

# Laser Treatment of AlN Co-doped ZnO Film for p-type ZnO Fabrication

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## 1. Introduction

Recently, much research about p-ZnO film has been carried out. In particular, various doping elements of group V, such as N, P, As and Sb atoms, were tested [1-2]. Among these acceptors, nitrogen dopant, which has a similar ionic radius to oxygen atoms, has long been considered to be the promising candidate for substituting oxygen atoms as  $N_o$  in ZnO. However, not only is the solubility of N in ZnO low enough, but Zn atoms prefer to bond with O atoms rather than with N atoms, owing to the higher chemical activity of oxygen atoms[3]. Therefore, it is difficult to reproduce and keep stable p-type ZnO using N dopant. As a result, N-III codoping method, such as N-Al, N-Ga, and N-In, has been reported to be a promising technique for the formation of p-type ZnO. In view of the point of thermodynamic behaviors, group III elements bond easily with oxygen under an oxygen atmosphere during the deposition process by using Zn-III alloy targets. Hence, p-type conduction for ZnO is still difficult to produce.

To increase the content of N atoms in the p-type ZnO films, a controllable method was proposed and studied in this work. The cosputtered ZnO-AlN films (ANZO) were deposited on silicon substrates using ZnO and AlN targets in a mixed Ar and  $N_2$  atmosphere. In addition, an ultraviolet laser operating at 355 nm was employed as the activation source. The aim of using UV laser irradiation instead of a conventional annealing process was to minimize heating and to prevent the out-diffusion of nitrogen atoms. The effects of laser irradiation for the ANZO films with various electrical properties, crystallographic structure and optical properties were investigated and compared with those without laser irradiation treatment.

## 2. Experimental

The pure ZnO and AlN co-doped ZnO thin films were cosputtered onto n-type Si (100) substrates using an rf magnetron co-sputtering system. In this study, 99.99% pure AlN and 99.99% pure ZnO were used as the target materials and the RF powers were fixed at 50W and 100W, respectively. During co-sputtering, both AlN and ZnO targets were inclined with respect to the normal direction of the substrates. Therefore, the AlN and ZnO could be deposited on the substrates simultaneously. The Ar flow rate was kept at 50 sccm and the  $N_2$ -to-Ar ( $N_2$ /Ar) flow ratios were set at 0%, 2%, 4% and 6% to control the nitrogen atmosphere. From a thermodynamic point of view,

it is a benefit for the N-doped ZnO in a non-equilibrium growth at a low temperature. Therefore, all the samples studied here were deposited at room temperature.

Moreover, activation treatment is the key issue to activate the dopants in p-type ZnO research. Therefore, a 355 nm UV laser with pulse duration of 30 ns (FWHM), and a repetition rate of 120 kHz was used to activate the dopants in the ANZO films. The number of impinging shots was set at 100. In the UV laser system, a homogenizer lens was used to achieve a uniform distribution of the laser beam intensity over a  $50 \times 50 \mu m^2$  spot. The activation treatment process was performed under ambient environmental conditions and single shot densities ranging from 100 to  $200 mJ/cm^2$ .

## 3. Experimental results and discussion

Table I shows the deposition conditions of the investigated samples, as well as their composition and carrier types, measured by EDS and Van der Pauw Hall measurements. The samples are labeled with letters A-E for abbreviation. It can be seen that the as-deposited ANZO thin films (samples B to E) have comparable alumina contents while the AlN target was fixed at 50W. Also, the nitrogen content increases with increasing  $N_2$ -to-Ar ( $N_2$ /Ar) flow ratios. On the other hand, due to the soluble limitation of nitrogen in the ZnO films, the N content in samples D and E were nearly unchanged in spite of the increased  $N_2$ /Ar flow ratio. Moreover, all the ANZO films exhibited the n-type conductive behavior. This implies that the N-related acceptors were electrically inactive in the as-deposited films.

With the aim of effective activation of the dopants, all the samples were laser-irradiated at 100, 150 and 200

**Table I** Process condition, composition and carrier type measured by EDX measurement and Hall measurement.

Sample	AlN Target(W)	$N_2$ /Ar (%)	Compositions Zn : O : Al : N	Carrier type
A	0	0	50.2: 49.8 : 0 : 0	n
B	50	0	48.6: 48.4 : 1.6:1.4	n
C	50	2	48.5: 46.1 :1.7 :3.7	n
D	50	4	48.5: 44.5 :1.7 :5.3	n
E	50	6	48.5: 44.3 : 1.7:5.5	n

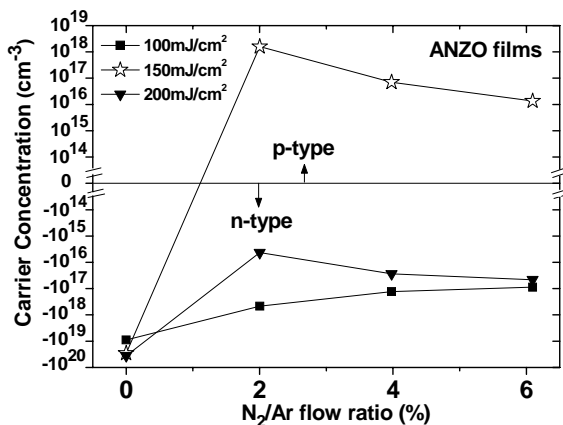


Fig. 1 Carrier concentration, and carrier type of the ANZO films under various laser activation energy density.

mJ/cm<sup>2</sup>, respectively. Figure 1 shows the effect of laser activation energy density on the carrier concentration in ANZO films. At a low laser energy density of 100 mJ/cm<sup>2</sup>, all of the co-doped ZnO films showed n-type conduction. This phenomenon indicated that the laser energy density was too low to activate the N-related acceptors. As the laser energy density increased from 100 mJ/cm<sup>2</sup> to 150 mJ/cm<sup>2</sup>, the electrical conduction of samples C, D and E were converted from n-type into p-type conduction, showing hole concentrations of 10<sup>17</sup>-10<sup>18</sup> cm<sup>-3</sup>. Therefore, the N-related dopants in the ANZO films seem to be activated in this laser irradiation condition. However, the hole carrier concentration decreased with increasing the N<sub>2</sub>-to-Ar (N<sub>2</sub>/Ar) flow ratios. This phenomenon is attributed to the incompletely dissociated N<sub>2</sub> molecules occupying the oxygen sites in the ZnO lattice, leading to the double-donor doping of (N<sub>2</sub>)<sub>o</sub> defects. As a result, N-related acceptors formed in p-type ZnO are being compensated by (N<sub>2</sub>)<sub>o</sub> defects in ZnO film to a higher degree, resulting in a low hole concentration. Moreover, a further increase in laser energy density leads to a decrease in hole concentrations. The carrier type of samples C, D and E were changed from p-type to n-type at a high irradiation energy density of 200 mJ/cm<sup>2</sup>. This type conversion may include the creation of native defects, such as oxygen vacancies or Zn interstitials, and the dissociation of Al-2N complexes.

X-ray diffraction spectra of the ZnO and ANZO films deposited on silicon substrates irradiated at 150 mJ/cm<sup>2</sup> are shown in Figure 2. The major diffraction peak observed was the (002) plane with the wurtzite crystallized phase. In addition, except for the ZnO-related diffraction peaks, a weak diffraction peak determined to be Zn<sub>3</sub>N<sub>2</sub> (222) was observed from the irradiated ANZO film diffraction pattern. The appearance of the zinc nitride phase was believed to be the nitrification reaction of the excess Zn and N atoms in the co-doped films. According to the theoretical prediction, the Zn-N bonds via the N-III-N complex were the basic requirement to accomplish p-type ZnO. As a result, our codoping method under laser energy density of 150 mJ/cm<sup>2</sup> promotes the formation of N-III-N complex.

Figure 3 shows the room-temperature EL spectra of the p-n heterojunction light-emitting diodes. The EL spectra of the forward biased p-ZnO(sample B, laser-irradiated at 150

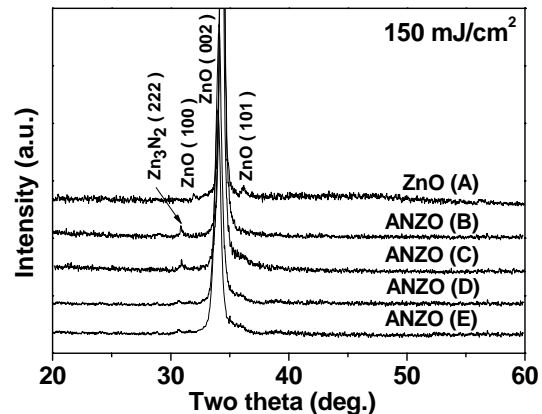


Fig. 2 The XRD spectra of ZnO and ANZO films under laser activation energy density at 150 mJ/cm<sup>2</sup>.

mJ/cm<sup>2</sup>) / n-GaN heterojunction consist of a broad emission band at 405 nm, which is attributed to the transition from the conduction band to the acceptor level ascribed to the AlN doped ZnO when electrons are injected from the n-GaN into the p-ZnO. The radiative recombination occurs mainly at the p-ZnO region because the depletion region of the p-n heterojunction resides mostly in the p-ZnO layer.

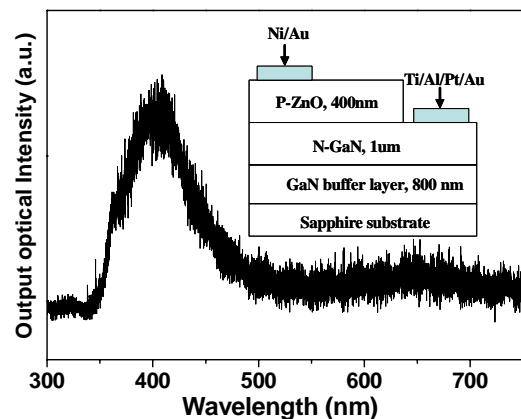


Fig. 3 The room-temperature electroluminescence (EL) spectrum of the p-n light-emitting diodes.

#### 4. Conclusions

High quality p-type ZnO film can be obtained by co-sputtering of ZnO and AlN targets under adequate N<sub>2</sub>/Ar flow ratio of 4% and laser activation energy density at 150 mJ/cm<sup>2</sup>. The appearance of the Zn<sub>3</sub>N<sub>2</sub> phase in the x-ray diffraction pattern of the laser-irradiated ANZO films provided evidence of the nitrification of zinc ions. The EL peak of 405 nm attributed to the radiative recombination occurred at the p-ZnO region.

#### Reference

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