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Study on the Hall-effect and photoluminescence of N-doped p-type ZnO thin films

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Abstract

N-doped, p-type ZnO thin films have been grown by plasma-assisted metal-organic chemical vapor deposition method. The results under optimized growth conditions included a resistivity of 1.72 Ω cm, a Hall mobility of 1.59 cm^2/V s, and a hole concentration of 2.29×10^{18} cm^{-3}, and were consistently reproducible. A N-related free-to-neutral-acceptor emission and an associated phonon replica were evident in room temperature photoluminescence spectra, from which the N acceptor energy level in ZnO was estimated to be 180 meV above the valence band maximum.

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1. Introduction

ZnO has now become an attractive material for short-wavelength optoelectronic devices, such as light emitting diodes and laser diodes, because of its wide band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature [1]. However, the realization of p-type ZnO, which is critical to practical applications of ZnO-based devices, has proven difficult and thought to be the bottleneck in the development of ZnO-based devices due to the asymmetric doping limitations in ZnO [2]. Among all possible acceptor dopants, including group-V and group-I elements, N substituting for O appears promising [3–6]. Moreover, homojunction light emitting diodes based on ZnO, containing N-doped ZnO as the p-type layer, have been successfully fabricated [7,8]. These achievements open the window for the practical applications of ZnO-based optoelectronic devices, and call for further investigation of N acceptor behaviors in ZnO. In addition, metal-organic chemical vapor deposition (MOCVD) is of particular interest because it has many advantages over other growth methods, such as the feasibility of large area growth as well as simple and accurate doping and thickness control. Thus, combining the N doping technique based on ZnO with the MOCVD method can be a promising way to overcome the bottleneck of p-type doping in the development of ZnO-based devices.

Despite the importance of the MOCVD technique, there have been relatively few reports on N-doped, p-type ZnO by the MOCVD method. This is probably due to the low solubility of the N element in ZnO, especially in a CVD process. In this work, N-doped, p-type ZnO thin films were grown by a plasma-assisted MOCVD. Dependences of electrical and optical properties of ZnO thin films on growth temperature were investigated.

2. Experiments

N-doped ZnO thin films were grown on a-plane (11–20) sapphire substrates by the plasma-assisted low-pressure MOCVD method. Diethyl zinc was used as the zinc source, and N_2 was used as the carrier gas. NO plasma, generated by a radio frequency (RF) plasma source operating at 150 W,

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Table 1
Electrical properties of the N-doped ZnO thin films grown at different temperatures

Growth temperature (°C)	Resistivity (Ω cm)	Hall mobility (cm^2/V s)	Carrier concentration (cm^{-3})	Carrier type
250	735	0.23	3.69×10^{16}	p
300	135	0.41	1.13×10^{17}	p
350	33.8	1.05	1.75×10^{17}	p
400	1.72	1.59	2.29×10^{18}	p
450	82.9	2.04	3.68×10^{16}	p
500	0.785	7.14	1.11×10^{18}	n

acted as both the oxygen source and the N dopant source. The growth temperature ranged from 250 to 500 °C and the chamber pressure was maintained at 5 Pa. Hall-effect measurements were carried out in the van der Pauw configuration (BIO-RAD HL5500PC) at room temperature. The insulating sapphire substrates assured that the measured p-type conductivity came from the ZnO thin films. The surface morphology of the N-doped ZnO thin films was characterized by scanning electron microscopy (FEI Sirion 200 FEG SEM). The optical properties were studied by photoluminescence (PL) measurements at room temperature using a He–Cd 325 nm laser as the excitation source.

3. Results and discussions

The average thickness of the N-doped ZnO thin films is approximately 300 nm measured by cross-sectional SEM. Only one peak corresponding to the (002) plane of ZnO is observed in the X-ray Diffraction pattern (Bede D1 X-ray diffraction system using CuKα (λ = 1.541 Å), data not shown), suggesting a high (002) preferential orientation for the N-doped ZnO thin films. The results of Hall-effect measurements are summarized in Table 1. It is seen that p-type conductivity can be achieved at all growth temperatures except 500 °C. The optimized result is realized at the temperature of 400 °C with a resistivity of 1.72 Ω cm, a Hall mobility of 1.59 cm^2/V s, and a hole concentration of 2.29×10^{18} cm^{-3}. It is possible that the high temperature growth such as 450 and 500 °C reduces the N acceptor incorporation in the ZnO thin films, which can account for the relatively low hole concentration of 3.68×10^{16} cm^{-3} or even the inversion to n-type conductivity. This is not unexpected, since the decreasing N concentration in ZnO with the increasing growth temperature has been reported [9–11], independent of the growth methods. In the moderate temperature of 400 °C, more N acceptors are incorporated into the ZnO thin film, leading to the increase of the hole concentration and the optimized p-type conductivity. When decreasing the growth temperature from 350 to 250 °C gradually, even though the incorporation of the N element in ZnO should be enhanced at low temperature [9–11], no further increase of the hole concentration is observed. This is probably because a high N concentration in ZnO could lower the formation energy of some undesirable defects, such as $(N_2)_O$ or $(NC)_O$ [12–14]. These "hole killer" defects form readily at low growth temperature and compensate the N_O acceptor. As we can see, the sample grown at the low temperature of 250 °C possesses a relatively low hole concentration of 3.69×10^{16} cm^{-3} and a low Hall mobility of 0.23 cm^2/V s. It is the undesirable $(N_2)_O$ or $(NC)_O$ defects, which act as the "hole killer" and the scattering center, that deteriorate the p-type conductivity at the low growth temperatures. Note that the dependence of electrical properties of the N-doped ZnO thin films on growth temperature is not accidental in our growth experiments. These optimized results of p-type conductivity and the above-introduced growth temperature dependence have been consistently repeated.

Fig. 1 illustrates the SEM surface images of the N-doped ZnO thin films grown at different temperatures. It is seen that the smooth surface is composed of dense grains with the uniform dimension. In addition, the crystallinity of the ZnO thin film is improved for the high temperature growth.

Fig. 2(a) shows the room temperature PL spectra for the N-doped ZnO thin films grown at different temperatures. The strong UV emission indicates that the ZnO thin films are of high optical quality. The PL intensity increases significantly with the increasing growth temperature. A similar trend is observed for the nominally undoped samples, but much less dramatically (data not shown here). These

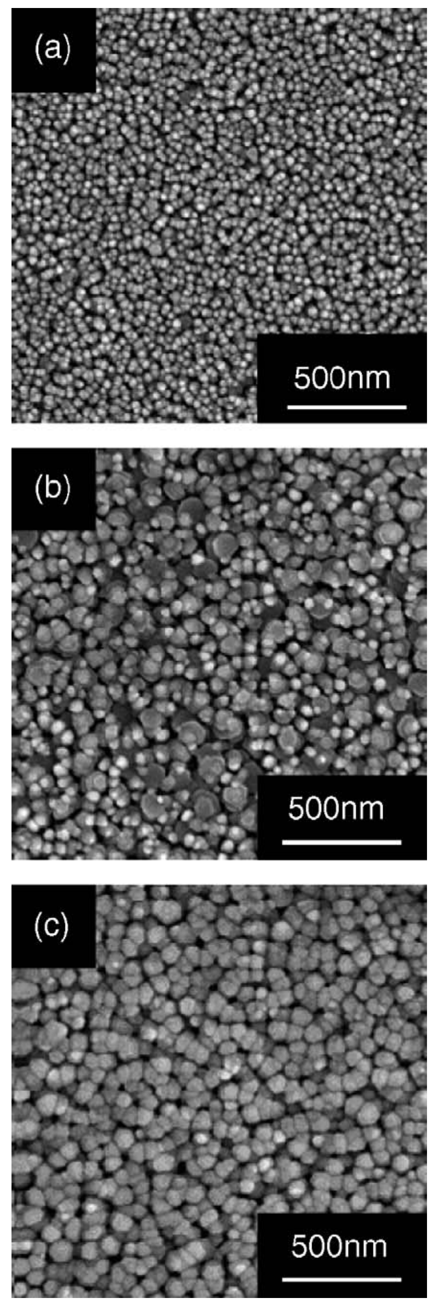

Fig. 1. SEM surface images of the N-doped ZnO thin films grown at different temperatures: (a) 300 °C; (b) 400 °C; (c) 500 °C.