Boron and Aluminum Codoped ZnO Transparent Conducting Films with High Electrical Stability

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Abstract
We suggest boron (B) and aluminum (Al) codoped ZnO (BAZO) transparent conducting thin films with high electrical stability for photovoltaic applications. The resistivity of widely used Al-doped ZnO (AZO) film decreased slightly by B doping. Above all, the resistivity of BAZO (4.9 at. % boron) increased by less than 1.5 times, whereas that of reference AZO film increased by over than 8 times after thermal annealing in atmospheric air. The carrier concentration and Hall mobility were much less degraded in BAZO films. X-ray photoelectron spectroscopy analysis showed that the peak portion related with chemisorbed oxygen at 100 nm-inside of the film was suppressed in BAZO film compared with AZO film. The B atoms would restrain the oxygen permeation into the film, which made the process of oxygen chemisorption inactive.

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Transparent conducting oxide (TCO) has been widely used in optoelectronic applications such as thin film solar cells and flat panel displays. 1–4 TCO requires low resistivity (<10–4 Ω cm) and high transparency (>80%) for transparent electrodes. 5 In addition, the reliability of resistivity is important to sustain device performance. The films should be further improved to replace ITO because ITO shows significant change under oxidizing atmosphere. Therefore, the electrical stability of AZO thin films is still degraded after thermal annealing. The AZO film as a reference sample was sputtered with a DC power of 300 W, and the proposed BAZO films were deposited via co-sputtering both AZO (300 W) and the BZO target. The different RF powers of the BZO target were 60 W, 90 W, and 120 W to control the B concentration in the BAZO films.

Thickness of all films was approximately 250 nm, which was measured by a profilometer. The chemical composition of the films was analyzed using Auger electron spectroscopy (AES) with multiplex mode to obtain precise spectrum and atomic concentration of compositional elements. X-ray diffraction (XRD) with a 0–2θ scan (Cu Kα, wavelength = 1.54056 Å) analysis was carried out to analyze the structural characteristics of the films. Hall measurement with van der Pauw method was used to measure the Hall mobility, carrier concentration, and resistivity of the films. The chemical states at film surface and 100 nm-inside part of deposited films were analyzed by X-ray photoelectron spectroscopy (XPS).

Results and Discussion

Figure 1 shows the atomic concentration (%) of compositional elements in the AZO and BAZO films analyzed by AES analysis. The B content in the BAZO films was controlled by RF power on the BZO target. The inset graph in Fig. 1a indicates the B concentrations which were 1.0, 1.8, and 2.6 (at. %) with the increase of RF power on BZO target from 60 to 120 W. The relative B content [B/(Zn+Al+B)] in BAZO films were 1.9 at. % (60 W), 3.3 at. % (90 W), and 4.9 at. % (120 W), respectively. Fig. 1b exhibits the relative B/Al ratio with the increase of RF power on BZO target. The B/Al ratio in the BAZO films was increased, which resulted from the increase of B content because the RF power on BZO target was increased from 0 to 120 W during the fixed DC power (300 W) on AZO target. When the RF power on BZO target was increased up to 120 W, the incorporated B level was about 60% of the Al content.

To analyze the crystal orientation and structural grain size of the BAZO films, XRD analysis was performed as indicated in Fig. 2. The BAZO films exhibited the diffraction peak near 34.4°, which is the diffraction angle of ZnO (0002) peak. It means the crystal structure of AZO with hexagonal wurtzite was not changed by B addition. Considering that the only ZnO (0002) peaks were observed, the incorporated B atoms did not form other phases such as zinc borate, and the prepared BAZO films have a strong c-axis texture perpendicular to the substrates. The crystallite sizes of the films can be deduced by Scherrer formula, 12 which was exhibited as follows.

$$t = \frac{0.9 \lambda}{\Delta \theta \cdot \cos \theta_g} \quad [1]$$

where $t$ is the crystallite size, $\Delta \theta$ is the full width at half maximum (FWHM), $\theta_g$ is the Bragg angle. Applying the appropriate values...
The relative B content in the BAZO films was increased with the RF power on the BZO target. The data of AZO film was indicated the point with the RF power of 0 W. The relative B content in the BAZO films was observed in Fig. 2. The diffraction peak position of BAZO film (1.9 at. %) shifted to a higher diffraction angle with the further increase of B doping (3.3 at. %). It means that the incorporated B atoms exist in interstitial sites as well as in substitutional sites. The lattice expansion is enhanced by the excess interstitial B atoms, which can be confirmed by the increased interplanar d-spacing (2.602 Å and (0002) diffraction peak position shifted to a higher diffraction angle by the Bragg's law. This phenomenon can support the result of increased carrier concentration as discussed in Fig. 3. The substituted B ions in ZnO sites provide excess free electrons to the ZnO, and it increases carrier concentration. On the other hand, the diffraction peak position shifted slightly back to lower diffraction angle with the further increase of B doping (3.3–4.9 at. %). It means that the incorporated B atoms exist in interstitial sites as well as in substitutional sites. The lattice expansion is enhanced by the excess interstitial B atoms, which can be confirmed by the increased interplanar d-spacing (2.605–2.607 Å).

Figure 3. (Color online) The Resistivity, Hall mobility, and carrier concentration of AZO and BAZO films with various B content (1.9, 3.3, 4.9 at. %) analyzed by Hall measurement. The BAZO films have the resistivity of about 1.4–1.7 × 10^{-5} Ω · cm, which was slightly lower than that (1.8 × 10^{-5} Ω · cm) of AZO film. The small increase of carrier concentration was observed, and a relatively constant Hall mobility was measured with the increase of B doping in BAZO films. The initial electrical characteristics of BAZO films are not quite different from that of AZO film.

such as λ = 1.54056 Å (Cu Kα line), Δθ = 0.29–0.36, and θB = 17.1–17.2, the crystallite size t were estimated to about 23–28 nm, indicating that the crystallinity of BAZO films was similar to that of AZO film.

The positional shift of diffraction peaks with the increase of B content in the BAZO films was observed in Fig. 2. The diffraction peak position of BAZO film (1.9 at. %) shifted to a higher diffraction angle (34.44°) compared with that (34.32°) of AZO film. It implies that incorporated B ions mainly substituted the Zn ions. Because the ionic radius of B (0.074 nm) is smaller than that of Zn ions (0.074 nm), the interplanar d-spacing was decreased from 2.612 to 2.602 Å and (0002) diffraction peak position shifted to a higher diffraction angle by the Bragg’s law. This phenomenon can support the result of increased carrier concentration as discussed in Fig. 3. The substituted B ions in Zn sites provide excess free electrons to the ZnO, and it increases carrier concentration. On the other hand, the diffraction peak position shifted slightly back to lower diffraction angle with the further increase of B doping (3.3–4.9 at. %). It means that the incorporated B atoms exist in interstitial sites as well as in substitutional sites. The lattice expansion is enhanced by the excess interstitial B atoms, which can be confirmed by the increased interplanar d-spacing (2.605–2.607 Å).

Figure 3 exhibits the electrical properties of AZO and BAZO films with various B content. Overall, little changes were observed for electrical parameters such as electrical resistivity, Hall mobility, and carrier concentration when B doping was increased up to about 5 at. %.

Hall mobility and carrier concentration when B doping was increased up to about 5 at. %. The resistivity of AZO film decreased slightly from 1.8 × 10^{-5} to 1.4 × 10^{-5} Ω · cm with the increase of B doping from 0 to 1.9 at. %, thanks to the increase of carrier concentration rather than Hall mobility. The carrier concentration increased from 2.9 × 10^{20} to 3.5 × 10^{20}/cm^3, which indicates that some of the incorporated B atoms work as a donor and provide free carriers to the ZnO.14,16 With the increase of B doping up to about 5 at. %, the resistivity of BAZO films slightly increased from 1.4 × 10^{-3} (1.9 at. %) to 1.7 × 10^{-3} Ω · cm (4.9 at. %). However, it is hard to interpret that the amount of such variation is meaningful. A similar Hall mobility was also observed between AZO (12 cm^2/V · s) and BAZO films (~11.5–12.5 cm^2/V · s), consistent with the XRD results that the crystallite sizes were similar among the AZO and BAZO films. From the analysis above, it is thought that there were neither remarkable improvement nor...
To evaluate electrical stability, the as-deposited AZO and BAZO films were annealed in air ambient at 300°C. Figure 4 shows the Hall mobility, carrier concentration, and resistivity of the films as a function of annealing time. The resistivity of AZO film (4.9 at. %) slightly varied from $1.7 \times 10^{-3}$ to $2.4 \times 10^{-3}$ Ω·cm after annealing, whereas that of BAZO degraded considerably from $1.8 \times 10^{-3}$ to $1.5 \times 10^{-2}$ Ω·cm. The carrier concentration and Hall mobility of BAZO films also showed much less degradation compared with those of AZO film.

Degradation in the structural and electrical properties by small amount of B doping (≈4.9 at. %).

To evaluate electrical stability, the as-deposited AZO and BAZO films were annealed in air ambient at 300°C. Figure 4 shows the Hall mobility, carrier concentration, and resistivity of the films as a function of annealing time. The resistivity of AZO film increased significantly from $1.8 \times 10^{-3}$ to $1.5 \times 10^{-2}$ Ω·cm (over 8 times) with annealing for 4 hours due to decrease both Hall mobility and carrier concentration. A considerable decrease was observed in carrier concentration (from $2.9 \times 10^{20}$ to $1.0 \times 10^{20}$ /cm$^3$) and Hall mobility (from 12 to 3.8 cm$^2$/V·s). This degradation phenomenon of AZO was reported in the literature, and the cause of the degradation had been mainly known as the chemisorption of oxygen at the grain boundaries. Oxygen from the air was chemisorbed at surface and/or grain boundaries in the film. The diffusion of oxygen into the film decreased the carrier concentration by removing oxygen vacancies and Zn interstitials. In addition, the trapping of electrons to chemisorbed oxygen results in an increase in the barrier height at the grain boundaries, which decreases the Hall mobility.

In contrast to AZO films, however, the resistivity of BAZO films showed much less changes than that of AZO after annealing. The resistivity of BAZO film (4.9 at. %) increased slightly from $1.7 \times 10^{-3}$ to $2.4 \times 10^{-3}$ Ω·cm (≈1.5 times) after 4 hour annealing. The carrier concentration of BAZO (4.9 at. %) decreased from $3.2 \times 10^{20}$ to $2.3 \times 10^{20}$ /cm$^3$, whose variation is smaller than that of AZO film. In addition, the degradation of Hall mobility in BAZO films was considerably suppressed compared with AZO film. The Hall mobility of BAZO films was maintained at about 10−11.5 cm$^2$/V·s, which was quite different from that (3.8 cm$^2$/V·s) of AZO film. These results indicate that the proposed BAZO films are highly reliable against oxidizing ambient compared with AZO film.

Three possible factors are considered for supporting the electrical stability. First, it can be originated from film crystallinity. Films with high crystallinity have large grain sizes and they should have less grain boundaries, which reduces the permeation path of oxygen into the film. However, the XRD analysis showed that the AZO and BAZO films have similar crystalline structure and grain size. These results imply that the film crystallinity is not proper factor for achieving the electrical stability. Second, the increase of extrinsic donor B on substitutional sites of Zn can affect the stability of ZnO. The extrinsic doping of Al$^{3+}$ or B$^{3+}$ substituted Zn in ZnO can be a stable donor compared with native donors such as Zn interstitials and oxygen vacancies. Thus, extrinsic B dopant in substitution can enhance the stability of BAZO films. To examine this possibility in BAZO films, the concentration of activated and inactivated B atoms was estimated as indicated in Table I. The concentration of B and B atoms in the BAZO films was estimated by using a ZnO bulk density of 5.67 g/cm$^3$ and molar mass (81.38 g/mol). From the amount of Zn (4.19 × 10$^{20}$ atoms/cm$^3$), the amount of B in the BAZO films were approximately $7.96 \times 10^{20}$ (1.9 at. %), $1.38 \times 10^{21}$ (3.0 at. %), and $2.05 \times 10^{21}$ (4.9 at. %). Assuming that the increment (= nBAZO - nAZO) of the carrier concentration with B doping resulted from the substitution of B$^{3+}$ into Zn$^{2+}$ sites, the concentrations of the activated and inactivated B atoms were calculated. The activated B atoms from Hall measurement were $5.70 \times 10^{20}$ (1.9 at. %), $2.40 \times 10^{20}$ (3.0 at. %), and $3.40 \times 10^{20}$ /cm$^3$ (4.9 at. %). Thus, the inactivated B atoms were $7.39 \times 10^{20}$ (1.9 at. %), $1.34 \times 10^{21}$ (3.0 at. %), and $2.02 \times 10^{21}$ /cm$^3$ (4.9 at. %). Based on these estimations, the very small portion (1.7−7.2%) of B atoms was possibly activated as a substitution. According to this point of view, it seems unreliable that the stability is mainly originated from the effect of substituted B in our BAZO films.

Next, the third possibility is that the chemisorbed-oxygen permeation into film through defects such as grain boundaries can be restrained by B atoms. Fig. 5 exhibits the XPS results of annealed AZO and BAZO films of various B content (1.9, 3.3, 4.9 at. %). Table I. The concentrations of estimated B atoms, activated B atoms, and inactivated B atoms in the BAZO films with various B content (1.9, 3.3, 4.9 at. %).

<table>
<thead>
<tr>
<th>B content (at. %) in the BAZO films</th>
<th>Incorporated B atoms</th>
<th>Activated B atoms</th>
<th>Inactivated B atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9</td>
<td>$7.96 \times 10^{20}$</td>
<td>$5.70 \times 10^{19}$ (7.2%)</td>
<td>$7.39 \times 10^{20}$ (92.8%)</td>
</tr>
<tr>
<td>3.3</td>
<td>$1.38 \times 10^{21}$</td>
<td>$4.20 \times 10^{19}$ (3.0%)</td>
<td>$1.34 \times 10^{21}$ (97.0%)</td>
</tr>
<tr>
<td>4.9</td>
<td>$2.05 \times 10^{21}$</td>
<td>$3.40 \times 10^{19}$ (1.7%)</td>
<td>$2.02 \times 10^{21}$ (98.3%)</td>
</tr>
</tbody>
</table>

In other words, chemisorbed oxygen peak (OII) was not detected in the 100 nm-inside part of the film by B addition. Thus, it is suggested that oxygen chemisorption into the film is suppressed by B addition. We additionally performed the analysis of energy dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) for mapping the B profile in grain boundary regions. However, they were...
not detected precisely because the atomic size of B is very small and very little concentration of B atoms was indeed incorporated in BAZO relative to other atoms. In the XPS analysis, the B 1s peak exhibited signals similar to noise level, and the chemical state of B atoms could not be clearly classified. Nevertheless, we speculate that the large amount of the neutral inactivated B atoms would locally stop up the grain boundaries through segregation, and the process of oxygen chemisorption became inactive. Thus, the process of annihilating donor levels formed by the oxygen vacancies and Zn interstitials would be less efficient in the BAZO film, resulting in much less reduction in the carrier concentration compared with that of AZO film as indicated in Fig. 4. As for the Hall mobility, the increase in the potential barrier height at grain boundaries by electron trapping could scarcely proceed due to suppressed oxygen chemisorption in the BAZO film.

In view of photovoltaic applications, the increase of TCO resistivity will lead directly to degradation of solar cell performances. Thus, the reliability of the BAZO films under harsh conditions was investigated. We have performed H2O vapor annealing at 300 °C to test the stability of the films as shown in Fig. 6. It was observed that the increase of resistivity was more severe in the H2O vapor annealing than the annealing in atmospheric air, which is attributed to permeation of H2O molecules and oxygen. In case of the AZO film, the resistivity was increased about 39 times after 4 hour in the H2O vapor annealing, whereas it was increased about 8 times in the air-annealing. In addition, it was increased about 110 times after 8 hour in the H2O vapor annealing. However, the BAZO films showed the better reliabilities than the AZO film under the H2O vapor annealing as well as the air-annealing. The resistivity of BAZO film (1.9 at. %) was increased about 8 times after 8 hour annealing. When the B content was increased about 3.3 ~ 4.9 at. % in the BAZO films, the resistivity was increased about only 4 times, which was significantly lower than that (110 times) of AZO film after 8 hour in the H2O vapor annealing. These experimental results imply that the corrosion of transparent electrode can be considerably retarded by using the BAZO films instead of AZO film.

For applications of transparent conducting electrode, the optical transmittance of BAZO films was measured by spectrophotometer.

![Figure 5](image-url) (Color online) The chemical states (O 1s) of (a) AZO and (b) BAZO (4.9 at. %) at surface and those of (c) AZO and (d) BAZO (4.9 at. %) at the 100 nm-etched part. The O1 peak indicates the oxygen in ZnO structure binding with Zn or substitutional Al (fully oxidized stoichiometric surrounding) and OII peak reflects the loosely bounded oxygen belonging to specific species (e.g., chemisorbed oxygen).

![Figure 6](image-url) The resistivity of AZO and BAZO films with various B content under H2O vapor annealing. The resistivity of BAZO films with B content (3.3~4.9 at. %) was increased about 4 times, whereas that of AZO film was increased about 110 times after 8 hour in the H2O vapor annealing.
The measured optical transparency of BAZO film was comparable to that of AZO film. The average transmittance in visible region of AZO and BAZO film was 96.4 and 95.5%, respectively. In addition, the transmittance in NIR region of AZO and BAZO film was 96.4 and 95.5%.

In conclusion, we have developed BAZO films with high electrical stability under oxidizing atmosphere. The resistivity of deposited BAZO film was slightly lower than that of AZO film. The resistivity of BAZO film (4.9 at.%) was slightly varied from $1.7 \times 10^{-3}$ to $2.4 \times 10^{-3}$ $\Omega \cdot cm$ (<1.5 times), whereas that of AZO increased significantly from $1.8 \times 10^{-3}$ to $1.5 \times 10^{-2}$ $\Omega \cdot cm$ (>8 times) after the annealing in atmospheric air. The Hall mobility of BAZO films was much less degraded compared with those of AZO film. In the XPS analysis, the chemisorbed oxygen peak was not detected at 100 nm inside of the BAZO film, implying that the oxygen chemisorption process would be suppressed by B addition. When the H2O vapor annealing was performed, the resistivity of BAZO films with B content (3.3 ∼ 4.9 at.%) was increased about 4 times, whereas that of AZO film was increased about 110 times after 8 hour. The much less increase of resistivity for BAZO films after annealing can be evaluated as a significant improvement in the electrical stability of the ZnO films considering that other ZnO-based TCO films such as ZnO:Al, ZnO:Ga, and ZnO:In typically show considerable deterioration of resistivity after annealing in oxidizing atmosphere. Our experimental results suggest that suitable B- and Al- codoping for ZnO can attain a reasonable and highly stable resistivity. From this aspect, it is strongly believed that the BAZO film can be a promising candidate of highly stable transparent conducting electrode, even in very thin films (<300 nm).

References