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Opto-mechanics driven fast martensitic transition in two-dimensional materials

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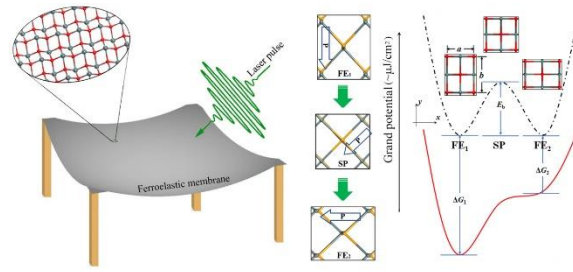
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Abstract

Diffusional phase-change materials, such as Ge-Sb-Te alloys, are used in rewritable non-volatile memory devices. But the continuous pursuit of readout/write speed and reduced energy consumption in miniaturized devices calls for optically driven, diffusionless phase change scheme in ultra-thin materials. Inspired by optical tweezers, in this work, we illustrate theoretically and computationally that a linearly polarized laser pulse with selected frequency can drive an ultrafast diffusionless martensitic phase transition of two-dimensional ferroelastic materials such as SnO and SnSe monolayers, where the unit-cell strain is tweezed as a generalized coordinate that affects the anisotropic dielectric function and electromagnetic energy density. At laser power of 2.0×10^{10} and 7.7×10^9 W/cm², the transition potential energy barrier vanishes between two 90°-orientation variants of ferroelastic SnO and SnSe monolayer, respectively, so displacive domain switching can occur within picoseconds. The estimated adiabatic thermal limit of energy input in such optomechanical martensitic transition (OMT) is at least two orders of magnitude lower than that in Ge-Sb-Te alloy.

Keywords: opto-mechanics, martensitic phase transition, ferroelasticity/ferroelectricity, two-dimensional materials, density functional theory, dielectric function

TOC graphic



Storing and reading information in an efficient, fast, and reversible way with low energy consumption are of great importance. Currently, the most widely used structural phase change material for non-volatile memory is Ge-Sb-Te alloy,¹ which could exist in both crystalline and amorphous phases with pronounced differences in electrical and optical properties. Upon heating, these two phases can be reversibly switched on a timescale of ten to one hundred nanoseconds by diffusion of atoms. This order-disorder transition has a latent heat and requires breaking of chemical bonds. It is highly desirable to explore new phase-change materials with degenerate, diffusionless order-to-order transitions to accelerate the read/write kinetics, reduce energy dissipation, and eliminate fatigue.

Since the isolation of graphene sheet in 2004,² two-dimensional (2D) materials with a few atomic layer thickness (e.g. hexagonal boron nitride,³ transition-metal dichalcogenides,⁴ and phosphorene⁵) have developed rapidly.⁶⁻¹² Some layered 2D materials (such as MoS₂ and analogues) have been found to possess multiple (meta-)stable structural phases or orientation variants, holding the possibility to function as non-volatile phase change memory materials with reduced size. For example, previous predictions have revealed that carrier doping, electrostatic gating, or tensile strain can induce phase transformation of MoTe₂ monolayer (and similar materials) between 2H and 1T' structures, or transition among different orientations in the 1T' phase.¹³⁻¹⁵ Such transitions have also been experimentally verified.¹⁶ Subsequent theoretical calculations also suggested that these 2D phase transformation can further decrease the required operation energy than the Ge-Sb-Te alloys.¹⁷ However, these methods typically require mechanical, electrical or

electrochemical contacts and patterning. Optical readout/write with focused laser would be preferable in many circumstances, especially for 2D materials which are easily optically accessible. For example, photostrictive property has been observed in BiFeO_3 , where a relative elongation of 10^{-5} when irradiated by a laser light of 70 kW/m^2 .¹⁸

Martensitic transitions are displacive, without the need for random diffusions of atoms which are thermally driven. Hence, the time scale of transformation can be greatly reduced. In this study, we propose a photonic, energy-assisted approach that could induce optomechanical martensitic transitions (OMT) of 2D ferroelastic (FE) materials. OMT differ from temperature-driven martensitic transitions (MT, e.g. in steel heat-treatment) in that the photonic energy couples strongly to only one generalized reaction coordinate ξ , and not with the other degrees of freedom, thus breaking the equi-partition character of a temperature-driven process. The benefit of laser scanning read/write compared to static electric field switching is the easy spatial addressability. Because 2D ferroelastic domains are unconstrained in the z -direction, the elastic energy required for switching is much reduced compared to 3D MT systems. Several 2D FE materials have been discovered.^{15,19,20} FE materials exhibit spontaneous symmetry-breaking strains (transformation strains) and consequently have at least two degenerate orientation variants, and the switching between these orientation variants is diffusionless.

Here we focus on recently-discovered SnO and SnSe monolayers.^{19,20} Because the two 90° -orientation variants of ferroelastic SnSe and SnO have rectangular symmetry, alternating electric field along different polarization directions will bias the variants differently. Hence, we predict that one can use a short pulse of linearly polarized light (LPL) to induce a phase transition from one orientation variant to the other. For example, a monolayer SnSe nanosheet with a lateral size of $L \sim 300 \text{ nm}$ has been fabricated via a colloidal route,²¹ SnO monolayer has also been grown using a liquid metal van der Waals exfoliation technique,²² and such size could be ideal for wholesale-switching in freely suspended mode (with slight pre-buckling in both x and y to give it some “slack” – zeroing tensile stresses and removing the in-plane elasticity constraints as well). By first-principles calculations, we show that the optical-frequency dielectric responses along different directions in these anisotropic FE monolayers exhibit a large orientational contrast. Like

optical tweezers that can change the spatial coordinates of a dielectric bead using the dielectric energy of the laser-bead interaction, in this case the unit-cell geometry (strain and internal atomic shuffling coordinates²³) as a generalized coordinate ξ , upon which the dielectric constant ε depends. The dielectric energy (proportional to $\langle E^2 \varepsilon(\xi) \rangle$ where E is the electric field amplitude) modifies the potential energy landscape of the martensitic transition. At a critical laser power this dielectric energy causes the transition barrier (measured in energy/area) to vanish across the entire sample, leading to barrier-free OMT. When this happens, one can avoid the typical nucleation-and-growth kinetics, and the transition can happen dynamically within picoseconds everywhere across the whole sample. Because the freely suspended sample is slightly pre-buckled, there will be no tensile transformation stress or long-range elasticity constraint in x , y or z , which is fundamentally different from the general case of 3D MT. Even though the required pulsed laser power maybe high, the extremely fast transition will cause the total heat absorption to be small, allowing efficient and damage-free operation.

We show our schematic setup of FE monolayer transformation under LPL exposure in Figure 1a and the typical FE potential energy change in Figure 1b. In a non-polarized SnO monolayer, a rectangular FE monolayer would have two vertical orientation variants (FE₁ and FE₂), while the saddle point (SP) state with high symmetry serves as an energy barrier to separate the FE₁ and FE₂ orientation variants (black curve in Figure 1b). Each orientation variant is thermodynamically stable and the energies of the different states per supercell satisfy $E_{\text{FE}_1} = E_{\text{FE}_2} < E_{\text{SP}}$. To induce a transition from FE₂ to FE₁ across a sample of linear dimension L , we apply LPL onto the sample. The LPL contains an oscillating electric field (e.g. $\mathbf{E}(\omega_0, t) = E e^{-i\omega_0 t} \hat{\mathbf{e}}_x$, where $\hat{\mathbf{e}}_x$ is unit vector along the x direction) that accelerates ions and electrons. The thermodynamic fundamental equation can be written as $dU = S \times \mathbf{E} \cdot d\mathbf{P}_0 + S \times \mathbf{E} \cdot d\mathbf{D}$, where U is internal energy and S is total area. Here we have ignored the entropy and stress effects. Under linear approximation and use electric field \mathbf{E} as natural variable, this induces an additional term in thermodynamical grand potential density (unit energy/area):

$$G(\mathbf{E}) = G(E = 0) - \mathbf{E} \cdot \mathbf{P}_0 - \frac{1}{2} \mathbf{E}^* \cdot \boldsymbol{\varepsilon}^{(1)}(\omega_0) \cdot \mathbf{E}, \quad (1)$$

where \mathbf{P}_0 is intrinsic static polarization and $\epsilon^{(1)}(\omega_0)$ is the real part of dielectric function tensor. The first term is intrinsic grand potential without electric field. The second term vanishes for non-polarized SnO monolayer FE₁/FE₂, with centro-symmetry even at ferroelastic state. The third term incorporates the response of both ion and electron subsystems to the electric field ($\epsilon = \epsilon_{\text{ion}} + \epsilon_{\text{electron}}$). Here we consider the frequency ω_0 on the order of 10^2 terahertz (THz). Considering that phonon frequencies are typically below 20 THz, the ion response (ϵ_{ion}) to the electric field would be small (see Supplementary Text and Figure S1 for detailed discussions) because they are far off-resonance due to the heavy masses of ions. In the following, we will only consider the dielectric function from electron subsystem contribution $\epsilon_{\text{electron}}$. In anisotropic FE 2D materials, the electronic dielectric function tensor components along the x and y directions are not equal ($\epsilon^{(1)}_{xx} \neq \epsilon^{(1)}_{yy}$). Therefore, LPL lifts the degeneracy of the FE₁ and FE₂ orientation variants. When the energy difference is sufficiently large, this effect creates a barrier-free OMT from FE₂ to FE₁ (Figure 1b, red curve) that avoids nucleation-and-growth kinetics.

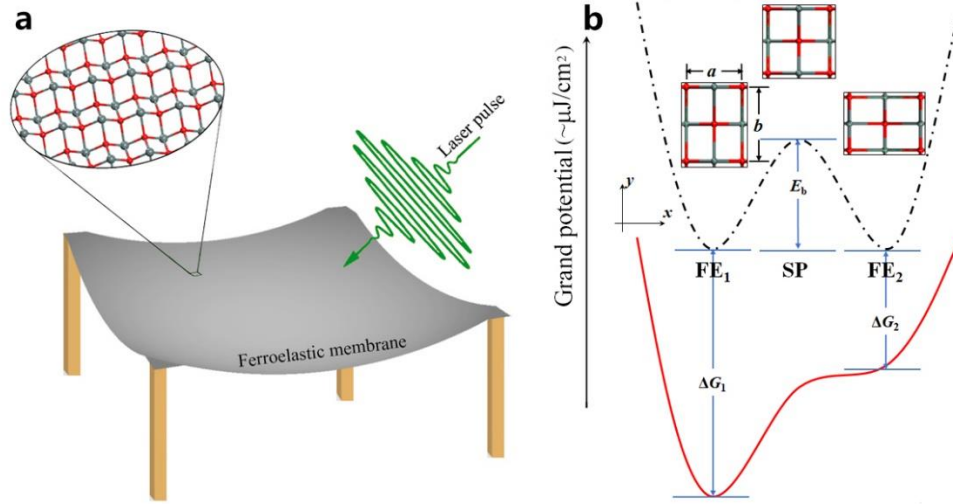


Figure 1. Schematic plot of SnO monolayer phase transition under optical exposure. (a) A SnO monolayer under LPL pulse exposure. (b) Elastic energy curve of intrinsic state (no exposure, black dashed dot curve), where FE₁ and FE₂ states are energetically degenerate. LPL lifts the degeneracy of thermodynamic grand potential of FE₁ and FE₂ orientation variants (red solid curve).

In this section, we use density functional theory (DFT,^{24,25} see Method) to show that OMT can be realized in FE SnO monolayers. After full relaxation, the SnO monolayer (inset of Figure 1b) shows a FE rectangular unit cell with $pmmn$ layer group. The FE state is energetically lower than the high symmetric SP by 0.61 meV per chemical formula unit (f.u.). Taking the SP structure as reference, we calculate that the 2D transformation strain tensor $\boldsymbol{\eta}$ of FE₁ and FE₂ is

$$\eta_{\text{FE}_1} = \begin{pmatrix} -0.048 & 0 \\ 0 & 0.048 \end{pmatrix}, \quad \eta_{\text{FE}_2} = \begin{pmatrix} 0.048 & 0 \\ 0 & -0.048 \end{pmatrix}. \quad (2)$$

These results agree well with previous work.¹⁹ These transformation strains are sufficiently small that a -5% biaxial pre-buckling of a freely-suspended sheet (like a hammock) would ensure that no tensile stress will be generated during the OMT. The calculated band dispersion of FE₁, SP, and FE₂ are shown in Figure 2a. We find that the FE SnO monolayer is a quasi-direct bandgap semiconductor. In the FE₁ structure, the valence band maximum (VBM) is along the $\Gamma \rightarrow X$ path ($\Sigma = 0.28 \times 2\pi/a, 0, 0$), and the conduction band minimum (CBM) is at the corner of Brillouin zone ($M = \pi/a, \pi/b, 0$). This gives an indirect bandgap of 2.92 eV. The direct bandgap is 3.11 eV, corresponding to optical transitions at the Γ point.

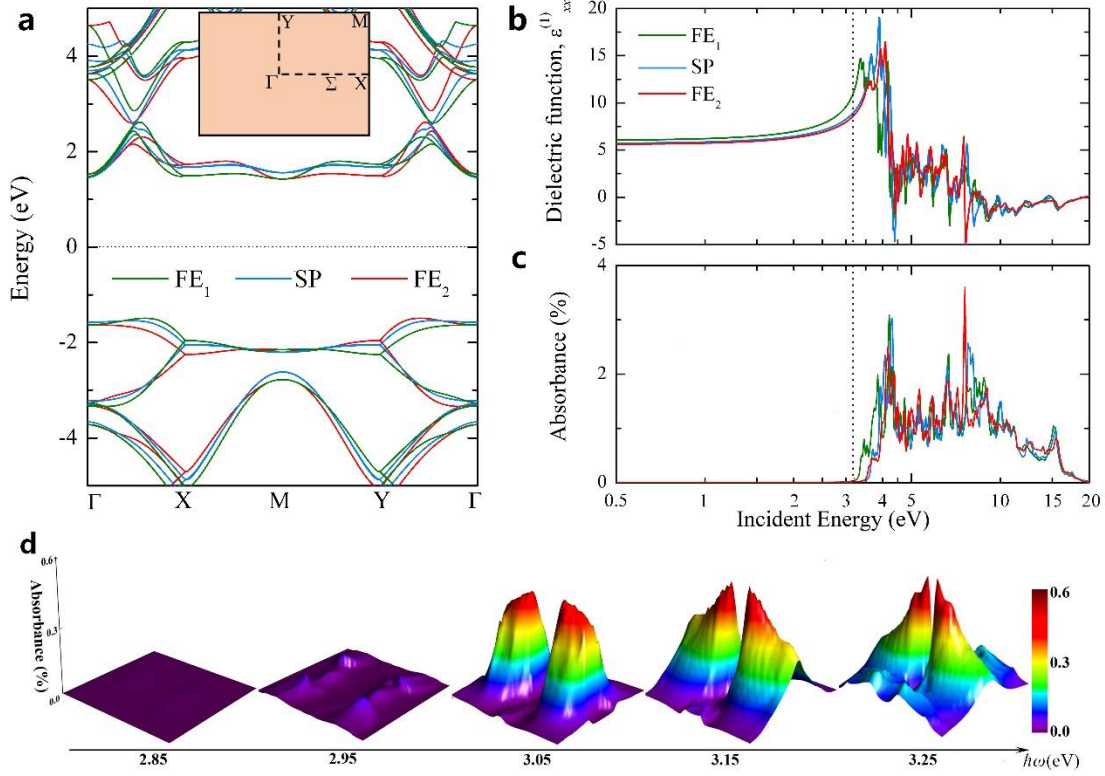


Figure 2. Electronic property of a SnO monolayer. (a) Band dispersions of FE₁, SP, and FE₂ states along high symmetry path in the first Brillouin zone. The direct coordinates are $\Gamma = (0, 0, 0)$, $X = (1/2, 0, 0)$, $M = (1/2, 1/2, 0)$, and $Y = (0, 1/2, 0)$. Inset shows the first Brillouin zone of FE₁ state. The Fermi level lies in the middle of VBM and CBM (dotted horizontal line at zero energy). (b) RPA calculated real part dielectric function $\epsilon_{xx}^{(1)}$ and (c) optical absorption spectra at the long wavelength limit. The dashed vertical line denotes energy $\hbar\omega_0 = 3.25$ eV. (d) Optical absorbance in the first Brillouin zone (finite q) in the vicinity of indirect bandgap.

We calculate the in-plane optical response using the random phase approximation (RPA). The relative dielectric function (cgs units, Ref. 26) in the long wavelength limit ($q \rightarrow 0$) is

$$\epsilon_{\alpha\alpha}(\omega) = 1 - \lim_{q \rightarrow 0} \frac{4\pi e^2}{q^2} \frac{1}{\Omega} \sum_{c,v,\mathbf{k}} w_{\mathbf{k}} \times \frac{|(u_{v,\mathbf{k}} | u_{c,\mathbf{k}+q\alpha})|^2}{E_{c,\mathbf{k}} - E_{v,\mathbf{k}} - \hbar\omega - i\zeta} \quad (\alpha = x, y). \quad (3)$$

The indices c and v refer to conduction and valence band states, respectively, and $|u_{n\mathbf{k}}\rangle$ is the cell-periodic part of the wavefunctions of the band- n at \mathbf{k} . Ω is the volume of simulation

supercell, $w_{\mathbf{k}}$ is the weight of each \mathbf{k} -point, and ζ is a phenomenological damping parameter taking to be 0.025 eV in our calculation. For 2D materials in a 3D-periodic supercell, one has to eliminate the vacuum contributions and spurious interactions between different periodic image layers. From Equation (3), the supercell calculated dielectric function inversely proportional to d , the thickness of simulating supercell. One scheme that can be used is to truncate Coulomb interactions,²⁷ which shows vacuum-independent optical response based on 2D electronic screening of Coulomb interaction.²⁸ Here, we employ another method to rescale the calculated in-plane (x and y) dielectric function, based on 3D electronic screening, which also eliminate the vacuum dependence. The supercell can be regarded as a parallel combination of the 2D SnO monolayer and the vacuum capacitance,²⁹ so that the real part of 2D SnO monolayer dielectric function satisfies

$$d \times \varepsilon_{\text{cell}}^{(1)} = (d - h) \times \varepsilon_{\text{vac}}^{(1)} + h \times \varepsilon_{2\text{D}}^{(1)}. \quad (4)$$

$\varepsilon_{\text{cell}}^{(1)}$, $\varepsilon_{\text{vac}}^{(1)}$, and $\varepsilon_{2\text{D}}^{(1)}$ represent the real parts of dielectric function of the supercell, the vacuum, and the 2D material, respectively. The distance parameters d and h are the thickness of simulating supercell and of the 2D material, respectively. We take the thickness of a SnO monolayer to be the distance between two adjacent layers in bulk SnO, $h = 4.276 \text{ \AA}$. In this way, the re-scaled $\varepsilon_{2\text{D}}^{(1)}$ is independent on the thickness of the simulating supercell.

Optical absorption can be evaluated from the imaginary part of dielectric function. The absorbance (A) of a 2D material is calculated as

$$A(\omega) = 1 - e^{-\frac{\omega}{c}\varepsilon^{(2)}d}, \quad (5)$$

where c is the speed of light. We plot $\varepsilon_{2\text{D},xx}^{(1)}$ for the three structures FE₁, SP, and FE₂ in Figure 2b, and corresponding absorbance $A(\omega)$ in Figure 2c. There are clear differences in the dielectric functions of the FE₁ and FE₂ variants. We note that ε_{xx} of FE₂ is ε_{yy} of FE₁, due to the structural anisotropy of the FE state. The first absorption peak appears at 3.44 and 3.57 eV for FE₁ and FE₂, respectively. This optical anisotropy can be understood by analyzing the group representations of the frontier orbitals (Table S1 in Supporting Information). Taking the FE₁ structure as the example, by examining the group

representations of the highest valence and lowest conduction bands, we find that optical absorption is prohibited at the Γ point. The lowest optical absorption of x -polarized light occurs at the X point (with a direct bandgap of 3.45 eV), and for the y -polarized light it corresponds to the transition at the M point (3.57 eV).

The optical anisotropy suggests that the phase transition between FE_1 to FE_2 could be triggered by LPL. For instance, if one fixes the incident energy at $\hbar\omega_0 = 3.25$ eV (dashed vertical line in Figure 2b and 2c), the real part dielectric functions in the x -direction satisfy $\epsilon_{\text{FE}_2}^{(1)} < \epsilon_{\text{SP}}^{(1)} < \epsilon_{\text{FE}_1}^{(1)}$. Note that small dielectric function refers to low screening effect and high electric field in SnO. Thus, the dielectric energy density in the FE_2 state is larger than those in the SP and FE_1 states. Under a finite intensity of LPL, a phase transition from FE_2 to FE_1 occurs with a reduced energy barrier. We estimate the critical electric field strength of barrier-free phase transition by $-\frac{1}{2}\epsilon_0\epsilon_{\text{FE}_2}^{(1)}E^2Sh = E_b - \frac{1}{2}\epsilon_0\epsilon_{\text{SP}}^{(1)}E^2Sh$, where S is the supercell area, ϵ_0 is the vacuum permittivity, and E_b is the original energy barrier (see Supporting Information for details). Using $\epsilon_{\text{FE}_2}^{(1)} = 8.952$ and $\epsilon_{\text{SP}}^{(1)} = 9.322$, we find that the critical electric field strength is $E_0 = 1.37$ V/nm. We found similar results using many-body GW-BSE calculations³⁰⁻³³ (see Method). If we choose an incident energy $\hbar\omega_0 = 4.36$ eV (for which $\epsilon_{\text{FE}_2}^{(1)} = 9.86$ and $\epsilon_{\text{SP}}^{(1)} = 14.29$), then the critical electric field strength and laser power can be reduced to $E_0 = 0.39$ V/nm and $I_0 = 2.05 \times 10^{10}$ W/cm² (Figure S2 and Table S3 in Supporting Information). This is achievable by visible spectrum pulsed lasers. Note that the self-energy in many-body GW calculations may change the band topology of 2D materials,³⁴ here we find that the indirect bandgap feature still remains for the SnO monolayer.

To illustrate the OMT process more explicitly, we calculate the total energy as a function of biaxial strain η_{11} ($=-\eta_{22}$) in a SnO monolayer and its corresponding dielectric function in the x -direction (Figure 3). The RPA-calculated $\epsilon_{xx}^{(1)}(\omega_0)$ decreases from FE_1 , to SP, to FE_2 . For biaxial strain beyond FE_2 ($\eta_{11} > 0.048$), the $\epsilon_{xx}^{(1)}(\omega_0)$ increases again. LPL lifts the degeneracy of FE_1 and FE_2 , and increasing the laser power causes the transition barrier to decrease and eventually to disappear. Throughout the FE_1 potential well is retained (Figure 3b). Thus, an FE_2 orientation variant can switch to FE_1

simultaneously throughout the sample by optical “tweezing”, with no barrier and no elastic energy constraint.

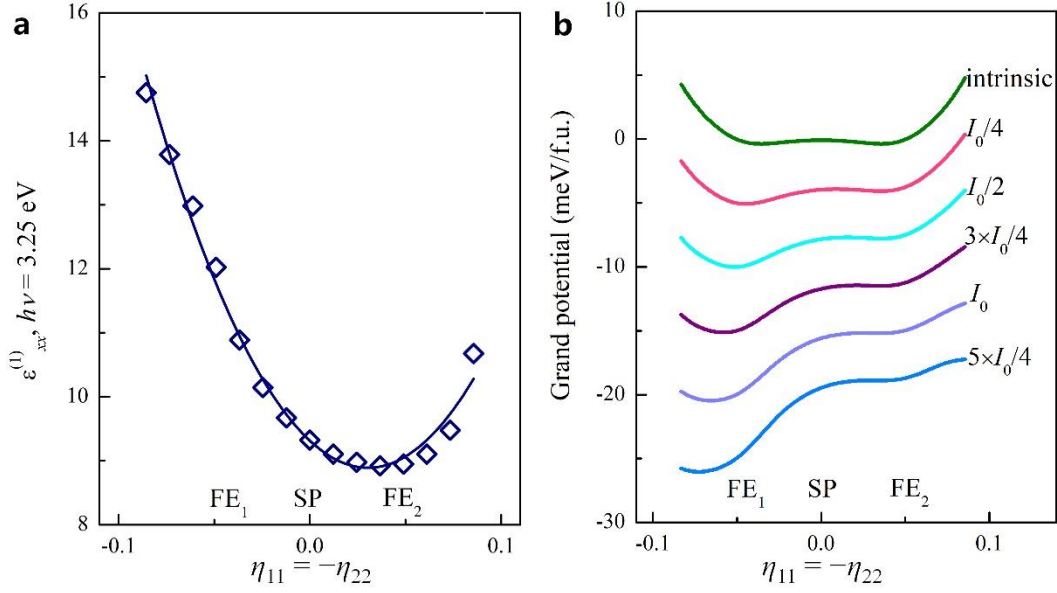


Figure 3. Laser power modulation of energy profile. (a) RPA-calculated real part of dielectric function in the x -direction, at incident energy of 3.25 eV, as a function of strain. (b) Grand potential of SnO monolayer per formula unit vs strain under different laser power. The energy is shifted with respect to the intrinsic (no LPL) SP state.

In $\text{Ge}_2\text{Sb}_2\text{Te}_5$ alloys, the adiabatic thermal limit of energy input is estimated to be ~ 1.17 aJ/nm³. Recent calculations of phase-transitions in MoTe_2 monolayers yield a lower estimate, on the order of 0.1 aJ/nm³ (Ref. 17). The lower limit of energy required for OMT can be simply evaluated from internal energy expression, $E_{\text{input}} = \frac{1}{2} \epsilon_0 \epsilon_{\text{FE}_2} S h E^2$. This energy is ~ 16 meV/f.u. (Figure 3b), which converts to 0.07 aJ/nm³, comparable to the predictions for MoTe_2 monolayers. Using the results of GW-BSE calculations, this energy density is further reduced to 0.006 aJ/nm³. If this energy is dissipated as waste heat, then using the heat capacity of bulk SnO (> 4.1 cal/mol·K, Ref. 35) we estimate that the temperature rise is below 11 K.

The barrier-free and diffusionless martensitic phase transition is ultrafast. We analyze its kinetics by taking the total mass of a SnO to be $\langle m \rangle = m_{\text{Sn}} + m_{\text{O}} = 134$ amu, and a characteristic displacement of $l = (b - a) = 0.32$ Å. The energy change in the transition is

$\Delta E = \Delta E_1 - \Delta E_2 = 5.1$ meV/f.u. According to a simplified constant acceleration motion model, the transition time can be approximated to be $\tau = l \times \sqrt{2\langle m \rangle / \Delta E} \approx 1.1$ ps. This indicates that the phase transition should occur on the order of picosecond, faster than that in Ge-Sb-Te alloys. Thus, a laser pulse as brief as 10 ps should be sufficient for switching.

The incident photon energy of $\hbar\omega = 3.25$ eV is higher than that of indirect bandgap (2.92 eV) of the SnO monolayer. Therefore, indirect band gap transition may occur at this frequency. In order to evaluate this effect, we fit the band dispersion of SnO monolayer (at the DFT level) by maximally localized Wannier functions,³⁶ as implemented in Wannier90 code.³⁷ Then we use Lindhard theory³⁸ to calculate the dielectric function at finite q under RPA,

$$\varepsilon(\mathbf{q}, \omega) = 1 - \frac{e^2}{\varepsilon_0 q^2} \int \frac{1}{(2\pi)^3} d\mathbf{k} \sum_{m,n} \frac{(f_{n,\mathbf{k}+\mathbf{q}} - f_{m,\mathbf{k}}) |\langle u_{n,\mathbf{k}+\mathbf{q}} | u_{m,\mathbf{k}} \rangle|^2}{E_{n,\mathbf{k}+\mathbf{q}} - E_{m,\mathbf{k}} + \hbar\omega - i\zeta}. \quad (6)$$

Here f is the Fermi-Dirac distribution. By adjusting the incident $\hbar\omega$ from 2.85 eV (lower than indirect bandgap) to 3.25 eV (incident laser energy), we plot the optical absorbance $A(\mathbf{q}, \omega)$ in the first Brillouin zone (Figure 2d). Below the indirect bandgap, the optical absorbance remains zero in the whole \mathbf{k} -space. Once the incident energy exceeds the bandgap, very small absorbance is found. The highest peak locates at the $q = (\pm 0.069, 0, 0) \times \text{\AA}^{-1}$ point when $\hbar\omega = 3.25$ eV, with absorbance of $A(q, \omega) = 0.57\%$. Thus, we expect marginal indirect bandgap transition occurs in the process, and can be omitted during a short picosecond pulse. In addition, the calculated long-wavelength dielectric function in the x -direction satisfies $\varepsilon_{\text{FE}_2}^{(1)}(\omega) \Big|_{\omega < \omega_0} < \varepsilon_{\text{SP}}^{(1)}(\omega) \Big|_{\omega < \omega_0} < \varepsilon_{\text{FE}_1}^{(1)}(\omega) \Big|_{\omega < \omega_0}$, even below the indirect bandgap 2.92 eV. Therefore, one can also apply lower-frequency light to trigger phase transition while avoiding inter-band transitions.

For readout, one can use the transmission/reflection contrast for LPL. From Figure 2c we see that the biggest contrast occurs at $\hbar\omega_{\text{readout}} = 3.35$ eV, for which there is a factor of 1.3 difference in reflectance between FE₁/FE₂, and optical absorption is marginal. At the GW-BSE level of theory, the readout energy can be selected as 4.46 eV with a factor of 2.2 change in reflectance. In addition, ferroelasticity can also be characterized by

photothermal induced resonance technique, which has been applied to study anisotropic perovskites.³⁹

SnO monolayers are centrosymmetric and have no polarization. In the following, we show that this scheme also works for a polarized 2D ferroelectric material. We consider a ferroelectric SnSe monolayer without centrosymmetry. It belongs to group-IV monochalcogenide family and has a simultaneous ferroelasticity and in-plane ferroelectricity.^{40,41} Thus, SnSe monolayers have two equivalent orientation variants (Figure 4a), and each orientation variant has two internal polarizations. Previous works have found that tensile strain can switch between the two orientation variants of SnSe monolayers, and a static in-plane electric field can switch the polarization within one orientation variant.²⁰ Here we will show that a LPL pulse can transfer its orientation variant and consequently rotate its polarization \mathbf{P}_0 by 90° . In Equation (1), the polarization \mathbf{P}_0 comes from non-centrosymmetric atomic structure. When the LPL frequency (on order of 10^2 THz) is much higher than phonon frequency (< 6 THz, see Figure S1), the vibrational amplitude of ions is small (Supporting Information). Therefore, the first term in Equation (1) ($\mathbf{E} \cdot \mathbf{P}_0$) vanishes on time-averaging, even though $|\mathbf{P}_0|$ is finite.

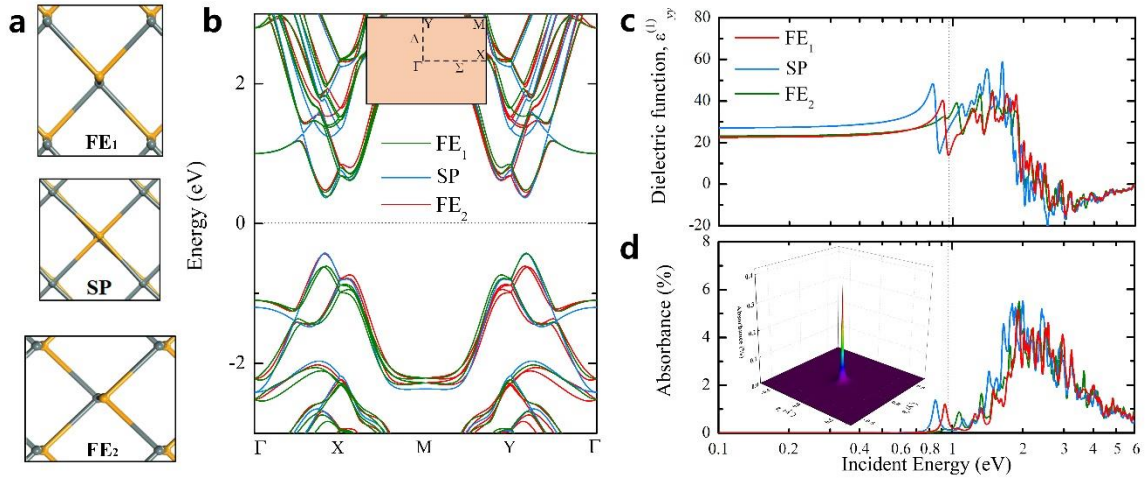


Figure 4. Optically-driven phase transition of a SnSe monolayer. (a) The atomic structures of a SnSe monolayer in FE₁, FE₂, and SP states. (b) DFT-calculated band dispersions. Inset shows the first Brillouin zone of FE₁ orientation variant. (c) RPA calculated real part dielectric function $\epsilon_{yy}^{(1)}$ and (d) optical absorbance spectra at the long wavelength limit ($q \rightarrow 0$). The vertical dashed line denotes an incident energy of 0.963 eV. Inset of (d) shows the absorbance of FE₁ in the whole k -space.

We again focus on the electric field response of the electron subsystem. The pathway is from FE₁ to SP and then to FE₂, as shown in Figure 4a (and Figure S3 in Supporting Information). Our DFT calculations find that the lattice constant of FE₁ orientation variant is $a = 4.275 \text{ \AA}$, $b = 4.401 \text{ \AA}$, and for the SP $a = b = 4.312 \text{ \AA}$, consistent with previous theoretical results.^{20,40,41} The thickness of one SnSe monolayer is taken to be $h = 5.895 \text{ \AA}$. Hence, the 2D transformation strain tensors are $\eta_{\text{FE}_1} = \begin{pmatrix} -0.008 & 0 \\ 0 & 0.021 \end{pmatrix}$ and $\eta_{\text{FE}_2} = \begin{pmatrix} 0.021 & 0 \\ 0 & -0.008 \end{pmatrix}$. The SP state is energetically higher than the FE state by 1.76 meV/f.u. The DFT-calculated band dispersions are plotted in Figure 4b. We find that the FE structure ($pm2_1n$ layer group) is again a quasi-direct bandgap semiconductor. For the FE₁ orientation variant, the VBM is along the $\Gamma \rightarrow Y$ path ($\Delta = 0, 0.40 \times 2\pi/b, 0$), and the CBM is along the $\Gamma \rightarrow X$ path ($\Sigma = 0.42 \times 2\pi/a, 0, 0$). The indirect bandgap is 0.82 eV. The direct bandgap at the Δ and Σ points are 0.91 and 1.00 eV, respectively. At the many-body GW level of theory, these two direct bandgaps are 1.72 and 1.91 eV, respectively (Supplementary Table S3). Group theory analysis reveals that the optical transition between the valence band and conduction band at the Δ point is allowed for y -polarized LPL and forbidden for x -polarized LPL (Table S2 in Supporting Information). These facts confirm that the electronic and optical transition properties of FE SnSe monolayer is anisotropic. The SP structure is a direct bandgap semiconductor (bandgap of 0.79 eV by DFT and 1.62 eV by GW), with degenerate extrema of the VBM and CBM at the $\Delta (0, 0.41 \times 2\pi/b, 0)$ and $\Sigma (0.41 \times 2\pi/a, 0, 0)$ points, owing to its $cm2e$ layer group symmetry.

The RPA-calculated real part of dielectric functions in the y -direction of the three variants are shown in Figure 4c. At a selected incident energy, $\hbar\omega_0 = 0.963 \text{ eV}$, the $\epsilon_{yy}^{(1)}$ of FE₁, SP, and FE₂ are 14.14, 27.30, and 33.22, respectively. Therefore, according to our previous discussion, a LPL with electric field strength of $E_0 = 0.29 \text{ V/nm}$ is sufficient to diminish the energy barrier and switch the orientation variant transition from FE₁ to FE₂ (Figure S3 in Supporting Information). The absorbance at this incident energy is very small (Figure 4d) with $A = 0.5\%$ in FE₁ and 0.1% in SP state, ensuring minimal parasitic absorption. We also calculate the dielectric function at the finite q (inset of Figure 4d). We

find that the pronounced absorbance peak is at the Γ point, demonstrating that the indirect band transition is suppressed. The adiabatic energy input limit is estimated to be 0.005 aJ/nm^3 , smaller than that found above for a SnO monolayer. As with SnO, this OMT is a barrier-free, displacive transition, and its time scale is on the order of picoseconds. Due to the lack of elasticity constraints and tensile stresses (and associated damage), good reversibility can be expected. The optical response is also reproduced under GW-BSE calculation (Figure S4 in Supporting Information), where we observe higher contrast at an incident energy of $\hbar\omega_0 = 1.51 \text{ eV}$. The calculated $\varepsilon_{yy}^{(1)}$ of FE₁, SP, and FE₂ are 3.85, 23.48, and 34.45, respectively. From these values we estimate a smaller laser power of $I_0 = 7.7 \times 10^9 \text{ W/cm}^2$ and adiabatic energy input limit of 0.001 aJ/nm^3 . From Figure 4c, one can use a readout energy $\hbar\omega_{\text{readout}} = 0.95 \text{ eV}$ (or 1.58 eV according to GW-BSE level of theory) to yield a reflectance change of 1.5 (or 1.9 based on GW-BSE) between FE₁ and FE₂.

The laser driven SnSe monolayer orientation variant transition is interesting. As discussed previously, different orientation variants have vertical polarizations. Hence we have shown that, using optical-frequency alternating electric field, one can modulate the electronic term (second order) to change the static polarization \mathbf{P}_0 in the first order term in Equation (1).

Note that due to anisotropic feature of the FE 2D material, a LPL with its power lower than the critical power could also lift the FE₁ and FE₂ degeneracy and induce a phase transition with a reduced energy barrier. In Figure 5 we plot the variation of (a) energy difference between two FE states and (b) transition barrier with respect to electric field intensity of incident LPL. The energy barrier per area is evaluated by $E'_b/S = E_b/S - \frac{1}{2}(\varepsilon_{\text{SP}}^{(1)} - \varepsilon_{\text{FE}}^{(1)})\hbar\varepsilon_0 E_0^2$. As the laser intensity increases, the FE₁ and FE₂ potential difference (transition energy barrier) increases (decreases) quadratically. These indicate that the phase transition could occur easily and fast under moderate LPL exposure, even before the critical laser power proposed previously.

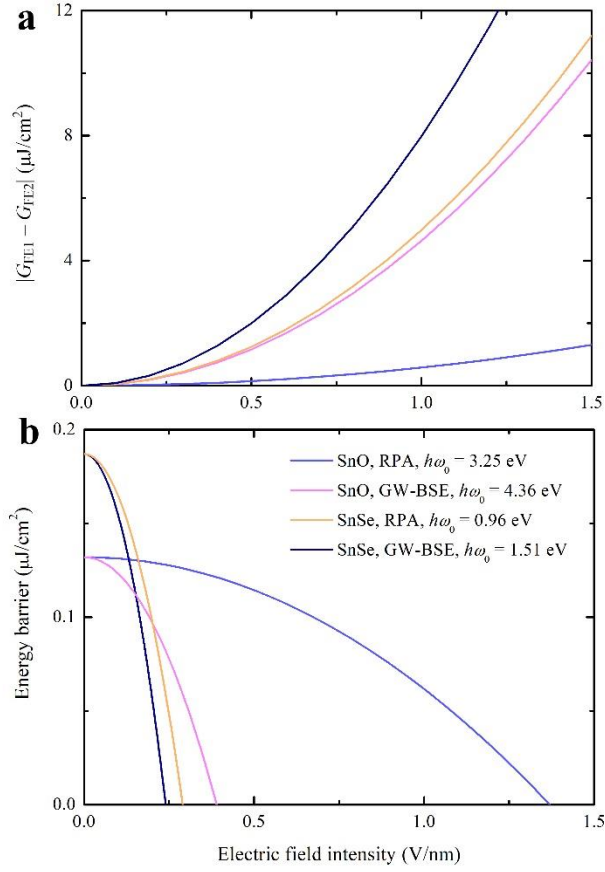


Figure 5. Variation of (a) FE₁/FE₂ grand potential difference and (b) transition energy barrier during phase transition as a function of incident LPL electric field intensity E_0 .

One may wonder if such strategy can be applied to group-V monolayers, such as black phosphorous (α -P). Our calculations reveal that the energy barrier separating the two orientation variants of α -P monolayer is 238 meV/atom. This value is much larger than that in SnO and SnSe monolayer. Considering this, this opto-mechanical strategy is not suitable for α -P monolayer to switch its ferroelastic phase.

In conclusion, we show that linearly polarized light provides a method to “tweeze” domain variant transitions in anisotropic 2D materials, akin to optical tweezers. These crystal structural transitions may occur within 1 picosecond through a macroscopic sample. Owing to this extraordinary speed, which approaches the upper limit of all possible atomic structural changes (e.g. one Debye oscillation period), the energy required for writing can be very small. Compared to orientation variant switching using static strain or static electric

field, a laser-based scheme does not require mechanical, electrical or electrochemical contact patterning, and could be preferable from cost considerations, especially for 2D materials which are highly optically addressable as they are “all surface”. Optomechanical martensitic transitions (OMT) in 2D material do not suffer from the same elasticity constraint of martensitic transitions in 3D, because a freely-suspended 2D membrane has no constraint in z . A small, -5% biaxial pre-buckling (like a hammock) in x and y would ensure that subsequently no tensile stress will be generated during the OMT. Thereby, tensile stress-induced damage and long-term fatigue can be avoided: the OMT is expected to be highly reversible. All of our computed optical properties are consistent with more accurate many-body GW calculations, including exciton binding energy correction. Unlike the currently-used chalcogenide Ge-Sb-Te alloys, the predicted structural transition is microscopically barrier-free and diffusionless, and thus exceptionally fast.

Theoretical Methods

Density functional theory. Our first-principles calculations are based on density functional theory (DFT)^{24,25} as implemented in the Vienna *ab initio* simulation package (VASP),^{42,43} where the electron exchange-correlation interactions are treated by the generalized gradient approximation (GGA) functional in the Perdew-Burke-Ernzerhof (PBE) form.⁴⁴ The core and valence electrons are treated by projector augmented wave (PAW) method⁴⁵ and a planewave basis set, respectively. The kinetic cutoff energy for SnO and SnSe monolayers are set to be 520 and 350 eV, respectively. The in-plane lattice constants and atomic coordinates are fully relaxed using the conjugated gradient algorithm without applying any symmetry constraints. The convergence criteria for electronic and atomic relaxations are set to be 1×10^{-7} eV and 1×10^{-3} eV/Å, respectively. Each simulation supercell contains two chemical formula units (f.u.). The first Brillouin zone is sampled by a $15 \times 15 \times 1$ Monkhorst-Pack \mathbf{k} -point mesh,⁴⁶ whose convergence has been tested in a $19 \times 19 \times 1$ mesh. We include self-consistent spin-orbit coupling effect in all calculations, which shows significant effects on the band dispersion (Figure S5). The geometric structure, energy profile, and band dispersion agree well with previous calculations,^{19,20,40,41} ensuring the accuracy of our simulation procedure. In order to analyze optical responses, we calculate the ion-clamped dielectric function according to random-phase approximation (RPA). More accurate quasi-particle GW calculations^{30,31} with exciton binding correction (Bethe-Salpeter equation, BSE)^{32,33} are also performed (Figure S6), giving qualitatively similar results compared with RPA approach. Convergence test of many-body calculations can be found in Table S4 and Table S5.

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