Enhancement in conductivity through Ga, Al dual doping of ZnO nanofibers

Minkyu Park, Seung Min Han *

Graduate School of Energy Environment Water and Sustainability, Korea Advanced Institute of Science & Technology, Daejeon 305-701, Republic of Korea

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A B S T R A C T
In this study, electrical conductivity of Al doped ZnO nanofiber was enhanced by using Ga co-doping over the maximum conductivity achievable with only Al dopants of 2 at.% in ZnO. Al and Ga have different atomic sizes that results in further doping with Ga up to 1 at.% Al. Ga co-doped ZnO nanofiber was fabricated by using electrospinning technique and structural analysis was investigated by X-ray diffraction. X-ray analysis indicates a change in lattice parameter (a-axis) of doped ZnO from 3.2497 Å to 3.2483 Å with added 1 at.% Al and from 3.2497 Å to 3.2488 Å with co-doping of 1 at.% Ga on top of the 2 at.% of Al doped ZnO. Therefore, Ga was incorporated into Al doped ZnO nanofiber without significant lattice parameter and grain size reduction to result in the enhanced conductivity up to a maximum value of 9.57 × 10^{-3} S/cm.

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1. Introduction

Transparent conductive oxides (TCOs) have been widely used for optoelectronic devices such as displays and solar cells [1]. In solar cells, transparent electrodes need to have low sheet resistance and high transmittance for high light conversion efficiency. Currently, ITO (indium tin oxide) shows the highest performance among the candidates for transparent electrode. However, it has some engineering problems like the high cost of indium so these drawbacks are motivated to develop alternative TCOs. Among several candidate materials, ZnO is one of the promising solutions due to its elemental abundance, non-toxicity and ease of doping for various purposes [2–5]. Some trivalent elements like Al, Ga can enhance conductivity of ZnO when they replace the Zn sites within the ZnO lattice, and AZO (aluminum doped zinc oxide) shows enhanced performance that is comparable to that of ITO.

For further improvement in optical and electrical properties, a few researchers have explored the possibility of Al, Ga co-doped ZnO (AGZO). Ionic radius of Al (r_{Al} = 67.5 pm) is significantly smaller than that of Zn (r_{Zn} = 88.0 pm) that causes lattice distortion when Al is substituted to Zn in ZnO matrix, which is partly the cause for deteriorated electrical conductivity. Ionic radius of Ga is still smaller than that of Zn but the degree of mismatch is much smaller than that of Al. Some researchers have shown some evidences that additional Ga doping in AZO can enhance the optical, electrical property. However, most of the reports so far have focused on usage of vacuum based thin film deposition methods for co-deposition. For example, the work by Kang et al. [6] has shown that additional Ga doping into AZO can relax the stress induced in film and also lower resistivity because of the smaller mismatch of ionic radius of Ga and Al.

Recently, electrospinning method has been proposed as an easy scalable doping method to produce AGZO nanofibers. Lin et al. [7] shows that fabrication and the morphology of ZnO nanofiber can be easily modified via controlling parameters of electrospinning technique and Zhou et al. [8] reported that introduction of Al^{3+} in ZnO nanofiber brings degradation of crystal quality of AGZO samples after calcinations. Both of these examples show that fabrication of ceramic nanofiber is a solution based process with the target material with desired dopants that can be easily operated by simply adding the dopant precursor. By utilizing electrospun nanofibers, mechanical flexibility can also be acquired that can overcome the limitations arising from the brittleness of conventional ITO thin film, similar to how Si can be made flexible by tuning the geometry [9]. In addition, nanoscale ceramic materials have been demonstrated to have suppressed fracture since crack extension becomes more difficult in smaller sized nanofibers [10].

Electrospun ZnO nanofibers with Al, Ga co-doping are, therefore, expected to have advantages in terms of enhanced conductivity as a result of additional co-doping with Ga, reduction in cost in comparison to that of high vacuum processed thin film, as well as having enhanced mechanical flexibility due to both the geometry and the ability to suppress fracture in nanomaterials. In this study, we report the characterization of Al, Ga co-doped ZnO fabricated by electrospinning technique for electrical, optical and structural properties.

2. Experimental details

Precursor solution was prepared in advance of beginning of electrospinning step. PVA (polyvinyl alcohol 96,000 Mw, Sigma-Aldrich) was dissolved in water up to 10 wt.% and zinc acetate...
dihydrate, aluminum nitrate nonahydrate, and gallium nitrate hydrate (Sigma-Aldrich) were then added into the polymer solution for making a viscous precursor solution with various dopant concentration. The precursor solution was injected in a syringe for electrosprining to get one-dimensional nanofibers. 15 kV was applied between tip of the needle and collector and distance of needle and collector was 12 cm. Nanofibers were collected using a special collector that is designed to synthesize free-standing fibers held between the two metal plates with a gap of 2 cm as shown in Fig. 1-a [11]. The collected nanofibers were then easily transferred by carefully scooping an individual free-standing fibers with SiO2/Si wafer. These nanofibers are still a composite of polymer with precursors and solvent. Post calcination treatment is required, where the nanofibers are annealed in a muffle furnace at temperature of 550 °C with 10 °C/min of heating rate. After calcination, PVA is removed and only the nanocrystalline ZnO nanofibers with alignment are fabricated. Scanning Electron Microscope (FEI sirion) at 20 kV was used to examine the morphology of the synthesized nanofibers. Dopant ratio in ZnO nanofiber was confirmed by ICP-MS (Agilent ICP-MS 7700S) measurements and compared against the precursor concentration as shown on Table 1.

Structural characterization of AZO and AGZO nanofiber was performed by using X-ray diffractometer (Rigaku, D/MAX-2500) with a Cu Kα radiation source (λ = 1.540562 Å) at 40 kV and 300 mA in 0–2θ can mode. JCPDS data (card no. 89-1397) was used to determine phase formation, presence of secondary formation and change of lattice parameter calculated based on peak shift as dopants are incorporated. Through those results, position of dopant of each sample is determined in the ZnO matrix. The effect of Al, Ga dual doping on the conductivity of ZnO nanofibers were investigated by measuring the I–V characteristics of individual AGZO nanofibers. An array of Al pads was deposited with a thickness of 500 nm on the top of ZnO nanofiber using E-beam evaporator. Here, Al pads were used for two probe measurement for proper electrical response of AGZO nanofibers under ohmic contact, and the suitability of Al for ohmic contact with n-type ZnO was explained in the work by Kim et al. [12]. Electrical properties of synthesized AZO and AGZO nanofibers were analyzed by measuring the current–voltage (I–V) curves using a probe-station (Keithley 4200SCS). The nanofibers that were well-aligned in between the two pads were selected for measurement as shown on Fig. 1-b. As shown in Fig. 1-d, all the I–V plots show linear behavior indicating that AZO and AGZO nanofibers have formed an ohmic contact with the electrode. In the I–V plots, resistance can be calculated and length and width of nanofiber are examined through SEM. Resistivity is calculated based on the measured geometry of the nanofiber, but nanofibers with similar dimensions were chosen for fair comparisons.

3. Result and discussion

The morphology of the synthesized nanofibers is examined using SEM as shown in Fig. 1-b. Nanofibers are smooth with a diameter of around 800 nm before calcination, but they become quite rough after calcination with a diameter of around 250 nm due to the loss of polymer and the solvent result in fine grained nanofiber. These nanofibers are cylindrical in shape and are well-contacted with the top surface of substrate. The diameter of synthesized nanofibers is carefully controlled by adjusting optimum voltage parameter in order to compare electrical resistivity of fibers with different dopant concentrations without any complications arising from the difference in geometry. High molecular weight of PVA (96,000 Mw) was used for electrosprining to allow for rigid template before calcination. Electrospun nanofibers can be flattened upon impact with the substrate, but rigid polymer template can avoid this problem to result in well-controlled cylindrical geometry. 

X-ray diffraction analysis of AZO and AGZO nanofibers was performed to ensure that the dopants are not forming a secondary phase. As shown on Fig. 2-a, our AGZO nanofibers with 2 at% Al and additional 1 at% Ga co-doping do not indicate any formation of secondary phases such as Al2O3, Ga2O3, ZnAl2O4 or ZnGa2O4 which have low conductivity. Furthermore, as shown in Fig. 2-b,c, the reduction in lattice parameter as Al and Ga dopants substitutionally replace the Zn sites is confirmed by shift in XRD peak. Since rAl < rGa < rZn, the ZnO matrix will result in higher distortion when Zn is replaced with Al in comparison to replacement with Ga. Therefore, even though additional Al doping

\[ \text{Fig. 1. (a) Schematic image of electrosprining setup, (b) SEM images of AGZO nanofiber with Al pads, (c) Change of conductivity as a function of dopant content in doped ZnO nanofiber, (d) I-V plots for pure ZnO, AZO and AGZO nanofiber.} \]
Table 1
ICP-MS analysis of Al, Ga dopant concentration in ZnO nano fiber.

<table>
<thead>
<tr>
<th>Analysis value</th>
<th>Target dopant concentration</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Al 1 at.%</td>
</tr>
<tr>
<td>Al ratio (at %)</td>
<td>0.66</td>
</tr>
<tr>
<td>Ga ratio (at %)</td>
<td>0</td>
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</table>

Beyond 2 at.% Al in ZnO will result in significant lattice distortion, which can induce lower crystallinity as well as electrical conductivity, Ga has smaller mismatch in dimension to that of Zn that allows for further doping of Ga beyond the maximum dopant concentration of 2 at.% Al. To investigate this idea, the lattice parameter was analyzed as a function of dopant concentration. The (002) peak (2θ = 34.4°) of ZnO was analyzed for the peak shift to calculate the difference in the lattice parameter as a result of dopant incorporation. As shown in Fig. 2-b,c, recognizable amount of decrease in lattice parameter of AZO is observed as Al dopant concentration is increased from 1 to 2 at.% Al, which is expected to be due to substitution of Zn sites (rZn = 88.0 pm) with smaller sized Al (rAl = 67.5 pm). As more Al dopants are added into AZO, lattice parameter is deviated further from the original ZnO lattice parameter. Interestingly, however, Ga addition to 2 at.% Al in ZnO does not cause further decrease in the lattice parameter. This result is as expected given that the atomic size mismatch of Ga is smaller than that of Al when replacing the Zn site.

Lattice distortion due to introduction of dopants of different atomic volume can induce excessive degree of strain in the matrix that can decrease the overall conductivity. Electrical conductivities of samples with various dopant concentrations are shown in Fig. 1-c. In the case of AZO with Al 2 at.%, highest electrical conductivity (σ = 4.37 × 10^-3 S/cm) is measured and further Al doping resulted in reduction in conductivity. The maximum Al doping concentration found in this study for AZO nanofiber is reasonable when compared with previous results for maximum solubility of Al in ZnO thin film of about 2 at.% [13–15]. Although the electrical conductivity of AZO is decreased with increasing amount of Al incorporated beyond the 2 at.% for Al, additional doping of 1 at.% Ga in Al 2 at.% of Al doped ZnO nanofiber can increase the electrical conductivity up to 9.57 × 10^-3 S/cm. This conductivity enhancement in AGZO nanofiber is in agreement with previous report on Al, Ga codoped ZnO film [16].

The electrical conductivity of doped semiconductor material is known to be proportional to the charge carrier concentration and carrier mobility as shown below.

\[ \sigma = e \cdot n \cdot \mu \]

Here, \( n \) is the charge carrier concentration and \( \mu \) is the mobility value. For sample with 3 at.% Al doping and 2 at.% Al + 1 at.% Ga doping in ZnO, the total carrier concentration is expected to be the same since Al and Ga both contribute one additional charge carrier in the ZnO matrix when the dopants replace the Zn site. Nevertheless, 2 at.% Al + 1 at.% Ga doping has higher conductivity than 3 at.% Al doping in ZnO, and this difference in conductivity must be from difference in mobility. Mobility, especially for doped ZnO, is known to be dependent on impurity scattering as well as from scattering from grain boundaries. Each of these factors will be considered below.

Previous reports have shown that the mobility of the AZO thin film decreases as dopant concentration is increased, but this is not an issue for the two samples with equal dopant concentration (3 at.% Al and 2 at.% Al + 1 at.% Ga). In addition, Conwell–Weisskoff formula stated below predicts the valence dependency of ionized impurity scattering [\( \mu_i \)] as stated below [17].

\[ \mu_i = \left( \frac{2}{m^*} \right)^{1/2} \cdot \frac{e^2E_F^2}{\Pi e^4N_iZ^2} \cdot \frac{1}{\ln \left( 1 + \frac{eE_F}{N_iZ^2} \right)} \]  

m* (=0.38 m0) is the effective mass of electron in conduction band, \( \varepsilon \) is a static dielectric constant of the base material, e is electron charge, \( N_i \) is concentration of the scattering center equal to the carrier concentration, \( Z \) is the valence of ion, and \( E_F \) is Fermi level. Since the ion valence (\( Z \)) is also the same for both Al and Ga, ionic scattering cannot account for the difference in mobility to explain the conductivity difference.

Mobility is also known to be dependent on the amount of scattering occurring at the grain boundaries [18,19]. In order to investigate the difference in grain sizes, we examined the full width at half maximum (FWHM) values from X-ray diffraction peak to compare the degree of crystallinity of 3 at.% Al doping vs. 2 at.% Al + 1 at.% Ga. Fig. 3 shows that FWHM values are increased by adding Al dopant to pure ZnO nanofiber, but are reduced by adding Ga dopants for AGZO nanofibers. Therefore, the AGZO nanofibers are expected to have fewer grain boundaries resulting in smaller FWHM in comparison to that of AZO that can in turn result in enhancement in conductivity in AGZO nanofibers. Our results are in agreement with the reported enhancement in crystallinity by incorporation of Ga in the case for thin films [6]. Therefore, we conclude that the enhancement in conductivity in AGZO nanofiber comparison to that of AZO nanofibers is from difference in crystallinity and not...
due to formation of secondary phases, which were not detected in our X-ray analysis.

4. Conclusions

In conclusion, AZO and AGZO nanofibers were fabricated by electrospinning technique and electrical and structural characteristics of each nanofibers were investigated. X-ray analysis revealed that the change in lattice parameter can be minimized when adding Ga beyond 2 at.% Al doping in ZnO due to smaller mismatch in atomic size to that of Zn. Therefore, additional Ga doping can be more effectively incorporated in the ZnO matrix without extensive strain. Our I–V curve analysis has revealed that the AGZO nanofibers with optimized concentration of 2 at.% Al + 1 at.% Ga had the highest conductivity of 9.57 × 10−3 S/cm. Addition of Ga to 2 at.% Al ZnO nanofiber was reported to significantly increase the crystallinity and turn cause less grain boundary scattering or increased mobility. Hence our increased conductivity of AGZO nanofibers in comparison to that of AZO is naturally expected. The outcomes of this study on Al, Ga dual doped ZnO nanofibers are expected to be of significant interest in development of easily scalable doped ZnO with enhanced conductivity for different transparent electrode applications.

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