Research Article

Research of Si-ZnO Thin-Film Transistors Deposited by Atomic Layer Deposition

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Si-ZnO thin-film transistors were fabricated using atomic layer deposition (ALD) then annealed in oxygen at 400°C for 1 hour and are demonstrated. Hexagonal wurtzite structure for ZnO was presented in all films, with a primary diffracted peak in the (100) direction regardless of the annealing treatment. First-principle density functional theory (DFT) calculations supported the observed crystalline characteristics. Electrical characteristics were improved with Si doping, increasing carrier concentration to 3.51 × 10²⁰ cm⁻³ and reducing film resistivity to 0.28 × 10⁻¹ Ω·cm with well-matched optical bandgap widening from UV-vis results using Tauc plot: Burstein-Moss (BM) effects. After implementing the oxygen ambient annealing and Si doping, the device parameters to realize the low power/energy consumption were improved to an SS value of 0.67 V/decade; threshold voltage (V th) of 0.68 V; and a field effect mobility (μ FE) of 5.22 cm²/V·s, respectively. The improved device parameters were related to the reduced interface trap densities due to annealing passivated oxygen vacancies, and the BM effect induced percolation conduction with increased carrier concentration due to Si doping, respectively. Thus, incorporating Si-based ZnO materials by ALD offers a viable candidate for superior device characteristics for energy-saving appliances.

1. Introduction

Metal oxide-based thin-film transistors (TFTs) for the display products have engendered considerable research interest recently due to their unique properties, including transparency in the visible range, excellent deposition uniformity onto large area substrates, and high field-effect mobility. Among them, amorphous In-Ga-Zn-O (a-IGZO) is widely used commercially to satisfy technical requirements for advanced display products [1, 2]. However, a-IGZO contains large quantities of indium (In) because it is the homologous compound (In₂O₃(ZnO)ₘ) of each In₂O₃ and ZnO layered structure [3]. Consequently, In toxicity and poor abundance limit further developments for metal oxide materials including IGZO. Therefore, developing alternative to In is critical for the TFT industry. However, as the recent research trend on oxide materials has been focused on the characteristics centered on the typical 3A element-doped ZnO or IGZO, there are relatively few reports of new materials. In this regard, incorporating new metal elements into ZnO could still be an effective and easy-customizing solution.

Many elements have been used to improve ZnO characteristics. In particular, the 3A elements Al, Ga, and In have been widely investigated, providing superior electrical and optical characteristics [4]. These typical 3A group elements
serve as shallow donors, supplying one electron each [5]. From the point of view of the introduction of a new element, silicon has also been shown to be an effective donor in the films fabricated using RF sputtering [6] and may be suitable as an effective dopant to improve various devices [7]. Since Si has atomic size of 1.17 Å, which is similar to or slightly less than Zn, using Si as ZnO film dopant could reduce lattice mismatch [8]. However, few previous studies considered Si-doped ZnO thin-film transistors; hence, further research is indicated.

One of the most important challenges for optoelectronic applications, including light-emitting diodes (LEDs), photodiodes, and transparent TFTs, is low power consumption [9]. Improving subthreshold swing (SS), field-effect mobility ($\mu_{FE}$), and threshold voltage ($V_{th}$) could reduce the required driving voltage and effectively reduce power consumption. In this regard, it is crucial to understand the relationship between the channel and insulators: interfacial trap density and $E_F$ (Fermi energy level) [10].

Various deposition processes can be used to fabricate ZnO thin films. Atomic layer deposition (ALD) has attracted significant attention since these films exhibit high uniformity and conformality and precise thickness and roughness control. The ALD process for thin-film deposition involves precursor source and purging gas injected and deposited onto the substrate in an alternating sequence; hence, film properties can be affected by various processing parameters, including metal-organic precursor type, substrate temperature, and precycle conditioning [11, 12].

Therefore, this study investigated Si doping influences on ALD-formed ZnO films and their device properties including SS, $\mu_{FE}$, and $V_{th}$ for TFTs with bottom gate structures. The devices were annealed under optimum conditions (400°C in oxygen for 1 hour) to further improve thin film characteristics and hence device properties.

2. Materials and Method

2.1. Material Deposition and Device Fabrication. We manufactured ZnO and Si-ZnO thin films on SiO$_2$ (100 nm)/Si (p-type, 100) substrates and glass substrates (Corning, Fusion 1737 for display use) using a traveling-wave Lucida D100 ALD system with 150°C substrate temperature and 1 Torr working pressure (NCD Technology, Inc., Korea). Diethylzinc (DEZ: (C$_2$H$_5$)$_2$Zn, Hansol Chemical Co., Ltd., Korea) and deionized (DI) water were used as Zn and O precursors, respectively, with tris (dimethylamino) silane (TDMAS: (Me$_2$N)$_3$SiH, Hansol Chemical Co., Ltd., Korea) as the Si doping precursor. DEZ was chilled to 10°C and supplied into the vacuum chamber at 20 sccm with high-purity N$_2$ (99.999%) carrier gas. TDMAS was heated to 60°C and flowed at similar rate to DEZ to avoid any antecedent condensation.

The cycle sequence for ALD growth to deposit ZnO and Si-ZnO thin films was as follows:

(a) ZnO thin films (Figure S1(a), Supplementary Information (SI)): DEZ pulse for 0.1 s, N$_2$ purge for 10 s, H$_2$O pulse for 0.1 s, and N$_2$ purge for 10 s

(b) Si-ZnO thin films (Figure S1(b), (SI)): DEZ pulse for 0.1 s, N$_2$ purge for 10 s, H$_2$O pulse for 0.1 s, N$_2$ purge for 10 s, TDMAS pulse for 0.1 s, N$_2$ purge for 10 s, H$_2$O pulse for 0.1 s, and N$_2$ purge for 10 s

Total ALD cycles (200 cycles) for both ZnO and Si-ZnO thin films and Si-doping concentration were controlled by modulating the ratio between the Zn-O and Zn-O-Si-O cycles, e.g., Si-1/10 was achieved by $20 \times (1 \times (b) + 9 \times (a))$. We fabricated Si-1/10, 1/20, 1/30, 1/40, and 1/50 Si-doped ZnO thin films.

Figures 1(a) and 1(b) show the TFT structure used in this study. Fabricated films for all conditions were post-annealed after ALD for 1 hour at 400°C in oxygen atmosphere. Mask aligner (M-150, Pro Win Co., Ltd., Korea) was used to shape the source/drain electrodes and channel layer, and bottom-gate TFT devices were constructed with channel width $W = 100$ μm and length $L = 5$ μm. An e-beam evaporator was used to deposit the 4 nm thick Ti adhesion layer and 30 nm Au source/drain electrodes.

2.2. Thin-Film and Device Characterization. Crystalline properties for the ZnO and Si-ZnO thin films were examined by X-ray diffraction (XRD; D/Max-2000, Rigaku, Japan) with Cu Kα radiation source ($\lambda = 1.5418$ Å) operated at 40 kV and 30 mA. Film thickness was verified using ellipsometry (GAERTNER, L117 C, USA) and atomic force microscopy (AFM; XE100, Park Systems, Korea). Electrical characteristics (resistivity ($\rho$), carrier concentration ($n$), and Hall mobility ($\mu_{H}$)) were determined using a Hall effect measuring device utilizing the van der Pauw technique (Ecopia, HMS-3000, Korea). Optical transmittance spectra 200–900 nm was acquired using an ultraviolet-visible-near infrared (UV-vis-NIR) spectrophotometer (V-570, JASCO, Japan). Photoluminescence (PL) spectroscopy (LabRam Aramis, Horriba Jovin Yvon, Japan) was used to monitor the films at room temperature using a 325 nm laser source. X-ray photoelectron spectroscopy (XPS; K-alpha, Thermo Scientific Inc., U.K.) using monochromated Al X-ray sources (Al ka line: 1486.6 eV) with 12 kV and 3 mA X-ray beam was used to analyze surface elemental composition for the films. A Keithley 2636B (USA) source meter was used to measure I–V characteristics for the constructed devices.

3. Results and Discussion

3.1. Thickness and Crystalline Structure. Figure 1(c) shows ellipsometry thickness for ZnO and Si-ZnO thin films deposited onto glass substrates using ALD with different cycle ratios before and after annealing. Average thickness = 37.25 and 37.16 nm for as-deposited (as-dep.) and annealed samples, respectively, with no significant changes due to Si doping or thermal treatment. Although ZnO film thickness was expected to reduce as more Si atoms were substituted into Zn sites, there is little difference in thickness between ZnO and Si-ZnO thin films because thickness change is primarily caused by ALD cycle ratio [13]. Figure 1(d) shows the annealed ZnO film thickness = 37.58 nm measured by AFM, which is similar to the ellipsometry results. Therefore, the
The overall average thin-film thickness for 200 ALD supercycles is 37.20 ± 1.50 nm.

Figures 1(e) and 1(f) show XRD results for ZnO and Si-ZnO films with as-dep. and annealed samples for Si-doping concentration, respectively. Hexagonal wurtzite structure was confirmed in all the films, with the highest peak at 31.92° (100) and others at 34.46° (002), 36.22° (101), and 56.73° (110). All diffraction peaks were consistent with reference code (JCPDS 96-210-7060). Generally, ZnO prefers the orientation for (002) planes since surface energy in that plane is lower than any other [14]. However, among the various ALD parameters, the deposition temperature has the largest effect on crystal orientation for ALD derived ZnO thin films [15]. Pung et al. showed that (100) and (002) oriented crystals were dominant in films at low temperatures (below 150°C), but the (100) orientation becomes dominant and (002) orientation reduces over 150–220°C, before switching back to (002) dominant at 220°C [16]. These orientation growths can be explained by a hindering process, proposed by Baji et al. [17]. Surface bonding sites are covered with -OH groups during chemisorption, with (100) sites 5.2 Å distant from one another, whereas (002) sites are 3.25 Å. DEZ has Zn-ethyl bond length = 1.95 Å. The DEZ molecule releases one ethyl group when chemisorbed...
onto the surface; therefore, the radius of the remaining spec-
imen is little under 2 Å. Thus, the molecules have sufficient
space to connect in the (100) direction without encountering
steric barriers. In contrast, (002) direction sites have atomic
spacing near the adsorbate size, and repulsion from sur-
rounding molecules is likely to rearrange them into the
next-closest packing configuration.

The peak intensities increased after the annealing treat-
ment, which aids atom migration to proper lattice locations
and crystal formation [18]. However, the intensity is reduced
in all conditioned samples as Si-doping concentration
increased, implying that Si doping into Zn sites degraded
thin-film ordered structure [19, 20]. Table 1 shows XRD
parameters referring to d-spacing and cell volume.

Grain size was calculated from XRD results using the
Scherrer equation [21]:

\[ D = \frac{K\lambda}{\beta \cos \Theta}, \]

where \( \beta \), \( K \), and \( \lambda \) are peak FWHM, shape factor = 0.9, and
Cu Ke wavelength, respectively, and interplanar distance \( d \)
was calculated as (\( d \))

\[ \frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{p^2}{c^2}, \]

where \( h \), \( k \), and \( l \) are Miller indices.

The cell volume in Table 1 is reduced with increasing Si-
doping concentration in the annealed samples. As previously
stated, this is related to the degradation of crystallinity
caused by Si doping. That is to say, the electrons are donated
as Si is substituted and ionized in the ZnO lattice, and in this
process, the Si ion size decreases, and the total unit cell
volume also decreases. This means that Si is stably doped
into the thin film and successfully releases electrons.

To clarify this discussion, we evaluated geometrical
optimization using first-principles density functional theory
(DFT) calculations with Cambridge Serial Total Energy
Package (CASTEP). Supplementary Information (SI) provides
relevant detailed DFT theory and calculation. Figures 2(a)–
2(d) show ZnO and Si-ZnO 2 x 2 x 2 supercell structural
changes with changing Si charge states. Si-doped ZnO structures
exhibit shortened bonding length to the oxygen around
Si-Zn compared with the original ZnO; more charged states
show more compressed structures, reducing \( d \) and cell
volume. Therefore, we could expect that delocalized Si ions
are incorporated in the ZnO thin film stably and can donate
electrons to form various ion states. However, we cannot
define which ion state in Si was more preferred, which
will be discussed in Section 3.3. Table 2 shows optimal
results for pure ZnO and Si-ZnO primitive cells with dif-
ferent charges, where finalized geometry parameters is
well matched to the experimental results.

Table 1: Lattice parameters from XRD data for as-deposited (as-dep.) and annealed (anneal) samples.

<table>
<thead>
<tr>
<th>Condition</th>
<th>d (Å) (100)</th>
<th>d (Å) (002)</th>
<th>Cell Vol. (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>2.801</td>
<td>2.601</td>
<td>47.128</td>
</tr>
<tr>
<td>Anneal</td>
<td>2.809</td>
<td>2.602</td>
<td>47.404</td>
</tr>
<tr>
<td>Si-1/50</td>
<td>2.801</td>
<td>2.601</td>
<td>47.111</td>
</tr>
<tr>
<td>Anneal</td>
<td>2.808</td>
<td>2.601</td>
<td>47.352</td>
</tr>
<tr>
<td>Si-1/40</td>
<td>2.801</td>
<td>2.600</td>
<td>47.115</td>
</tr>
<tr>
<td>Anneal</td>
<td>2.809</td>
<td>2.602</td>
<td>47.419</td>
</tr>
<tr>
<td>Si-1/30</td>
<td>2.808</td>
<td>2.599</td>
<td>47.258</td>
</tr>
<tr>
<td>Anneal</td>
<td>2.820</td>
<td>2.600</td>
<td>47.123</td>
</tr>
<tr>
<td>Si-1/20</td>
<td>2.828</td>
<td>2.600</td>
<td>47.334</td>
</tr>
<tr>
<td>Anneal</td>
<td>2.804</td>
<td>2.600</td>
<td>47.187</td>
</tr>
<tr>
<td>Si-1/10</td>
<td>2.806</td>
<td>2.597</td>
<td>47.237</td>
</tr>
</tbody>
</table>

3.2. Electrical Properties. Figure 3 shows electrical properties
from Hall effect measurements in the Van der Pauw geo-
metry for ZnO and Si-ZnO thin films before and after anneal-
ing. N-type conductivity properties are cruised into all
conditions of the films.

Carrier concentration increased from 0.02 x 10^20 to
3.51 x 10^20 and 0.010 x 10^20 to 2.94 x 10^20 cm^-1 as Si-
doping concentration increased, whereas Hall mobility
reduced from 6.99 to 2.18 and 11.36 to 4.99 cm^2/Vs for
as-deposited and annealed samples, respectively, due to
increased charge carrier scattering probability. Carrier
mobility behavior can be further described by investigation
the direct relationship with carrier concentration.

Hall mobility for metal oxide increases with carrier
concentration is generally opposite to that for Si-based
crystalline material. This conduction mechanism is known
as percolation conduction and helps charge carriers to move
in the conduction band by lowering the barrier height [22].
However, increasing mobility is ultimately restricted by
another barrier, i.e., ionized impurity scattering [23]. Thus,
reduced mobility despite increased carrier concentration
from Si doping indicates these films have highly ionized
scattering probability. Therefore, increased charge carrier
concentration and internal defects, such as V_{O}, could limit
film mobility despite increase carrier concentration from Si
doping. These internal defects are discussed in more details
in the subsequent XPS section.

Resistivity reduced from 6.15 x 10^{-1} to 0.28 x 10^{-1} and
25.68 x 10^{-1} to 12.49 x 10^{-1} cm for as-deposited and
annealed samples, respectively.

Electrical resistivity (i.e., conductivity) within thin films
reduces in proportion to the product of mobility and carrier
concentration:

\[ \frac{1}{\rho} = \sigma = ne\mu, \]

where \( \rho \), \( \sigma \), \( n \), \( e \), and \( \mu \) are the resistivity, conductivity, carrier
concentration, electron charge, and Hall mobility, respectively.

Electrical properties also improved after annealing, exhi-
biting reduced carrier concentration and increased mobility.
Thermal energy delivered into the films during annealing helps atoms migrate to appropriate lattice positions, as discussed in the XRD section. Thus, electron donation properties are lost due to oxygen vacancies which are being filled with incoming oxygen [24]. Therefore, thin film electrical properties were improved by both Si doping and oxygen annealing; hence, Si dopant was stably activated in annealed samples.

3.3. XPS Results. Figure 4 shows XPS spectra to investigate additional phase formation, Si cation valence state, and O chemical states with increasing Si-doping concentration in ZnO and Si-ZnO films. Carbon (C) 1s at 284.5 eV was applied to compensate for charging effects in all spectra [25]. Figures 4(a) and 4(b) confirm Zn 2p binding energy = 1021.08 ± 0.1 and 1044.13 ± 0.1 eV for Zn 2p_{3/2} and Zn 2p_{1/2} peaks, respectively, which closely match with the previous study (1021.8 ± 0.5 and 1045.0 ± 0.5 eV, respectively) [26]. Also, energy difference for spin-orbital splitting between Zn 2p_{3/2} and Zn 2p_{1/2} remained constant at 23.1 eV for both ZnO and Si-ZnO, confirming that Si was stably doped in ZnO without generating secondary phase artifacts, such as zinc silicates (e.g., Zn_{x}Si_{y}O_{z} : Zn 2p_{3/2}−1023.0 ± 0.5 eV) [27].

Table 2: Optimized parameters for primitive ZnO and Si-ZnO cells with different Si charge states.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Lattice parameter (Å)</th>
<th>Angle (deg.)</th>
<th>d (Å)</th>
<th>Cell volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>c</td>
<td>A</td>
<td>c</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.248</td>
<td>5.228</td>
<td>90.000</td>
<td>120.000</td>
</tr>
<tr>
<td>Si-ZnO (0) : Si^{2+}</td>
<td>3.262</td>
<td>5.210</td>
<td>90.000</td>
<td>120.000</td>
</tr>
<tr>
<td>Si-ZnO (+1) : Si^{3+}</td>
<td>3.214</td>
<td>5.127</td>
<td>90.000</td>
<td>120.000</td>
</tr>
<tr>
<td>Si-ZnO (+2) : Si^{4+}</td>
<td>3.169</td>
<td>5.039</td>
<td>90.000</td>
<td>120.000</td>
</tr>
</tbody>
</table>
Figures 4(c) and 4(d) show Si 2p XPS spectra for Si-ZnO thin films. Si 2p peak intensity increased as Si precursor pulse cycles increased. However, Si concentration is quite small compared with previous reports, remaining about 2 at% for Si-1/10, as shown in Table 3. This low doping concentration was attributed to low decomposition rate for Si-H species in the Si source precursor (TDMAS) due to low substrate temperature. Burton et al. confirmed that SiO$_2$ growth rate using this precursor depends on the substrate temperature [28], suggesting that these Si-H species could be fully decomposed using higher reaction temperatures and/or more oxidant agents. This outcome was confirmed by comparing with Yuan results in Ref. [20], which achieved higher Si dopant concentration than the current study due to higher substrate temperature (300°C) and increased oxidant precursor (H$_2$O$_2$). Since the highest intensity is the Si$^{3+}$ state in this research, Si dopant mainly donates electrons into the conduction band in form of Si$^{3+}$ rather than Si$^{2+}$ or Si$^{4+}$. Previous studies have also shown that Si mainly replaces Zn sites in Si$^{3+}$ states and hence only contributes one electron to the conductivity [19, 30]. Therefore, the most defect equation for Si substitution into Zn site could be expressed as:

\[ \text{Zn}^{2+} + \text{Si}^{3+} \rightarrow \text{Zn}^{2+}_\text{Si} + e^- . \]  

The Si 2p core level could be deconvoluted into three subordinate chemical states corresponding to Si$^{3+}$ (103.2 eV; SiO$_2$), Si$^{3+}$ (102.1 eV; Si$_2$O$_3$), and Si$^{2+}$ (101.0 eV; SiO), respectively [29]. Since the highest intensity is the Si$^{3+}$ state in this research, Si dopant mainly donates electrons into the conduction band in form of Si$^{3+}$ rather than Si$^{2+}$ or Si$^{4+}$. Previous studies have also shown that Si mainly replaces Zn sites in Si$^{3+}$ states and hence only contributes one electron to the conductivity [19, 30]. Therefore, the most defect equation for Si substitution into Zn site could be expressed as:

\[ \text{Zn}^{2+} + \text{Si}^{3+} \rightarrow \text{Zn}^{2+}_\text{Si} + e^- . \]  

Figures 4(e) and 4(f) show O 1s spectra for ZnO and Si-ZnO thin films before and after annealing. Chemical states for the O 1s peak could be categorized into three groups of O$^\circ$ in Zn-O (O$_{\text{f}}$: 530 ± 0.3 eV); oxygen vacancies, i.e., $V_O$
Figure 4: X-ray photoelectron spectroscopy (XPS) spectra for ZnO and Si-ZnO films: (a) Zn 2p for as-dep., (b) Zn 2p for annealed, (c) Si 2p for as-dep., (d) Si 2p for annealed, (e) O 1s for as-dep., and (f) O 1s for annealed samples.

Table 3: Si concentration and areal ratio for O 1s constituents O_{II}/O_{I} in ZnO and Si-ZnO in as-deposited (as-dep.) and annealed (anneal) samples.

<table>
<thead>
<tr>
<th>Group</th>
<th>Condition</th>
<th>Cycle ratio</th>
<th>As-dep. Si (at%)</th>
<th>Anneal Si (at%)</th>
<th>O_{II}/O_{I} As-dep.</th>
<th>O_{II}/O_{I} Anneal</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-dep</td>
<td>ZnO</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Si-ZnO</td>
<td>Si-1/50</td>
<td>0.62%</td>
<td>0.78%</td>
<td>13.09%</td>
<td>11.47%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si-1/40</td>
<td>1.22%</td>
<td>1.16%</td>
<td>14.41%</td>
<td>9.32%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si-1/30</td>
<td>1.35%</td>
<td>1.34%</td>
<td>16.41%</td>
<td>15.25%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si-1/20</td>
<td>1.40%</td>
<td>1.32%</td>
<td>17.66%</td>
<td>12.15%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si-1/10</td>
<td>1.68%</td>
<td>1.53%</td>
<td>21.30%</td>
<td>19.27%</td>
</tr>
</tbody>
</table>
(OII: 531.0 ± 0.3 eV); and carbon contamination or hydrated oxides (OIII: 531.9 ± 0.3 eV), respectively [30]. Table 3 summarizes relative peak ratios for OII/OI.

The ratio for OII/OI chemical states (i.e., VO ratio) for the annealed samples is lower than that of as-dep. samples. It means that VO began to be filled by oxygen atoms outside the films during annealing process. Previous studies have shown that higher oxygen ambient pressure reduces VO when ZnO thin films deposited using metal-organic chemical vapor deposition (MO-CVD) [31]. However, OII/OI ratio changed from 13.09 to 25.13% and 11.47 to 19.27% for as-dep. and annealed samples with increasing Si-doping concentration, respectively, which indicates that VO increased. This means that Si ions combine with O of the Zn-O lattice to form SiO2, thereby generating Vo around the Zn atoms. Previous study reported that SiO2 was created at the ZnO expense as SiOx and ZnO combination, which becomes oxygen-deficient in Si-ZnO thin films [32]. These results were attributed to free energy differences between SiOx and ZnO. Si atoms can be easily thermally oxidized to SiO2 because the free energy for SiO formation at ~300 K (GO ≈ -304 kcal/mol) is much lower than for the ZnO layer (GO ≈ -161 kcal/mol) [33, 34]. Therefore, SiO2 is relatively more stable than zinc metal oxide [35]. Figure S2 (SI) shows overlapped normalized O 1s spectra for all conditions to further clarify chemical state for related Si-O compounds. Chemical states for Si-O compounds were investigated with SiO2 (SiI: 532.5 eV) and SiOx (SiI: 531.7 eV) [36]. OII, SI, and SiII properties increased with increasing Si-doping concentration for both as-dep. and annealed samples. This result confirms that Si-ZnO thin films promoted VO generation at Zn-O bond expense and subsequently generated SiO2 compounds. Since SiI intensity exceeds that for SiI, Si ionization states more dominant to Si3+ (SiO2) than Si4+ (SiO2). Thus, Si functions more as an electron donor than SiO2 insulator form. Therefore, defects for electron donation to oxygen vacancies after Si doping can be expressed as

\[
\text{O}^{2-} + \text{Si}^{3+} \rightarrow \text{SiO}_2 + \text{V}_0 + e^- .
\]  

(5)

Therefore, although Si dopant is widely acknowledged to be a multidonor, in this case, it mainly donates a single electron in the Si3+ form from Zn sites (Si-Zn). Consequently, oxygen vacancies (VO) are formed by consuming lattice oxygen in ZnO.

3.4. Optical Properties. Figure S3 (SI) shows UV-vis transmittance spectra for the Si-ZnO thin films before and after annealing. Average transmittance in the visible range (400 – 800 nm) = 79.89%, 80.21%, 80.46%, 80.38%, 81.61%, and 82.74% for ZnO, Si-1/50, 1/40, 1/30, 1/20, and 1/10 as-dep.; and 84.75%, 84.41%, 84.41%, 83.95%, 85.12%, and 86.14% for annealed samples, respectively, with the absorption edge between 300 and 400 nm. Previous studies have reported similar transmittance results, as summarized in Table S1 (SI) [37, 38]. These transmittances are sufficient for various commercial products such as LEDs, liquid crystal devices, touch screens, and optical windows for photovoltaic applications [4, 39, 40]. Although the spectra profile changed slightly with Si-doping level, no significant transmittance changes occurred. However, transmittance increased after annealing compared with as-dep. (average = 80.88 ± 1.08% and 84.81 ± 0.76%, respectively), due to enhanced crystallinity, as shown in XRD analysis (Section 3.1) [41].

Figures 5(a) and 5(b) show the optical band gaps for as-dep. and annealed samples. The Tauc’s equation expresses the relationship between the absorption edge and the optical band gap as follows [42]:

\[
a h v^n = C (h v - E_g),
\]  

where n = 2 for direct band gap materials, C is a constant, hv is photon energy, and α is the absorption coefficient derived from the Beer-Lambert law [43]:

\[
a = \frac{1}{t} \cdot \ln \left( \frac{1}{T_r} \right),
\]  

where t and Tr are thin-film thickness and transmittance, respectively. Thin-film direct band gap characteristics were calculated from the (ahv)2 wrt hv plot, extrapolating the linear region fit to the intercept.

The interband absorption edge from 300 to 400 nm shifted to higher energy (blue shift) as Si-doping concentration increased, indicating that Si doping widened the optical bandgap in the films, which can be attributed to the BM effect [19, 20, 30, 44]. Through the BM effect, the conduction band minimum gradually filled as the Fermi level increased into the conduction band, preventing low-energy transitions and increasing the optical bandgap.

Figure S4 (SI) shows that calculated optical bandgap monotonically increased from 3.173 to 3.174, 3.177, 3.198, 3.246, and 3.322 eV for Si-1/50, Si-1/40, Si-1/30, Si-1/20, and Si-1/10 as-dep. and 3.167, 3.169, 3.172, 3.174, and 3.183 eV for annealed samples, respectively. Thus, the calculated optical bandgap and their increment rate in the annealed samples are lower than in the as-dep. samples. This phenomenon could be due to interactions between two mechanisms:

(1) Decrease of band gap of thin film by the heat treatment

(2) Increase of band gap of thin films by the BM effect (i.e., Si doping)

Generally, at a higher temperature, the crystallites in films may agglomerate, causing band gaps to shrink [45]. These band gap tailoring may be a result of quantum confinement effects, which are correlated with the relative grain size [46]. However, the BM effect from Si doping induces bandgap widening. The BM effect slightly increases the band gap with Si-doping concentration, whereas bandgap is reduced by annealing. Thus, optical bandgap behavior for these samples was mostly affected by quantum confinement
rather than BM effects. Similar results have been reported previously: Sengupta et al. found the bandgap grew as Al-ZnO concentration increased for the same annealing temperature, but bandgap reduced with increasing heat treatment temperature at the same dopant concentration [47]. Irimpan et al. showed that the optical band for ZnO thin films reduced with increasing annealing temperature [48].

3.5. Photoluminescence. Figures 5(c) and 5(d) show PL spectra for ZnO and Si-ZnO thin films before and after annealing. The films generally exhibit two significant peaks in the visible region: one high intensity PL peak at 382 nm (near band edge, NBE), and another broad emission band around 500 nm (deep level emission, DLE), due to $V_O$ and/or $Zn_i$ in the ZnO crystal, respectively [49, 50].

Annealed samples initially exhibit higher NBE peaks than as-dep. samples, since film crystalline quality influences NBE emission, implying that the crystallinity of the annealed films have improved [51]. However, the NBE peak reduced with increasing Si-doping concentration because thin film crystallinity reduced with increasing Si ions in the ZnO crystal lattice [20]. Also, the BM effect could explain the NBE shift toward shorter wavelengths [52]. These results are consistent with XRD and optical results, discussed in Sections 3.1 and 3.4, respectively.

Figures 5(a) and (b) (SI) show relative peak intensity $I_{rel}$ to help confirm DLE effects for Si doping and annealing [51, 53]:

$$I_{rel} = \frac{I_{DLE}}{I_{NBE}},$$

Figure 5: Tauc's plots for (a) as-dep., and (b) annealed samples and photoluminescence (PL) spectra for (c) as-dep., and (d) annealed samples.
where $I_{\text{DLE}}$ and $I_{\text{NBE}}$ are DLE and NBE emission intensities, respectively. The relative peak strength close to the green emission range increased with Si-doping concentration, hence $V_O$ increased with increasing Si doping. However, the increase rate for $V_O$ in annealed samples was less than for as-dep. samples, which is confirming that the competition between increased $V_O$ due to Si doping and reduced $V_O$ due to oxygen annealing.

### 3.6. Device Properties.

Figures 1(a) and 1(b) show layered and top views for the fabricated TFT using a bottom-gate (BG) structure with heavily doped p-type Si substrates as a common-gate electrode and 100 nm thermally grown SiO$_2$ as a gate insulator. TFT featured with $W/L$ ratio = 100/5 was used for characterization purposes. TFTs' performance parameters were determined using the standard MOSFET equation [54]:

$$I_{ds} = \frac{W}{2L} \mu_{\text{sat}} C_{\text{ox}} (V_{gs} - V_{th})^2,$$

where $W$, $L$, $C_{\text{ox}}$, and $V_{gs}$ are channel layer width and length, gate oxide capacitance per unit area, and gate-source voltage, respectively. $I_{\text{on}}$ and $I_{\text{off}}$ denote the on and off-state currents, respectively. $V_{th}$ is the threshold voltage. $\mu_{\text{sat}}$ is the saturation mobility.

#### Table 4: Extracted device parameters from annealed ZnO and Si-ZnO samples with various Si concentrations for the current and previous studies.

<table>
<thead>
<tr>
<th>Condition</th>
<th>$V_{th}$ [V]</th>
<th>$\mu_{\text{FE}}$ [cm$^2$/V s]</th>
<th>SS [V/decade]</th>
<th>$I_{\text{on}} / I_{\text{off}}$</th>
<th>$D_{\text{n, max}}$ [cm$^{-2}$ eV$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>18.91</td>
<td>1.72</td>
<td>6.63</td>
<td>$7.22E+05$</td>
<td>$2.42E+13$</td>
</tr>
<tr>
<td>Si-1/50</td>
<td>15.61</td>
<td>1.36</td>
<td>4.01</td>
<td>$1.39E+05$</td>
<td>$1.46E+13$</td>
</tr>
<tr>
<td>Si-1/40</td>
<td>10.36</td>
<td>2.55</td>
<td>2.68</td>
<td>$8.82E+05$</td>
<td>$9.66E+12$</td>
</tr>
<tr>
<td>Si-1/30</td>
<td>7.89</td>
<td>2.61</td>
<td>2.16</td>
<td>$1.39E+06$</td>
<td>$7.74E+12$</td>
</tr>
<tr>
<td>Si-1/20</td>
<td>3.44</td>
<td>5.22</td>
<td>1.70</td>
<td>$4.14E+05$</td>
<td>$6.05E+12$</td>
</tr>
<tr>
<td>Si-1/10</td>
<td>0.68</td>
<td>2.91</td>
<td>0.67</td>
<td>$7.00E+05$</td>
<td>$2.25E+12$</td>
</tr>
<tr>
<td>Lee et. al</td>
<td>0.80</td>
<td>0.70</td>
<td>0.28</td>
<td>$1.66E+07$</td>
<td>—</td>
</tr>
<tr>
<td>Liu et. al</td>
<td>18.50</td>
<td>1.02</td>
<td>2.6</td>
<td>$4.00E+07$</td>
<td>—</td>
</tr>
<tr>
<td>Yang et. al</td>
<td>3.40</td>
<td>5.10</td>
<td>0.60</td>
<td>$3.20E+06$</td>
<td>$1.90E+12$</td>
</tr>
</tbody>
</table>

#### Figure 6: Transfer curves for ZnO thin-film transistors with increasing thermal treatment time oxygen atmosphere: (a) as-dep., (b) 0.5 hour at 300°C, (c) 1 hour at 300°C, and (d) 1 hour at 400°C.
respectively. Subthreshold swing (SS) was calculated as follows [55]:

$$\text{SS} = \left( \frac{d \log (I_{ds})}{dV_{gs}} \right)^{-1}, \quad (10)$$

at the steepest point of the transfer slope. Table 4 shows extracted TFT performance parameters for different doping levels. The derived values from this study are comparable with previous study results [56–58].

Figures 6(a)–6(d) show ZnO TFT transfer curves using annealed samples, for gate voltage $V_{gs} = -50$ to $+50$ V with drain voltage $V_{ds} = 0.5$ V. The device made by as-dep. samples (Figure 6(a)) showed a horizontal transfer curve of the metallic properties (i.e., no device characteristics) due to its relative highly conductivity in the channel layer allowing better electrons flow to traverse the source and drain. $I_{off}$ is related to channel layer conductivity [59]:

$$I_{off} = \frac{\sigma W}{L} V_{ds} t_{ch}, \quad (11)$$

where $\sigma$ is electrical conductivity for the channel layer and $t_{ch}$ is the active layer thickness. Calculated conductivity from Hall measurements reduced from 1.63 S/cm for as-dep. sample to 0.39 S/cm for annealed sample after the annealing treatment. The reduced conductivity decreased $I_{off}$, confirming the device’s characteristics. The final device achieved $n$-channel enhancement, as evidenced by the requirement for positive gate voltage to induce a conducting channel [60].

Table 4 shows that the device threshold voltage ($V_{th}$) decreased with increasing Si doping from 18.91 to 0.68 V. The donated electron from Si tail states contributes to the device current with increasing Si-doping concentration [61]. Furthermore, the $V_O$ induced from Si doping generated more free electrons, which also contribute to the device current. The device’s field effect mobility ($\mu_{FE}$) improved from 1.72 to 5.22 cm$^2$/V·s until the Si-1/20 doping condition and decreased back to 2.91 cm$^2$/V·s in the Si-1/10 condition. As already mentioned, it is well known that the charge mobility for metal oxide devices increases with increasing carrier concentration. As the $E_F$ of the thin film is uplifted into the conduction band due to the BM effect by Si doping, the energy barrier height existing in the conduction band is lowered, and the mobility of electrons in the band is increased without the scattering between the energy barriers, which can be attributed to the percolation conduction [62]. That is, the additional electrons from the subgap state as $\text{Si}_{2\alpha}$ and $V_{O}^{2+}$ with increasing Si doping elevated the device current, and finally, the $V_{th}$ decreased, and the $\mu_{FE}$ increased. However, as you can see in Si-1/10 condition, the increase in mobility is finally limited by ionized impurity scattering [23, 63].

Figure 7 shows transfer curves for TFTs fabricated from annealed ZnO and Si-ZnO (1/50, 1/40, 1/30, 1/20, and 1/10) samples.
films. The subthreshold slope becomes steeper with increasing Si doping, i.e., subthreshold swing (SS) reduced. The small swing value is important for the device in terms of power and energy saving, which means that the device can turn on faster [64]. The interfacial trap density ($D_{it}$) may be calculated using SS from the following equation [65]:

$$D_{it} = \left( \frac{SS\log(e)}{k_B T/q} - 1 \right) \frac{C}{q}, \quad (12)$$

where $e$ is the natural constant, $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, $q$ is the electronic charge, and $C$ is the insulator capacitance per unit area, respectively. The calculated $D_{it}$ values were shown in Table 4. It can be seen that the interfacial trap density was effectively reduced. For further verification of reduction for interfacial trap density, the hysteresis of the transfer curves was measured under gate voltage sweeping from -50 V to 50 V back and forth for ZnO and Si-ZnO 1/10 cases, which is shown in Figure S6 (SI). The large difference of hysteresis around the subthreshold region in ZnO indicates the high trap density between the insulator and active layer, while it is suppressed in Si-ZnO 1/10, which means that the device drives faster and has an energy-saving effect [66].

Figure 8 shows the energy band diagram with BM effect in the channel/dielectric interface for Si-ZnO TFTs. The density of states ($g(E)$) and Fermi-Dirac distribution ($f_F(E)$) relationship can be expressed as follows [54]:

$$N(E) = f_F(E) = \frac{1}{1 + \exp ((E_{CBE} - E)/k_B T)}, \quad (13)$$

where $N(E)$, $E_{CBE}$, $E_F$, $k_B$, and $T$ are the distributed electron count, conduction band edge, Fermi energy, Boltzmann’s constant, and absolute temperature, respectively. Thus, carrier concentration is dependent on ($E_{CBE}$-$E_F$), where smaller difference improves concentration up to saturation ($E_{CBE} \ll E_F$). This effect is similar to BM effect derived from Si doping, i.e., since the Si tail state forms under the conduction band edge, continually increasing carrier concentration will promote $E_F$ into the conduction band at the gamma ($\Gamma$) position in the reciprocal lattice for direct semiconductors. Therefore, $E_F$ lies above the conduction band [67]. The device is accumulated with electrons when the bottom of the conduction band edge is filled with charge carriers. These accumulated electrons contribute to $I_{on}$ and induce increased $\mu_{FE}$, followed by negative $V_{th}$ shift applying the gate voltage.

4. Conclusion

This study investigated fabricated transistors employing ZnO and Si-ZnO thin films produced with ALD and doping influences after annealing. XRD scans confirmed that the ZnO films all contained hexagonal wurtzite structures, with no preferred orientation change for Si doping, and crystallinity improved with annealing. Si is a multivalence donor and hence can exist in various oxidation states, including Si$^{4+}$, Si$^{3+}$, and Si$^{2+}$, but this study confirmed that it primarily occurs as Si$^{3+}$, which donates one electron to the matrix. Si doping also generated $V_O$ in the thin film, resulting in donating one electron due to environmental thermal stress. These increased charge carrier concentrations induced the BM effect. Consequently, Si achieves superior electron donation efficiency compared with other dopants. However, optical band gap in annealed Si-doped ZnO is narrowed due to quantum confinement. This study confirmed that these band gap behaviors could be explained by interactions between bandgap narrowing from annealing and widening from BM effects. These results are strongly consistent with many previous Hall, XPS, UV-vis, and PL investigations. Optimized devices were operated as an enhancement mode, and the improved device parameters from the reduced interfacial trap density and the increased $\mu_{FE}$ by the percolation conduction would help to realize the low power and energy saving devices/applications. Advanced multivalence material research and commercialization, including Si and indium-free alternatives, are expected to result from the outcomes identified in this study.

Data Availability

Data will be made available on request.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
Acknowledgments

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Supplementary Materials

Supplementary information for this article includes theory and calculation using DFT; O 1s XPS spectra, UV-vis transmittance, calculated optical bandgap, and $I_{DLE}/I_{NBE}$ ratio from PL spectra for as-deposited and after annealed Si-doped ZnO samples; sweeping curves of transfer characteristics for ZnO and Si-ZnO samples; and comparison results of the efficient optical properties with previous results. (Supplementary Materials)

References

[27] Y. Liu, J. M. Shen, Z. L. Chen, L. Yang, Y. Liu, and Y. Han, “Effects of amorphous-zinc-silicate-catalyzed ozonation on...


