Origin of Prestress-Driven Optical Modulations of Flexible ZnO Thin Films Processed in Stretching Mode

Hong Je Choi,†§ Woosun Jang,†§ Bhaskar Chandra Mohanty,†§ Ye Seul Jung,† 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

Supporting Information

ABSTRACT: Experimental verification of optical modulation with external stress has not been easily available in flexible systems. Here, we intentionally induced extra stress in wide band gap ZnO thin films by a unique prestress-driven deposition process that utilizes a stretching mode. The stretching mode provides homogeneous but biaxial stresses in the hexagonal wurtzite structure, leading to the extension of the c-axis and the contraction of the a-axis. As a result, the reduction of the optical band gap by ∼150 meV was observed for the strain of ~4.87%. The band gap narrowing was found to occur from the respective downward and upward shifts of the conduction band minimum and valence band maximum under the applied stress. The experimental evidence of optical modulations was supported by the theoretical calculations using density functional theory. The reduced strong interactions between Zn d and O p orbitals were assumed to be responsible for the band gap narrowing.

Train engineering has been considered as an effective way to modulate the electrical, optical, magnetic, and mechanical properties of inorganic thin films.1–4 In particular, optical properties can be significantly strain-dependent by inducing crystallographic deformations, such as extension or contraction of bond lengths, with the changes in electronic structure and molecular orbitals.5–10 Consequently, tuning the band structure and band gap of semiconducting thin films via an applied strain has been demonstrated so far mostly based on the theoretical calculations of electronic structure.8–10 The modulation of the band structure with stress can be practically used, for example, to achieve a favorable band offset between different junction layers in a device, leading to higher charge transfer and better performance.

Meanwhile, a number of studies have reported the meaningful changes in optical band gap/band edges due to the stress induced unintentionally in rigid inorganic thin films mostly as a result of the physical relation between the film and substrate and processing conditions, e.g., lattice and thermal mismatches at the interface,11 cation substitutions,12,13 and even film thickness.9,14 Although these studies reported unintended and isolated variations of optical properties due to stress and no systematic attempt was made to vary the stress directly (i.e., not via the processing conditions), these results are remarkable in that they suggest the potential manipulation of the band gap and band edges by modulating the stress and strain in the films. Notably, reports of band gap modulation in flexible thin films (especially those of high relevance in optoelectronics) by explicit strain engineering remain very scarce.

At variance with the earlier reports on explicitly non-adjustable strain and its effects, this work introduces an innovative approach to induce strain in flexible thin films in a controllable manner, in order to modulate band structure and thus optical properties. The present result may be the very first report demonstrating that an intentional extra stress changes optical band gap in a flexible thin film. An in situ stretching mode is used here to modulate the level of compressive stress in a selected wide band gap thin-film semiconductor of ZnO deposited on a flexible plastic substrate. The ZnO thin film was selected because of its multifaceted applications in a wide range of optoelectronic devices.15–17 The degree of stretching during deposition provides a different level of strain up to ~4.87% without cracking of films after the final releasing step. In addition, the results of density functional theory (DFT) calculations fully support the experimentally observed modulations of optical properties by the adjustable strain introduced in the flexible thin-film system.

Figure 1a illustrates the experimental in situ stretching procedure for sputter-depositing a 200 nm thick ZnO thin film on a flexible polyethylene terephthalate (PET) substrate. Prior to the deposition of the ZnO thin film, the PET substrate (~175 μm) was linearly stretched using a fixture designed to allow homogeneous strain (denoted as prestretching strain or prestrain in the following) and to control its magnitude by adjusting the level of stretching. ZnO films were then...
deposited on the PET substrate subjected to prestretching strains of 0.49, 1.98, and 4.87% using radiofrequency (RF) magnetron sputtering at room temperature (see the Supporting Information for the experimental details). After the films were deposited, the samples were released from their stretched condition and recovered to their normal (nonstretched) state. The released films are expected to experience uniaxial contraction with the residual compressive stress in the interior of the films.

Figure 1b compares glancing-incidence X-ray diffraction (XRD) patterns of zinc oxide thin films grown with different prestretching strains and the reference sample grown without prestretching. The XRD patterns indicate that the ZnO thin films were predominantly oriented along the c-axis (out-of-plane direction) of the hexagonal wurtzite structure. The (002) peak was progressively shifted toward lower 2θ values with increasing prestretching strain, corresponding to an increase in the lattice constant c along the c-axis of the ZnO thin films from 5.22 to 5.31 Å. This variation, originating from the in situ processing in the stretching mode, suggests the presence of out-of-plane tensile strain and is expected to be accompanied by in-plane biaxial compression. In-plane stress, σ, in ZnO thin films was estimated by the biaxial strain model using the following equation:

\[
\sigma = \frac{2C_{13} - C_{33} \left( C_{11} + C_{12} \right)}{C_{13}} \left( \frac{d - d_0}{d_0} \right)
\]

where \(C_{ij}\) are the elastic stiffness constants for ZnO; \(d\) is the interplanar spacing corresponding to (002) reflection in the XRD patterns, and \(d_0\) is the spacing for stress-free system. As expected from the shift of the (002) peak toward lower 2θ angles, the resulting compressive stress \(-\sigma\) was found to increase with the degree of stretching as demonstrated in the inset of Figure 1b. Compressive residual stresses of about -1.44, -2.72, -5.58, and -9.00 GPa were obtained for the ZnO thin films processed with prestretching strains of 0, 0.49, 1.98, and 4.87%, respectively.

The presence of intentional stress in the in situ-processed ZnO/PET thin films was also investigated by direct observation. Figure 2a shows a TEM image of a 200 nm thick ZnO film on the PET substrate. A well-defined film layer with columnar structure is easily seen. The interplanar spacing of (100) and (002) planes (i.e., \(d_{100}\) and \(d_{002}\), respectively) in the thin films was estimated from the high-resolution transmission electron microscopy (HR-TEM) images of Figure 2b–d. The results, as expected, revealed an anisotropic distortion of the ZnO unit cell, to an extent controlled by the in situ processing in the stretching mode. For example, it revealed that the \(d\)-spacing of the (002) plane, \(d_{002}\), increased from 2.61 to 2.66 Å and that of the (100) plane, \(d_{100}\), decreased

\[
L_0 + \Delta L \quad \text{Sputter Deposition} \quad \text{Stretching Mode} \quad \text{Releasing} \quad L_0
\]

**Figure 1.** (a) Schematic illustration of the processing steps for the in situ stress-driven ZnO thin films and (b) X-ray diffraction patterns of as-deposited ZnO thin films with different levels of in situ strain. The inserted plot indicates the variation of calculated compressive stress (\(\sigma\)) as a function of applied in situ strain.

**Figure 2.** (a) Cross-sectional TEM image of ZnO thin films on PET and HR-TEM images of the thin films processed with in situ strain of (b) 0%, (c) 0.49, and (d) 4.87% (with inserted diffraction patterns). The interplanar spacing corresponding to the (002) and (100) planes (i.e., \(d_{002}\) and \(d_{100}\), respectively) are marked in the images. (e) Variations in lattice parameters of \(a\) and \(c\) as a function of applied in situ strain and (f) schematic crystal structures reflecting unit cell distortion as a result of biaxial stress.
Figure 3. (a) $\alpha hv^2$ versus $hv$ plots of the flexible ZnO thin films processed with different levels of in situ strain and the changes in (b) optical band gap (obtained from Figure 2a) and (c) PL peak position (obtained from Figure S2 of the Supporting Information) of the ZnO thin films as a function of applied in situ strain. The PL peak corresponds to the near-band-edge UV emission at $\sim$380 nm. (d) Schematic illustration of energy band diagrams of the thin films according to different levels of in situ strains, obtained from the UPS and optical absorption measurements.

Figure 4. (a) Calculated electronic density-of-states (DOS) of ZnO with $c = 5.22$ Å and $c = 5.35$ Å and the real-space partial electron density plot for the VBM (left inset) and CBM (right inset), respectively. The isosurface level was set to 0.02 and 0.01 for the partial electron density at the VBM and that of CBM, respectively. The DOS above the Fermi level is magnified by 100 times to aid displaying the different orbital contributions. (b) The electronic band gap as a function of lattice parameter, $c$, and their % differences, $\Delta c$. The structure at $\Delta c = 0$ corresponds to the experimental structure without applied strain.

from 2.79 to 2.76 Å going from the 0% to the 4.87% prestrained samples, respectively, while the corresponding lattice constants $a$ and $c$ varied from 5.22 to 5.32 Å and from 3.22 to 3.19 Å, respectively. The variations of lattice constant $c$ and $a$ with prestrain, obtained from the HR-TEM images, are seen in Figure 2e. As a result, the ZnO thin films deposited under the prestretching strain of 4.87% are supposed to have anisotropic lattice strains of $\sim$1.61% along the $a$-axis and 2.14% along the $c$-axis. Figure 2f illustrates the schematic change in the unit cell of wurtzite ZnO as a function of the prestrain, based on the estimated structural values. It represents a unit cell distortion driven by the extended $c$-axis and contracted $a$-axis with prestrains.

Spectral transmittance and reflectance curves of the ZnO thin films were investigated to estimate the optical band gap depending on the level of in situ strain (Figure S1). As seen in the plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$), where $\alpha$ is the absorption coefficient, in Figure 3a, the optical band gap, $E_g$, was determined by extrapolating the linear portion of the curves. $E_g$ markedly decreased from 3.37 to 3.22 eV as the compressive stress in the films increased from $-1.44$ to $-9.00$ GPa. Figure 3c shows the change in band position of the emitted photon energy of the ZnO thin films in response to different levels of prestrain, which was obtained from the photoluminescence (PL) spectra measured at 4 K (Figure S2). The peak shift of the near-band-edge UV emission at $\sim$380 nm showed the same trend as that of the optical band gap, confirming that the intentional stress induces the optical modulation. A large shift of peak position by $\sim$200 meV, relative to the reference sample, was found for the $-4.87%$ thin film.

The strain-dependent optical modulation of the ZnO thin films enabled by the prestretching process was further analyzed through the experimental determination of band edges. Ultraviolet photoelectron spectroscopy (UPS) was used to obtain the relative position of the energy levels for the purpose of gaining insight into the effects of strain on the optical properties, as seen in Figure S3. The valence band maximum (VBM) was determined by extrapolating the linear region at low binding energies of the UPS spectra. The work function, $\Phi$, was determined as the energy difference between the incident photon energy of 21.2 eV and the intersection of the secondary electron cutoff in the high-binding energy...
The conduction band minimum (CBM) was calculated by adding the optical band gap energy to the VBM. Finally, the valence and conduction band-edge energies of the ZnO thin films were obtained from the work function and optical band gap values. The position of the band edges of ZnO thin films with different prestretching strains is illustrated in Figure 3d, and the details are provided in Table S1. These results suggest that the band gap narrowing caused by the prestretching strain comes from both the upward shift of the VBM and the downward shift of the CBM. This is the first experimental interpretation of the origin of the optical modulation of ZnO thin films induced by adjustable stress, in terms of the evolution of the electronic band structure.

The strain-driven modulation on the electronic structure of ZnO was further investigated using first-principles hybrid DFT calculations. Figure 4a shows the DFT-calculated density-of-states (DOS) for two different ZnO structures with lattice parameter $c = 5.22\ \text{Å}$ ($\Delta c = 0\%$, where $\Delta c = (c - c_0)/c_0 \times 100\%$) and $5.35\ \text{Å}$ ($\Delta c = 2.51\%$), reflecting the effects of strain found in experiments. For the structure with $\Delta c = 0\%$, the valence band edge is predominantly composed of $O\ p$ states, followed by $Zn\ p$ and $Zn\ d$ ones, whereas the conduction band edge consists of $Zn\ s$, $O\ s$, and $O\ p$ states. This agrees well with previous theoretical studies. In agreement with the experiments, very minor changes in the orbital contributions to the band edges were observed upon applied strain ($\Delta c = 2.51\%$), with only a small red shift in the DOS peak near $−1.5\ \text{eV}$.

The DFT-calculated partial electron density for the band edges at the $\Gamma$ point, plotted in Figure 4a, highlights the very small changes in both the VBM and CBM upon applied strain. The figure clearly shows that the partial electron density for the VBM states does not significantly change under the applied strain, while that for the CBM states exhibits a larger delocalization effect around Zn atoms when strain is applied. These subtle changes in the partial electron densities near the band edges support the shifts in the band edge positions observed experimentally (Figure 3d), with a larger shift in the CBM than in the VBM.

Based on the calculated band structure shown in Figure S4, the applied strain appears to influence the relative energy positions of the sub-bands near the VBM, especially for the second and third uppermost valence band states near the $\Gamma$ point. Moreover, these strain effects on the valence bands are in good agreement with previous theoretical studies, where the nominal shift in the absolute VBM position of ZnO (with larger shifts observed in the sub-bands) were reported. This is consistent with the present electronic band structure (Figure S4) and partial electron densities (Figure 4a) calculated by DFT. In addition, a downward shift of the valence band states at the $A$ and $M$ points has been observed around $−1.5\ \text{eV}$, corresponding to a red shift of the $O\ p$ states (as seen in the DOS of Figure 4a). The strain-induced changes in the $Zn\ s$ states dominating the CBM are reflected in a small (but not negligible) upward shift of the energy band (Figure S4). This is consistent with both the experimental CBM shifts and the calculated partial electron densities at the CBM discussed in this work. Considering all these effects, this work provides both experimental (Figure 3d) and theoretical (Figure 4b) evidence of a reduction in $E_g$ as a function of strain. These experimental and theoretical results can be understood in terms of changes in electronic structure and orbital interactions resulting from strain-induced structural deformations. Indeed, ZnO preferably crystallizes in the hexagonal wurzite structure where each Zn atom is surrounded by four O atoms at the corners of a tetrahedron. When the ZnO thin films experience uniaxial compression, the Zn–O bond lengths contract, altering the orbital coupling of neighboring atoms because of increased repulsion between the orbitals involved. This may lead to the change of the band gap.

The band edge position and their shifting in ZnO system are closely related to their atomic structure, especially entangled with the axial (out-of-plane direction, aligned to (0001)) and radial (in-plane direction) Zn–O bonds. In wurzite ZnO, the valence band edge is a bonding state from the coupling of anion $p$ and cation $p$ states, whereas a considerable amount of contribution from the coupling of anion $p$ and cation $d$ states. When the radial bond length decreases, the $p–d$ repulsion increases as the effective overlapping of the orbital dominates, consequently pushing up one of the degenerate valence band states at the $\Gamma$ point. In the conduction band edge where the anion $s$ and cation $s$ orbitals form an antibonding state, the increase of the axial bond length weakens the orbital interaction and finally shifts down in energy.

In conclusion, we demonstrated the origin of optical modulations in the semiconducting ZnO thin films processed by the in situ deposition process. The stretching mode with variable stresses was utilized during the deposition to deliberately provide compressive stress in the films. The experimental and theoretical results, to determine the changes of band structure, supported well the effects of the intentional extra stress on the band gap and band structure of the flexible semiconducting film films. Apparent structural changes, depending on the level of extra stress, were confirmed by the XRD and HR-TEM analyses. As an example, optical band gap was found to decrease by $\sim 150\ \text{meV}$ with a compressive strain of $\sim 4.87\%$, implying the stress dependency of optical properties. Subsequent band structure calculations also confirmed that the band gap narrowing originated from the respective downward and upward shifts of the CBM and VBM under the applied stress.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b02474.

Detailed experimental procedures, UV–visible transmittance/reflectance, UPS spectra with estimated energy levels, and computational details (PDF)

### AUTHOR INFORMATION

#### Corresponding Authors

*E-mail: aloysius.soon@yonsei.ac.kr.*

*E-mail: ycho@yonsei.ac.kr.*

#### ORCID

Woosun Jang: 0000-0003-1274-1714

Bhaskar Chandra Mohanty: 0000-0002-9823-8548

Aloysius Soon: 0000-0002-6273-9324

Yong Soo Cho: 0000-0002-1601-6395

#### Author Contributions

H.J.C. and W.J. contributed equally to this work.

#### Notes

The authors declare no competing financial interest.

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Hong Je Choi,1,† Woosun Jang,1,† Bhaskar Chandra Mohanty,2 Ye Seul Jung,1 Aloysius Soon,1,* and Yong Soo Cho1,*

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

Corresponding Author
*E-mail: aloysius.soon@yonsei.ac.kr, ycho@yonsei.ac.kr
1. Experimental details

**In situ deposition process of ZnO thin films.** An in situ deposition process was designed to provide extra compressive stress during the growth of films by stretching intentionally a flexible polymer substrate along the two ends of the substrate. A mechanical fixture of clamping both ends of the substrate was fabricated with an adjustable knob to control the stretchability. The fixture was inserted to the sputter chamber prior to the deposition. The magnitude of extra stress was assumed to be associated with the extended length of the substrate compared to the original length. For the in situ deposition, a 2-inch ZnO target (CERAC Inc., USA) was used. The distance between the target and substrate was maintained at ~10 cm. The chamber was evacuated to $1 \times 10^{-6}$ Torr before the introduction of Ar gas and the operating pressure was kept at 2 mTorr. The deposition of a 200 nm-thick ZnO thin film was conducted at room temperature with an RF powder of 100 W in pure Ar atmosphere (65 sccm). After deposition, the stretched substrate was released back to the original length and maintained for 4 hours for stabilization. No mechanical cracking on the surface of the released thin films was confirmed by optical microscopy up to the maximum strain of -4.87%.

**Characterization.** Crystal structure of the thin films was analyzed by X-ray diffraction in the $2\theta$ range of 20–70°, with a PANalytical X’pert PRO diffractometer using Cu K$_\alpha$ radiation in Bragg-Bretano($\theta/2\theta$) geometry. Cross-sectional TEM sample of the films was prepared using a focused ion beam (FIB) technique. HR-TEM (FEI Tencai G2 F30 S-Twin, USA) was used to characterize highly magnified TEM images of strained ZnO thin films. Diffraction patterns were analyzed from the HR-TEM images using the Gatan Digital Micrograph software. Optical transmittance and reflectance spectra of the thin films were obtained by a UV-visible near-infrared (NIR) spectrophotometer (JASCO V530, Japan). Ultraviolet photoelectron spectroscopy (UPS: PHI 5000
Versa Probe™, ULVAC-PHI) operating with a He(I) discharge lamp at 21.2 eV was used in an ultrahigh vacuum condition of ~1×10⁻⁸ Torr to obtain information on energy levels. Photoluminescence (PL) spectra of the thin film samples were acquired at 4 K by a Raman microscope (LabRam HR800, Horiba Jobin-Yvon, France) using a 266 nm Nd-YAG laser as light source.

2. UV-visible transmittance/reflectance spectra of strain-ZnO thin films

The optical bandgap \( E_g \) of ZnO thin film samples was determined by extrapolating the linear region of \( (αhν)^2 \) vs. photon energy \( (hν) \) plots, where \( α \) is the absorption coefficient, obtained from UV-visible transmittance and reflectance spectra in the 300–900 nm wavelength range.

Figure S1. (a) Optical transmittance and (b) reflectance spectra of ZnO thin films with different levels of pre-strain.

Figure S2 shows the low-temperature (4 K) photoluminescence spectra of ZnO/PET thin films with different pre-strain values. An intense and sharp peak around 380 nm represents the near-band-edge emission of each sample. The position of the PL peak shifted from 3.35 to 3.15 eV with
applying pre-stress. The maximum shift of ~200 meV is significant and believed to come from extra compressive stress present in the thin films.

**Figure S2.** PL spectra of ZnO/PET thin films at 4 K as a function of applied pre-strain.

4. UPS spectra with estimated energy levels

**Figure S3.** UPS spectra of the ZnO thin films processed with applied in situ strain, indicating the (a) valence and (b) secondary cut-off regions
Table S1. Calculated energy levels obtained from the UPS spectra, with optical bandgaps (unit: eV)

<table>
<thead>
<tr>
<th>Pre-strain (%)</th>
<th>$E_{\text{cut-off}}$</th>
<th>Work function</th>
<th>$E_{\text{onset}}$</th>
<th>VBM</th>
<th>$E_g$</th>
<th>CBM</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>17.15</td>
<td>4.05</td>
<td>2.88</td>
<td>-6.930</td>
<td>3.37</td>
<td>-3.560</td>
</tr>
<tr>
<td>0.49</td>
<td>17.14</td>
<td>4.06</td>
<td>2.84</td>
<td>-6.900</td>
<td>3.31</td>
<td>-3.590</td>
</tr>
<tr>
<td>1.98</td>
<td>17.11</td>
<td>4.09</td>
<td>2.8</td>
<td>-6.890</td>
<td>3.29</td>
<td>-3.600</td>
</tr>
<tr>
<td>4.87</td>
<td>17.06</td>
<td>4.14</td>
<td>2.73</td>
<td>-6.870</td>
<td>3.22</td>
<td>-3.650</td>
</tr>
</tbody>
</table>

5. Computational details

All density-functional theory (DFT) calculations performed in this work were carried out using the projector augmented wave (PAW) method, as implemented in the Vienna ab initio Simulation Package (VASP) code. A plane-wave basis set with a kinetic cutoff energy of 500 eV was employed, together with the hybrid DFT exchange correlation ($\chi c$) functional proposed by Heyd, Scuseria, and Ernzerhof (HSE). It has been previously reported that a combination of 36% Hartree-Fock exchange and 64% semi-local exchange accurately predicts the band gap of ZnO; this setup was thus used in this study. A $\Gamma$-centered $8 \times 8 \times 6$ k-point grid mesh was adopted to sample the Brillouin zone. To describe the atomic structure of ZnO, we used the experimentally determined lattice parameters and included an additional structure with $a = 3.154$ Å and $c = 5.353$ Å ($\Delta c = 2.51\%$). Dielectric function ($\varepsilon$) of ZnO is calculated under the independent-particle approximation (IPA) formalism where the excitonic and local effects are neglected. With obtained dielectric function, extinction coefficient ($k$) and optical absorption coefficient ($\alpha$) is calculated.
with the following equations: 

\[ k = \sqrt[2]{\frac{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1}{2}}, \quad \alpha = \frac{4\pi k}{\lambda}, \]

where \( \varepsilon_1, \varepsilon_2 \) and \( \lambda \) denotes the real part of dielectric function, imaginary part of dielectric function, and wavelength, respectively.

**Figure S4.** DFT-calculated band structure of ZnO with \( c = 5.22 \text{ Å} (\Delta c = 0\%), \) red curves and \( c = 5.35 \text{ Å} (\Delta c = 2.51\%), \) blue curves.

**Figure S5.** DFT-calculated absorption coefficient (\( \alpha \)) of ZnO with different \( c \) values.
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