



Experimental investigation on nitrogen related complex acceptors in nitrogen-doped ZnO films



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ABSTRACT

In this article, experiments have been designed to investigate the nature, introduction, and control of the shallow acceptor states in nitrogen-doped ZnO material. With the help of a batch of characterizing experiments, we have confirmed shallow acceptor states in the form of $(\text{NH}_4)_{\text{Zn}}$ and $(\text{N}_2)_{\text{Zn}}$. The content of the acceptor-like nitrogen complexes could be tuned by varying the VI/II ratio in gas phase during growth. The formation mechanism of the complexes has also been discussed. The formation energy of the $(\text{NH}_4)_{\text{Zn}}$ complex could be lower than that of V_{Zn} at O-rich condition, making its formation at zinc site energetically favorable. However, although the formation energy of the $(\text{N}_2)_{\text{Zn}}$ complex is slightly higher than that of V_{Zn} , the complex could be stabilized by binding to adjacent lattice oxygen or additional hydrogen, which could lower the total energy through transferring electrons to the high energy states. Furthermore, direct introduction of $(\text{N}_2)_{\text{Zn}}$ via growth has been suggested to be more efficient as compared to that via post-growth process demonstrated previously. All these mechanisms lead to a reasonable co-existence of the $(\text{NH}_4)_{\text{Zn}}$ and $(\text{N}_2)_{\text{Zn}}$ acceptor-like complexes in ZnO lattice, which is responsible for the experimentally observed shallow acceptor state in nitrogen-doped ZnO material.

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1. Introduction

As an excellent material candidate for ultraviolet (UV) laser, zinc oxide (ZnO) has attracted a great deal of interest from global interdisciplinary researchers. Recently, an ultra-fast UV laser based on ZnO nanowire with an ultra-small mode volume has been demonstrated [1]. This prestigious work has again proven the outstanding UV luminescence efficiency of the ZnO material. However, the nano-laser was optically pumped due to the unavailability of p-type ZnO. In fact, the lack of high-quality p-type-ness in ZnO has critically hindered the development of ZnO-based optoelectronic devices for decades accompanied by debates [2,3]. No unified conclusion has been made on the correct route towards controllable p-type ZnO. As a result, in order to fully realize the potential of ZnO material, more efforts are required on searching for proper dopant and technique for better control of the doping level.

Traditionally, nitrogen (N) has been thought as the most appropriate p-type dopant due to similar electronegativity and

ionic radius to oxygen. Nowadays, although doubted by theoretical calculations [4,5], doping with nitrogen is still the state-of-the-art approach for efficient p-type doping in ZnO because it gives the most evident experimental results of p-type realization [6–9]. If the calculations are correct, i.e., the substituting nitrogen on oxygen site (N_O) is quite deep in terms of ionization energy, the successful realization of p-type nitrogen-doped ZnO implies that the actual shallow acceptor is not in the form of simply N_O . Two categories of shallow acceptor forms have been proposed. One is complexes involving intrinsic zinc vacancies (V_{Zn}) and nitrogen [10,11], the other is the nitrogen dopant in complex forms [12–14]. Apparently, intrinsic defects cannot be ‘doped’ and are impossible for fine tuning of the doping level. Therefore, zinc vacancy related shallow acceptors are of less practical importance. On the contrary, the concentration of the nitrogen complex acceptors is closely linked to the dopant concentration during the material growth process and thus can be controlled.

Theoretical works by Bang [12] and Lambrecht [14] have predicted the possible shallow acceptor states in the form of $(\text{NH}_4)_{\text{Zn}}$ and $(\text{N}_2)_{\text{Zn}}$, respectively. They also have relatively low formation energy indicative of high solubility in ZnO lattice. Therefore, they are proposed as the possible origins for shallow acceptor states, which can explain the p-typeness observed in nitrogen-doped ZnO.

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However, there is rare experimental investigation on the introduction, control, and properties of these novel acceptor-like complexes. Ton-That et al. [13] have studied the effect of nitrogen plasma treatment on the ZnO nanowire samples. They have identified that the doped nitrogen can be in the form of $(N_2)_{Zn}$ which may create a shallow acceptor state. Experiments on the introduction of $(NH_4)_{Zn}$ complex have never been seen. Besides, the experimental characterization methods regarding the novel complex acceptors have not been well-established yet. In our opinion, by clear identification of the acceptor-like nitrogen complex, one can try to intentionally introduce and control the acceptor-like nitrogen complexes by proper tuning of the growth recipe. With this demand, in this work, we report the experimental introduction and control of the nitrogen-related complex acceptors by metal-organic chemical vapor deposition (MOCVD) technique. Net p-type has been realized for a wide window of nitrogen plasma flow rate. The acceptor dopant concentration has been successfully tuned by varying the nitrogen plasma flux during growth. By utilizing a series of characterization methods, we have confirmed the shallow nature of the complexes as predicted [13,14].

2. Experiments

According to the theoretical results, we have to push the nitrogen dopants to zinc sites in order to realize $(N_2)_{Zn}$ and $(NH_4)_{Zn}$ complexes. From the aspect of tuning the growth condition, it requires a crystal growth at oxygen (O)-rich ambience [14]. Considering that the O-rich condition is also beneficial to the suppression of popular intrinsic compensating donors, like zinc interstitials and oxygen vacancies, we fixed our O/Zn ratio during growth to a high value. Samples were grown by a home-built MOCVD apparatus. Dimethyl zinc (DMZn) [$-10\text{ }^\circ\text{C}$, 2 standard cubic centimeter per minute (SCCM)] and oxygen gas (O_2 , 100 SCCM) were employed as zinc precursor and oxidant, respectively. The substrate temperature and chamber pressure were set to optimized values of $400\text{ }^\circ\text{C}$ and 4 kPa, respectively. Relatively low substrate temperature guarantees efficient nitrogen incorporation. (0001) sapphire wafers were used as the substrates. Nitrogen doping source was provided by employing nitrous oxide (N_2O) plasma. Five nitrogen-doped samples were grown with different N_2O flux of 6, 12, 24, 50, 100 SCCM, and marked as samples A-E respectively. All samples have similar thickness of $230\text{ nm} \pm 10\text{ nm}$ due to that the growth rate is determined by the amount of zinc precursor. A batch of characterizations were employed to study the properties of the samples, including capacitance-voltage (C-V), Raman, X-ray photoelectron spectra (XPS), and photoluminescence (PL). Details of the measuring parameters can be referenced in our previous papers [15–17].

3. Results and discussion

Initially, the electrical properties have been characterized by high-frequency C-V measurement. The shape of the curves for all samples shows that the concentration of the acceptors overcomes that of the donors, indicating that acceptors are major (positive $N_A - N_D$ value). The curve for sample C, representing a typical p-type conduction, has been shown in the inset of Fig. 1. The capacitance shows a sharp decline when the bias goes positively indicates a gradual process of free holes from an accumulation to a depletion, and finally to an inversion [18,19]. The net doping concentration ($N_A - N_D$) for all samples have been derived from the relation between $d(C^{-2})/dV$ and $N_A - N_D$ in the depletion region, and plotted in Fig. 1 [20]. As the N_2O flux increases, the net acceptor concentration increases first and then decreases, with the max value obtained for sample C. Noticing that the $N_A - N_D$ value is in the order of $10^{15} \sim$

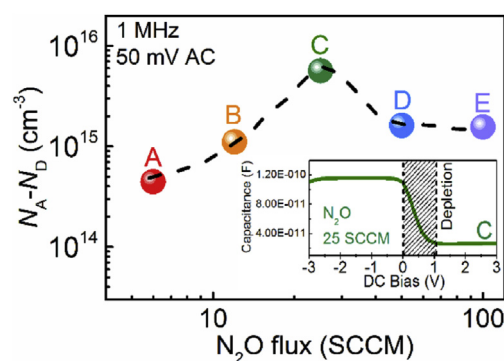


Fig. 1. The net doping concentration ($N_A - N_D$) of all samples derived from C-V measurement. The inset shows the C-V curve of sample C.

10^{16} cm^{-3} , such a trend illustrates that the net acceptor concentration can be tuned by varying N_2O flux, and the compensating donors exist.

In order to further investigate the forms of the acceptor- and donor-like defects, Raman spectra have been employed and the results are shown in Fig. 2. For the spectra at low-wavenumber region [Fig. 2(a)], only vibration modes of sapphire and ZnO can be detected. The intensities of the ZnO $E_2(L)$, $E_2(M)$, and $E_2(H)$ modes are nearly identical among different samples, implying that the change of N_2O flux does not almost affect the lattice quality and the amount of intrinsic defects in the samples [21]. Furthermore, the additional mode at 275 cm^{-1} , which is attributed to the vibration of Zn in small interstitial clusters $[(Zn-Zn)_i]$ has been suppressed [22]. It indicates that such a complex is not responsible for the compensating donors.

For the spectra at high-wavenumber region from 2250 to 2340 cm^{-1} [Fig. 2(b)], we have found additional peaks or humps. The peaks ranging from 2327 to 2338 cm^{-1} are attributed to the nitrogen vibrations in molecule N_2 . The origin for this is due to the absorption from air [13]. Besides, small humps raise at around 2305 cm^{-1} , which are visible for all samples. According to Soudi et al. [23] and Haboeck et al. [24], this peak is related to complexes involving nitrogen and hydrogen (NH_x). The formation of N-H is very common in MOCVD-grown nitrogen-doped materials since hydrogen is ubiquitous and abundant in the MO precursors [25]. Another peak around 2280 cm^{-1} can be prominently detected for sample C. While for other samples, it can be hardly observed. Based on the discussion and attribution from Ton-That et al. [13] and Haboeck et al. [24], this peak is ascribed to the lattice-bound nitrogen molecules (N_2), which may reside at oxygen $[(N_2)_O]$ [26], interstitial $[(N_2)_i]$ [27], or zinc $[(N_2)_{Zn}]$ sites [14]. The emergence of this peak implies the existence of lattice bound N_2 in sample C. Additionally, a minor hump in the vicinity of 2290 cm^{-1} , which were reported to emerge simultaneously with the 2280 cm^{-1} peak [24], can be marked. It is also attributed to the lattice bound double nitrogen complex. Considering the multiple forms and different electrical activity of the nitrogen related complexes, it is expected that they would affect the electrical conduction of the samples. Nitrogen chemical states have thus been checked by XPS.

Fig. 3(a) shows the N 1s XPS fine lines for samples A, C, and E, respectively. Utilizing the area ratio of N 1s over Zn 2p [28], we have determined the samples to have almost identical nitrogen concentration. We do not see a direct tuning of nitrogen concentration with increasing N_2O flux, possibly due to the solubility limitation. However, different nitrogen chemical configurations have been observed. Generally, three components, located at 403.7 , 399.9 , and 398.6 eV , have been deconvoluted from the original data. According to the XPS database from various species containing nitrogen [29],

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