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p-Type ZnO Thin Films Grown by MOCVD

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ABSTRACT

ZnO has demonstrated a possibility to be doped as a *p*-type by using nitrogen and other group-V elements. A high nitrogen doping concentration by metalorganic chemical vapor deposition (MOCVD) with nitric oxide (NO) gas has been achieved. However, the processing window for obtaining the *p*-type ZnO:N film is very narrow, and the hole concentration is typically low. Possible compensation and passivation effects have been studied. Hydrogen and carbon elements are detected by secondary-ion mass spectroscopy (SIMS). Considering the other experimental and modeling results, we believe that the impurities inadvertently incorporated with the zinc precursor could be compensating or passivating the nitrogen acceptor and result in the low hole concentration.

INTRODUCTION

ZnO, a wide-bandgap semiconductor material, is widely used in various applications. It can be easily doped to *n*-type, but is difficult to dope to *p*-type [1]. Low impurity solubility, excessive accepter ionization energy, and possible compensating mechanisms are the three main factors that could make *p*-type doping of ZnO difficult. In addition to being of interest for ultraviolet light emitters, *p*-type ZnO has a potential advantage in the fabrication of novel solar cell structures: inverted CdTe devices, improved contacts to both *p*-type absorbers, and organic semiconductors. The recent reports on *p*-type ZnO brings this potential close to reality [2-9].

In this report, we discuss the achievement and the issues that have been observed on the nitrogen-doped *p*-type ZnO films formed by MOCVD. Special focus is put on the low hole concentration and possible compensation mechanisms.

EXPERIMENTAL

P-type ZnO films have been fabricated by MOCVD, using diethylzinc (DEZn) and nitric oxide (NO) precursors. NO gas serves as both the oxidizer and nitrogen dopant in this reaction. The substrate is Corning 1737 glass. More information on ZnO:N sample fabrication can be found in previous papers [10].

The composition of the ZnO films was analyzed by a CAMECA IMS 5f SIMS. Film topography was taken by atomic force microscopy (AFM, Auto probe LS from Park Scientific Instruments with Si Cantilevers). Electrical and optical properties were measured using Hall analysis (BioRad Model HL5500), capacitance-voltage (double-Schottky surface contact with mercury probe), and a Cary 5G spectrophotometer.

RESULTS AND DISCUSSION

The MOCVD-formed ZnO:N films on glass substrate are randomly oriented polycrystalline with a light yellow color. The

transparent spectra of the ZnO:N compare with the ZnO film shown in Fig. 1. The increased absorption around the band edge of the ZnO:N made the film look yellow. The topography of the ZnO:N on glass substrate is illustrated in Fig. 2.

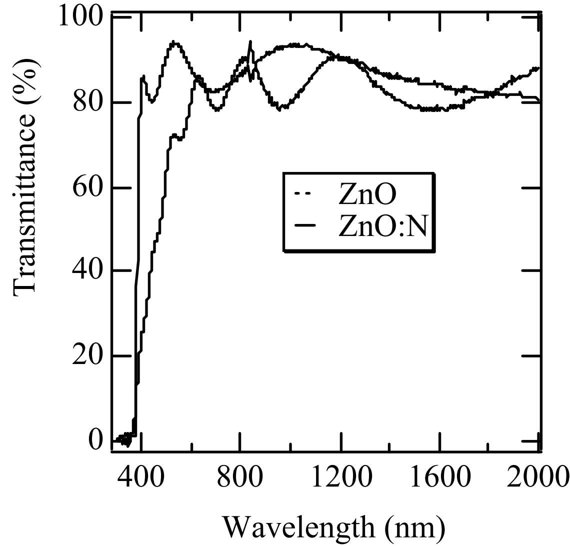

Figure 1. Optical transmittance spectra of ZnO and ZnO:N films.

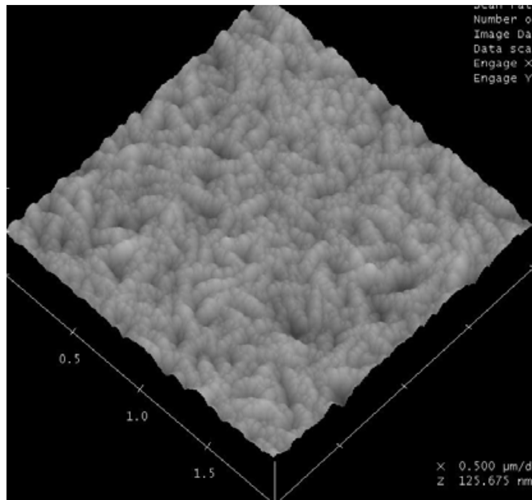

Figure. 2. The topography of a 0.74-µm-thick ZnO:N film grown on a glass substrate.

An O-poor growth ambient is required for nitrogen doping. Therefore, all the ZnO:N films studied here were formed with NO gas as the oxidizer. When NO gas is the only oxidizer, nitrogen concentration levels in the range of $1.75 \times 10^{21} \sim 2.60 \times 10^{21}$ cm^{-3} have been achieved. The high nitrogen concentration level can be achieved in a wide processing range, but the growth window for fabricating the *p*-type ZnO:N is narrow. The *p*-type films are observed only in a temperature range of 400°-440°C [10]. Although some of the ZnO:N films deposited in this temperature range are remain insulating.

Results of Hall probe analysis of several ZnO samples are shown in Table 1. Undoped ZnO is *n*-type with a carrier concentration in the range of $10^{16} \sim 10^{18}$ cm^{-3}. The nitrogen-doped ZnO samples are no long *n*-type but are insulator or weak *p*-type. The hole concentration is around 10^{13} to 10^{18} cm^{-3} and the resistivity is in the range of 2 to few hundred Ω–cm. The capacitance-voltage (C-V) technique was used to confirm the Hall results. Without post-deposition heat treatment, the C-V analysis indicated that the as-deposited ZnO:N sample is weak *p*-type.

Table 1. Electrical properties of ZnO films deposited at a temperature of 400°C.

Doping	C. C. (cm^{-3})	μ (cm^2/V)	ρ (Ω-cm)
ZnO	-8.42×10^{18}	3.2	0.235
ZnO	-8.38×10^{16}	6.3	11.8
ZnO:N	9.24×10^{13}	236	286
ZnO:N	8.36×10^{17}	4.55	1.64

The measured carrier concentration is several orders of magnitude lower than the nitrogen concentration. With the achieved nitrogen doping concentrations, it is clear that the limitation is not due to the dopant solubility. Several other reasons could be: (1) a small fraction of the nitrogen acts as an acceptor. There is a possibility that the nitrogen forming the [$(N_2)_O$] (two nitrogen atoms substitute on an oxygen site) double shallow donor instead of (N_O) single deep acceptor [11]. (2) The nitrogen acceptors' energy levels lie well above the valence band

edge. And (3), a strong compensation or passivation mechanism exists. The second possibility has been discussed previously [10]. The calculations indicated that the ionization energy needs to be as much as ~350 meV to explain the observed difference between the nitrogen and the carrier concentration. Considering the recent experimental result that the ionization energy N_O is about 160 meV, a much larger carrier concentration should result [12]. With the knowledge of the possible impurities introduced by MOCVD procedures, in this study, we shall focus our attention on the third possibility: compensation or passivation effects by possible impurities introduced during MOCVD deposition.

The depth profiles of hydrogen and carbon in ZnO:N films were obtained using SIMS. In both ZnO and ZnO:N films, both hydrogen and carbon have been found. Figure 3 indicates hydrogen and carbon concentrations are strongly affected by deposition temperature. This observation indicates that the hydrogen and carbon elements are possibly introduced as the products of the zinc precursor ($(C_2H_5)_2Zn$) decomposition process.

It has been found that the other zinc metal-organic precursor ($(CH_3)_2Zn$) introduced some carbon into the ZnO film [13]. There are not many studies on the function of the carbon in ZnO film. In nitrogen-doped ZnO, there is evidence that carbon has possibly bonded with nitrogen [14]. The recent theoretical study conducted at NREL indicated that the carbon-related defect in ZnO:N film most possible are donor type. Thus, the carbon is an undesirable impurity for *p*-type ZnO film [15].

The role of hydrogen in ZnO has been well studied [16-18]. It has been indicated that hydrogen acts only as a donor in ZnO. There are not many studies on the function of hydrogen in a nitrogen-doped ZnO film. Considering the difficulty associated with nitrogen doping by MOCVD and the high level of hydrogen concentration in the ZnO film, we believe that hydrogen could be one of the important factors in determining the efficiency of nitrogen doping.

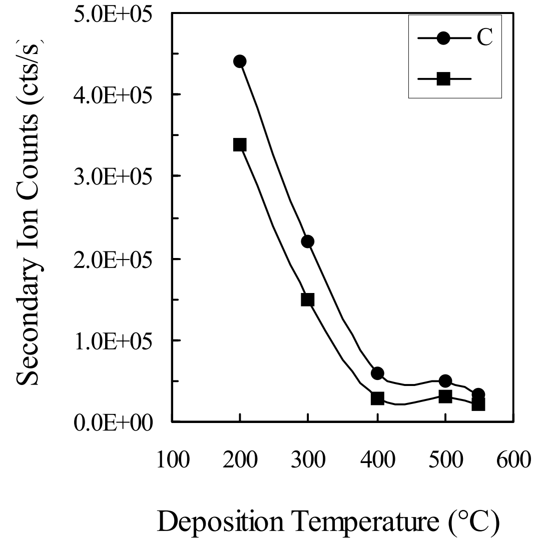

Figure 3: The hydrogen and carbon impurity levels varied with deposition temperature in MOCVD-formed ZnO films.

Our study by Fourier transform infrared spectroscopy (FTIR) and first-principles calculations indicated that there is a strong tendency for N_O^- and H^+ defects to form a neutral combined defect complex [19]. In undoped ZnO samples, hydrogen bonded with oxygen. With nitrogen doping, the intensity of the absorption peak due to O-H decreased, and the absorption line at 3007 cm^{-1} due to the N_O-H (anti-bonding) emerged. This observation implies that one of the possible reasons for low hole concentration in heavily doped ZnO:N is due to the hydrogen passivation effect.

In summary, we have fabricated *p*-type, nitrogen-doped ZnO by MOCVD. The nitrogen concentration achieved using this method is as high as 2.60×10^{21} cm^{-3}. However, low hole concentration is observed. Hydrogen and carbon elements have been detected by SIMS analysis. This, together

with FTIR, XPS, and modeling results, provides strong evidence that compensation or passivation of nitrogen acceptors by inadvertently incorporated impurities exist in ZnO:N films, thereby resulting in the low hole concentration.

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