Journal of Crystal Growth 483 (2018) 236–240

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/crys

P-type single-crystalline ZnO films obtained by (Na,N) dual implantation through dynamic annealing process

Zhiyuan Zhang, Jingyun Huang *, Shanshan Chen, Xinhua Pan, Lingxiang Chen, Zhizhen Ye *

State Key Laboratory of Silicon Materials, Cyrus Tang Center for Sensor Materials and Applications, School of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

ARTICLE INFO

Article history:
Received 26 September 2017
Received in revised form 4 November 2017
Accepted 1 December 2017
Available online 5 December 2017
Communicated by A. Ohtomo

Keywords:
P-type single-crystalline ZnO films
Ion implantation
Molecular beam epitaxy
Dynamic annealing

ABSTRACT

Single-crystalline ZnO films were grown by plasma-assisted molecular beam epitaxy technique on c-plane sapphire substrates. The films have been implanted with fixed fluence of 130 keV Na and 90 keV N ions at 460 °C. It is observed that dually-implanted single crystalline ZnO films exhibit p-type characteristics with hole concentration in the range of 1.24×10^{16}–1.34×10^{17} cm^{-3}, hole mobilities between 0.65 and 8.37 cm^2 V^{-1} s^{-1}, and resistivities in the range of 53.3–80.7 Ω cm by Hall-effect measurements. There are no other secondary phase appearing, with (0 0 2) (c-plane) orientation after ion implantation as identified by the X-ray diffraction pattern. It is obtained that Na and N ions were successfully implanted and activated as acceptors measured by XPS and SIMS results. Also compared to other similar studies, lower amount of Na and N ions make p-type characteristics excellent as others deposited by traditional techniques. It is concluded that Na and N ion implantation and dynamic annealing are essential in forming p-type single-crystalline ZnO films.

1. Introduction

As a wide gap semiconductor, today ZnO has become one of the hottest research fields in advanced materials and devices, emerging as one of the most important photonic and electronic materials, which shows great potential applications in gas sensor [1], photoelectrochemical immunosensor [2], solar cell [3], piezoelectric material [4], transparent electrode [5], UV-shielding material [6], thermoelectric material [7], biosensor [8], thin film transistor [9], photocatalytic material [10], and so on. Solid-state-lighting has a great tendency to replace the traditional bulb, which represents the future of human light source. High-efficiency blue light-emitting diodes (LEDs) become commercialized attributing to the successful fabrication of high quality p-type GaN films. It is obtained that ZnO possesses a series of advantages over GaN in fabricating light-emitting diodes, such as availability of large bulk single crystal, radiation hardness and high exciton binding energy [11,12]. For many advanced applications, the development of ZnO based devices such as p-n homojunctions can be realized by utilizing both n-type and p-type ZnO films of high quality. Due to a large number of intrinsic defects such as Zn interstitials (Zn_i) and oxygen vacancies (V_o), ZnO occurs as naturally as n-type semiconductor. Nevertheless, despite decades of worldwide research, p-type ZnO film is still difficult to achieve attributing to deep acceptor level, limited acceptor solubility, and various donor compensation [13]. So the difficulty in improving p-type conductivity hampers the development of the performance of ZnO-based LED. And in order to overcome the problem, considerable efforts have been made in research of creating p-type ZnO films, by doping with group IA, VA and IB elements, such as Li [14], Na [15], K [16], N [17], P [18], As [19], Sb [20], Cu [21], Ag [22], and so on. It is important that choosing appropriate acceptor and doping method is the key obstacle to obtain stable p-type ZnO films with excellent p-type characteristics after a period time [23,24]. Among group V elements, N is regarded as the most promising p-type dopant of ZnO films, attributing to similar radius and electronic structure between N and O [25,26]. Although considerable efforts have been focused on realize N-doped p-type ZnO films and ZnO based p-n diodes, it is difficult to achieve reproducible and good quality p-type conduction in N-doped ZnO films. One way to achieve a good solubility of N into ZnO is to use a dual acceptor method that uses two acceptors. There are reports on the successful preparation of stable p-type ZnO films attributing to using Li and N as p-type dopants, which were grown by pulsed laser deposition (PLD) [27], molecular beam epitaxy (MBE) [28], RF-magnetron sputtering [29], and so on. Nevertheless, Wardle points out that lithium may prefer to be on interstitial site in ZnO lattice and is more easily to form Li_{Zn}-H, Li_{Zn}-Li_i complexes than sodium [30]. Recently, theoretical studies indicate that it produces shallow acceptor state for

* Corresponding authors.
E-mail address: huangjy@zju.edu.cn (J. Huang).

https://doi.org/10.1016/j.jcrysgro.2017.12.001
0022-0248/

Na_{Zn}. The investigations on Na-doped ZnO films should receive more attentions, not only for illustrating the possible behaviors of sodium in ZnO, but also for the potential application. It is an interesting question that is very worthy of consideration that what will happen if Na and N simultaneously doped in ZnO? There are a few reports on Na-N dual acceptor doping of ZnO films, and there still exists a scope for an extensive investigation of the properties of the p-type ZnO films doped by Na and N fabricated by various deposition techniques.

Today, a large number of studies towards p-type ZnO films have focused on choosing traditional deposition techniques. Low solubility of dopants is the obstacle to hinder obtaining p-type ZnO films with high hole concentration. So in order to solve the problem, ion implantation is a widely used method in semiconductor processing, which is established owing to compatibility with planar device technology and its simplicity. The doping concentration can be precisely controlled by in situ ion beam current monitoring while the depth profile of the implanted ions can be controlled by ion beam energy. It shows clear advantages in controlling and productivity, compared to other existing deposition techniques [31]. The crystal damage and lattice disorder caused by ion implantation possesses negative effect on resistivity and mobility. Therefore, crystal recovery and dopant activation through dynamic annealing are needed [32].

In this paper, molecular beam epitaxy, ion implantation, and dynamic annealing have been combined to obtain p-type single-crystalline ZnO films. The impacts of Na and N ion implantation and the dynamic annealing process on the p-type conductivity have been discussed.

2. Material and methods

ZnO film was grown by plasma-assisted MBE technique on c-plane sapphire substrate. Elemental zinc (6N grade) and oxygen radio frequency (RF) plasma (O_2 gas of 6N grade) were used as the sources. The c-plane sapphire substrates were cleaned ultrasonically with acetone, ethanol, and deionized water for 10 min at room temperature, respectively. Prior to beginning growth, the substrate was thermally cleaned by heating at 300 °C in the preparation chamber for 3 h and then treated at 250 °C for 20 min in oxygen plasma exposure in the growth chamber with further cleaning at 800 °C for 30 min under ultrahigh vacuum achieved by a liquid nitrogen supply. After these cleaning processes, a MgO buffer layer was first grown at 650 °C for 5 min. Then the ZnO buffer layer was deposited at 300 °C for 5 min and annealed at 750 °C for 5 min. Then the top ZnO layer was deposited at 700 °C for 2.5 h and annealed at 750 °C for 5 min for better film crystallinity and smoother surface, during which the Zn cell temperature, oxygen flow rate and RF excitation power were fixed at 270 °C, 1.0 sccm and 350 W, respectively. After growth, the substrate temperature was decreased slowly at a rate of 5 °C per minute. The as-grown ZnO films were implanted with 90 keV N ions to fluence at 1.7×10^{15} cm^{-2} and 130 keV Na ions to fluence at 2.0×10^{14} cm^{-2} at 460 °C [33]. The as-grown ZnO film was about 300 nm, which is used as total thickness of the implanted layers, and the projected range was calculated to be 150 nm by the TRIM code. Na and N concentrations predict skew-Gaussian profiles with maximum implanted concentration at a depth of 150 nm simulated by SRIM.

Hall-effect measurements were conducted by using the Van der Pauw configuration and using Sn as contact metal at room temperature and in dark environment, with sample size as 1 cm^2 and applied magnetic field as 0.32 T. The reproducibility of repeated measurements is within the margin of error. The crystal structure of the unimplanted and implanted were investigated by X-ray diffraction measurements by using a Cu Kα radiation source (λ = 1.54,056 Å) at 2θ ranging from 20° to 80°. The chemical states of the elements present in the implanted ZnO films were analyzed by XPS measurement and calibrated by the C 1s peak. The distribution of elements of implanted ZnO films was analyzed by SIMS measurement. Raman spectra were performed at room temperature by using an Ar laser as excitation source with wavelength at 514 nm, with spectroscopic ratio of the spectroscope as 50:50.

3. Results and discussion

The electrical properties of both unimplanted and implanted ZnO films have been studied by Hall-effect measurements in van der Pauw method, as listed in Table 1. In order to make sure of reliability of the electrical properties, Hall-effect measurements were conducted several times and similar results were obtained. After ion implantation and dynamic annealing, it is observed that the single-crystalline ZnO films exhibited changing from n-type characteristics to p-type characteristics. It is deduced from the conversion that Na and N ions are successfully implanted in single-crystalline ZnO films and activated to produce holes and lattice disorder and crystal damage has been recovered by performing dynamic annealing caused by high energy ion implantation. In dual acceptor doping, Na ions replace the Zn sites while N ions occupy the O sites, forming Na_{Zn}-N_o acceptor complexes, which attributes to the conversion of the single-crystalline ZnO films [34]. Also stable p-type conduction results from the shallow acceptor with energy level of Na_{Zn} at 164 meV [30]. The aging analysis has been performed to confirm the stability and reliability of the electrical properties of p-type single-crystalline ZnO films. The p-type characteristics of the dually-implanted single-crystalline ZnO films remains relatively stable and don't convert to n-type characteristics after four months with hole concentration in the range of 8.4 $\times 10^{15}$–9.7×10^{16} cm^{-3}, hole mobilities between 0.5 and 5.4 $cm^2\,V^{-1}\,s^{-1}$, and resistivities in the range of 54.5–79.2 Ω cm by Hall-effect measurements, which implies the good stability and reliability of the dually-implanted single-crystalline ZnO films. Compared to N, O is so electronegative that the absorbed O tends to occupy its own site, resulting in forcing N ions from substitutional site to interstitial sites and stable Zn—O bond. As a result, it has negative effect on p-type characteristics that the N ions slowly migrate from substitutional sites to neighboring interstitial sites.

The comparison of the crystallinity of the unimplanted and implanted single-crystalline ZnO films has been studied in Fig. 1.

Table 1
Electrical results of unimplanted and implanted ZnO films.

Samples (N cm^{-2})/Na cm^{-2}	Temp (°C)	Resistivity (Ω cm)	Mobility ($cm^2\,V^{-1}\,s^{-1}$)	Carrier concentration (cm^{-3})	Carrier type
Unimplanted		0.15	37.7	2.08×10^{18}	n
1.7×10^{15}	460				
2.0×10^{14}		80.7	8.37	1.24×10^{16}	p
1.7×10^{15}	460				
2.0×10^{14}		53.3	0.65	1.34×10^{17}	p