p-n Heterojunction Composed of n-ZnO/p-Zn-doped InP

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A p-n junction was obtained by the deposition of an n-type ZnO thin film on a p-type Zn-
doped InP substrate. The Zn-doped InP substrate has been made by the diffusion of Zn with
sealed ampoule technique. The ZnO deposition process was performed by pulsed laser
deposition (PLD). The p-n junction was formed and showed typical I-V characteristics. We
will also discuss about the realization of an ultraviolet light-emitting diode (LED). The
structure of n-ZnO/p-Zn-doped InP could be a good candidate for the realization of an
ultraviolet light-emitting diode or an ultraviolet laser diode.

Keywords : ZnO, InP, PLD, p-n junction, LED

1. INTRODUCTION

ZnO has been studied as a short-wavelength light-emitting material[1], because it has the direct band gap
of 3.28 eV at 300 K. Compared with other wide band gap materials, ZnO has larger exciton binding energy (59
meV)[2], which assures more efficient excitonic emission at higher temperatures. Recently, there have
been a number of efforts of studying the characteristics of ZnO for the application to optoelectronic devices.
However, only a few successes have been reported about the fabrication of ZnO LEDs[3,4] due to the difficulty of
preparing p-type ZnO.

In our work, we have fabricated a ZnO based diode. Our approach to realize the ZnO diode was unique in
that we used a p-type Zn-doped InP substrate, rather than forming p-n homojunctions of ZnO. The combination of
p-type Zn-doped InP with n-type ZnO would lead to the formation of p-n heterojunctions.

In this paper, the structural and optical properties and the I-V characteristics of ZnO thin film will be discussed.

2. EXPERIMENT

ZnO films were grown on 1 cm x 1 cm (100) Zn-
doped InP substrates. The substrates were prepared by
Zn diffusion. The zinc diffusion processes were
performed via sealed ampoule technique using a
diffusion furnace maintaining temperature of about
495°C for 60 minutes. The details of the doping process
have been described elsewhere[7]. We have deposited
ZnO films using the pulsed laser deposition technique.
The chamber was evacuated by a turbomolecular pump
to a base pressure of 1 x 10^-6 Torr. The laser energy
density was 2.5 J/cm². We have used a ceramic ZnO
target (1-inch diameter, 99.999% purity). A pulsed
Nd:YAG laser was operated at a wavelength of 355 nm
and repetition rate of 2 Hz. A substrate holder was
placed at 50 mm from the target. The target was rotated
at 2 rpm to preclude pit formation in the target and to
ensure uniform ablation of the target[5]. The ZnO films
were deposited at the oxygen pressure of 350 mTorr, and
at a substrate temperature of 400°C. This condition has
been found to be optimal condition to emit UV light,
elsewhere[6,10-12]. Prior to deposition, Zn-doped InP
substrates were ultrasonically degreased in acetone and
methanol for 3 min. The deposition time was 10 min.
and the film thickness was measured to be about 3200 Å
by the cross-section scanning electron microscopy
(SEM) image. The structural properties of the sample
were investigated by the θ - 2θ method of X-ray
diffraction (XRD) where a Ni-filtered CuKα (λ=1.5418
× 10^-10 m) source was used. The optical properties of the
ZnO thin films were characterized by photoluminescence
with an Ar ion laser as a light source using the excitation
wavelength of 351 nm and a power of 100 mW. All the
spectra were taken at room temperature by a grating
spectrometer and a photomultiplier detector. Electrical
properties were investigated by Keithley 236 SMU.
3. RESULTS AND DISCUSSION

The XRD pattern of the ZnO film is shown in Fig. 1. Only the (002) ZnO and (200) InP peaks were observed. The XRD patterns show that the ZnO films are strongly c-axis oriented. The FWHM (full width at half maximum) of 20 values reveals the crystallinity of the film. Our result of FWHM was about 0.25°, and that is a relatively large value compared with the FWHM values of ZnO films deposited on sapphire substrates[6]. While InP has Zincblende structure, ZnO and sapphire have Wurzite structure. Therefore, it should be considered that the crystallinity was affected by the structural difference of ZnO thin films and InP substrates.

Earlier work[8] indicated that ZnO exhibited three PL bands centered around 390, 510 and 640 nm, labeled near ultra-violet (UV), green and orange bands respectively. It is known that the green luminescence of polycrystalline ZnO is related to the amount of oxygen vacancies in the films and the green PL comes from oxygen deficient films as reported by Vanheusden et al. [9]. In this work, the ZnO film emitted intensive UV emission and very weak visible light emission as shown in Fig. 2. The visible photoluminescence was much weaker than UV light emission (visible light was not detectable in our setup). Therefore, It could be thought that there are only a very few defects, such as oxygen vacancies, zinc vacancies or other impurities. Composition measurements such as SIMS could help to estimate the purity of the films. Also, we have considered that the major impurity might be due to In or P, because In or P of InP substrate could diffuse into the film. In SIMS data, secondary ion count of In or P was three order smaller than that of Zn or O. Therefore, it could be thought that the ZnO thin film has a very low number of impurities.

![Fig. 1. The XRD pattern of a 3200 Å thick ZnO film.](image)

![Fig. 2. PL spectrum of the ZnO thin film taken at room temperature.](image)

![Fig. 3. (a) The I-V characteristics of n-ZnO/p-Zn-doped InP heterojunction. (b) I-V characteristics of Au-ZnO-Au and (c) I-V characteristics of Au-InP-Au.](image)

The I-V characteristics of the ZnO/Zn-doped InP diode are shown in Fig. 3. In our I-V measurement system, we have used gold electrodes. The inset of Fig. 3 shows I-V characteristics of Au-ZnO-Au and Au-InP-Au contacts. Figures indicate that both ZnO-Au and InP-Au contacts show ohmic characteristics. The physical reason for the ohmic contact of p-type InP-Au contact has been discussed as follows. The work function of Au has been reported as to be about 5.1-5.5 eV[13]. For InP, the summation of band gap and electron affinity has been reported as to be about 5.75 eV[13]. Since InP substrate was heavily doped in our study, the work function might be near 5.75 eV, which is over the work function of Au. Generally, the ideal metal-semiconductor contact formed from a metal and a p-type semiconductor contact is to be rectifying contact if the work function of the metal is
smaller than that of the semiconductor. However, metal-degenerated p-type semiconductor contact in which the work function of semiconductor is larger than that of metal might be a narrow Schottky barrier. The narrow width of Schottky barriers might cause tunneling of carriers. Therefore, InP–Au contact has ohmic characteristic. The reason for the ohmic n-type ZnO–Au contact could be discussed as the same mechanism.

The main difference between the result of Fig. 3 and the typical I–V characteristics of diode is that the breakdown voltage is very small. The physical reason for the small breakdown voltage could be due to tunneling of carriers caused by both heavily doped n-type ZnO and p-type Zn-doped InP.

4. CONCLUSION

A ZnO based diode has been fabricated by the deposition of ZnO thin films on Zn-doped InP substrates. The ZnO thin film shows strong c-axis orientation, and intensive UV luminescence has been observed in the PL spectrum. While the breakdown voltage was very small in the reverse bias in the ZnO diode, the typical I–V characteristics have been observed in the forward bias. This could suggest a few successes to fabricate ZnO based diodes and show the possibility of the realization of ZnO LEDs.

REFERENCES