

Optical Effects on Polarization States in van der Waals Ferroelectric α -In₂Se₃

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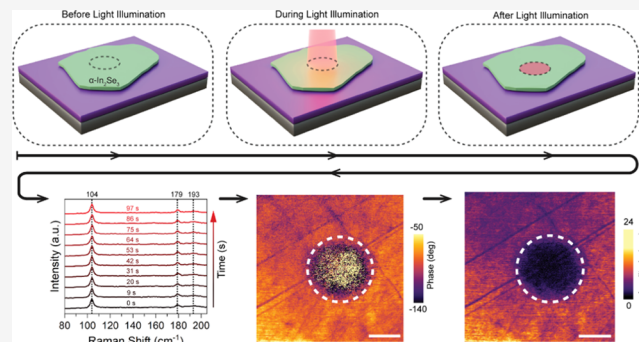


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Supporting Information

ABSTRACT: Optically controlled ferroelectricity represents a scalable approach to engineering desirable ferroelectric properties for various device applications. With van der Waals ferroelectric α -In₂Se₃ being extensively explored for optoelectronic memory and photonic neuromorphic computing technologies, an understanding of the light–ferroelectric interactions is necessary but has not been clearly established. In this study, we show the significant effects of optical illuminations on ferroelectric properties in α -In₂Se₃, particularly the changes from monodomain to disordered polarization states and associated variations of surface electric potentials. We attribute these photoinduced changes to the screening effects from photogenerated carriers that allow for the formation of domain walls and the corresponding multidomain state. These multidomains are metastable under ambient conditions, persisting for tens of days, but begin to disappear after $\sim$ 100 days. In addition, they can be returned to the aligned polarization state through external electrical poling. We also demonstrate the reversible optical modulation of device electrical resistance, which is promising for reconfigurable electronics. These findings reveal rich and new phenomena of light–ferroelectric interactions and provide critical microscopic insight that forms the basis for future explorations of novel device concepts based on ferroelectric α -In₂Se₃.



INTRODUCTION

The ability to control spontaneous electric polarization represents the most important aspect in ferroelectrics and is central to many applications including memory, tunneling diodes, and field-effect transistors.^{1–4} Typically, an external electric field is applied across the material to reverse the polarization. In addition to conventional metal electrodes, using a biased atomic force microscope (AFM) probe as the electric field source is particularly appealing, as it allows for on-demand reconfigurable local domain patterning for desired device functionality.^{5–9} However, such an approach is inherently slow and is not readily applicable to large-scale device fabrication. On the other hand, it has been shown^{10–14} that light–material interactions in ferroelectrics can drive polarization changes and domain wall motion, opening an alternative and scalable path to modifying domain configurations and associated ferroelectric properties.

The recent emergence of van der Waals ferroelectric materials^{4,15–23} provides greater flexibility in integrating materials with distinctive properties into heterostructures with novel functions, such as multiferroicity, polarization-controlled electrical conductivity, and ferroelectric field-effect transistors. Among the materials being explored, two-dimensional α -phase In₂Se₃ (α -In₂Se₃) features above-room-temperature ferroelectricity and unique interlinked in-plane (IP) and out-of-plane (OOP) ferroelectric polarizations.^{11,24–29} This

IP/OOP polarization coupling allows for ferroelectric switching using either an IP or an OOP electric field, and therefore, it is capable of accommodating various device designs and integrations such as planar memristors, ferroelectric field-effect transistors, nonvolatile memory, and neuromorphic computing circuits.^{19,30–34} In addition, recent studies have revealed that optical illuminations can tune the electrical conductance of 2D α -In₂Se₃ nonvolatily, demonstrating potential for multifunctional devices³⁵ and photonic synapses.³⁶ The mechanism of such a phenomenon, however, remains open to debate. Particularly, domain wall motion driven by optical illuminations³⁶ and polarization reversal due to the neutralization of screening charges by photogenerated carriers³⁵ have been suggested as the underlying processes.

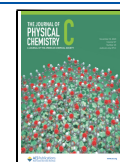
Here, we show that optical illuminations introduce significant changes to the ferroelectric properties and surface electric potential of α -In₂Se₃; we attribute these photoinduced changes to the emergence of multidomains due to the

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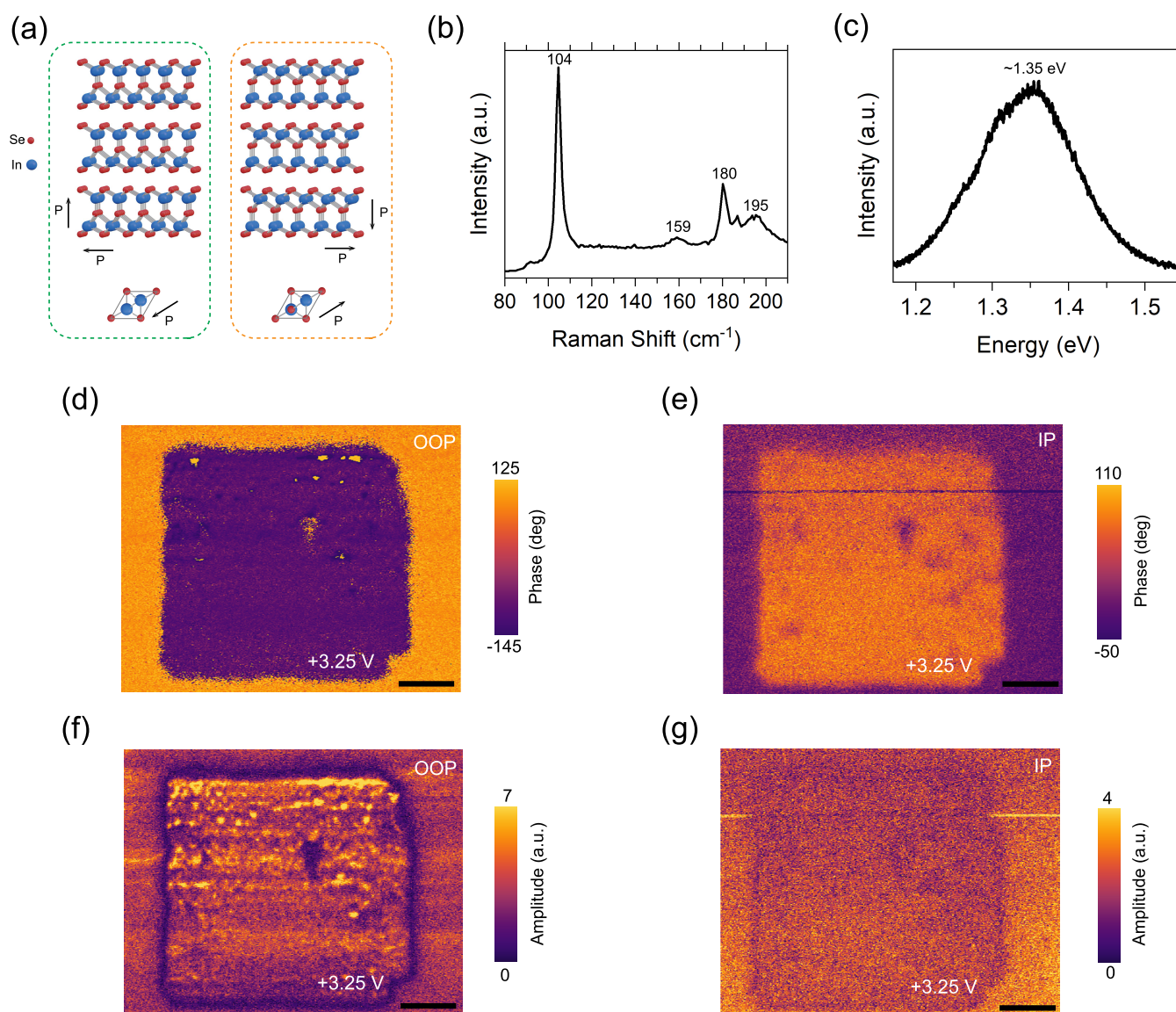


Figure 1. Structural and ferroelectric properties of α - In_2Se_3 . (a) Schematic side (top panel) and top (bottom panel) views of α - In_2Se_3 crystal structures with two opposite polarization directions (indicated by arrows); (b) Raman and (c) PL spectra of α - In_2Se_3 layers; (d–g) OOP-PFM and IP-PFM phase (upper) and amplitude (lower) images of a box pattern written by a biased AFM tip at +3.25 V. Scale bars in panels (d–g) are 200 nm. The α - In_2Se_3 layer in panels (d–g) was exfoliated onto a gold-coated substrate. See the [Supporting Information](#) for details on substrate parameters.

screening effect from the photogenerated carriers. This multidomain state is metastable under ambient conditions, persisting over approximately tens of days, but begins to revert to the original single-domain state over a longer period of time (~ 100 days). In addition, external electrical poling can also be used to erase the multidomain state and reverse the polarization to a single-domain state, demonstrating reconfigurability. We also show that the optically illuminated multidomain states can be implemented in device applications by demonstrating reversible optically modulated electrical resistance. These results reveal the new phenomena of light–ferroelectric interactions and associated mechanisms and could enable further novel device concepts such as more advanced reconfigurable memory and neuromorphic computing.

RESULTS AND DISCUSSION

Figure 1a shows the schematic layered structures of ferroelectric α - In_2Se_3 that represent two opposite polarization states. The interlinked OOP and IP spontaneous polarizations can be seen from the side and top views of the crystal structure. The Raman spectrum of an as-exfoliated α - In_2Se_3 layer (Figure 1b) exhibits main characteristic α -phase lattice phonon modes³⁷ at 104, 159, 180, and 195 cm^{-1} . Room-temperature photoluminescence (PL) emission at ~ 1.35 eV is observed (Figure 1c) from these layers, consistent with a recent study²³ that has shown that α - In_2Se_3 layers have a band gap at ~ 1.45 eV. The PL spectra have also been fitted (Figure S1) to reveal any additional peaks in the spectra. To verify the ferroelectricity and intercorrelation between polarization states in α - In_2Se_3 , we used a biased AFM tip (experimental details provided in the [Supporting Information](#)) to pole the original ferroelectric polarization into the opposite direction and then

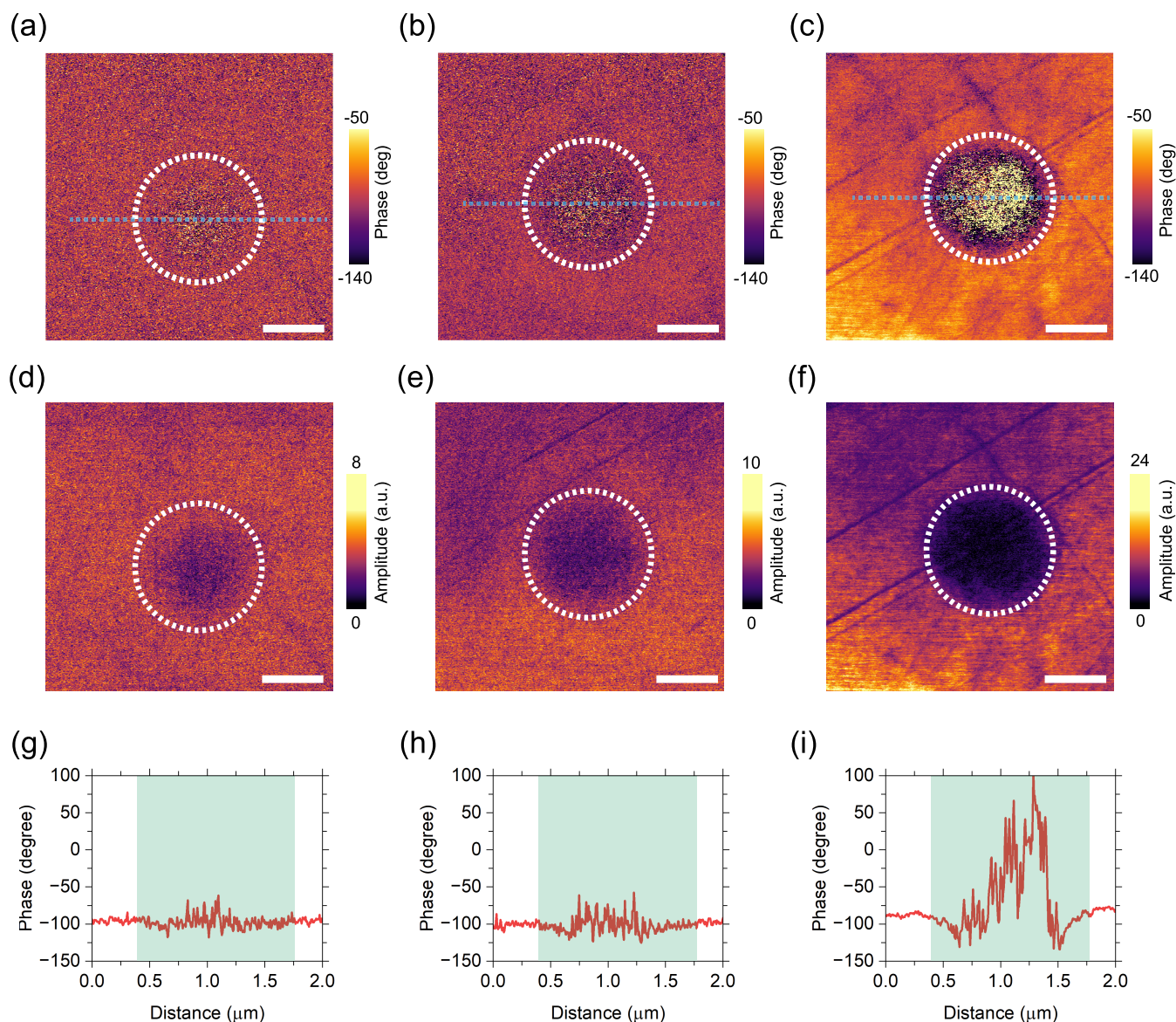


Figure 2. Effects of local optical illuminations. (a–c) PFM phase and (d–f) PFM amplitude images of optically illuminated regions (indicated by circles) with various illumination times (15, 30, and 60 s, respectively) in an α - In_2Se_3 layer (67 nm in thickness); (g–i) spatial profiles of the PFM phase across the optically illuminated regions in panels (a–c), respectively, with the shaded areas representing illuminated regions. Scale bars in panels (a–f) are 0.5 μm . The α - In_2Se_3 layer was exfoliated on a SiO_2/Si substrate.

used piezoresponse force microscopy (PFM) to probe the piezoresponse phase and amplitude. As shown in Figure 1d–1g, the square area was poled by scanning the AFM probe biased at +3.25 V. The OOP-PFM (Figure 1d,1f) and IP-PFM (Figure 1e,1g) images show clear correlated phase differences between the original and patterned domain and the diminished piezoresponse amplitude at the domain wall. We further conducted local poling measurements with the OOP-PFM phase and amplitude as functions of the AFM tip bias, showing characteristics consistent with ferroelectric switching (see Figure S2 and discussion).

To investigate the effect of optical illumination, we used 633 nm laser emission focused through a microscope objective as the local optical excitation source. As the laser energy (~ 1.96 eV) is above the band gap of α - In_2Se_3 , we expect efficient optical absorption and photon–material interactions. Figure 2a–f shows the OOP-PFM phase and amplitude images of an α - In_2Se_3 layer exfoliated on a SiO_2 (90 nm)/Si substrate with

multiple locations exposed to local optical illuminations with a laser power density of ~ 60 kW/cm^2 . We emphasize that no surface topographical changes are observed following the optical illuminations (Figure S3). On the other hand, areas with distinctive piezoresponse amplitude and phase can be clearly observed within the illuminated regions (indicated by circles). Particularly, the PFM amplitude is suppressed within these regions, with the phase signal showing significant fluctuations compared to that from outside the illuminated areas. Similar features are also observed in α - In_2Se_3 layers exfoliated on Au-coated Si substrates (Figure S4). Figure 2g–i further shows that longer laser exposure times lead to more pronounced variations in PFM phases. The extent of these photoinduced changes is also dependent on the laser power density (Figure S5). Furthermore, we have observed similar photoinduced changes across single domains with opposite polarization directions (Figure S6).

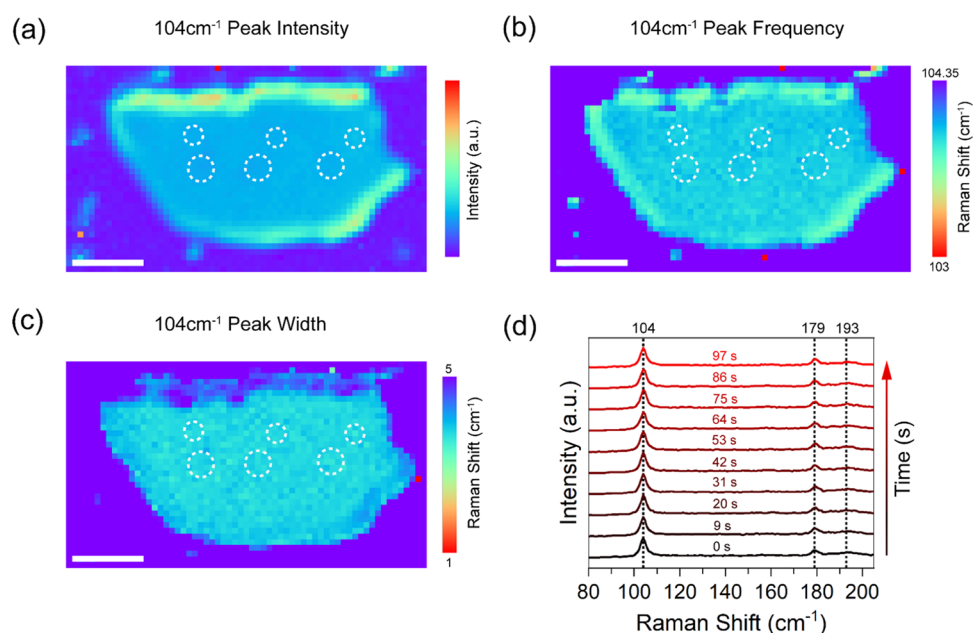


Figure 3. Raman characterization of the illuminated α - In_2Se_3 layer and investigation of heating effects. (a–c) Intensity, frequency, and width maps of the characteristic α - In_2Se_3 104 cm^{-1} Raman mode with dashed circles indicating the illuminated regions; (d) Raman spectra collected at time intervals during illumination; dashed lines indicate the three main Raman modes (104 , 179 , and 193 cm^{-1}) of α - In_2Se_3 . Spectra vertically shifted for clarity. Scale bars in panels (a–c) are $5\text{ }\mu\text{m}$. The α - In_2Se_3 layer was exfoliated on a SiO_2/Si substrate.

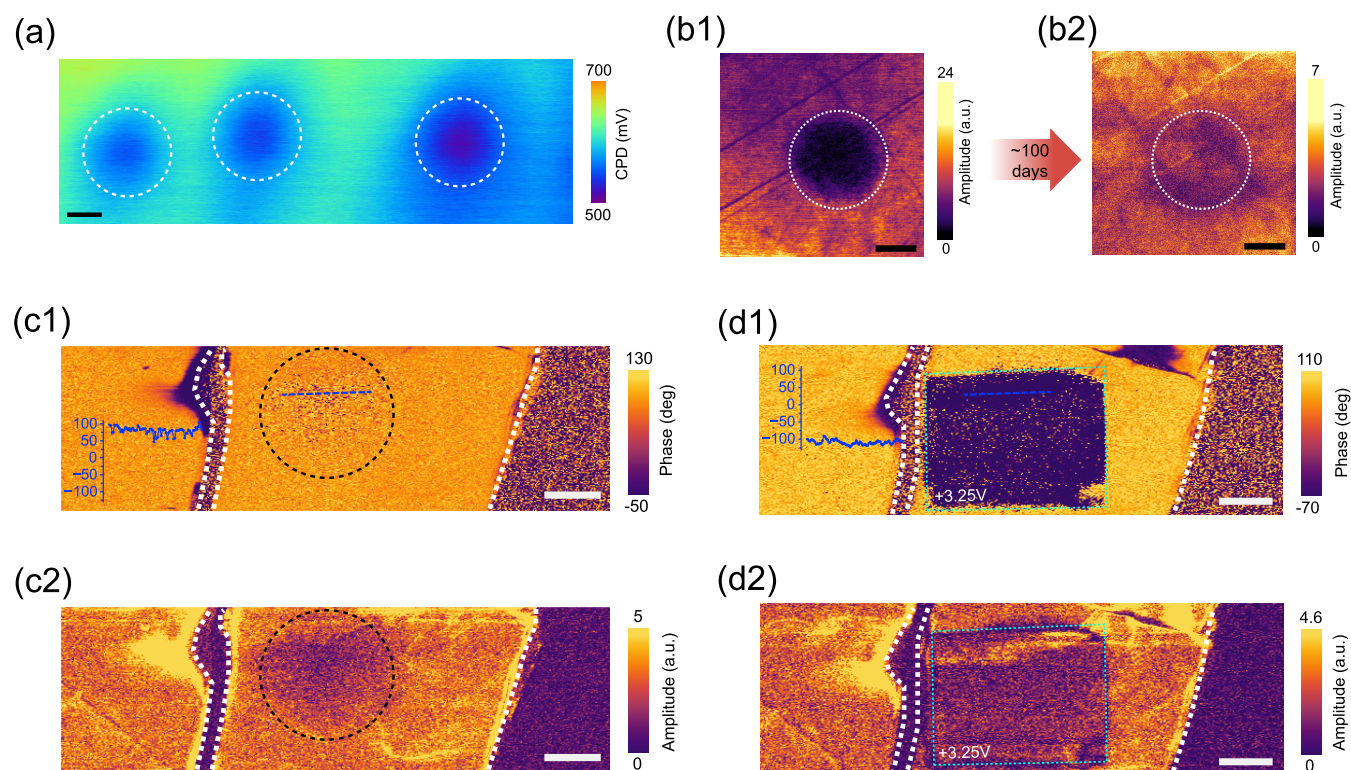


Figure 4. Surface potential measurements, retention, and ferroelectric control of optically illuminated regions. (a) KPFM imaging of illuminated regions in an α - In_2Se_3 layer with varying exposure times (from left to right: 60, 90, and 120 s as indicated by dashed circles); (b1) initial OOP-PFM amplitude image after illumination (circled) and (b2) OOP-PFM amplitude image taken after ~ 100 days, with panel (b1) reproduced from Figure 2f; (c1) OOP-PFM phase and (c2) amplitude of an area illuminated (circled) for 30 s at 30 kW/cm^2 ; (d1) OOP-PFM phase and (d2) amplitude of the same area where the illuminated region was poled with an AFM tip biased at $+3.25\text{ V}$ to pattern the region into a single-domain state (outlined); insets to panels (c1) and (d1) are the line profiles from the corresponding dashed blue lines. Scale bars are 500 nm . The α - In_2Se_3 layers in panels (a, c, d) were exfoliated on gold-coated substrates and the layer in panel (b) was exfoliated on a SiO_2/Si substrate.

We note that surface topography-related PFM signal variations can be excluded as shown in Figure S3. To probe

the possibility of structural phase changes due to laser heating,³⁸ we conducted micro-Raman spectroscopy to analyze

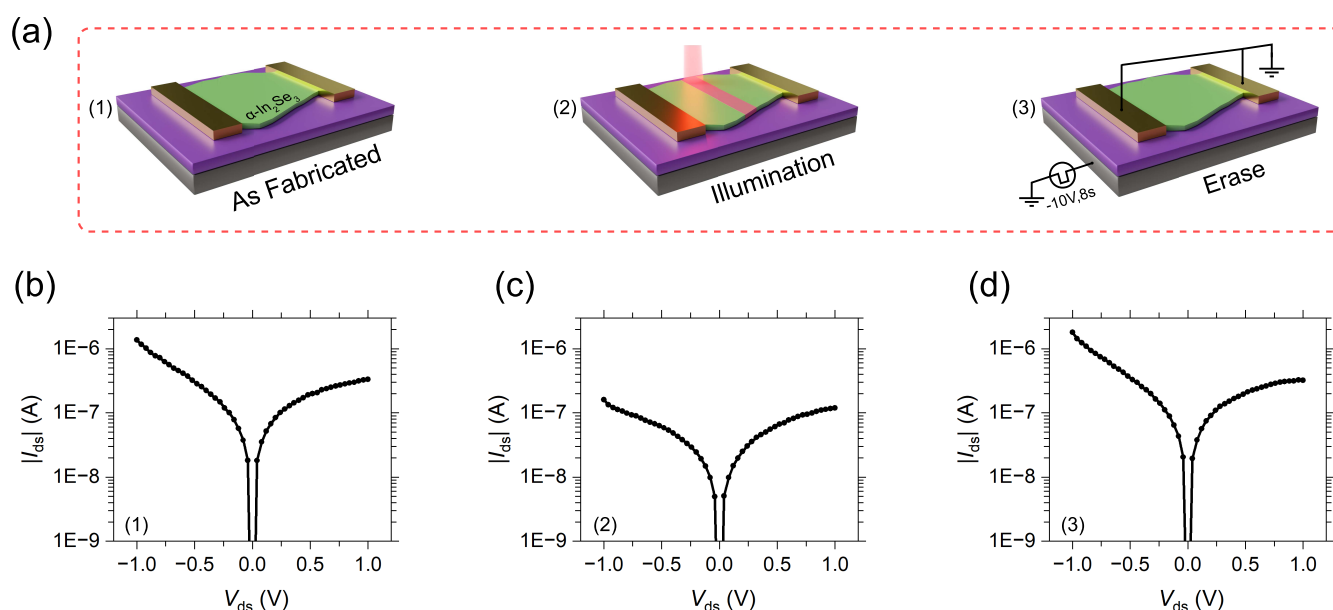


Figure 5. Prototype α -In₂Se₃ device. (a) Schematic detailing the device operations; (b) as-fabricated, (c) after-illumination, and (d) after-gate-pulse device current–voltage characteristics. The α -In₂Se₃ layer was exfoliated on a SiO₂/Si substrate.

the intensity, frequency, and full width at half-maximum variations of the main 104 cm⁻¹ phonon peak of the α -phase lattice (Figure 3a–c, respectively) across optically illuminated regions (marked by circles) in a layer. The absence of any variations in the main phonon peak characteristics indicates that the lattice structure remains in the α phase. Additionally, we have also recorded (Figure 3d) the Raman spectra at time intervals during laser illumination with the same power density used in Figure 2. As no significant variations are observed, this indicates minimal laser heating effects. Furthermore, the PFM phase and the amplitude as functions of the tip bias measured inside the optically illuminated regions (Figure S7) still retain the characteristic hysteretic behavior, further confirming the ferroelectric nature of the lattice in the illuminated regions. These observations indicate that the observed changes in the PFM images are due to the photoinduced variations in the local polarization states, which we attribute to the emergence of multidomains. Particularly, as ferroelectric polarization in α -In₂Se₃ has the in-plane component, the domain walls are likely to be charged.³⁶ As such, the formation of new domains, while favored to reduce the energy associated with the depolarization field,³⁹ needs to overcome the increase in the electric potential energy associated with the charged domain walls.⁴⁰ When under optical illumination, this energy barrier to the multidomain state formation is minimized via enhanced screening provided by photogenerated carriers. This allows for the nucleation and growth of new domains, as observed here. This disordered multidomain state is consistent with the observed random fluctuations in the PFM phase spatial profiles (Figure 2g–i) and also accounts for the decrease in the PFM amplitude signals (Figure 2d–f) as the antiparallel polarization states result in a reduced overall polarization magnitude within the area.

Moreover, as ferroelectric polarizations lead to the presence of surface-bound charges at the ferroelectric interface, changes in the polarization direction and magnitude are correlated with variations of the surface-bound charges and thus the surface potential, which can be measured by Kelvin probe force microscopy (KPFM).⁴¹ Our KPFM measurements (Figure 4a;

see also discussion on possible charge trapping effects in Figure S8) demonstrate that the surface potential decreases in the optically illuminated regions, and such changes become more significant with increasing illumination time. This observation is consistent with light-induced multidomain formations with corresponding changes to local polarizations and surface potentials.

We have found that these photoinduced changes under ambient conditions can persist for tens of days (~ 40 days) as shown in Figure S9. However, for longer periods of time (~ 100 days), we have observed diminishing of photoinduced changes (Figure 4b1,b2). This is consistent with the presence of unscreened charged domain walls that become metastable, and the multidomain state reverts to a single-domain state. The return to a single-domain state can also be achieved by an external poling field. As shown in Figure 4c,d, scanning a biased (at +3.25 V) AFM tip over the layer surface erases the PFM phase contrast associated with the optically illuminated region.

With the capability to define areas with distinctive surface potentials via optically driven multidomain formation, we next explore device applications by demonstrating reversible optical modulation of electrical resistance. Figure 5a,b shows the device schematics and the as-fabricated device current–voltage characteristics, respectively. By scanning a focused laser beam across the channel, we can observe a notable decrease in the device conductance (Figure 5c). This can be attributed to the surface potential variations within the illumination region, which creates potential barriers that impede carrier transport. The device conductance state can be restored to the initial state by applying a -10 V gate voltage pulse for 8 s (Figure 5d), which erases the potential variations through the realignment of the ferroelectric polarizations inside the device channel.⁴²

CONCLUSIONS

We have shown that local optical illumination can drastically modify the ferroelectric properties in α -In₂Se₃ by randomizing the spatial distribution of polarization state directions. These

optically induced multidomains can persist for a certain period of time (approximately tens of days) and can be reversed to a single polarization state by an external poling field. An important consequence of the changes in the domain configuration is the variations in the surface electric potentials, which evolve with the illuminations. Furthermore, our results show that controlled optical illuminations can be used to define desired electronic patterns in ferroelectric α -In₂Se₃ for device applications and open the possibility for further implementations such as in optical memory and memristive and photonic neuromorphic computing. More fundamentally, our results provide critical microscopic insight into light–ferroelectric interactions.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.3c05148>.

α -In₂Se₃ fitted PL spectrum; ferroelectric hysteresis of exfoliated α -In₂Se₃; α -In₂Se₃ layer topography before and after illuminations; PFM for illuminations on α -In₂Se₃/Au; threshold power density for multidomain state formation; PFM for illuminations on antiparallel domains; ferroelectric hysteresis inside and outside illuminated regions; control experiments on MoS₂/Au, MoS₂/SiO₂, and SiO₂ surfaces; and temporal stability of multidomain states (PDF)

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Notes

The authors declare the following competing financial interest(s): Y.G. has equity interest in Klar Scientific.

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