panel) and -9.0 V/0.5 ms (lower panel) and (f) MRS and LRS by applying voltage pulses of $+1.0$ V/5.0 ms (upper panel) and -1.0 V/5.0 ms (lower panel). The insets are the waveforms of applied voltage pulses.

while the standard deviation (Δ) to mean (μ) ratios (Δ/μ) of R_{HRS} , R_{MRS} , R_{LRS} , V_{SET} and $|V_{\text{RESET}}|$ are 0.0524, 0.0984, 0.1556, 0.0455 and 0.0556, respectively (Figs S9 and S10). The large κ and small Δ/μ values again indicate the uniformity of the switching parameters [34]. Furthermore, the programmed resistance states (HRS, MRS and LRS) possess good retention over 4500 s at room temperature (Fig. 3d). In addition, the multi-state programming speeds of the device were also explored. As shown in Fig. 3e, f, by applying a write voltage pulse of +1.0 V/5.0 ms (top inset of Fig. 3f), the device is changed from the MRS to LRS. In contrast, the device is switched from the LRS to MRS under an erase voltage pulse of -1.0 V/5.0 ms (lower panel). The switch between the HRS and LRS needs a pulse width of 0.5 ms and voltage amplitude of ± 9.0 V (Fig. 3e). These results demonstrate that short pulses of millisecond scale are able to successfully switch polarization and suggest the reliability of polar-order-tailored multi-state memory in 2H α -In₂Se₃-based devices.

As a semiconductor with a narrow bandgap (~ 1.4 eV), α -In₂Se₃ is sensitive to light [35]. We also investigated the photoresponse under different resistance states. Surprisingly, although 2H α -In₂Se₃ has a suitable optical bandgap, there is no obvious photocurrent in the as-exfoliated initial device under white light illumination (Fig. 4d). This is different from 3R α -In₂Se₃ that has the obvious photoresponse under the stimulation of light with appropriate wavelength [36]. It means that the photogenerated carriers cannot be separated quickly in the fresh 2H α -In₂Se₃. When the device is in the MRS, there is still no obvious photocurrent (Fig. 4e, lower panel). When the device is switched to the LRS, the photocurrent appears (Fig. 4e, upper panel). When

the device is in the HRS, a prominent photocurrent is observed (Fig. 4f). Similar phenomenon also occurs in the 51-nm-thick sample (Fig. S11). The results of these different photoresponses could be attributed to that the different polar order configurations (shown in Fig. 2d) produce distinct E_{bi} that separates the photogenerated carriers in different extents. In its initial state, 2H α -In₂Se₃ has an interlayer anti-parallel polar order arrangement owing to its stacking structure of the 180-degree IP rotation with respect to the adjacent layers (Fig. 4a). This anti-parallel polar order arrangement will lead to the smaller E_{bi} than that of IP-E aligned polarizations (Fig. 4c). Although the electron-hole pairs of the as-exfoliated 2H α -In₂Se₃ can separate transiently under white light illumination, it would be difficult for the smaller E_{bi} to suppress the recombination of the electron-hole pairs, thus there is no obvious photoresponse in the fresh device. On the contrary, the larger E_{bi} can effectively separate the photogenerated carriers (electrons and holes) to generate photocurrent (Fig. 4b, c) [37–39]. Considering antiparallel polar order being unfavorable for the separation of photogenerated electron-hole pairs, it is further illustrated that a few polarization orientations are aligned in the MRS and LRS. Above all the different polar order states are discovered to exhibit distinctive photoresponse in the 2H α -In₂Se₃ based planar device.

CONCLUSIONS

In summary, we have demonstrated that the special polar order of interlayer IP polarization anti-parallel alignment in the vdW 2H α -In₂Se₃ ferroelectric can be tailored by the electric field to control the resistance state and photocurrent in the 2H α -In₂Se₃-

Figure 4 The different photoresponses of three-state in the ML 2H α -In₂Se₃-based planar device. (a, b) Schematic illustration of the different photoresponses in (d) and (f) with photoexcited carriers related to polarization orientation arrangements. (c) Schematic of photoelectric measurement in planar device at initial (upper panel) and IP-E- poling (lower panel) states. (d–f) The photoresponses of (d) fresh, (e) IP-E- poling and (f) IP-E- poling devices under white light ($P = 10.5$ mW cm⁻²) illumination.

based planar device. Through applying different IP poling voltage biases, the device shows three resistance states including HRS, MRS and LRS. These resistance states hold relatively fast switching speed on the millisecond timescale, excellent endurance (>300 cycles) and retention (>4500 s) performances. Specifically, the MRS and the LRS can be switched reversibly by an ultralow electric field of $\sim 5.7 \times 10^2 \text{ V cm}^{-1}$, being 1–2 orders of magnitude smaller than those currently reported in 2D ferroelectrics. Furthermore, the device exhibits distinctive photoresponse under the HRS, MRS and LRS with different polar order configurations. This is because different polar order states produce distinct E_{bi} that separates the photogenerated carriers in different extents. These results suggest that 2H α - In_2Se_3 has special and engineered polar order for flexible controllability of photoelectric characteristics, as well as demonstrate great opportunities in nonvolatile high-density memories and advanced optoelectronic devices.

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devices; Yan Z and Yang R helped analyze the results; Zhu W contributed to the theoretical analysis. Lv B, Xue W, and Xu X co-wrote the manuscript. All the authors discussed the results and commented on the manuscript.

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Supplementary information Supporting data are available in the online version of the paper.

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2H α - In_2Se_3 铁电体中极序工程控制的光电流和多态存储器

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摘要 控制铁电材料的极序可以丰富其特性和功能的多样性, 为设计新型电子和光电子器件提供新的机会. 本文报道了一种基于二维(2D)范德瓦尔斯(vdW)层状铁电材料2H α - In_2Se_3 的面内多态存储器件. 通过施加面内电场调控铁电 α - In_2Se_3 层的极序, 实现了可以相互切换的三种电阻态, 其具有快的切换速度、良好的耐久性和保持性. 值得注意的是, 中间阻态(MRS)和低阻态(LRS)之间可以通过比其他基于2D铁电材料的存储器小1-2个数量级的超低电场来实现可逆切换. 此外, 还发现这三种不同的极序态表现出了特有的光响应. 以上结果表明, α - In_2Se_3 在非易失性高密度存储器和新型光电器件中具有很大的应用潜力.