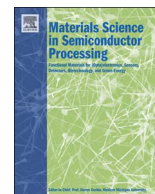




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Limitation of Na-H codoping in achieving device-quality p-type ZnO

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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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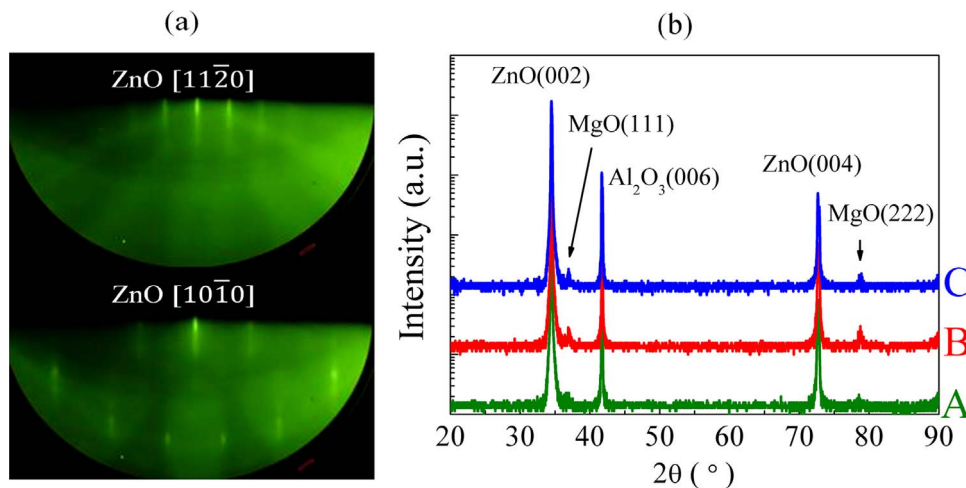


Fig. 1. (a) typical in-situ RHEED patterns of the Na-H codoped ZnO thin films (Sample B) and (b) X-ray diffraction θ - 2θ scan results of samples A, B and C.

Na-H codoped layer was around 250 nm. The as-grown samples were cut into several 10 mm \times 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			

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