Strain enhanced inplane ferroelectricity in few layer SnS

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Abstract. Two dimensional (2D) materials such as graphene and transition metal dichalcogenide (TMDC) like MoS2, WTe2 have brought widespread attention as their novel 2D confined properties and applications in nano devices. Among them, SnS draws people’s attention as the rise of inplane ferroelectricity study. Using first principle DFT calculation, we find the structure shrinking more flatten when monolayer SnS isolated from its bulk matrix. Our result shows that monolayer SnS is much flexible with elastic modulus about 4.4 GPa. The size of the band gap can be tuned from 0.06eV to 0.11 eV by strain. Under positive armchair strain/negative zigzag strain there is even a band gap transition between direct and indirect, which can be applied in PL control. And the born effective charge for strained monolayer SnS can be tuned up to 10% by 5% strain, indicating the great tunability in monolayer SnS. Our results pave the way for further study of controlling the electronic and ferroelectric properties in monolayer SnS and similar inplane FE 2D materials.

1. Introduction
Two dimensional materials like graphene, transition metal dichalcogenide (TMDCS), and black phosphorus are been well studied as their potential applications in electronic, optical devices. Also, they are famous for their novel properties like superconductivity, spin waves, spin hall effect due to the dimension reduce caused by quantum confinement in the thickness dimension [1-10].

Ferroelectricity in ultrathin films is technologically important for memories, sensors and optoelectronic devices. Among them, 2D FE in layer materials draws attention. They can be categorized as out-of-plane ferroelectricity, intercorrelated ferroelectricity, and in-plane ferroelectricity. Inplane FE retains the ferroelectric properties even as thickness decreases, thus allowing it to be stable against out-of-plane perturbations. SnS is predicted to exhibit a larger polarization than that of SnTe [11-13]. Strain engineering and layer tuning are important method for tuning the structural properties, electronic properties and optical properties for nanocrystals such as graphene, black phosphorus and many other 2D crystal materials [14]. Different type and amount of strain can change the band gap size and even open or close a band gap [15]. Another way to tune the properties for layer crystal materials are layer thickness control. As the layer number changed, the electronic properties [16] and transport properties [17] changed due to the quantum confinement effect. Thus it is important for both experimental and theoretical study for the strain and layer tuned properties of these 2D crystal materials. By using the first principle calculation base on density functional theory, we studied the ferroelectricity of inplane SnS by straining and testing its responses. We find that inplane SnS is highly tunable comparing with other 2D materials with sensitive responses to straining due to its anisotropy. These properties can have a potential application in the tunable optical devices and electronic devices.
2. Result and analysis

**Figure 1.** Structure and band structure of bulk and monolayer SnS. a Ball-stick model for bulk SnS in perspective, top and side view. b Zigzag direction and armchair direction for monolayer SnS. c The first Brillouin Zone and high symmetry path. d Band structure for monolayer SnS along high symmetry path. Fermi energy is allocated to zero; the band gap is illustrated as the blue arrow, the forbidden region is shown as the green shadow ribbon.

Bulk SnS is an orthorhombic crystal type with space group Pnma. The ball-stick structure model for bulk SnS in perspective, top and side view are shown in figure 1a, respectively. The bulk SnS unit cell contains two monolayer SnS with stacking order of AB type, in which the A and B layers are half b vector different in y direction. Each monolayer has two sub atomic layer by Sn and S in an substitution way in a planar square pattern, with the Sn atom slightly tilted out of the plane. We fully relaxed the monolayer SnS structure and the top view is shown in figure 1b. Along x direction (a vector direction) the Sn and S atoms alternate arranging forms zigzag chains similar with that in graphene and phosphorene, thus we name it as zigzag direction, following the name in previous literature. Likewise, we call the y direction (b vector direction) armchair direction. The sublayer Sn atoms shrinks within the monolayer SnS comparing with that in the bulk form, due to the enhanced quantum confinement and the redistribution of the electron density in the free standing monolayer SnS. The first Brillouin zone (reduced reciprocal k space) along with the high symmetry points are shown in figure 1c. Our DFT (density functional theory) band calculation shows that monolayer SnS possess an indirect BG (band gap) with its BG value about 0.11eV, meaning that SnS is a typical semiconductor.
Figure 2. Elastic modulus fitting. Red point line indicated the total energy (reduce to reference energy $E_0$) as a function of the deformation of the crystal structure $\Delta l/l_0$. The blue curve is the quadratic fit using the calculated total energy.

Elastic modulus is a good aspect to evaluate the strain tunability of a system. Here we use the energy-volume relationship with quadratic form fit to estimate the elastic modulus of monolayer SnS as shown in figure 2. The red point line indicate the total energy we calculated correspond to seven different deformation ranging from -0.08 % to 0.08 % respect to a reference energy $E_0$. The blue curve is the fitted quadratic function with quadratic coefficient equals to 22.09. The elastic modulus $C$ can be determined by quadratic fitting of the total energy $E$ with respect to the dilation $\Delta l/l_0$:

$A_0$ is the area at equilibrium, here is the cross section of the monolayer SnS perpendicular to the strain direction, which is approximately 10 Å$^2$. The elastic modulus $C$ is calculated to be 4.4 GPa, which is smaller than its bulk counterpart 23 GPa and much smaller than other 2D materials’’, graphene’s 30 GPa, for instance.[18] Our result shows that monolayer SnS is highly tunable and of great flexibility respond to strain.
Figure 3. Band structure for uniform and uniaxial strain. a-b monolayer SnS band structure under uniform strain from -8%, -5%, -2%, 2%, 5%, 8%, respectively. c-d monolayer SnS band structure under armchair direction strain from -8%, -5%, -2%, 2%, 5%, 8%, respectively. e-f monolayer SnS band structure under zigzag direction strain from -8%, -5%, -2%, 2%, 5%, 8%, respectively. The Fermi energy is set to zero and the band gap are indicated as blue arrows.
For an ideal semiconductor, a high tunability allows people to modify the band gap size and type, which control the optical absorption of a certain material. For this reason, we continue to detect the change in electronic structures corresponding to different types of strain. For uniform strain, as shown in fig3a and fig3b, the band gap type remains indirect, pointing from k point near X along X - Γ direction to k point near Y along Γ - Y direction. The band gap value increase from 0.07 eV to 0.1 eV when apply -8% uniform strain to 0% uniform strain, indicating the sensitive electronic respond for the press stress in monolayer SnS. When we apply stretch strain even to uniform 8%, the band gap still remains close to the unstrained state. This is probably due to the renormalization of the band structure while the electron density redistributes and maintains the band feature.

Uniform strain performs the most sensitively, while other two seems more resistant to strain, and there are some slight differences between zigzag direction and armchair direction caused by anisotropic: when stretched, zigzag direction band structures are mostly indirect BG type, but become direct when shrunk, but armchair direction band structure behaves oppositely. Nonetheless, the overall pattern can still be identified. Also, we can see that the forbidden gap doesn’t change significantly, but the distribution becomes more concentrated as we shrink the materials. This means the density of states (DOS) is higher comparing with the one in normal condition, leading to a denser charge distribution since more states are allowed to occur with the same energy difference. This inspires us that we can modify the electric quality of SnS by straining. A general pattern of the corresponding change is that the more we stretch, the denser the charge distribution (CD) and DOS would be, but there’s no obvious change in band gap, and compared to stretch or shrink in a single direction, do it uniformly can be more effective, and band structure in zigzag direction and armchair direction behaves opposite in type under strain. Because it is easier to excite electron directly without the k momentum change (if crystal momentum changed, there should be an absorption of phonon, which cost energy), the indirect-direct band gap transition can largely enhanced the photoluminescence (PL). So by the specific type and amount of strain, the monolayer SnS can switch the efficiency for PL.

Figure 4. Born effective charge as function of uniform and uniaxial strain. Orange, blue and pink line point illustrated the uniform, zigzag and armchair type of strain, respectively.

The strain can tune the atomic structures and the electron density distribution will change correspondently, as we demonstrated in the above calculation result analysis. It is intriguing to wondering how the born effective charge, which is determined by the departure of positive charge center and negative charge center, will be changed while strain are applied. The main result are shown in figure 4, which, in general, indicate a large tunability for inplane born effective charge under strain. The intrinsic born effective charge for unstrained monolayer SnS is -9.6. Under uniform strain from -5% to 5%, the born effective charge change linearly from -8.8 to -10.3, almost 10% varied. The armchair direction strain shows the similar ferroelectricity (FE) respond with that in uniform, with a smaller variation under the 5% uniaxial strain. To our great surprise, under zigzag direction strain the monolayer SnS behave the anomaly FE respond (blue line point in figure 4),
which presented as an increase born effective charge under press strain. The reason for this anomaly FE respond may probably due to the reshape of overlap wave function from the nearest neighbor atomic orbital, which caused the armchair direction positive/negative charge center separate even larger. Thus, the application of stretch uniform/armchair direction strain or compress in zigzag direction can enhance the born effective charge in monolayer SnS, which can be used for achieving more functionalized electronic and optical nano devices.

3. Conclusions
Using first principle DFT calculation, we studied the structure, electronic band structure, and inplane ferroelectricity of monolayer SnS under uniform and uniaxial strain. We find the structure shrunk more flatten when monolayer SnS isolated from its bulk matrix. Our elastic modulus calculation shows that monolayer SnS is much flexible with elastic modulus about 4.4 GPa. The size of the band gap can be tuned from 0.06 eV to 0.11 eV by strain. Under positive armchair strain/negative zigzag strain there is even an indirect-direct band gap transition, which can be applied in PL control. Finally, the born effective charge for strained monolayer SnS can be tuned up to 10% by 5% strain, indicate the great tunability in monolayer SnS, which can be used for achieving more functionalized electronic and optical nano devices.

4. Simulation method
First we show the method of density functional theory, starting from single particle approximation. And then hartree fork equation was lead to solve the exchange energy problem. Hogenberg theorem build the connection between the electron charge density distribution with ground state energy, followed by Kohn-Sham equations which not only include exchange interaction but also the correlation interaction.

Single particle approximation.

For system with electron N, assuming no interaction between these electrons, the total Hamiltonian H can be written as the sum over single particle Hamiltonian \( h(\mathbf{r}_i) \)

\[
H = \sum_i h(r_i) + \sum_i V(r_i) = -\frac{\hbar^2}{2m} \nabla_i^2 + V(r_i)
\]

The question simplified as the solution of electron movement in periodic lattice field \( V(r_i) = V(\mathbf{r}_i + \mathbf{R}_j) \):

\[
h(r_i)\phi_i = \varepsilon_i \phi_i
\]

that is the single particle approximation. The ions can be considered to be fixed with respect to the electron movement, as the mass of ion is far big than that of electrons. Under the single particle approximation, the N electron many body question can be described as the following H:

\[
H = \sum_i \left( -\frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{j=1}^{n-1} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{l=1}^{Z} \frac{Ze^2}{|\mathbf{r}_i - \mathbf{R}_l|} \right)
\]

\( Z \) stand for the charge number of ion. In solid state physics, we use Slater determinant as a start to solve this kind of problem

\[
\Psi(x_1 \ldots x_n) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \ldots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \ldots & \psi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(x_1) & \psi_N(x_2) & \ldots & \psi_N(x_N) \end{vmatrix}
\]

\( x \equiv (r, \sigma) \), and satisfy orthogonal normalization condition

\[
\int \psi_i^* (x) \psi_j (x) dx = \delta_{ij}
\]

When \( Z=1 \), and the single ion potential \( V(\mathbf{r} - \mathbf{R}_l) = -\frac{e^2}{|\mathbf{r} - \mathbf{R}_l|} \). last term on the right side of equation (3) stand for periodic lattice potential

\[
V(\mathbf{r}) = \sum_i V(\mathbf{r} - \mathbf{R}_l) = -\sum_{l=1}^{Z} \frac{Ze^2}{|\mathbf{r} - \mathbf{R}_l|}
\]

The mean energy of the system is

\[
E = \int \Psi^* \mathbf{H} \Psi dx_1 dx_2 \ldots dx_N
\]
Substitute into (4) with arrange, we get $E$ in the form of

$$E = \sum_i \int d^3r \psi_i^*(r) \left[ \frac{-\hbar^2}{2m} \nabla^2 + V(r) \right] \psi_i(r) + \frac{1}{2} \sum_{i,j} \int d^3r d^3r' |\psi_i(r')|^2 \frac{e^2}{|r-r'|} |\psi_j(r')|^2 - \frac{1}{2} \sum_{i,j} \int d^3r d^3r' \psi_i^*(r') \psi_j(r') \frac{e^2}{|r-r'|} \psi_j(r) \psi_i(r')$$

(7)

The second term on the right indicate Coulomb interaction between electrons, the third term derives from the exchange interaction between parallel spin electrons based on Pauli exclusive principle. Using equation (5) as restrict condition to variation the equation (7), one can get $\psi_i(r)$ satisfied the following single electron equation:

$$\left[ \frac{-\hbar^2}{2m} \nabla^2 + V(r) + \sum_j \int d^3r' |\psi_j(r')|^2 \frac{e^2}{|r-r'|} \right] \psi_i(r) - \sum_{i,l} \int d^3r' \frac{e^2}{|r-r'|} \psi_j(r') \psi_i(r') = \epsilon_i \psi_i(r)$$

(8)

This is the Hartree-Fock equation, left side square brakets stand for periodic lattice potential of ions and the mean Coulomb potential generated by all the electrons. Left side last term(exchange interaction potential) is related to the electron state $\psi_i(r')$, which can only be solved by self-consistent iteration. Alternatively, one can write Hartree-Fock equation in the single electron effective equation:

$$\left[ \frac{-\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r)$$

$$V_{\text{eff}}(r) = V(r) + V_C(r) + V_{\text{xc}}(r)$$

(9)

in which $V_C(r) \equiv \int d^3r' \rho(r') \frac{e^2}{|r-r'|}$ indicate all the mean Coulomb potential generated by all the other electrons from the system that a single electron can feel, and $V_{\text{xc}}(r)$ is a localization exchange potential decided by $\rho_{\text{av}}^{HF}$ (mean non-local exchange density distribution)

$$V_{\text{ex}}(r) \equiv -\int d^3r' \rho_{\text{av}}^{HF}(r, r') \frac{e^2}{|r-r'|}$$

(10)

Hohenber-Kohn theorem

Interaction many body system particle number density is the basic variable to decide the physical properties of a ground state system.

Kohn-Sham equation

Kohn-Sham equation is derived from energy functional of HK variation minimum respect to $\rho(r)$.

HK energy functional can be written as

$$E[\rho, V] = T_0[\rho] + V_H[\rho] + E_{\text{xc}}[\rho] + \int d^3r V(r) \rho(r)$$

(11)

in which $T_0[\rho] = \sum_i \int d^3r \psi_i^*(r) \left[ \frac{-\hbar^2}{2m} \nabla^2 \right] \psi_i(r) = \sum_i < \psi_i(r) \left| \frac{-\hbar^2}{2m} \nabla^2 \right| \psi_i(r) >$ is the kinetic term with same ground state density in non-interacting electronic system, and $V_H[\rho] = \frac{1}{2} \sum_{i,j} \int d^3r d^3r' \rho(r') \frac{e^2}{|r-r'|} \rho(r') = \frac{1}{2} \sum_{i,j} < \psi_i \psi_j \left| \frac{e^2}{|r_{ij}|} \right| \psi_i \psi_j >$ is the direct Coulomb interaction term for electron in Hartree apprximation. $E_{\text{xc}}[\rho]$ is the exchange correlation functional, defined as

$$E_{\text{xc}}[\rho] \equiv \int [F[\rho] - T_0[\rho] - V_H[\rho] + (V_{\text{ex}}[\rho] - V_{\text{xc}}[\rho])$$

(14)

Since functional $F[\rho]$ is unknown, $E_{\text{xc}}[\rho]$ is unknown, but include exchange and correlation interact effect, and also all the other unknown many body effect when substitute many body kinetic functional $T[\rho]$ with non-interacting electron system kinetic term $T_0[\rho]$. So HK energy functional can be written as

$$E[\rho, V] = \sum_i < \psi_i \left| \frac{-\hbar^2}{2m} \nabla^2 + V(r) \right| \psi_i > + \frac{1}{2} \sum_{i,j} < \psi_i \psi_j \left| \frac{e^2}{|r_{ij}|} \right| \psi_i \psi_j > + E_{\text{xc}}[\rho]$$

(15)

As for the non-interacting independent electron system,

$$V_{\text{eff}}(r) \equiv V(r) + V_C(r) + V_{\text{xc}}(r)$$

(16)

$$V_C(r) = \int d^3r' \rho(r') \frac{e^2}{|r-r'|}$$

(17)

$$V_{\text{xc}}(r) \equiv \delta E_{\text{xc}}[\rho]/\delta \rho(r)$$

(18)

$V_{\text{xc}}(r)$ functionialized depend top(r) density in the whole space distribution. After variation $\delta \rho_i^*$, one get interacting electron system single electron equation

$$\left[ \frac{-\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r) \right] \psi_i(r) = \epsilon_i \psi_i(r)$$

(19)
Can be interpreted as independent electron movement equation in effective potential $V_{\text{eff}}(r)$, at the same time this effective potential depend on the ground state density

$$\rho(r) = \sum |\psi_i(r)|^2$$

so, for many body system equation (18) and (19) should solve in self consistent union, this is the KS self consistent equation set.

By iteration calculation under particular convergence threshold, we can solve the wave functions and the energy eigenvalue.

The whole calculation are performed by PWscf implemented in Quantum Espresso (QE)[19] based on density functional theory (DFT). We use the General Gradient Approximation (GGA) Perdew, Burke, and Ernzerhof (PBE) functional [20]. All the structures are fully relaxed according to the force and stress calculated in PWscf until the force is less than 10^{-4} eV/angstrom and the total energy changed within 10^{-5}eV. We use 9*9*1 kpoints to optimize the structure and do the self-convergence field and the band calculation. A vacuum space between neighboring layers is set to be more than 15 Å to avoid the artificial interactions between neighboring slab structures.

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