Experimental Demonstration of in Situ Stress-Driven Optical Modulations in Flexible Semiconducting Thin Films with Enhanced Photodetecting Capability

Seung Min Lee,†,‡ Woosun Jang,†,‡ Bhaskar Chandra Mohanty,†,‡ Jisu Yoo,§ Jin Woo Jang,‡ Da Bin Kim,‡ Yeonjin Yi,§ Aloysius Soon,*,† and Yong Soo Cho*,∥

†Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Korea
‡School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala 147004, India
§Department of Physics, Yonsei University, Seoul 03722, Korea

Supporting Information

ABSTRACT: Flexible semiconducting thin films have a broad coverage of future competitive electronic and optoelectronic devices. Although the stress present in thin films has been long known to affect optical properties, the experimental verification of the optical modulations in flexible systems has not been available so far. Here, we propose an in situ deposition process of inducing intentional compressive or tensile stress in the flexible thin films, ultimately to define the actual level of optical bandgap and photosensitivity modulations using an example of narrow bandgap p-type semiconductor PbS thin films. We experimentally and theoretically prove the stress dependency of bandgap changes from 1.23 to 1.73 eV in the strain range of −0.88 to +0.88%. A metal–semiconductor–metal device with compressive strain-induced PbS thin film exhibited a higher photoresponse compared to the unstrained ones, because of combined effects of favorable band edge positions as well as generation of a higher number of electron–hole pairs due to absorption of a wider range of photon energies owing to its lower bandgap.

INTRODUCTION

In recent years, strain engineering and its effects on electrical, optoelectronic, magnetic, and mechanical properties of materials have drawn significant interest owing to its multifaceted potentials in device applications. In the growth of thin films, stress that usually arises from the lattice mismatch and/or thermal expansion difference between films and substrates plays a critical role in determining film orientation and quality. Meanwhile, flexible optoelectronics has earned tremendous research interest because of its potential applications in the next-generation devices for the foreseeable future. With the growing demands of devices with improved performance, it has become very important to assess the effects of external stresses, for example, due to bending/stretching/twisting, on optoelectronic properties for efficient designing of the devices.

More specifically, the external stress (or strain) applied on the crystalline solids can strongly perturb their electronic structure by distorting the crystal symmetry or inducing unexpected defects and, therefore, can markedly change the material’s intrinsic properties such as band edge positions and effective masses. Especially, in thin films and low-dimensional nanomaterials which are often used in modern optoelectronic devices, there are increasing number of studies reporting such intentional modulation of the electronic structure upon applied mechanical strain. Incidentally, it has been suggested that the electronic structure of technologically important chalcogenide-based compounds can be tailored by strain engineering. In order to successfully design and engineer these key functional materials for desired optoelectronic performances, it is important to understand the effect of external stresses on their electronic structures.

There are, however, very limited reports on flexible systems, which demonstrate experimentally the changes in material properties when an external compressive or tensile stress is applied to typical thin films, except for the studies on the stress-driven mechanical failure. In the field of optoelectronics, the recent studies on the effect of stress on optical properties, e.g., bandgap and band positioning, of semiconducting materials are based on the theoretical calculations of electronic structure.
The reason why the experimental verification of the stress dependency of optical properties in the flexible system has been unavailable may lie in the difficulty in fabricating inorganic semiconducting thin films inherently possessing a considerable level of compressive or tensile stress. Usually fracture occurs first in the films since, being brittle, these cannot withstand a significant level of stress which is required for noticeable changes in the film properties. Second, finding crystalline semiconducting thin films which can be directly deposited onto the flexible polymer substrates that restrict the deposition temperature to typically less than 100 °C has also been a limiting factor. Another reason may be related to the limitation of easily available optical measurement techniques since most of the semiconductor thin films are fabricated on nontransparent substrates.

Here, we propose for the first time a way to induce in situ compressive or tensile stress on semiconducting thin films deposited at near room temperature so that flexible polymer substrates can be used for maintaining transparency and flexibility. The stress-dependent change of optical bandgap is first demonstrated here in a selected narrow bandgap semiconducting thin film, i.e., PbS, with an actual device fabrication in the form of a photodiode showing the optical properties. Theoretical calculations of electronic bandgap with stress modulations benefitting the photosensing performance. The experimental verification of the stress dependency of optical properties in the flexible system has been unavailable since, being brittle, these cannot withstand a significant level of stress which is required for noticeable changes in the film properties. Second, finding crystalline semiconducting thin films which can be directly deposited onto the flexible polymer substrates that restrict the deposition temperature to typically less than 100 °C has also been a limiting factor. Another reason may be related to the limitation of easily available optical measurement techniques since most of the semiconductor thin films are fabricated on nontransparent substrates. Here, we propose for the first time a way to induce in situ compressive or tensile stress on semiconducting thin films deposited at near room temperature so that flexible polymer substrates can be used for maintaining transparency and flexibility. The stress-dependent change of optical bandgap is first demonstrated here in a selected narrow bandgap semiconducting thin film, i.e., PbS, with an actual device fabrication in the form of a photodiode showing the optical properties. Theoretical calculations of electronic bandgap with stress modulations benefitting the photosensing performance. The experimental verification of the stress dependency of optical properties in the flexible system has been unavailable since, being brittle, these cannot withstand a significant level of stress which is required for noticeable changes in the film properties.
negative sign indicates the compressive strain in the film deposited in the outward bent substrate.

X-ray diffraction measurements of the PbS thin films on PET with different levels of prebending strain revealed well-defined Bragg peaks (Figure 1b) corresponding to the polycrystalline cubic PbS phase (JCPDS file: 05-0592) regardless of the magnitude of strain albeit shift of the peak positions that depended on the level of prebending strain. Increasing the tensile prebending strain resulted in progressive shift of the peaks toward lower 2θ values indicating tensile lattice strain \( \varepsilon_{\text{lattice}} \) in the films, and similar was the case for the compressive prebending strain. The quantitative variation of the lattice parameter and, thus, the lattice strain with the prebending strain are summarized in Table S1 of the Supporting Information.

Figure 1c shows the background-subtracted and normalized Raman spectra of the PbS thin films of prebending strain of \(-0.88\%\), 0%, and 0.88%. The corresponding Raman spectra in the wider range of wavenumber can be seen in the inset. Peaks at \(~157\) cm\(^{-1}\) and \(~453\) cm\(^{-1}\) are noticeably observed, corresponding to the 1LO and 2LO phonon modes of PbS, respectively. The normalized Raman spectra of the 1LO mode clearly show the shift of the spectrum according to the type of strain, confirming the existence of stress in the films. As can be anticipated, the shift toward the higher wavenumber for the \(-0.88\%\) strain indicates that a compressive strain exists in the PbS thin film. According to an estimation from the shift of the 1LO peak by the curve-fitting, the average strain dependency of peak shift is evaluated as \(-11.1\) cm\(^{-1}\)/%.

The corresponding high resolution TEM (HR-TEM) images and the FFT (fast Fourier transformed) patterns of the films are shown in Figure 2. The clear lattice fringes of the (111) and (200) lattice planes (I and II images of each sample) indicate high crystallinity of the films which is also supported by the corresponding FFT images as shown in inset of I and II. As analyzed from the lattice fringe images, interplanar spacing corresponding to the (111) plane, \(d_{111}\), was found to vary depending upon the prebending strain. The value of \(d_{111}\) increased from 3.45 Å for the 0% sample to 3.53 Å for the 0.88%-strained films, whereas it decreased to 3.39 Å for the compressive \(-0.88\%\) strain. The \(d\)-spacing of the (200) plane has the same varying tendency with the strain. These observations clearly indicate, again, that the current in situ processing definitely affected the crystallographic state of the flexible thin films with intentional compressive or tensile strain.
The optical bandgap $E_{\text{opt}}$ of the films was estimated from the plots of $(a h \nu)^2$ versus $h \nu$ (Figure 3a), where the absorption coefficient $\alpha$ was determined from the spectral transmittance and reflectance curves as seen in Figure S1 of the Supporting Information. The unstrained PbS films showed an optical bandgap of $\sim 1.62$ eV, which is consistent with our previous report, whereas that for the strained films strongly depended on the applied strain. An increased bandgap of 1.73 eV was observed for the 0.88% strain while the compressive strain decreased the bandgap to 1.43 eV for the $-0.88\%$ strain. It is remarkable to note the wide variation ($\sim 21\%$) in the bandgap of the films easily accessible through a facile modulation of the film deposition strategy. The microstructure of the films as the possible origin of the observed bandgap change is precluded based on the surface SEM images (Figure S2) that showed little variation of surface features with strain. The details of the shift of the band edges (i.e., conduction band minimum $E_C$ and valence band maximum $E_V$) leading to the observed variation in the $E_{\text{opt}}$ was studied by ultraviolet photoelectron spectroscopy. The Fermi levels $E_F$ and $E_V$ for the films were directly evaluated from the UPS spectra (Figure S3), and $E_C$ was determined by adding $E_{\text{opt}}$ to $E_V$. The quantitative results of our analysis of the experimental data of band edge shifting of the films with the applied strain during the in situ processing are summarized in Figure 3b,c. As evidenced, the relative position of $E_C$ and $E_V$ was dependent on the type and level of the strain. The energy levels tended to decrease with compressive strain and to increase with tensile strain. A compelling observation, however, is that not only the band edges but also the Fermi level position is significantly affected by the in situ stress during deposition of the films (Table S2). We find that the $E_F - E_V$ values progressively increased from 0.41 eV for $-0.88\%$ prebending strain to 0.53 eV for $+0.88\%$ strain, while the $E_F - E_C$ values increased from 1.02 to 1.20 eV implying the movement of the Fermi level away from the band edges deeper into the bandgap. Consequently, the electrical properties, namely, carrier concentration, Hall mobility, and dark resistivity, were considerably affected (Figure S4), and as expected, the films grown at a prebending strain of $+0.88\%$ exhibited the highest dark resistivity among all films.

Further analysis of PbS electronic band structure through the density-functional theory (DFT) calculations (see Section V of the Supporting Information for calculation details) revealed that the change in the electronic bandgap ($\Delta E_{\text{elec}}$) monotonically increases with the applied strain (Figure 4a), which is very much in line with the trend of experimentally measured optical bandgap, though the absolute amount of the calculated electronic bandgap is smaller than the optical bandgap (where the underestimation of the energy gap in DFT calculations due to the generalized gradient approximation (GGA) exchange-correlation functional is well-known). The same tendency is also found for the relative positions of the
valence and conduction band edges (Figure 4b). Here, we find that the applied strain (within ±2%) may vary the ionization potential (IP) of PbS by ∼0.6 eV while the electron affinity (EA) is changed by a larger extent of ∼1 eV. Specifically, within an applied strain of ±2%, bandgap is found to decrease by ∼0.2 eV when a compressive strain is applied, while a tensile strain increases the bandgap by a similar value. Upon tensile strain, the Pb–S chemical bonds are stretched, and this affords a less effective overlap of the bonding S 3p and Pb 6s orbitals, thus opening up the bandgap. This is rationalized by the calculated projected density-of-states (Figure 4c). In the valence band region, the dominant S 3p occupied states are clearly more localized upon applied tensile strain, while the Pb 6s empty states are upshifted as the strain increased in a positive direction. And vice versa, the opposite is true when a compressive strain is employed.

We then demonstrated the effects of the in situ induced stress by fabricating an actual device in the form of a photodetector having a metal–semiconductor–metal (MSM) configuration with the selected PbS thin films processed with the applied prebending strains of −0.88, 0, and 0.88%. Figure 5a demonstrates the time-resolved photocurrent under the AM 1.5 illumination (100 mW/cm²) at a bias of 3 V. A distinct, stable, and repeatable current change was observed by switching the light on and off for several cycles for all samples, albeit the significant difference in the magnitude of the change in the current for a differently stressed sample. As noted from the inset to Figure 5a (that depicts photoresponse in a single cycle), the total current Iₜₚₚ increased remarkably from 0.50 μA in dark to 3.02 μA with 100 mW/cm² illumination at a biasing of 3 V for the unstrained sample. The corresponding changes, however, were from 0.8 μA to 4.85 μA in the −0.88% sample and from 0.25 μA to 1.95 μA in the +0.88% sample, clearly suggesting the strong prebending strain dependence of the dark as well as photo-current of the devices. As expected, linear dark I–V characteristics were observed (Figure 5b), suggesting the Ohmic nature of the interface.

The photoresponse of the devices to different power densities ranging from 10 to 100 mW/cm² is shown in Figure 5c. The photocurrent Iₚₚ is almost linearly proportional to the incident light intensity for all samples because the excited charge density increased with the increased density of photons. Further characterization of the photoresponse behavior at different bias voltages (0.01 and 1.0 V) with an illumination power density of 100 mW/cm² revealed an increasing Iₚₚ with the bias voltage (Figure S5).

The mechanism of the remarkable modulation in the photoresponse of the devices by the induced in situ strain is illustrated by a schematic diagram of the band structure at the interface shown in Figure 5d. Considering that the in situ strain affects the band edge of the films differently (Table S2), differences in the barrier characteristics are expected when the contact is made between Al (work function of 4.28 eV) and the p-type PbS films. When a bias is applied, tilting of the bands leads to an asymmetric band profile across the length of the MSM device. Under illumination and biasing, the induced electron–hole pairs are separated and collected by the applied external field. As illustrated, for the ∼0.88% strain sample, the resulting band profile (Figure 5d) is expected to promote the separation of the holes and electrons, and their transport and collection at the contacts leading to an enhanced photocurrent. Furthermore, the ∼0.88% strain sample has the lowest bandgap resulting in absorption of a wider range of photons, which, in turn, created more number of electron–hole pairs compared to other samples. The −0.88% sample that exhibited significant enhancement in photocurrent at higher illumination intensity indicates the generation of a higher number of electron–hole pairs as associated with a favorable band alignment that culminates in better photoresponse of the device.

■ CONCLUSIONS

We have shown that the band edge positions and optical bandgap of flexible thin films can be modulated through an in situ deposition process imposing intentional compressive and tensile stress. As an example, PbS thin films were studied theoretically and experimentally to prove in situ stress dependence of the optical bandgap and the resulting photoresponse of flexible metal–semiconductor–metal devices. The modulation of the band edges by inducing in situ stress during deposition itself may offer a novel approach unavailable in conventional technologies for use in future tunable optoelectronic devices. Optical excitation, semiconducting properties, and band alignment achieved through in situ stress can be holistically integrated for potential development of flexible novel adaptable optoelectronics.

■ ASSOCIATED CONTENT

6 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.8b03177.

(1) Calculation of applied prebending strain, (2) lattice strain, optical spectra, and microstructures of PbS thin films, (3) analysis of ultraviolet photoelectron spectroscopy (UPS) results, (4) Hall measurements, (5) computational details, and (6) photocurrent–voltage characteristics of in situ-stress driven photodetectors (PDF)

■ AUTHOR INFORMATION

Corresponding Authors
*(A.S.) E-mail: aloysius.soon@yonsei.ac.kr.
*(Y.S.C.) E-mail: ycho@yonsei.ac.kr.

ORCID
Woosun Jang: 0000-0003-1274-1714
Blakshar Chandra Mohanty: 0000-0002-9823-8548
Yeonjin Yi: 0000-0003-4944-8319
Aloysius Soon: 0000-0002-6273-9324
Yong soo Cho: 0000-0002-1601-6395

Author Contributions
S.M.L., W.J., and B.C.M. contributed equally to this work.

Notes
The authors declare no competing financial interest.

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Supporting Information

Experimental demonstration of *in situ* stress-driven optical modulations in flexible semiconducting thin films with enhanced photo-detecting capability

Seung Min Lee¹⁺, Woosun Jang¹⁺, Bhaskar Chandra Mohanty²⁺, Jisu Yoo³, Jin Woo Jang¹,
Da Bin Kim¹, Yeonjin Yi³, Aloysius Soon¹⁺, Yong Soo Cho¹⁺

¹Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Korea
²School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala 147004, India
³Department of Physics, Yonsei University, Seoul, 03722, Korea.

*Corresponding author: aloysius.soon@yonsei.ac.kr, ycho@yonsei.ac.kr
⁺These authors contributed equally.
I. Calculation of applied pre-bending strain

The level of strain was changed by adjusting the curvature of the loaded polymer substrate. The bending curvature radius $r$ was calculated by a simple relationship of $\pi r = L$, where $L$ is the length of substrate. The pre-bending strain, $\varepsilon_p$, applied to the substrate was calculated using the following general relationship between the film/substrate thicknesses and the bending radius:

$$\varepsilon_p = \left( \frac{t_f + t_s}{2r} \right) \left( 1 + 2\eta + \chi^2 \eta^2 \right) \left( 1 + \eta \right) \left( 1 + \chi \eta \right)$$  \hspace{1cm} (S1)

where $t_f$ and $t_s$ are the thickness of the film and the substrate, respectively, $\eta = t_f / t_s$, $\chi = E_f / E_s$, and $r$ is the radius of the curvature of the center of the bent sample. The reported Young's modulus values of 70.2 and 2.3 GPa respectively for PbS and PET were used for the $\varepsilon_p$ estimation.\(^1\)\(^2\) We used sample fixtures to maintain the fixed curvature $r$ for each deposition in the chemical bath as shown in the schematic below for the compressive stress case. The two different levels of strain, 0.67% and 0.88%, were applied by changing the value of curvature. Two fixtures were needed to give the two different $r$ values for each stress case. The sample length $L$ was carefully determined to give the exact half of the circle of the substrate in the fixture, at which the precise $r$ value is applied. Note the relation of $L = \pi r$. When calculating the actual $\varepsilon_p$ from the equation S1, we assumed that the film thickness was zero because the pre-bending stress was applied to the substrate.\(^3\) This simplifies the equation S1 to $\varepsilon_p = t_s / 2r$. As a result, pre-bending with the radius of curvatures of 13 mm and 10 mm was estimated to create pre-bending strains of 0.67% to 0.88%, respectively.
An example of the sample fixture for the induction of compressive stress in the film

II. Lattice strain, optical spectra and microstructures of PbS thin films

**Table S1.** Lattice parameter and calculated lattice strain $\varepsilon_{\text{lattice}}$ of PbS thin films. The lattice strain can be estimated using the equation as a function of lattice parameter, which corresponds to $\varepsilon=(a-a_0)/a_0\times100\%$, where $a$ is the strained lattice constant and $a_0$ is the stress-free lattice constant.

<table>
<thead>
<tr>
<th>$\varepsilon_p$</th>
<th>a (Å)</th>
<th>$\varepsilon_{\text{lattice}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.88%</td>
<td>5.951</td>
<td>-0.432</td>
</tr>
<tr>
<td>-0.67%</td>
<td>5.955</td>
<td>-0.368</td>
</tr>
<tr>
<td>0%</td>
<td>5.977</td>
<td>0</td>
</tr>
<tr>
<td>0.67%</td>
<td>5.990</td>
<td>0.209</td>
</tr>
<tr>
<td>0.88%</td>
<td>5.999</td>
<td>0.371</td>
</tr>
</tbody>
</table>

**Figure S1.** (a) Optical transmittance and (b) reflectance spectra of PbS thin films with different strains.

Optical bandgap $E_{g,\text{opt}}$ of all the films was calculated using the relation of $(\alpha h\nu)^{1/n} = A(h\nu-E_{g,\text{opt}})$, where $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy and $n$ is $\frac{1}{2}$ for direct transition. $\alpha$ was calculated using the expression $\alpha = (1/d)\ln[(1-R)^2/T]$ with the obtained information of the thickness $d$, the transmittance $T$ and the reflectance $R$. 
Figure S2. Surface and cross-sectional images of PbS thin films with different levels of strain.

III. Analysis of ultraviolet photoelectron spectroscopy (UPS) results

Figure S3 shows UPS spectra of the secondary electron cutoff (SEC) region and the low binding energy cutoff valence band region of PbS thin films with different strains. Work function $\Phi$ was determined by the difference between the incident photon energy (21.2 eV) and the binding energy of the SEC region (Figure S3a). For example, the work function of 0% PbS thin film is $\Phi=21.2-16.74=4.46$ eV; that is, the Fermi level $E_F$ is -4.46 eV with respect to the vacuum level $E_{\text{VAC}}$. The valence band edge was determined by extrapolating the linear portion of the low binding energy region (Figure S3b), indicating the onset of photoelectron intensity in the low binding energy region ($E_F$ at 0 eV) of the UPS spectrum. The conduction band minimum ($E_C$) is calculated by adding the optical bandgap, as determined by the position of the lowest exciton absorption peak, to $E_V$. The numerical band positions are plotted in Figure 2a and summarized in Table S2.

![Figure S3. UPS spectra of (a) secondary cutoff region and (b) low binding energy region of the PbS thin films](image_url)
Table S2. Energy band levels with respect to the vacuum level as deduced from the UPS spectra of Figure S3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_C$</th>
<th>$E_F$</th>
<th>$E_V$</th>
<th>$E_F-E_V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.88%</td>
<td>-3.27</td>
<td>-4.29</td>
<td>-4.70</td>
<td>0.41±0.03</td>
</tr>
<tr>
<td>-0.67%</td>
<td>-3.17</td>
<td>-4.26</td>
<td>-4.69</td>
<td>0.43±0.03</td>
</tr>
<tr>
<td>0%</td>
<td>-3.06</td>
<td>-4.24</td>
<td>-4.68</td>
<td>0.44±0.05</td>
</tr>
<tr>
<td>0.67%</td>
<td>-2.97</td>
<td>-4.22</td>
<td>-4.67</td>
<td>0.45±0.03</td>
</tr>
<tr>
<td>0.88%</td>
<td>-2.91</td>
<td>-4.11</td>
<td>-4.64</td>
<td>0.53±0</td>
</tr>
</tbody>
</table>

IV. Hall measurements of PbS thin films

![Graph showing carrier concentration, electrical resistivity, and mobility as a function of strain.]

*Figure S4.* Carrier concentration $n$, electrical resistivity $\rho$ and mobility $\mu$ of the PbS thin films as a function of strain, obtained by Hall measurement

V. Computational details

For the density-functional theory (DFT) calculations, we have used the Vienna Ab initio Simulation Package (VASP) code with the projector augmented wave (PAW) method to describe the ion-
electron interactions. The Kohn-Sham orbitals are expanded with a plane-wave basis set and the kinetic cutoff energy is taken as 500 eV. For all calculations, the generalized gradient approximation (GGA) due to Perdew, Burke, and Ernzerhof (PBE) to the DFT exchange-correlation (xc) functional is adopted. The Brillouin-zone is sampled by adopting a Γ-centered k-point mesh with an equivalent k-spacing of 0.1 Å^-1. The influence of spin-orbit coupling (SOC) to the total energies and the electronic band structure is tested, and we find that the effect of SOC to the total energy is usually limited in a few meV, but the computational cost is not trivial. We have also found that the impact of SOC on the overall electronic band structure is appreciable, i.e. the electronic bandgap energy is further reduced but in poorer agreement with experiments. More importantly, its influence on the variation of the electronic bandgap energy is negligible (Figure SA). Hence, we have neglected such SOC effects in our discussion.

Using DFT within the PBE approximation, we have obtained the optimized lattice constant for bulk PbS (6.01 Å) which is in agreement with previous reports. To mimic our experiments and understand the effect of mechanical strain on its electronic band structure, we have applied isotropic strain, ε on bulk PbS and ε can written as ε=(a-a_0)/a_0, where a and a_0 denotes the modified lattice constant upon strain, and the lattice parameter of zero-strain case, respectively. In our calculations, ε is varied from -2 to 2%. Having obtained the corresponding lattice constants under the applied strain, we then proceed to calculate their electronic band structures (including SOC) to obtain the electronic bandgap energy, E_{g,elec} as well as their valence and conduction band edges. The bandgap of zero-strain bulk PbS is calculated to be 0.50 eV (which is in a good agreement with previous works).

Figure SA shows the calculated electronic bandgap of PbS system upon applied strain, which ranges from -2 to 2%, with and without considering the spin-orbit coupling effect. It is clearly shown
that the spin-orbit coupling effect only laterally downshifts $E_{g,\text{elec}}$ approximately by 0.4 eV, without changing the relative difference of $E_{g,\text{elec}}$ between distinctively strained PbS structures. Here, the negative magnitude of $E_{g,\text{elec}}$ denotes the gap measured from the inverted position of the valence and the conduction band due to the band inversion, as shown in Figure SB. According to the S 3$p$ projected-band structure near band edges, no band inversion has been found in the unstrained PbS structure, while the VB-CB band inversion has been observed in the -2% strained PbS structure, only under the consideration of spin-orbit coupling effect.

![Figure SA](image.png)

**Figure SA.** Calculated electronic bandgap ($E_{g,\text{elec}}$) of strained PbS system with and without considering spin-orbit coupling.
Figure SB. Projected electronic band structure of sulfur 3p near L point, with and without considering spin-orbit coupling.
Upon applied hydrostatic pressure, our theoretically calculated band gap change was found to be slightly more responsive to the compressive stress, as shown in the Figure 4a of the main text. When the bond is compressed out from the equilibrium bond length, the potential energy (i.e. total energy) increases more drastically compared to that under the tensile stress (see Figure SC). Likewise, the magnitude of the band gap change exhibits an anisotropic response upon the hydrostatic pressure applied, and is well reflected on the inset figure.

**Figure SC.** Total energy-volume curve of PbS under the hydrostatic pressure ($E^{\text{tot}}$, black solid line). The absolute number of the band gap change with respect to the non-strained PbS ($\Delta E_{g,\text{elec}}$, blue square) is superposed on the energy-volume curve.
VI. Photocurrent-voltage characteristics of in situ-stress driven photodetectors

![Graph showing photocurrent-voltage characteristics](image)

**Figure S5.** Dependency of photocurrent on bias voltage under 100mW/cm² light intensity.

References