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NO GAS DOPING OF ZnO FILMS USING Ir HOT-WIRE IN CATALYTIC REACTION-ASSISTED CHEMICAL VAPOR DEPOSITION

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Abstract

Nitrogen doping of ZnO films by the decomposition of NO gas using a heated Ir wire during film growth was attempted through the reaction between dimethylzinc (DMZn) and high-temperature H_2O. High-temperature H_2O was produced by the Pt-catalyzed reaction between H_2 and O_2. Although p-type ZnO films were not obtained, the residual carrier concentration decreased upon the addition of NO gas. In X-ray photoelectron spectra, multiple overlapping N-1s peaks were observed from 395eV to 408eV. By deconvoluting the spectra, components such as Zn-N, N-H, N-N, and N_xO_y were identified. The relative intensity of the Zn-N peak at 395.5eV-396.8eV increased when a heated Ir wire was used to decompose the NO gas.

Keywords and phrases: ZnO, catalytic reaction, Ir hot-wire, nitrogen doping.
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1. Introduction

Zinc oxide (ZnO) has drawn considerable interest owing to its potential applications in the ultraviolet wavelength range [1]. ZnO offers significant advantages for optoelectronic applications, such as light-emitting diodes and laser diodes in the ultraviolet range, because of their large binding energy (~60meV) [2]. We have previously developed a new chemical vapor deposition (CVD) method for ZnO film growth using a catalytic reaction between hydrogen and oxygen gases on Pt nanoparticles [3]. In order to fabricate optical emission devices, n-type and p-type ZnO crystals are required [4]. Doping with Al and Ga has been attempted by many groups, resulting in high-quality, highly conductive n-type ZnO films [5-10]. Although n-type ZnO with low resistivity has been grown by the doping of donor impurities, reproducible fabrication of p-type ZnO is very difficult. In order to fabricate p-type ZnO, a high concentration of nitrogen atoms is required. Nitrogen doping of ZnO by CVD can be achieved through the addition of nitrogen oxide gases. For some cases of nitrogen doping, the addition of N_2O and NO gases has been considered [11-14]. However, the addition of N_2O during our CVD method did not result in nitrogen doping [15]. NO is more reactive than N_2O. Gases can be decomposed effectively on heated refractory metal surfaces. For the decomposition of NO, refractory metals that can withstand oxygen atmosphere, such as platinum (Pt) and iridium (Ir), are suitable [16].

In the present work, we have tried nitrogen doping using NO gas and investigated the effect on NO decomposition by a heated Ir wire during ZnO film growth.

2. Experimental

The CVD apparatus used in this study had the same structure as that reported in a previous paper [3], except for the addition of an Ir wire, as shown in Figure 1. H_2 and O_2 gases were introduced into a catalyst cell containing a Pt-dispersed ZrO_2 catalyst, following which the temperature of the catalyst cell quickly rose above 1000ºC, owing to the exothermic reaction between H_2 and O_2 over the catalyst. After 10 min of the introduction of H_2 and O_2, the catalytic cell temperature stabilized, at which time the shutter located between the skimmer cone and the substrate holder was opened. The skimmer cone between the H_2O nozzle and the substrate served to selectively direct only high-velocity H_2O molecules to the substrate. The generated high-temperature H_2O molecules were ejected from a de Laval nozzle into the reaction zone in the chamber and allowed to collide with DMZn gas ejected from another small nozzle (inner diameter: 1.0mm). The H_2 and O_2 gas flow rates during growth were set at 400 and 130sccm, respectively. The DMZn gas flow rate was adjusted so as to maintain a partial pressure of $4.6 \times 10^{-3}\,\text{Pa}$. Epitaxial ZnO films were grown on a-plane sapphire substrates at a substrate temperature of 500ºC for 60 min without a buffer layer. The NO gas pressure was varied in the range from $1.0 \times 10^{-3}\,\text{Pa}$ to $3.0 \times 10^{-1}\,\text{Pa}$. The total reaction gas pressure in the chamber during deposition ranged between 0.4Pa and 0.8Pa, depending on the NO gas pressure. An Ir wire, 0.5mm in diameter and 50mm in length, was heated at 1200ºC. The pressure was measured by using an ionization vacuum gauge, however, the measured value was not multiplied by the correction factor for the specific gas species. The sapphire substrates were degreased by washing with methanol and acetone in an ultrasonic cleaner, etched with a H_2SO_4/H_3PO_4 solution, rinsed with ultrapure water, and finally, set on a substrate holder in the CVD chamber. The film thicknesses obtained were 2.0-3.0μm. The crystallinity and crystal orientation for each ZnO film were characterized by X-ray diffraction (XRD, Bragg-Brentano configuration, $\omega - 2\theta$ scan and ω rocking curve) using Cu-$K\alpha_1$ radiation (Rigaku, Smart Lab). The surface morphology was observed by using atomic force microscopy

(AFM, Shimadzu 9500J2). The carrier concentration of the ZnO films was determined by the van der Pauw method (ECOPIA, HMS-5000) under a magnetic field of 0.57 T at room temperature. The incorporation of nitrogen atoms and their bonding structure in the ZnO films were evaluated from N-1s spectra and their deconvolution measured by an X-ray photoelectron spectrometer (XPS, JEOL JPS-9010TR).

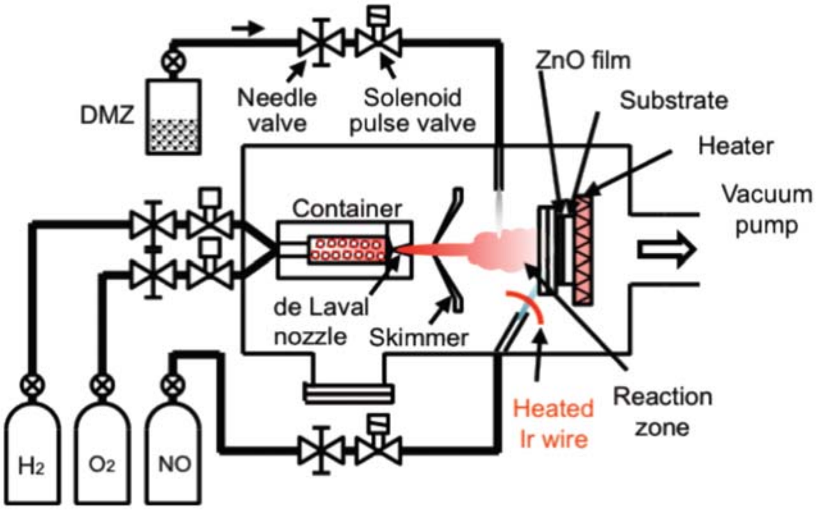


Figure 1. Schematic of CVD apparatus used in this study.

3. Results and Discussion

In the XRD patterns of all films, an intense (0002) peak at $2\theta = 34.44^\circ$, associated with c-plane ZnO, was observed (not shown). Figure 2 shows the ω-rocking curves of the ZnO (0002) peak for undoped and NO-doped ZnO films. The FWHM of the ω-rocking curve of ZnO (0002) also increased with increasing NO pressure, which indicates the degradation of crystal orientation along the c-axis upon the addition of NO gas.

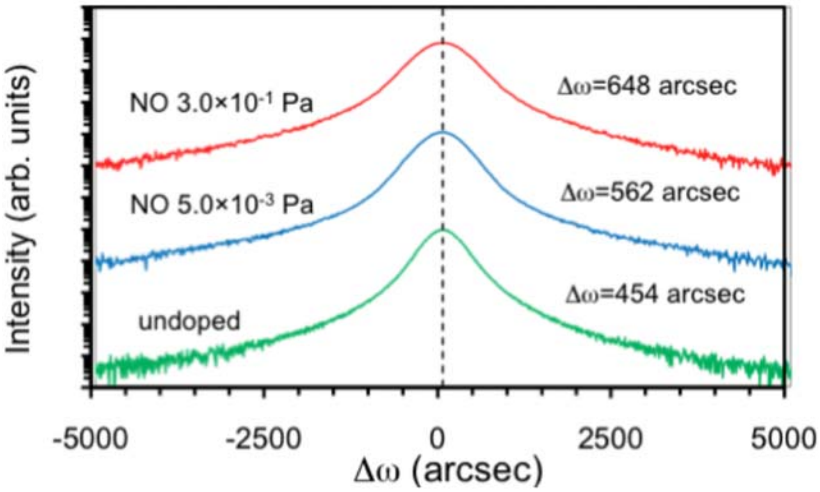


Figure 2. ZnO (0002) ω-rocking curves for the films grown with and without NO gas.

Figure 3 shows AFM images of the surface of ZnO films grown with and without NO gas. Although hexagonal facets can be observed for all films, the facet dimensions are small for the ZnO films grown with NO gas. This indicates that the crystallite size of the ZnO film decreased during growth in the presence of NO.

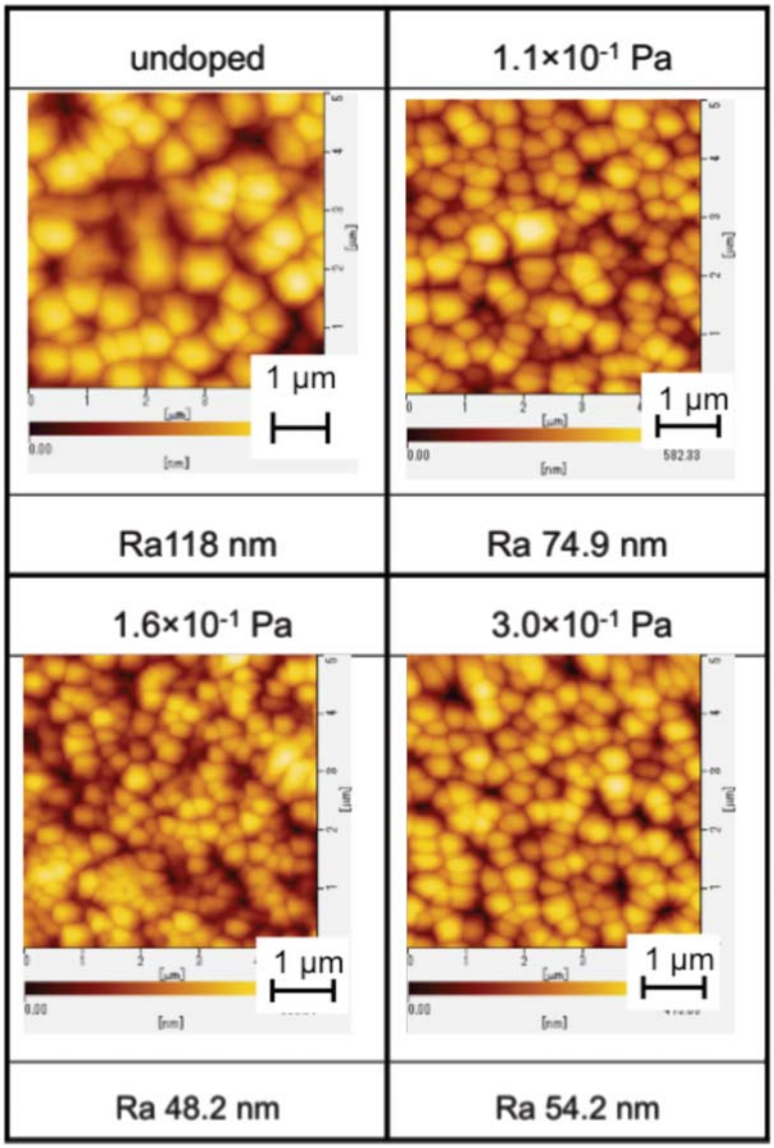


Figure 3. Atomic force microscopy images of ZnO films grown at various NO gas pressures (5×5 μm).

Figure 4 shows the dependence of the residual carrier (electron) density in the NO gas pressure measured by Hall effect measurement. All films showed the n-type characteristics. Although the residual carrier concentration was reduced by the addition of NO as shown in this figure, the ZnO films with low carrier concentrations were obtained at relatively low NO gas pressures of 2.5×10^{-3} Pa to 5.0×10^{-3} Pa.

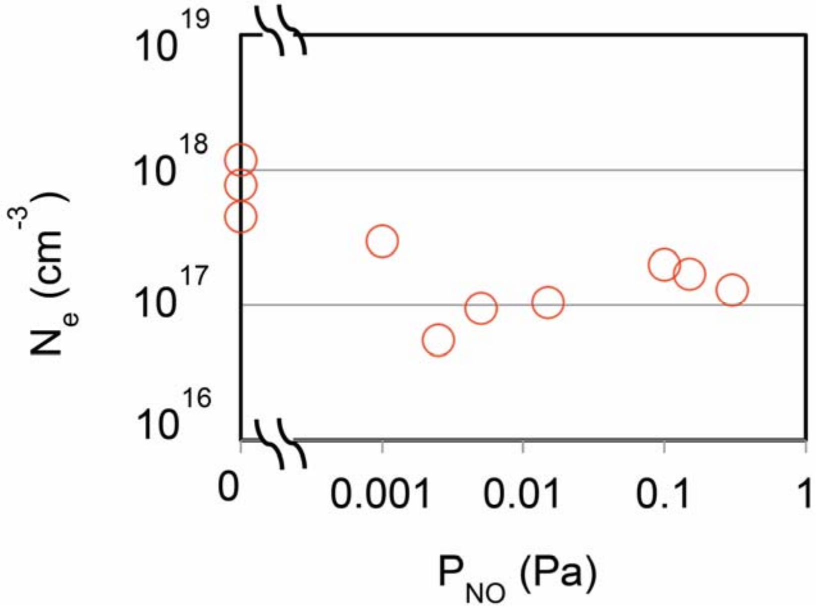
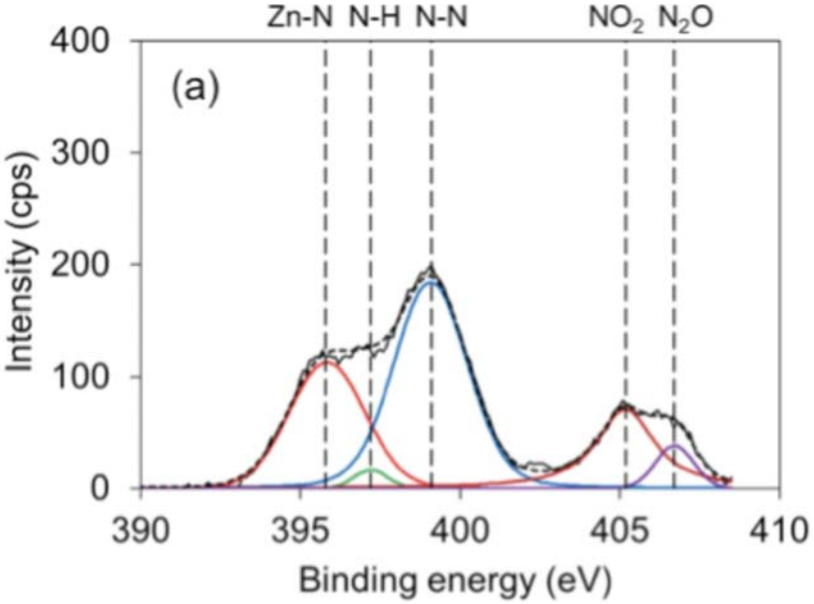
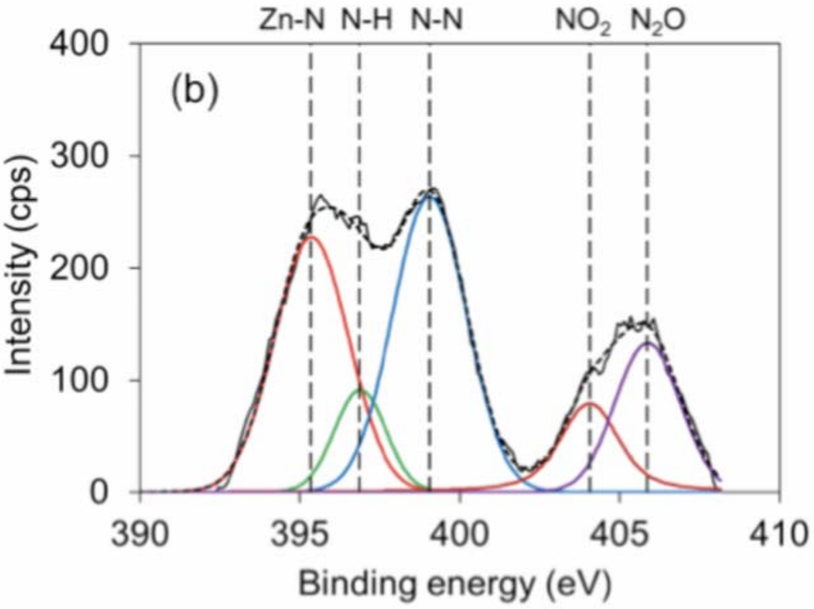


Figure 4. Dependence of carrier concentration of ZnO films on the NO gas pressure.

In the X-ray photoelectron spectra, multiple overlapping N-1s peaks were observed from 395eV to 408eV, as shown in Figure 5. Figure 5(a) is a result of the ZnO film grown with unheated Ir wire. On the other hand, Figures 5(b) and (c) are the results of them grown with heated Ir wire. By deconvolving the spectra, components such as Zn-N, N-H, N-N, NO_2 and N_2O were identified [17]. The relative intensity of the all N-1s components increased when the heated Ir wire was used. In particular, the relative intensity of the Zn-N peak became large at NO pressures of 2.5×10^{-3} Pa with the heated Ir wire.


Zn-N
N-H
N-N
NO_2
N_2O
(a)
Intensity (cps)
400
300
200
100
0
390
395
400
405
410
Binding energy (eV)


Zn-N
N-H
N-N
NO_2
N_2O
(b)
Intensity (cps)
400
300
200
100
0
390
395
400
405
410
Binding energy (eV)

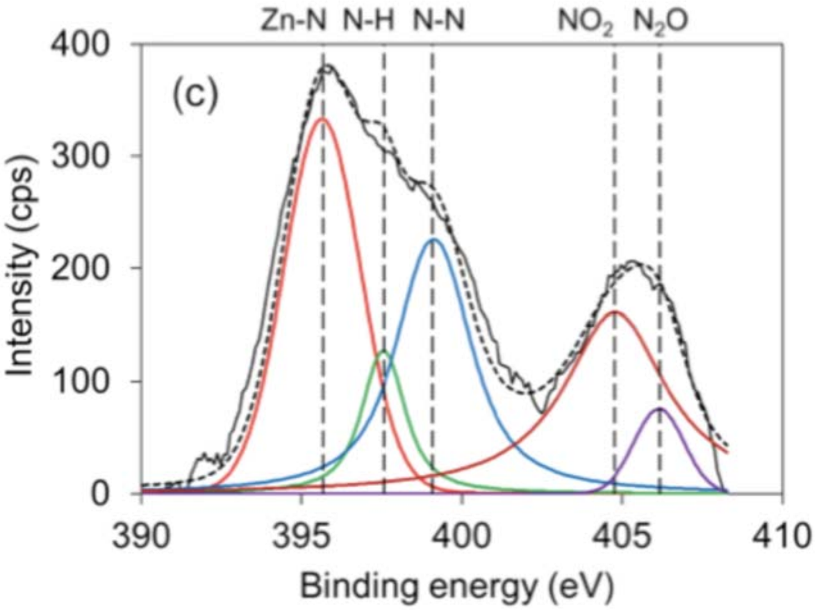


Figure 5. XPS spectra of N-1s region of ZnO films grown with Ir wire. (a) NO gas added sample (1.3×10^{-1} Pa, without heating of Ir wire), (b) NO gas added sample (1.3×10^{-1} Pa, with heated Ir wire), and (c) NO gas added sample (5.0×10^{-3} Pa, with heated Ir wire).

Figure 6 shows the relative integrated intensity ratios of the Zn-N, N-N and N_x-$O_y(NO_2 + N_2O)$ components. The relative integrated intensity ratio of the Zn-N peak was large at a NO gas pressure at 2.5×10^{-3} Pa, as shown in Figure 6. The Zn-N component is ascribable to the N atoms that substitute the O atoms in the ZnO crystal, which act as acceptors. On the other hand, the N-N component is ascribable to the N atoms that act as shallow double-donors [18]. In order to obtain the p-type ZnO, therefore, the higher-density Zn-N bonds and lower-density N-N bonds are required. The X-ray photoelectron spectra revealed that the formation of Zn-N bonds in the ZnO films using a heated Ir wire during film growth, in particular at NO gas pressures from 2.5×10^{-3} Pa to at 5.0×10^{-3} Pa, was effective. At high NO gas pressure higher than 1.0×10^{-1} Pa, total gas pressure in the chamber becomes high. Nitrogen radicals generated on the heated Ir wire would be deactivated by the scattering with gas molecules in the area between the Ir and the substrate. The deactivation may result in the decrease of the Zn-N bond concentration.

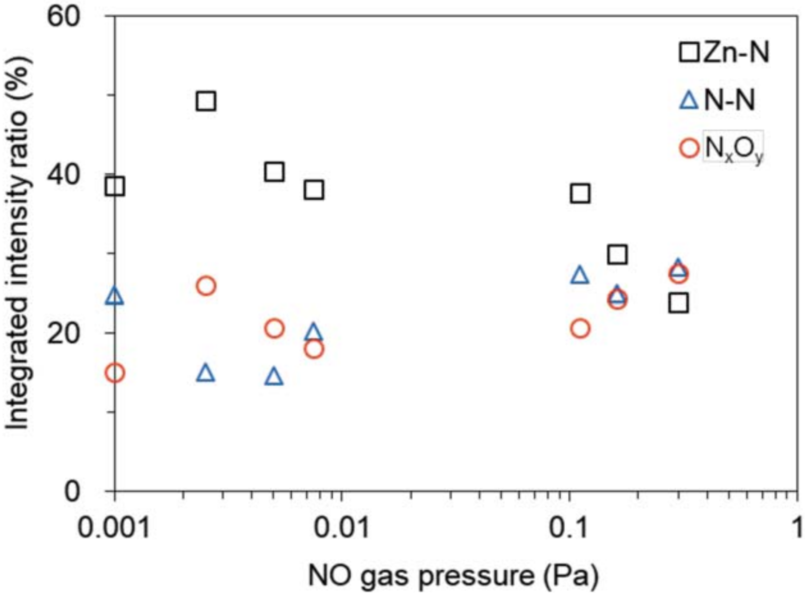


Figure 6. Relative integrated intensity ratios of Zn-N, N-N and N_x-O_y components.

4. Conclusion

The effect of a heated Ir wire during ZnO film growth on nitrogen doping by decomposition of NO gas was investigated by CVD using high-temperature H_2O generated by the Pt-catalyzed reaction between H_2 and O_2. Upon the addition of NO gas, the crystal orientation along the c-axis deteriorated. Although no p-type ZnO films were obtained, nitrogen incorporation increased when the heated Ir wire was used. The relative intensity of the Zn-N component in the N-1s peak became large at NO gas pressures from $2.5 \times 10^{-3}\,\mathrm{Pa}$ to at $5.0 \times 10^{-3}\,\mathrm{Pa}$. Thus, it was found that the use of the heated Ir wire during film growth was effective for the nitrogen doping.

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