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Growth and photoluminescence for undoped and N-doped ZnO grown on 6H-SiC substrate

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Abstract

Growth and photoluminescence (PL) spectra of undoped and N-doped ZnO grown on 6H-SiC substrate by plasma-assisted molecular beam epitaxy (P-MBE) method were especially studied. Compared with PL spectrum of undoped ZnO, a broadening of near-band-edge (NBE) emission was observed in N-doped samples at room temperature. The low-temperature (5 K) PL spectrum confirmed that some acceptor levels associated with N doping were presented in the N-doped ZnO sample. The NBE emission of undoped and N-doped ZnO samples grown on 6H-SiC showed a small blue-shift compared with that grown on Al_2O_3, it was relate to the change of band gap caused by stress. The intensity of dominant NBE emission from ZnO films grown on 6H-SiC is stronger and the FWHM is smaller than that grown on Al_2O_3 substrate. The deep-level emission can be observed on both samples, but the intensity ratio of NBE to deep-level emission is larger for ZnO samples grown on 6H-SiC.

Keywords: ZnO; 6H-SiC; Al_2O_3; PL; XRD; MBE

1. Introduction

Recently, ZnO is attracting considerable attention as a potential candidate material for the use of ultraviolet light-emitting diodes (LEDs) and laser diodes (LDs). However, there is big challenge for device fabrication using ZnO material: improvement of crystal quality. At present, p-type conductivity, which is another difficulty for using ZnO electronic material, could be achieved by doping with N, As, P or by codoping N with Al or Ga. Among them, N-doped ZnO is most promising [1,2]. However, the crystal quality of p-type ZnO is also not satisfied, because Al_2O_3 has been commonly used as substrate to grow undoped and doped ZnO films. As the in-plane lattice parameters of ZnO and c-Al_2O_3 material are 3.25 and 4.785 Å, respectively [3], It will introduce a mismatch of 18%. Furthermore, the thermal mismatch between them is also as large as 24% [4]. The large lattice and thermal mismatch between ZnO epilayers and substrates will lead to the failure of lasers and breakdown of p–n junctions.

6H-SiC is a more suitable substrate to grow high-quality ZnO thin films, because the lattice and thermal mismatch between ZnO and 6H-SiC is 5% and 1%, respectively. But only Ashrafi et al. [3–5] reported some properties of undoped ZnO grown on 6H-SiC substrate using metalorganic chemical vapor deposition method (MOCVD). As for N-doped ZnO grown on 6H-SiC substrate, to our knowledge, no reports was available so far.

In this paper, X-ray diffraction (XRD) and photoluminescence (PL) spectra were mainly used to investigate the quality of undoped and N-doped ZnO films grown on 6H-SiC. For comparison, undoped and N-doped ZnO films grown on Al_2O_3 were also investigated.

2. Experimental

ZnO epilayers in the experiment were grown by plasma-assisted molecular beam epitaxy (P-MBE) method on 6H-SiC and sapphire substrate, respectively. The VG-V80H

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twin-chamber MBE equipment was purchased from abroad. The zinc (Zn) source was supplied by evaporating metal zinc with 99.9999% purity through a Knudsen effusion cell. NO activated by an Oxford Applied Research radio-frequency (13.56 MHz) plasma source with a power of 300 W was used as oxygen (O) source and nitrogen (N) source for the growth of N-doped ZnO. Pure oxygen gas (O_2) also activated by the plasma was used for the growth of undoped one. An electrosatalic ion trap was operated at 500 V during the growth process to suppress interference of ion in the plasma. Prior to growth, it is necessary to clean the substrate thoroughly. The as-received 6H–SiC (0 0 0 1) substrates were treated chemically using the conventional organic solvents and then dipped into the HF solutions particularly to remove the Si–O bonds. For the Al_2O_3 substrate, it was ultrasonically cleaned in acetone, followed in ethanol for 5 min and etched in hot (160 °C) H_2SO_4:$H_3PO_4 = 3:1$ solution for 15 min, then the 6H-SiC and Al_2O_3 substrates were rinsed in deionized water (18.2 MΩ cm^{-1}) and dried by high pure nitrogen gas. To obtain a highly crystallized surface, 6H-SiC and Al_2O_3 substrates were treated thermally in MBE preparing chamber under a vacuum of 1×10^{-7} Pa at 800 °C for 30 min before growth. During growth, Zn beam pressure was fixed at 4×10^{-4} Pa in the growth chamber.

The photoluminescence (PL) of the as-grown samples were investigated using a He-Cd laser with the 325 nm line. X-ray diffraction (XRD) was carried out on a Rigaku O/max-RA X-ray system using CuK$_\alpha$($\lambda = 1.5418$ Å)

3. Result and discussion

Fig. 1 shows the XRD spectra of undoped and N-doped ZnO samples grown on 6H-SiC. From this figure, it can be seen that besides the (0 0 6) diffraction peak of 6H-SiC, only one peak related to wurtzite structural ZnO (0 0 2) could be observed. It proved that we have fabricated c-axis preferred orientation wurtzite ZnO. The FWHM of XRD is 0.200° and 0.224° for undoped and N-doped sample grown on 6H-SiC, respectively. The FWHM is decreased by 0.025° and 0.010° compared with the XDR spectra of undoped and N-doped ZnO grown Al_2O_3. It indicates that the crystal quality of ZnO grown on 6H-SiC is superior to that grown on Al_2O_3 for both undoped and N-doped samples. It is due to the small stress between ZnO films and 6H-SiC substrate. From the PL spectra (Figs 2 and 3) measured at room temperature (RT), all undoped and N-doped samples showed intense near-band-edge (NBE) emission and weak deep-level emission. For undoped samples grown on 6H-SiC and Al_2O_3, the NBE peak energy located at 3.285 and 3.276 eV, and the FWHM is 100 and 118 meV, respectively. For N-doped ones, no distinct shift of peak energy between undoped and N-doped samples was observed, but the FWHM increased to 115 and 139 meV. Compared with that grown on Al_2O_3, the intensity of NBE is stronger and the FWHM is smaller

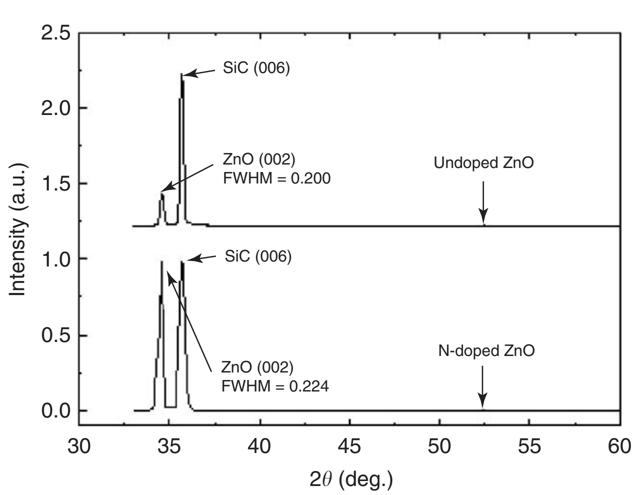

Fig 1. XRD spectra for undoped and N-doped ZnO grown on 6H-SiC.

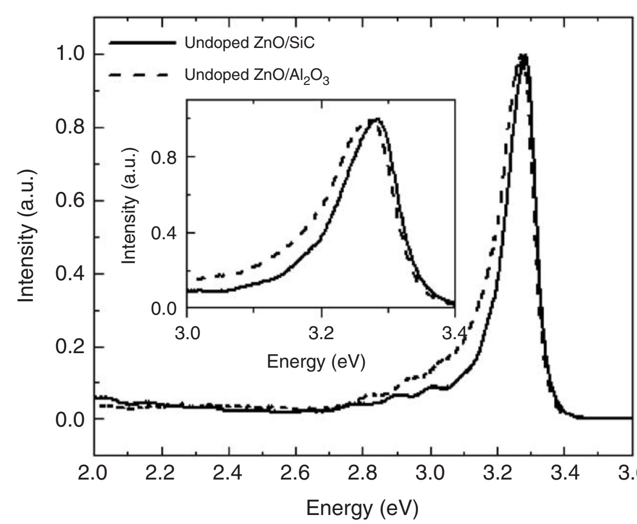

Fig 2. PL spectra (at RT) for undoped ZnO films grown on 6H-SiC and c-Al_2O_3.

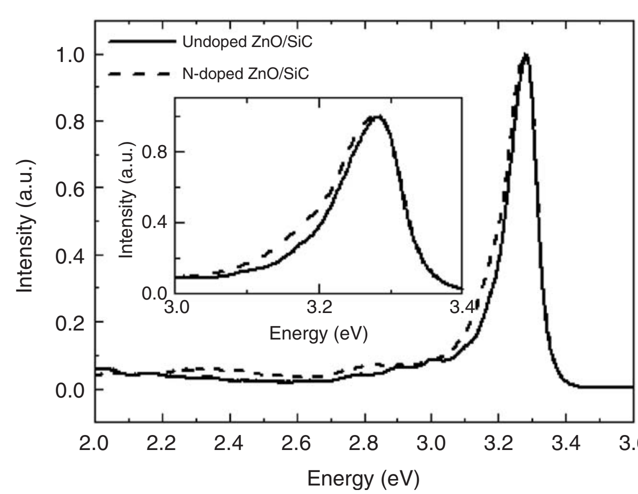

Fig. 3. PL spectra (at RT) for undoped and N-doped ZnO films grown on 6H-SiC.

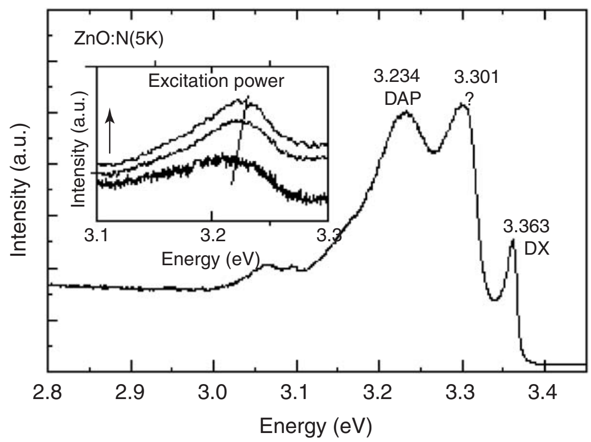

Fig. 4. PL spectra (5 K) for N-doped ZnO films grown on 6H-SiC, the insert shows the excitation power dependent on the DAP emission position.

for ZnO grown on SiC regardless undoped and N-doped ones. It shows that ZnO grown on 6H-SiC also have a superior optical property. The blue shift of NBE emission peak for ZnO grown on SiC relative to that grown on Al_2O_3 is due to the change of band gap caused by different stress. This stress comes from lattice and thermal mismatches between ZnO and substrate. Similar blue shift of NBE peak for GaN grown on SiC and Al_2O_3 substrates were also observed by Fischer et al. [6]. Considering the change of FWHM in PL (Fig. 3) and XRD (Fig. 1) spectra between undoped and N-doped samples grown on SiC substrate, it is believed some changes were caused by N-doping. However, Hall-effect showed n-type conductivity for both undoped and N-doped samples. In order to investigate the behavior of N atoms in doped sample, low-temperature (5 K) PL spectrum (Fig. 4) of ZnO grown on 6H-SiC was performed. This spectrum shows three main peaks in the ultraviolet region, which locate at 3.234, 3.301,and 3.363 eV. The peak position at 3.234 shifted towards higher energy with increasing the excitation power as shown in the inset, it is a characteristic of emission from donor–acceptor pairs (DAP). It is also close to the result of DAP recombination from ZnO:N grown on ZnO substrate by Look et al. [7]. It proved that some N atoms have occupied the positions of O atom, but these acceptors could not compensate all the donors in ZnO.

4. Conclusion

The undoped and N-doped samples grown on 6H-SiC showed an improved crystal and optical properties. An intense near-band emission (NBE) and weak deep-level emission were shown in the PL spectra. For N-doped ZnO samples, a broadening of the NBE peak were observed. Regardless of undoped and N-doped samples, the NBE emission peak of ZnO grown on 6H-SiC showed a blue shift relative to that grown on Al_2O_3. It is due to the different stress for ZnO grown on different substrates. DAP emission which located at 3.234 eV (5 K) was observed in N-doped ZnO grown on 6H-SiC.

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