

Limitation of Na-H codoping in achieving device-quality p-type ZnO

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ABSTRACT

Na-H in-situ codoping in single crystalline ZnO films was carried out by plasma assisted molecular beam epitaxy. It is found that Na-H codoping dramatically enhances the formation of substitutional Na (Na_{Zn}) in ZnO lattice due to the unchanged Fermi level. The annealing temperature needed to kick out H, however, is very high, which would concurrently result in a notable decrease of Na concentration to its solution limit in ZnO, namely, in the range of 10^{17} cm^{-3} . Our results suggest that Na-H codoping method has a limited effect on enhancing the p-type conductivity of ZnO.

1. Introduction

ZnO, a wide bandgap semiconductor material ($E_g=3.37 \text{ eV}$) with large exciton binding energy (60 meV), has been studied intensively due to its potential in optoelectronic applications [1,2]. In spite of the big progress made in ZnO-related materials and technology in recent years, synthesis of reliable p-type ZnO remains a formidable challenge. Na and Li have been proposed to act as shallow acceptors when substitute Zn in the lattice (Na_{Zn} and Li_{Zn}) [3–5], but stable p-type conductivity in Na or Li doped ZnO is still difficult to achieve due to the limited solid solubility of Na and Li in ZnO, and even more crucially, the formation of donor defects – interstitial Na (Na_i) or Li (Li_i). Specifically, calculations show that when the Fermi-level (E_F) decrease towards the valence band maximum (VBM), Na_i and Li_i become energetically more favorable than Na_{Zn} and Li_{Zn} , resulting in self-compensation [4,5]. Addressing this issue, Lee et al. proposed a codoping method with H [5]. The trick is that incorporation of H, a well-known shallow donor in ZnO [6,7], will compensate Na_{Zn} and Li_{Zn} , restraining E_F close to the conduction band minimum (CBM), where formation of Na_i and Li_i is unfavorable, especially under oxygen-rich condition. Meanwhile, the solubility limits of Na and Li can be greatly increased to 10^{20} cm^{-3} [5]. In that situation, H would bond with Na or Li to form neutral defect complex $\text{Na}_{\text{Zn}}\text{-H}_i$ or $\text{Li}_{\text{Zn}}\text{-H}_i$, so the codoped ZnO is highly compensated. However, the electrical activity of the substitutional acceptors can be retrieved by driving H out through subsequent annealing, providing that the complex can dissociate during the annealing process, which is just similar to Mg doped GaN [8]. To date, experimental research on Na-H or Li-H codoped p-type

ZnO thin films, as well as effort on clarifying the codoping mechanism, is surprisingly rare and far from success.

2. Materials and methods

In this work, we studied the Na-H codoped single crystalline ZnO thin films synthesized by molecular beam epitaxy. Hall measurements and SIMS were performed to evaluate the defect types and concentrations in the film. It was demonstrated that Na indeed occupied at Zn site when codoped with H, presumably in $\text{Na}_{\text{Zn}}\text{-H}_i$ configuration. Nevertheless, the elimination of H was much more difficult than expectation, implying a high activation energy for dissociation of the $\text{Na}_{\text{Zn}}\text{-H}_i$ complex, which was disadvantageous for practical p-type doping.

Na-H codoped ZnO thin films were deposited at 450 °C on undoped ZnO/MgO/ $\alpha\text{-Al}_2\text{O}_3$ templates by radio-frequency plasma assistant molecular beam epitaxy (rf-MBE) with a base pressure around $1 \times 10^{-7} \text{ Pa}$ [9]. Elemental zinc (7N) was evaporated by Knudsen effusion cell (Veeco), and oxygen radicals were produced by a plasma system (SVTA) using high-purity oxygen gas (5N5). Anhydrous NaOH (5N), after further dehydration in vacuum at 730 °C, was used as the dopant for in-situ Na-H codoping as it excluded undesired impurities which would impact the research [10]. Three samples labeled as A, B and C, were fabricated with different doping levels, where the NaOH-cell temperatures were 370 °C, 400 °C and 420 °C, respectively, and Zn-cell temperature was fixed at 320 °C. The rf power and oxygen flux were 340 W and 2.8 sccm (standard cubic centimeter per minute) respectively, which ensured an oxygen rich condition. The thickness of

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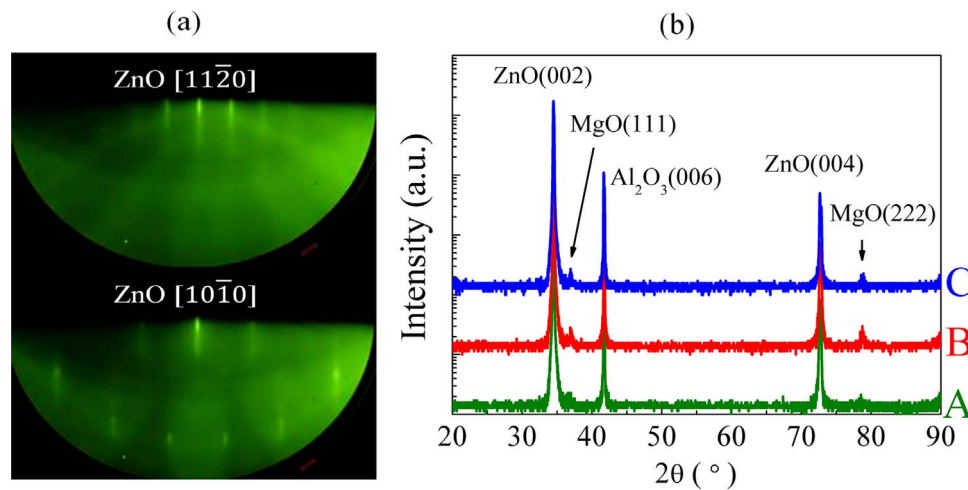


Fig. 1. (a) typical in-situ RHEED patterns of the Na-H codoped ZnO thin films (Sample B) and (b) X-ray diffraction θ - 2θ scan results of samples A, B and C.

Na-H codoped layer was around 250 nm. The as-grown samples were cut into several 10 mm×10 mm pieces for 10 min post-annealing under oxygen plasma environment in MBE chamber at 700 °C and 900 °C. X-ray diffraction (XRD) and the reflection high energy electron diffraction (RHEED) were employed to evaluate the crystal quality of the Na-H codoped ZnO films. Hall measurements were performed using a home-made Hall system (EMO 600, IPCAS), which was capable to exclude the influence of persistent photoconductivity in ZnO films by tracing the transverse voltage during measurements, guaranteeing a precise Hall voltage with correct sign extracted for the calculation [11]. The concentrations of Na and H versus depth profiles were measured in a Cameca IMS 7 f microanalyzer. Na concentrations were calibrated by using implanted reference samples, while H concentrations were simply characterized by the SIMS signal intensity.

3. Results and discussion

Fig. 1(a) shows the RHEED patterns of Na-H codoped samples which presents bright and fine sharp lines with high contrast, revealing a smooth surface and high quality single crystalline ZnO. Fig. 1(b) shows the XRD θ - 2θ scan results of the as grown sample A, B and C. Only five diffraction peaks were detected, corresponding to the diffraction from ZnO (002), MgO (111), α -Al₂O₃ (006), ZnO (004) and MgO (222), respectively. The full widths at half maximum of ZnO (002) peaks were smaller than 0.3° and the lattice constant c was calculated to be 0.5202 nm, in accordance with to the bulk value [12]. These results indicated a high crystalline quality of the Na-H codoped single crystalline ZnO thin films and ruled out the existence of any undesired phase. Note that the RHEED patterns and XRD results remained unchanged after anneal.

Hall measurement results of the as-grown and annealed samples were summarized in Table 1. For the as grown samples, A and B exhibits n-type conductivity, and the electron concentrations were $5.6 \times 10^{16} \text{ cm}^{-3}$ and $2.5 \times 10^{15} \text{ cm}^{-3}$, respectively, while sample C, with

the highest doping level, was semi-insulating. Taking into account that the undoped reference ZnO film possessed a background electron concentration around $7 \times 10^{16} \text{ cm}^{-3}$, the intrinsic donors must have been partly compensated by extrinsic acceptors, presumably Na_{Zn}. Thus we concluded that in the codoped ZnO films, Na indeed occupied the Zn sites when codoped with H, and more importantly, the amount of H incorporated in ZnO was less than that of Na in these samples. In another word, Na_{Zn}-H_i complex and isolated Na_{Zn} coexisted in the films and the latter passivated the intrinsic donors, leading to a decrease of the electron concentration. Note that the formation of Na_i was also a consideration as it might passivate part of Na_{Zn}, however, the content of Na_i should be orders of magnitude less than that of Na_{Zn} because its formation energy was much higher under oxygen rich condition with an upper E_F [5]. It is anticipated that increasing the H incorporation efficiency would further suppress the formation of Na_i due to the elevated E_F.

To kick out H and activate Na_{Zn}, annealing treatment is necessary. Isolated H in ZnO is easy to mobile and can completely diffuse out after annealing treatment at 500 °C. However, the mobile H can be easily trapped by impurities or defects [13,14]. Employing H implanted ZnO, Ip et al. found that the anneal temperature required to remove the trapped H increased to about 700 °C [14,15]. Therefore, to eliminate H efficiently, two anneal temperature for Na-H codoped samples was chosen in our study, specifically 700 °C and 900 °C. As shown in Table 1, all the 700 °C annealed samples turned to be semi-insulating. This is partly because the amount of residual H after 700 °C annealing is still high, which has been proved by SIMS (see Fig. 2(a)) and will be discussed later. In short, H trapped by Na cannot be efficiently removed at 700 °C, which is in accordance with previous research on Li-H and Na-H complex in bulk ZnO [16–18]. For the 900 °C annealed samples, p-type conductivity with a hole concentration of $\sim 2.6 \times 10^{16} \text{ cm}^{-3}$ was obtained in sample A. The conversion of conductive type after anneal was attributed to the decrease of H concentration. Interestingly, sample B and C were still semi-insulating after

Table 1

Summary of the electrical properties of as-grown and 900 °C annealed samples.

Sample	As-grown				Annealed at 700 °C	Annealed at 900 °C			
	Type	Carriers concentration (cm ⁻³)	Mobility (cm ² /Vs)	Resistivity (Ω cm)		Type	Carriers concentration (cm ⁻³)	Mobility (cm ² /Vs)	Resistivity (Ω cm)
A	n	5.6×10^{16}	30.5	3.66	semi-insulating	p	2.6×10^{16}	2.1	53
B	n	2.5×10^{15}	7.1	352	semi-insulating	semi-insulating			
C	semi-insulating				semi-insulating	semi-insulating			

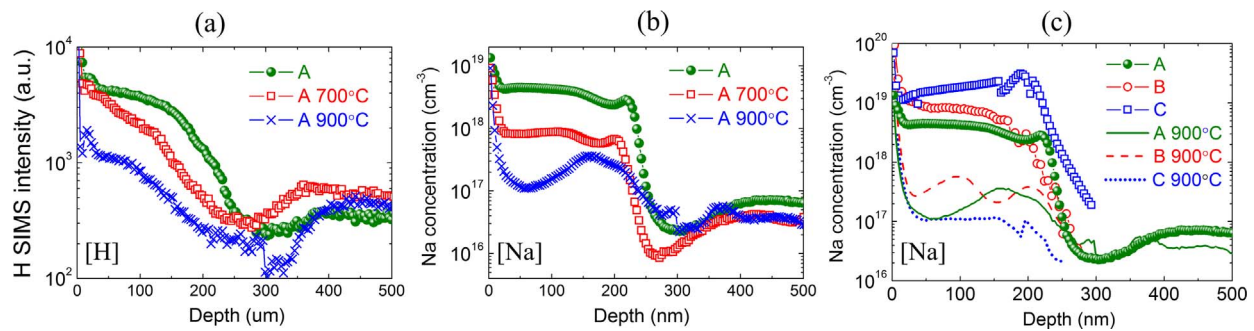


Fig. 2. (a) H and (b) Na concentration versus depth profiles for the as grown and annealed samples A. (c) Na concentration versus depth profiles for all samples.

anneal at 900 °C despite their higher doping level. Another notable fact is that the p-type conductivity of sample A is not stable that an alternation to ambiguous conduction type within a couple of days had been verified, which was attributed to the influence of H incorporated from air.

SIMS measurements provided further information of the samples to explore the doping mechanism. Figs. 2(a) and (b) shows sample A's H and Na concentration profiles, respectively. Apparent interface can be observed at a depth of ~ 250 nm for both, indicating simultaneous incorporation of Na and H in the codoped layer. The out diffusion of H at high temperature was demonstrated in Fig. 2(a), more than 15% H, however, remained in the film even after anneal at 900 °C, implying that the activation energy for dissociation of $\text{Na}_{\text{Zn}}\text{-H}_i$ complex was sufficiently high [17,18]. Moreover, Na_{Zn} was also revealed to diffuse out during the annealing process, which would definitely add to the difficulties to obtain a better p-type conductivity. The residual Na of sample A after anneal at 900 °C was less than 10% of its initial amount, yet p-type ZnO was still produced, which supported our assumption that $\text{Na}_{\text{Zn}}\text{-H}_i$ complex and Na_{Zn} co-existed in the as grown films, otherwise the remaining H (15%) would dominate, producing n-type conductivity. For samples annealed at 700 °C, about 50% H remained while Na concentration dropped at least one magnitude, consequently the compensation condition altered, which accounted for the high resistance.

Fig. 2(c) shows the evolution of Na concentration for the three samples. It can be observed that before anneal, the Na concentrations increased from $4.4 \times 10^{18} \text{ cm}^{-3}$ to $\sim 2.2 \times 10^{19} \text{ cm}^{-3}$ with the doping level. Interestingly, we found that the residual Na concentrations after anneal at 900 °C were all in the lower range of 10^{17} cm^{-3} regardless of the doping level [19]. One explanation is that at high temperature the concentration of Na, in the form of Na_{Zn} in our case, was restricted by the solution limit. This finding was in accordance with the results of Neuvonen et al., who reported that annealing Na implanted ZnO at high temperature (≥ 800 °C) resulted in Na redistribution with a plateau concentration level in the range of $\sim 2\text{--}5 \times 10^{17} \text{ cm}^{-3}$, regardless of the implantation dose [20].

In addition, sample B and C were semi-insulating after anneal at 900 °C, despite the similar residual Na contents in line with sample A. Two possible reasons were proposed responsible for this: 1) more H remaining in these two samples after anneal, passivating part of Na_{Zn} , because the amount of residual H was determined by its initial amount and the annealing temperature while that of residual Na was set by the solution limit at a certain temperature. 2) much more Zn vacancies (V_{Zn}) were formed in sample B and C after anneal due to the out-diffusion of Na_{Zn} , and these V_{Zn} tended to form vacancy clusters that passivated Na_{Zn} . This passivation mechanism has been well established in Li implanted ZnO [21].

4. Conclusion

In this work, Na-H codoped single crystalline ZnO thin films were fabricated by MBE. The evaluation of electrical properties and

impurities concentrations by annealing treatment was studied. Codoping with H indeed enhances the concentration of substitutional Na [Na_{Zn}]. However, $\text{Na}_{\text{Zn}}\text{-H}_i$ complex possesses a high bonding energy, hence removing the H donors requires annealing at very high temperature, namely, above 900 °C, where Na is revealed to diffuse out as well due to the low solution limit in the range of 10^{17} cm^{-3} . Our results suggests that Na-H co-doping technique is incapable to produce p-type ZnO with sufficient hole concentration on account of this dilemma.

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