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On the origin of intrinsic donors in ZnO

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ABSTRACT

As-grown undoped zinc oxide (ZnO) films have been annealed in zinc-rich, oxygen-rich and vacuum ambient, and the electron concentration varied greatly after the annealing process. It decreased nearly two orders of magnitude after the sample was annealed in oxygen, while increased nearly three times after annealed in metallic zinc ambient, and increased slightly after annealed in vacuum. It was found that the variation trend of the electron concentration is always the same with the expected variation of oxygen vacancy (V_O) under the three investigated conditions, it is thus speculated that V_O may be the dominant donor source in ZnO. By supplying more oxygen during the growth process to suppress V_O, ZnO films with lower electron concentration were obtained, which verifies the above speculation.

1. Introduction

Zinc oxide (ZnO) has been considered as one of the strongest candidates in a variety of applications including light-emitting devices, laser diodes, photodetectors, transistors, etc. [1–4]. However, such applications are drastically hindered by the difficulty in realizing reliable and reproducible *p*-type ZnO. It is widely accepted that the difficulty derives mainly from the strong compensation caused by the intrinsic donors and/or background impurities in ZnO. Therefore, clarifying the origin of the intrinsic donors, then taking measures to suppress these donors, is a fundamental step towards *p*-ZnO. However, up to now the origin of such donors is still under heated debate [5–9]. Some suggested that hydrogen may act as donors in ZnO [10–12]. However, many reports [13,14] have shown that hydrogen exhibits a rapid diffusion in ZnO films and subsequent annealing at 600 °C and above is sufficient to expel hydrogen out of the ZnO films. Moreover, it is found that ZnO films with low structural quality such as polycrystalline films usually have relatively high electron concentration [15], which suggests that the predominant origin of the residual donors may be intrinsic defects. Two major intrinsic defects have been considered as possible donor source in ZnO in previous literature: oxygen vacancy (V_O) [8,16,17] and interstitial zinc (Zn_i) [10,17–19]. However, some theoretical studies claimed that V_O has relatively deep energy level, and may be responsible for the so-called "green emission" in ZnO [20], while such a deep level excludes the possibility of V_O being the dominant origin of the relatively high residual electron concentration (as high as 10^{19-20} cm^{-3} in some cases) in undoped ZnO. Thermal treatment has been used extensively to investigate the defect chemistry of ZnO for decades, and effect of annealing on native defects have been studied in great detail [21]. It is speculated that by intentionally increasing/decreasing a certain kind of intrinsic defects in ZnO, for example, by annealing the as-grown sample in different ambient, the origin of the intrinsic donors in ZnO may be clarified.

In this paper, by annealing the as-grown ZnO films in oxygen, metallic zinc and vacuum ambient, it is found that the electron concentration of the film has the same variation trend with V_O in all the three investigation conditions. Therefore, V_O-related defects have been attributed to the dominant donor source in ZnO.

2. Experiment

The ZnO thin films were grown on *c*-plane sapphire (Al_2O_3) substrates by a plasma-assisted molecular beam epitaxy (MBE) technique. The substrates were treated by ethanol and acetone in

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an ultrasonic bath, then etched in hot (160 °C) H_2SO_4:H_3PO_4 = 3:1 solution for 15 min, and then rinsed with deionized water (18.2 MΩ cm^{-1}) and blown dry by nitrogen gas. To obtain a fresh clean surface, the substrate was annealed in vacuum ($\leq 1 \times 10^{-5}$ Pa) at 750 °C for 30 min in a pretreatment chamber. Metallic zinc (99.9999%) and oxygen gas (99.9999%) were employed as the precursors for the ZnO growth. A Knudsen effusion cell was used to evaporate elemental zinc, and the O_2 was activated by an Oxford Applied Research radio-frequency (13.56 MHz) atomic source (Model HD25) operating at 300 W. The substrate temperature was kept at 650 °C, and the O_2 flow at 0.50 sccm (sccm denotes standard cubic centimeter per minute) during the growth process. In this way, ZnO films with a thickness of about 1000 nm were attained. The as-grown samples were cut into small pieces and annealed in a tube furnace at 600 °C in oxygen ambient (about 1×10^5 Pa), metallic zinc, and vacuum (10^{-5} Pa). To test the influence of the oxygen pressure on the electrical properties of the ZnO films, another set of samples were annealed at different oxygen pressures (0.25 Pa, 1.8 Pa, 16 Pa, and 10^5 Pa) at 600 °C. The annealing was carried out isochronally in a systematic manner for 30 min. The ZnO films were also annealed in the aptotic oxygen pressure (about 1×10^5 Pa) at 650 °C for 0.5 h, 3 h, 6 h, 8 h, and 10 h to test the influence of the annealing duration on the electrical properties of the ZnO films. To suppress the oxygen vacancy-related defects during the growth process, a series of growths have also been carried out in our MBE technique experimentally. The growth conditions were almost the same with those stated above except that the flow rate of oxygen was maintained at 1.0, 1.6, and 2.0 sccm for three growths. The crystal structure of the samples was characterized by X-ray diffraction (XRD) with Cu Kα radiation (λ = 0.15406 nm), and the electrical properties were measured in a Hall system (LakeShore 7707) under Van der Pauw configuration at room temperature.

3. Results and discussion

Fig. 1 shows a typical XRD pattern of the as-grown ZnO films. Besides (0 0 6) peak of the Al_2O_3 substrate, only a strong (0 0 2) diffraction peak with its full width at half maximum of 0.18° is observed, indicating the as-grown ZnO films have single wurtzite structure with (0 0 2) preferential orientation. The effect of the annealing ambient on the electrical properties of the ZnO films is shown in Table 1. As evidenced from the table, the electron concentration of the ZnO film decreases nearly two orders of magnitude after the sample is annealed in oxygen, while it increases nearly three times after annealed in metallic zinc ambient, and increases slightly after annealed in vacuum. We note that the above data are not occasional, three similar experiments have been designed and carrier out, and the same variation trend has been obtained. It is rational to speculate that if the hydrogen is the dominant donor, the 600 °C annealing can expel hydrogen out of the ZnO films [13], so it would cause a dramatic decrease in the carrier concentration. However, in our experiments, the electron concentration decreases nearly two orders of magnitude after the sample was annealed in oxygen, but it increases nearly three times after annealed in metallic zinc ambient, and increases slightly after annealed in vacuum. Therefore, the obvious different variation of the carrier concentration after the annealing process reveals that hydrogen cannot be the dominant electron source in undoped ZnO.

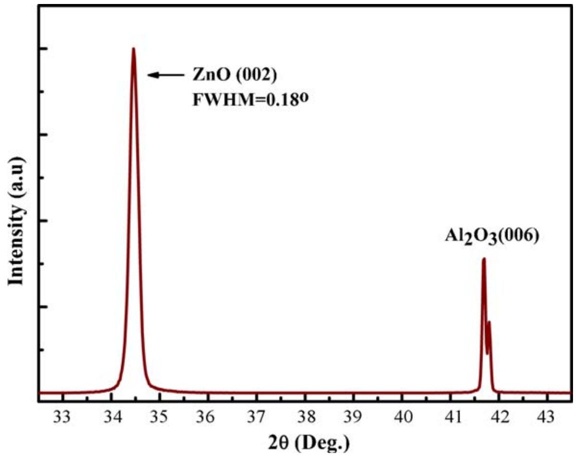

Fig. 1. A typical XRD pattern of the as-grown ZnO films.

Table 1
The Hall data of the as-grown ZnO film and those of the films after an annealing process in oxygen, metallic zinc, and vacuum ambient at 600 °C for 30 min.

Annealing ambient	Carrier concentration (cm^{-3})	Hall mobility ($cm^2 V^{-1} S^{-1}$)	Resistivity (Ω cm)	Conduction type
As-grown	3.6×10^{18}	1.8	1.01	n
O_2	3.9×10^{16}	3.2	51.43	n
Zn	1.3×10^{19}	30.9	0.02	n
Vacuum	6.2×10^{18}	13.4	0.07	n

Another possible donor source in ZnO is the intrinsic defects [5]. Amongst the common intrinsic defects Zn_i, V_O, and zinc vacancy (V_{Zn}) in ZnO, it is expected that the concentration of Zn_i and V_O will decrease, while that of V_{Zn} will increase when ZnO is annealed in O_2 ambient [22,23]. Meanwhile, electron paramagnetic resonance experiment revealed that the concentration of V_O and Zn_i will increase, while that of V_{Zn} will decrease when ZnO is annealed in Zn-vapor [24], However, there is a broad consensus both V_O and Zn_i are donors, while V_{Zn} is an acceptor in ZnO film from both theoretical and experimental points of view [25,26]. So the decrease of V_O and Zn_i, and the increase of V_{Zn} after the annealing process in O_2 ambient will lead to a decrease of the electron concentration jointly, which agrees well with the nearly two orders of magnitude decrease after the annealing in O_2 in our experiment, so it is impossible to identify the donor source in ZnO merely based on the Hall data of the samples annealed in O_2 ambient. Similarly, the origin of the residual electrons cannot be determined just from the three times increase of the carrier concentration after an annealing in metallic zinc ambient because the increase of Vo and Zn_i, and the decrease of V_{Zn}, that have been proved by the electron paramagnetic resonance experiment, can all cause a increase of electron concentration when ZnO is annealed in Zn-rich ambient.

Meanwhile, when the ZnO film is annealed in vacuum, both the concentration of V_{Zn} and V_O will increase [27,28], while that of Zn_i will decrease [27,29]. The variation of V_O will lead to an increase in the electron concentration, while the variation of Zn_i and V_{Zn} will result in a decrease of the electron concentration. The electron concentration increases slightly after the annealing in vacuum in our experiment, which has the same variation trend with V_O. Therefore, V_O should be the dominant source for the residual electrons in ZnO, while Zn_i and V_{Zn} can be excluded.

In order to confirm the above conclusion, two additional experiments have been designed and carried out. Firstly, the as-grown ZnO film is annealed in different oxygen partial pressures (0.25 Pa, 1.8 Pa, and 16 Pa) at 600 °C for 30 min, the electrical data of which are shown in Table 2. With increasing the partial pressure of O_2, the electron concentration of the films decreases gradually, which can be understood as follows: by increasing the oxygen pressure, more and more V_O-related defects will be occupied by oxygen, thus fewer electrons can be released, and the electron concentration in the ZnO film is decreased. Secondly, another series of ZnO films are annealed in O_2 ambient (about 1×10^5 Pa) at