Comparative study of ZnO and GaN films grown by MOCVD

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Abstract

ZnO and GaN films were grown by MOCVD. AFM, DCXRD and photoluminescence were used to study the surface morphologies, structural and optical properties of the films. By a comparison of the measurement results, it was shown that the structural and optical properties of the ZnO films are superior to the GaN films. The (102) FWHM and the free/bound exciton intensity ratio of the ZnO films are the best results ever reported for ZnO films. To evaluate the overall quality of the GaN films, an InGaN/GaN MQW LED was fabricated and the LED showed good I-V characteristics and its light output power was 6mW at 20mA, which indicated the good quality of the GaN layers and then indirectly suggested the high quality of the ZnO films.

1. Introduction

GaN is a direct wide gap semiconductor. Owing to the excellent work done by research groups all over the world since early 1990s, now high quality GaN layers can be grown by various methods and many high-performance GaN based devices have been fabricated, such as LEDs and LDs[1]. In recent years, with the progress in material growth, many new devices were designed to exploit new applications for GaN. For example, power GaN LEDs for lighting, GaN HEMT and other GaN based high temperature high power electronic devices are all in developing. To meet the higher requests for these new applications, many new material growth techniques were developed for GaN in the recent years. Meanwhile, researchers began to study new materials to complement the shortcomings of GaN for some applications. Among these new materials, ZnO attracted most interest, partly due to the surprising similarity of crystal structure and lattice constants between GaN and ZnO. In 1996, Z, K, Tang *et, al* [2]reported room temperature lasing in a microstructured ZnO film, which inspired world wide interest to ZnO research. By using MBE or PLD, ZnO with high crystallne perfection and high optical quality can be grown[3,4]. But considering the advantages in large-scale production and the success in GaN layers growth, MOCVD method shall be a promising technique to grow ZnO. For this technique, the most important problem to be overcome is the pre-reaction. In this article, we report high quality ZnO films grown by a home made atmospheric pressure MOCVD. For reference, GaN films were grown and a detailed comparison of their properties was conducted.

2. Experiment

ZnO films were grown by a homemade vertical AP-MOCVD system. To reduce the pre-reaction, the reactor was designed that the group II and VI reactant gas were delivered separately and mixed at only 5mm above the substrate surface. Meanwhile, large flow carrier gas (15L/min) was used to obtain high velocity. The susceptor is rotatable which ensure the uniformity of the films. 2-inch c-plane sapphire was used as the substrate. DEZn and H_2O were used as the Zn and O precursors and their flow rate were 92 μ mol /min and 0.036mol/min, respectively. The two-step growth process was adopted, a 150Å buffer layer was deposited at 160℃. After annealing the buffer layer at 685℃ for 5min, the epitaxial layer was grown under the same temperature. The growth time was 1 hour and the total film thickness was 3.0μm.

GaN films were grown by a Thomas Swan CS12712 MOCVD system. First, a 250 Å buffer layer

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was deposited at 530℃, 500Torr. Then the epi-layer was deposited at 1030℃.The total growth time was 2 hours and the total film thickness was 3.0μm. To evalute the overall quality of the GaN layer, an 5 periods InGaN/GaN MWQ structure and a p-type GaN layer were grown and LEDs were fabricated using Ti/Al and Ni/Au ohmic contacts.

The contact-mode AFM (Benyuan Nano Instrument, China) measurements were performed under ambient conditions. Rocking curves of the films were measured using a double crystal X-ray diffractometer (QC200, BEDE Instruments, UK), Cu $K_{\alpha 1}$ line was used as the source and Ge (004) was used as the reference crystal. Photoluminescence of the films were measured from 15K to room temperature using 325 nm line of a He-Cd laser (10mW) as the excitation source.

Results and discussion

Fig1. shows the morphology of the ZnO and GaN films. The GaN film have a very flat surface, the RMS roughness is 2.2nm for a 30x30 μm scan area. For the ZnO sample, hexagonal-like pyramid growths can be clearly seen. The grain size is about 15μm, which is the largest ever reported for ZnO films. The RMS roughness is about 17μm for the 30x30 μm scan area. The morphology of the ZnO film is different from that of our GaN sample but it is very similar to that of atmospheric pressure MOCVD grown GaN films reported by Nakamura[1]. And it is a common phenomenon that the atmospheric pressure MOCVD grown GaN films have larger grain size and rougher surface than low pressure MOCVD. The mechanism for the formation of larger grains by AP-MOCVD has been studied by several researchers[5,6]. It is believed that the nucleation density for atmospheric pressure growth is less than that for low-pressure growth. So in AP-MOCVD system, the lateral growth of nucleated islands will proceed for a longer time before they coalesce, thus form the larger grains. The similarity between the surface morphology of our ZnO sample and AP-MOCVD grown GaN films indicates that they have the same growth mode.

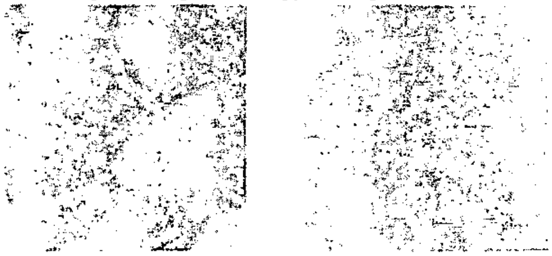

Fig1: AFM morphology of the ZnO and GaN sample

To evaluate the structural quality of the ZnO and GaN films, both (002) and (102) rocking curves were measured by double crystal XRD, as shown in Fig2. The FWHM of ZnO (002) is 118arcsec. This value is larger than that for MBE grown ZnO films reported in Ref[3].But it is much less than that of our GaN sample, which has the common device-level value of 234arcsec and close to the value of 106arcsec for a bulk ZnO

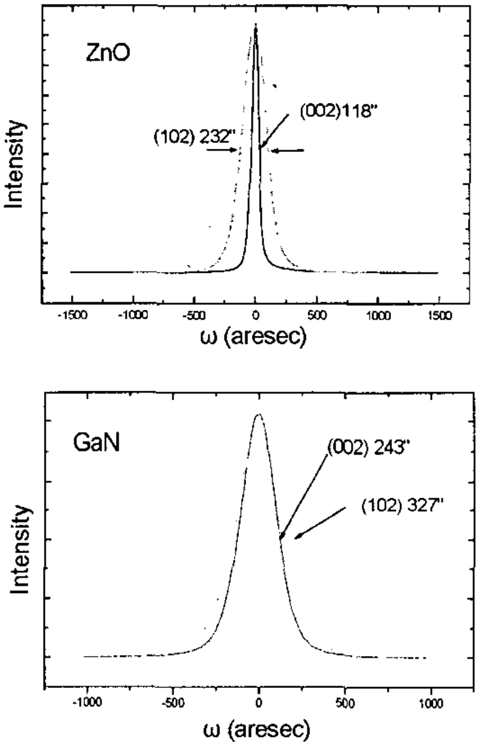

Fig2: XRD ω-rocking curves of the ZnO and GaN films

sample measured by our XRD system. Moreover, the (102) rocking curve of the ZnO sample has a very small FWHM of 232 arcsec, it's the best result for ZnO films ever reported. It is also much smaller than the 327"of the device-level GaN sample. B. Heying *et al* [7]has reported that the (002) rocking curves are sensitive only to the screw or mixed dislocations while the (102) rocking curves are sensitive to all the dislocations content in the GaN films. Similar result has been observed in ZnO. Thus, the broadening of (102) rocking curve is more reliable indicator of structural quality. In their research, the GaN sample studied had a (102) FWHM 413 arcsec and its total threading dislocation density was 4 x 10^8 cm^{-2}, so we estimate that the dislocation density of our ZnO sample will be less than 4 x 10^8 cm^{-2}, and probably in the order of .10^7 cm^{-2}

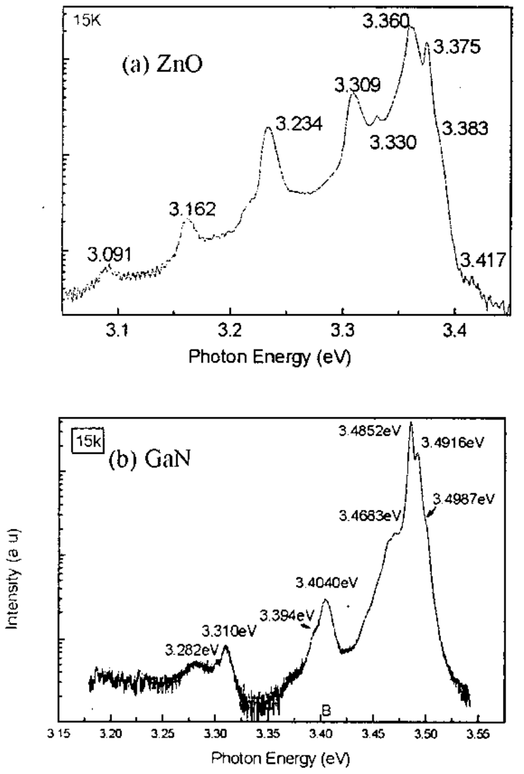

Fig3: PL specta of the ZnO and GaN films measured at 15K.

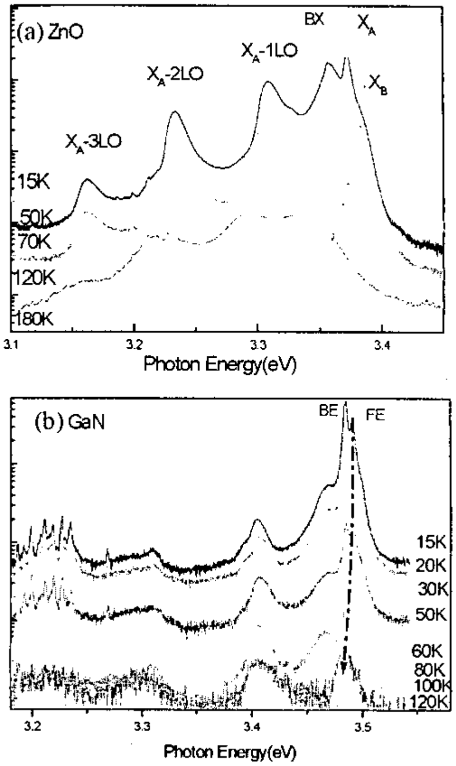

Fig4: Temperature dependent PL specta of the ZnO and GaN films.

Low temperature PL spectra is an important tool to study the properties of impurities and defects, as well as the band structure. The free and bound exciton peaks measured at very low temperature provide abundant information for the materials purity, lattice strain and defects energy level, etc. The low temperature PL spectra of the ZnO and GaN films and their evolution with increasing temperature are shown in Fig3 and Fig4. The 15K spectra of ZnO film dominated by a strong peak at 3.360eV, as shown in Fig3(a), which was attributed to the emission of D^0X.. The three peaks at 3.375eV, 3.383eV and 3.417eV are attributed to free exciton X_A, X_B and X_C, because the peak positions are very close to that of bulk ZnO[8] and the small red-shift are probably caused by tensile strain composed in the film. Evolution of the 3.360 and 3.375 peaks with the increasing temperature in Fig4(a) shows a typical free/bound exciton competition, which supported the identification of these peaks. Peaks at 3.309eV, 3.234eV, 3.162eV and 3.091eV have the regular space of about 72 meV, so it cant be attributed to the LO phonons of X_A. Similar line profile and peaks evolution can be seen in Fig3.(b) and Fig4.(b) for the GaN sample. The peak positions of D^0X and X_A, are blue shifted by several meV compared to bulk-like GaN, as commonly observed in most GaN films grown on sapphire [9]. The different peaks shift direction indicates a different stress releasing mechanism during the cooling down process for ZnO and GaN because their have the very close mismatch to the sapphire substrate. From Fig3.(a), the X_A/ D^0X ratio for ZnO was calculated to be about 2/3, which is the highest ever reported for ZnO. And the X_A/ D^0X ratio for the GaN sample is 1/3. The stronger free exciton intensity suggests the higher material purity. This is proved by the temperature dependence of the PL spectra: the ZnO X_A peak surpass the D^0X peak and become dominant at 50K while the GaN sample at 80K.

Fig5. shows the I-V characteristics of the InGaN/GaN MQW LED, the Vf is 3.2V and the IR <0.1 μA at -5V, the light output power is about 6mW. These are all satisfying parameters for high bright GaN LEDs. The good performance of the LED suggest that the quality of the GaN layer is fine and then indirectly indicate the high quality of the ZnO film.

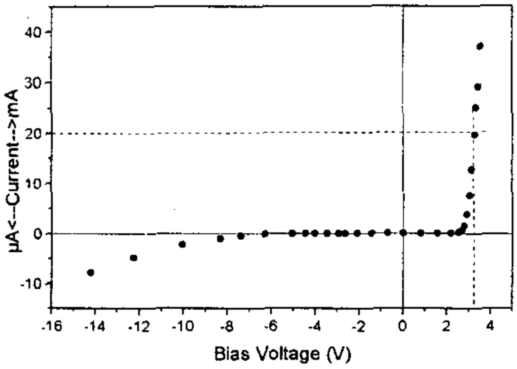

Fig5: I-V characteristics of InGaN/GaN MQW LED.

Summary

ZnO and GaN films were grown by MOCVD. The grain size, (102) FWHM and X_A/D^0X ratio are all the best values ever reported for ZnO film. By a comparison of the ZnO film to a GaN sample, it was shown that the ZnO sample has better structural and optical properties than the common device-level GaN film. And it was found that ZnO and GaN were grown under the same growth mode by MOCVD but have different strain release mechanisms. Our results suggest that MOCVD is suitable for ZnO growth.

Acknowledgements

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