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Short technical note

High quality p-type ZnO films grown by low pressure plasma-assisted MOCVD with N_2O rf plasma doping source

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ARTICLE INFO

Article history:
Received 12 July 2007
Received in revised form
16 February 2008
Accepted 9 March 2008

Keywords:
Photoluminescence
Metalorganic chemical vapor deposition
Zinc oxide films
p-type doping
Light-emitting devices

ABSTRACT

N-doped ZnO films have been grown on (0 0 0 1) sapphire substrates by a novel low-pressure plasma-assisted metalorganic chemical vapor deposition system using N_2O plasma as doping source. X-ray photoelectron spectroscopy analysis confirmed the incorporation of N into the ZnO films. Room temperature p-type conduction was achieved for the N-doped ZnO film at suitable substrate temperatures, with the resistivity of 8.71 Ω cm, hole concentration up to 3.44×10^{17} cm^{-3} and mobility of 2.09 cm^2/V s. In the photoluminescence (PL) measurement, a strong near-band-edge emission was observed for both undoped and N-doped films, while the deep-level emission was almost undetectable, which confirmed that the obtained ZnO-based films were well close to stoichiometry and of optically high quality.

1. Introduction

Recently, ZnO has attracted great interest for its wide bandgap (3.37 eV) and relatively large exciton binding energy (60 meV) at room temperature (RT). It has been regarded as one of the most promising candidates for the next generation of ultraviolet (UV) light-emitting diodes (LEDs) and lasing devices (LDs) operating at high temperatures and in harsh environments (Bian et al., 2004a, 2007; Polyakov et al., 2007). The ZnO-based LEDs will be brighter than the current state-of-art nitride light emitters, and at the same time, the production cost will be reduced significantly compared with current technology. However, the realization of stable and reproducible p-type ZnO with acceptable electrical and optical properties for optoelectronic devices has long been the bottleneck for ZnO-based materials applications. To date, many potential acceptors candidates have been attempted to realize p-type doping, including group 1 elements substituting on Zn site

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0924-0136/$ – see front matter
doi:10.1016/j.jmatprotec.2008.03.007

and group V elements substituting on O site (Tsukazaki et al., 2005; Look, 2005; Look et al., 2004). Though great progress has been made in fabricating p-type ZnO and even ZnO-based p–n junction light-emitting devices, this challenge still represents a major problem since the light-emitting efficiency was generally very limited due to the poor quality of the p-type layer (Ye et al., 2007; Lim et al., 2006; Wei et al., 2007; Ryu et al., 2006). Theoretical calculations of the electronic band structure predicated that N is the best candidate for producing a shallow acceptor level in ZnO compared with other group V elements, because it has almost the same ionic radii as that of O (Ozgur et al., 2005; Park et al., 2002; Wang and Zunger, 2004; Bian et al., 2004b). Nevertheless, there have been only very limited reports on the N-doped p-type ZnO mainly due to the too low solubility of the N dopant and only a small fraction of the incorporated N can be ionized to form the desired shallow acceptors (Polyakov et al., 2007). Moreover, the choice of dopant and growth technique remains controversial and the reliability and reproducible of p-type ZnO is still under debate (Look, 2005; Look et al., 2004).

Several N-containing dopants have been attempted as N doping source to grow N-doped ZnO films, such as N_2, NO, NH_3, NO_2 and N_2O (Iwata et al., 2000; Guo et al., 2002; Li et al., 2003; Look et al., 2002). N_2O was considered to be the best doping source for p-type ZnO compared with other nitrogen compound, the advantages were elucidated as follows: (I) N_2O can not only act as a N dopant source but also provide active O to suppress self-compensation from native donor defects such as V_O or Zn_i; (II) no other impurities will be incorporated into ZnO by N_2O doping source; and (III) N_2O was less toxic compared with other nitrogen compound. The only disadvantage with N_2O source seems to be that it was hard to decompose under normal condition due to the large atomic binding energy. In this article, N-doped ZnO films have been grown on sapphire substrates by a novel low-pressure plasma-assisted metalorganic chemical vapor deposition (MOCVD) system using N_2O plasma as doping source. p-type ZnO films with acceptable electrical and optical properties for optoelectronic applications were achieved. Compared with results obtained by other research groups, success in synthesizing p-type ZnO films as reported here provides convincing evidence that high reactive species containing atomic N could be produced through N_2O radio-frequency (rf) plasma source and act as an effective acceptor. The realization of p-type ZnO film by MOCVD technique paves the way for future industrialization.

2. Experiments

A novel low-pressure plasma-assisted MOCVD system was employed to grow N-doped ZnO films. Fig. 1 shows the schematic diagram of our patented MOCVD equipment. As shown in Fig. 1, Diethylzinc (DEZn) and O_2 gas (99.999% purity) were employed as the sources of Zn and O, respectively, which were introduced into growth chamber through separate injectors to effectively avoid the pre-reaction of precursors (Du et al., 2005). N_2O plasma was introduced into reactor through a quartz tube installed on the top of the growth chamber, which was fixed in a rf field. To exclude the influence of substrate on the measurements of electrical properties, the low-cost insulating (0 0 0 1) sapphire was selected as the substrates. It was pre-treated as follows: firstly, to remove the organic contamination, it was ultrasonically cleaned in toluene, acetone, ethanol and deionized water in sequence, then chemical etched in the mixture solution of H_2SO_4 and H_3PO_4 (3:1) for 15 min at 160 °C, and then blow dried with high pressured N_2 gas, and to the end, it was set into the pre-treatment chamber. Before growth, the substrates were physically cleaned by discharged Ar^+ in order to remove the atoms absorbed on substrates, which had been proved to be detrimental to the crystalline quality of as-grown film. After that, it was transported to the growth chamber and heated to the designated growth temperature. During the growth process, ultrahigh purity Ar was used as the carrier gas for DEZn with the flow rate of 4 sccm, rf power was fixed at 200 W, the flow rate of O_2 and N_2O were kept at 200 and 70 sccm, respectively. The reactor pressure was controlled to be ∼70 Pa, the appropriate low pressure was suggested to be essential to introducing plasma

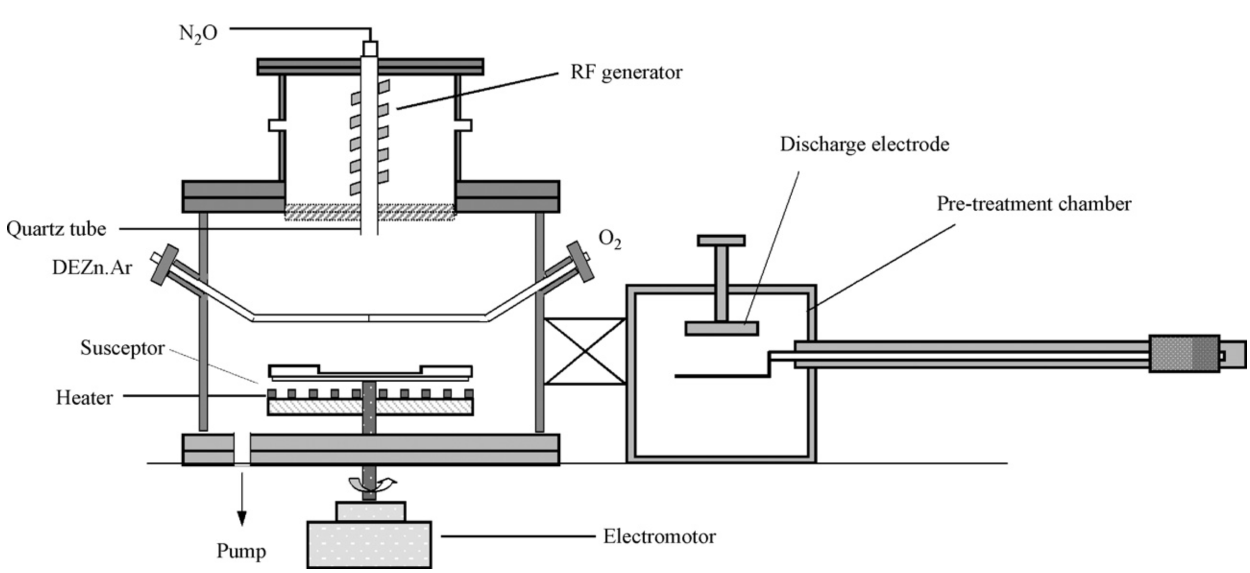

Fig. 1 – A schematic diagram of the plasma-assistant MOCVD system.