Realization of \(p\)-type ZnAgO:N thin films on flexible polyimide substrates through co-sputtering for wearable thermoelectric applications

Cite as: AIP Advances 10, 075201 (2020); https://doi.org/10.1063/1.5140618
Submitted: 29 November 2019 . Accepted: 11 June 2020 . Published Online: 01 July 2020

Buil Jeon, Chongsei Yoon, and Giwan Yoon

COLLECTIONS

Paper published as part of the special topic on Chemical Physics, Energy, Fluids and Plasmas, Materials Science and Mathematical Physics

ARTICLES YOU MAY BE INTERESTED IN

Effect of post-deposition treatment on electrical properties of solution-processed a-IGZO Schottky diodes
AIP Advances 10, 075104 (2020); https://doi.org/10.1063/5.0005970

The role of hafnium acetylacetonate buffer layer on the performance of lead halide perovskite solar cells derived from dehydrated lead acetate as Pb source
AIP Advances 10, 075006 (2020); https://doi.org/10.1063/5.0012646

Thermoelectric transport control with metamaterial composites
Journal of Applied Physics 128, 025104 (2020); https://doi.org/10.1063/5.0004037

NEW!
Sign up for topic alerts
New articles delivered to your inbox
Realization of $p$-type ZnAgO:N thin films on flexible polyimide substrates through co-sputtering for wearable thermoelectric applications

Cite as: AIP Advances 10, 075201 (2020); doi: 10.1063/1.5140618
Submitted: 29 November 2019 • Accepted: 11 June 2020 •
Published Online: 1 July 2020

Buil Jeon, Chongsei Yoon, and Giwan Yoon

AFFILIATIONS
School of Electrical Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, South Korea

Author to whom correspondence should be addressed: gwyoon@kaist.ac.kr

ABSTRACT

In this study, we deposited a series of Ag and N co-doped ZnO thin films (ZnAgO:N) with different Ag atomic percentage (at. %) ratios on flexible polyimide (PI) substrates to realize $p$-type ZnO-based thin films for wearable thermoelectric applications by in situ co-sputtering of ZnO and Ag by RF and DC magnetron sputtering in a mixture of Ar and N$_2$O gases. To evaluate the thermoelectric performance of these ZnAgO:N thin films, we measured the Seebeck coefficient $S$ and electrical conductivity $\sigma$ of the thin films with various Ag at. % ratios and calculated the power factor $S^2\sigma$. These measurements confirmed that the co-doping of Ag and N into ZnO is an effective method for fabricating $p$-type ZnAgO:N thin films with $\sigma$ in the range of about $10^5$–$3.3 \times 10^6$ S/m, as a function of Ag at. % ratio on the flexible PI substrates. In addition, the presence of an optimal Ag at % ratio that leads to a maximum $S^2\sigma$ for the $p$-type ZnAgO:N thin films was observed. Raman spectroscopy and x-ray photoelectron spectroscopy revealed that the $p$-type conductivity in ZnAgO:N thin films originates from the acceptors Ag$_{\text{Zn}}$ and N$_{\text{O}}$ formed by the co-dopants Ag and N. As a result, the $S$ and $\sigma$ of the $p$-type ZnAgO:N thin films were investigated to be affected significantly by the acceptors and defects formed by the Ag and N co-dopants in the thin films. The influence of Ag$_{\text{Zn}}$ and N$_{\text{O}}$ on the appearance of the $p$-type conductivity in ZnAgO:N thin films and $S$ and $\sigma$ of the thin films was intensively studied.

© 2020 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5140618

Zinc oxide (ZnO) is frequently used to fabricate thin-film-based devices because of its attractive properties such as superior biocompatibility, a direct band gap of $\sim$3.4 eV, and appropriate electrical conductivity. However, fabricating ZnO thin-film-based devices remains challenging because intrinsic donors, such as zinc interstitials (Zn$_{\text{i}}$) and oxygen vacancies (V$_{\text{O}}$), make it difficult to deposit $p$-type ZnO thin films. Therefore, major effort has been expended to find a way to deposit $p$-type ZnO thin films. To resolve this issue, diverse techniques have been used to deposit $p$-type ZnO thin films using dopants.

Given its atomic size and electrical role in ZnO, N has been considered as a substituting element for O. Nevertheless, $p$-type conductivity in N-doped ZnO remains uncertain because N-related acceptors are easily compensated by intrinsic donors in ZnO. The group IB elements, such as Cu and Ag, have also been considered as dopants because of their low self-compensation, but $p$-type ZnO thin films are difficult to be fabricated because Cu tends to form deep acceptors and Ag is an amphoteric dopant in ZnO. Meanwhile, after Yamamoto et al. suggested that co-doping of donor and acceptor dopants could make shallow acceptors in ZnO, various $p$-type ZnO thin films have been deposited by co-doping of donor and acceptor dopants, such as Ga–N and Al–N.

In this study, the $p$-type Ag and N co-doped ZnO thin film ZnAgO:N were deposited on flexible polyimide (PI) substrates for thermoelectric applications by in situ co-sputtering of ZnO and Ag in a mixture of Ar and N$_2$O gases for N doping into thin films.
The Seebeck coefficient $S$ and electrical conductivity $\sigma$ for these films with varying Ag atomic percentage (at. %) ratio were measured. The results indicate that the co-doping of Ag and N into ZnO is effective for depositing $p$-type ZnAgO:N thin films with various electrical characteristics depending on the Ag at. % ratios. These thin films were analyzyed by using various analytic techniques to investigate their electrical characteristics.

As detailed in Table I, ZnAgO:N thin films of varying Ag at. % ratios were deposited by co-sputtering of ZnO and Ag targets by RF and DC magnetron sputtering in a mixture of Ar and N$_2$O gases. The DC sputtering power for Ag was adjusted to control the Ag at. % ratio. The RF sputtering power for ZnO was held constant, as was the Ar/N$_2$O ratio. The deposition temperature ranged from 300 K to 310 K. After deposition, the thin films were post-annealed for 4 h in N$_2$ at 1 atm, 573 K. Ag thin-films were formed on these films as electrodes by electron-beam evaporation. Table I lists the Ag and N at. % ratios of ZnAgO:N thin films along with the ratio of DC sputtering power for Ag to RF sputtering power for ZnO (power ratio). Although the Ag at. % ratio is proportional to the power ratio, the N at. % ratio varies irregularly regardless of the power ratio.

Figures 1(a)–1(c) plot $S$, $\sigma$, and power factor $S^2\sigma$ for ZnAgO:N thin films as functions of the Ag at. % ratio at the hot-side temperature of these films. The $S$ of the ZnAgO:N thin films was measured under a lateral temperature gradient (Fig. S1, supplementary material) and the corresponding $\sigma$ was measured by using the van der Pauw method. As shown in Fig. 1(a), $S$ was measured only for thin films D3-2–D7-2 because the other thin films were too resistive to measure $S$. Likewise, $\sigma$ for the ZnAgO:N thin films was also measured only for D3-2–D7-2, as shown in Fig. 1(b). Although the positive $S$ for D3-2–D7-2 confirms $p$-type semiconductivity (Fig. S2, supplementary material), $S$ decreases as the Ag at. % ratio increases. Meanwhile, $\sigma$ increases until the Ag at. % ratio reaches that of D5-2. Thus, the maximum $\sigma$ is $\sim 3.0 \times 10^6$ S/m obtained for D5-2. The opposite slope of $S$ and $\sigma$ as a function of Ag at. % ratio in the range of 0.132–0.307 reflects the fact that they are inversely proportional. In this range of Ag at. % ratio, $S'\sigma$ increases, as shown in Fig. 1(c). However, when the Ag at. % ratio exceeds 0.307, $S'\sigma$ decreases because $S$ and $\sigma$ decrease in that range of Ag at. % ratio.

### Table I

<table>
<thead>
<tr>
<th>Thin films</th>
<th>Power ratio</th>
<th>Ag at. % ratio</th>
<th>N at. % ratio</th>
<th>Post-annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1-1</td>
<td>0</td>
<td>0</td>
<td>0.034</td>
<td>x</td>
</tr>
<tr>
<td>D1-2</td>
<td></td>
<td></td>
<td></td>
<td>o</td>
</tr>
<tr>
<td>D2-1</td>
<td>0.031</td>
<td>0.101</td>
<td>0.072</td>
<td>x</td>
</tr>
<tr>
<td>D2-2</td>
<td></td>
<td></td>
<td></td>
<td>o</td>
</tr>
<tr>
<td>D3-1</td>
<td>0.056</td>
<td>0.132</td>
<td>0.033</td>
<td>x</td>
</tr>
<tr>
<td>D3-2</td>
<td></td>
<td></td>
<td></td>
<td>o</td>
</tr>
<tr>
<td>D4-1</td>
<td>0.075</td>
<td>0.221</td>
<td>0.044</td>
<td>x</td>
</tr>
<tr>
<td>D4-2</td>
<td></td>
<td></td>
<td></td>
<td>o</td>
</tr>
<tr>
<td>D5-1</td>
<td>0.094</td>
<td>0.307</td>
<td>0.064</td>
<td>x</td>
</tr>
<tr>
<td>D5-2</td>
<td></td>
<td></td>
<td></td>
<td>o</td>
</tr>
<tr>
<td>D6-1</td>
<td>0.113</td>
<td>0.404</td>
<td>0.064</td>
<td>x</td>
</tr>
<tr>
<td>D6-2</td>
<td></td>
<td></td>
<td></td>
<td>o</td>
</tr>
<tr>
<td>D7-1</td>
<td>0.131</td>
<td>0.489</td>
<td>0.057</td>
<td>x</td>
</tr>
<tr>
<td>D7-2</td>
<td></td>
<td></td>
<td></td>
<td>o</td>
</tr>
</tbody>
</table>
The transition to p-type ZnAgO:N thin films infers that the Ag in the annealed films plays a key role in the formation of acceptors, such as Ag$^{+}$ substitution for Zn$^{2+}$ (Ag$_{Zn}$) and N-ion substitution for O (No). The x-ray diffraction (XRD) spectra of the p-type thin films contain the peaks related to ZnO and Ag (Fig. S3, supplementary material).

The appearance of the p-type conductivity in annealed ZnAgO:N thin films confirms the feasibility of fabricating p-type ZnAgO:N thin films by co-doping with Ag and N. However, the cause of p-type conductivity in the thin films remains uncertain. Thus, ZnAgO:N thin films were analyzed by Raman spectroscopy to investigate the types of defects in the ZnAgO:N thin films.

The Raman spectra of non-annealed ZnAgO:N thin films reveal only a single peak near 520 cm$^{-1}$ whereas the Raman spectra of annealed ZnAgO:N thin films reveal peaks near 507 cm$^{-1}$ and 570 cm$^{-1}$, related to No and N$_{p}$, respectively. The Raman peak near 395 cm$^{-1}$ is more significant in D$_{7}$-2 than in D$_{6}$-2. The Raman peaks from N$_{p}$-type conductivity in D$_{6}$-2 and D$_{7}$-2 is less than that in D$_{5}$-2, which indicates that the decrease in $\sigma$ of D$_{6}$-2 and D$_{7}$-2 is caused by a decrease in the concentration of Ag$_{Zn}$. Furthermore, the noticeable decrease in the Raman peak near 507 cm$^{-1}$ of D$_{7}$-2 indicates that the decrease in $\sigma$ is more significant in D$_{7}$-2 than in D$_{6}$-2.

Unlike $\sigma$, S as a function of Ag at. % ratio decreases in p-type ZnAgO:N thin films. The decrease in $S$ for D$_{3}$-2–D$_{5}$-2 is due to the inverse proportionality between $S$ and $\sigma$. The further decrease in $S$ for D$_{6}$-2 and D$_{7}$-2 seems to be related to defect-induced distortions. The Raman peak near 570 cm$^{-1}$ indicates the presence of defects such as Zn$_{\text{vac}}$, V$_{O}$, and No in ZnO. The concentration of such defects would increase with increasing dopant concentration in these thin films, which means that distortions degrading the electrical characteristics of thin films could be formed by the defects. Moreover, the metallic Ag formed by the over-doping of Ag could degrade the doping efficiency of acceptors, thereby lowering $\sigma$ and $S$ further. Consequently, the decrease in $S$ for D$_{6}$-2 and D$_{7}$-2 is attributed to defects stemming from the over-doping of Ag.

By x-ray photoelectron spectroscopy (XPS), we investigated in detail how the acceptors affect electrical characteristics of ZnAgO:N thin films. Figures 3(a)–3(c) show the XPS spectra of Ag 3d, O 1s, and N 1s, respectively. The deconvolution of the O 1s spectrum of D$_{1}$-2 into three spectra reveals three types of O$^{2-}$ ions. The O$^{2-}$ ions surrounded by Zn$^{2+}$ correspond to the O 1s spectrum with a binding energy (BE) of $\sim$529.6 eV. The O$^{2-}$ ions in O-deficient regions (V$_{O}$) or bonded on the surface correspond to the O 1s spectra with a BE of $\sim$531.4 eV or 532.2 eV, respectively. The N 1s spectrum of D$_{1}$-2 looks like noise, which means that No is not present in this film. Therefore, D$_{1}$-2 is not the p-type.

The N 1s spectrum of D$_{2}$-2 is similar to that of D$_{1}$-2. Although the O 1s spectrum with a BE of $\sim$528.8 eV and the Ag 3d$_{5/2}$ spectrum with BEs of $\sim$367.2 eV and 367.4 eV indicate the presence of Ag–O bonds in D$_{2}$-2, this film is not likely to be p-type because most Ag ions in this film are in the +3 or +4 oxidation state.

The peak near 399.3 eV in the N 1s spectrum of D$_{3}$-2 implies the absence of No acceptors. However, the Ag 3d$_{5/2}$ spectrum deconvoluted into two spectra with BEs of $\sim$367.8 eV and 368.5 eV indicates the presence of Ag$_{Zn}$ and metallic Ag, respectively. The presence of Ag$_{Zn}$ acceptors is also confirmed by the O 1s spectra with BEs of $\sim$530.1 eV and 531.4 eV. Thus,
the appearance of $p$-type conductivity in D3-2 is caused by Ag$_{Zn}$ acceptors.

D4-2 has Ag $3d_{5/2}$ spectra with BEs of $\sim 367.6$ eV and 368.6 eV derived from Ag$_{Zn}$ and Ag, respectively, indicating the greater concentration of Ag$_{Zn}$ in D4-2 because the Ag $3d_{5/2}$ spectrum derived from Ag$_{Zn}$ is farther from that derived from Ag in D4-2 than in D3-2. The O 1$s$ spectra with BEs of $\sim 530.1$ eV and 531.4 eV in D4-2 support the presence of Ag$_{Zn}$, as does in D3-2. In addition, the peak derived from N$_0$ in Ag$_{Zn}$–N$_0$ bonds appears near 398.8 eV in the N 1$s$ spectrum. The BE of N 1$s$ electrons in Ag$_{Zn}$–N$_0$ bonds is greater than that in Zn–N$_0$ bonds because of the greater electronegativity of Ag than of Zn. However, the concentration of N$_0$ seems low because no Ag $3d$ spectrum derived from Ag$_{Zn}$–N$_0$ is observed. Thus, the enhanced $p$-type conductivity in D4-2 is due to the enhanced Ag$_{Zn}$ concentration and a small amount of N$_0$ in Ag$_{Zn}$–N$_0$ bonds.

Only the Ag $3d_{5/2}$ spectrum derived from Ag$_{Zn}$ appears at $\sim 367.5$ eV, farther from the BE of Ag, which means that the concentration of Ag$_{Zn}$ increases further in D5-2. Like in D4-2, the O 1$s$ spectrum indicates the presence of Ag$_{Zn}$ in D5-2. The peak with low intensity near 398.2 eV in the N 1$s$ spectrum of D5-2 indicates N$_0$ acceptors in Zn–N$_0$ bonds. Therefore, the largest $\sigma$ measured in D5-2 is attributed to the further enhanced Ag$_{Zn}$ concentration and N$_0$ in Zn–N$_0$ bonds.

However, the Ag$_{Zn}$ concentration in D6-2 and D7-2 is lower than that in D5-2 because the Ag $3d_{5/2}$ spectrum derived from Ag$_{Zn}$ shifts to slightly higher BE, $\sim 367.6$ eV. In addition, the Ag $3d_{5/2}$ spectrum with low intensity derived from Ag appears near 368.4 eV in both thin films. Thus, the doping efficiency of Ag$_{Zn}$ would be degraded by Ag. Moreover, the peak derived from N$_0$ in Zn–N$_0$ bonds is significantly blurred in D6-2 and D7-2, therefore, the concentration of N$_0$ in these films is lower than in D5-2. Accordingly, the decrease in $\sigma$ for D6-2 and D7-2 is attributed to the significantly decreased concentrations of Ag$_{Zn}$ and N$_0$.

In summary, the $p$-type ZnAgO:N with different Ag at.% ratios were deposited on flexible PI substrates by co-sputtering of ZnO and Ag in a mixture of Ar and N$_2$ gases. To evaluate their thermoelectric performance, the Seebeck coefficient and electrical conductivity of the $p$-type ZnAgO:N thin films were measured and their power factors were calculated. The $p$-type thin film D5-2 has the best thermoelectric performance in terms of $S^2\sigma$.

The $p$-type ZnAgO:N thin films were analyzed by Raman spectroscopy and XPS to investigate their $p$-type characteristics. The Raman spectroscopy and XPS spectra reveal that the $p$-type conductivity in ZnAgO:N thin films originates from the Ag$_{Zn}$ and N$_0$ formed by the co-dopants Ag and N, and S and $\sigma$ for these films are affected strongly by the Ag$_{Zn}$ and N$_0$ concentrations. However, over-doping of Ag may induce distortions and formation of metallic Ag, which degrade the electrical properties of these films.

Finally, the $p$-type ZnAgO:N thin films having moderate $\sigma$ on flexible PI substrates are expected to meet the demand for $p$-type thin films required to fabricate flexible or wearable thermoelectric thin-film devices.

The supplementary material includes a schematic diagram of the apparatus used to measure the Seebeck coefficient $S$, the graphs of thermoelectric voltages generated by the Al-doped ZnO thin film ($n$-type thin film) and $p$-type ZnAgO:N thin film D3-2, the XRD spectra of ZnAgO:N thin films, the XPS spectra of Ag 3$d$ for annealed ZnAgO:N thin films edited to compare the intensities of Ag 3$d_{5/2}$ spectra derived from Ag$_{Zn}$ acceptors, the three-dimensional graphs of $S$, $\sigma$, and $S^2\sigma$ for ZnAgO:N thin films plotted as a function of Ag at.% ratio for the hot-side temperature of the thin films, and
a table for the Hall effect measurement results for $\sigma$ of the $p$-type ZnAgO:N thin films.

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (Grant No. 2016R1D1A1B01007074).

**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**REFERENCES**