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High Electron Mobility, Low Carrier Concentration of Hydrothermally Grown ZnO Thin Films on Seeded a-Plane Sapphire at Low Temperature

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Abstract

Hydrothermal growth of ZnO thin films were performed on a-plane sapphire substrates utilizing thick chemical vapor deposition (CVD) ZnO seed layer. The effects of growth temperature and molarity on the morphology, crystallinity, optical and electrical properties were investigated. All X-ray diffraction (XRD) patterns were dominated by the (002) peak, indicating the highly oriented growth along the c-axis direction. Many samples exhibited stacking hexagonal shaped end facets where their sizes and thicknesses increased with temperatures and molarities. Taking into account the XRD and photoluminescence (PL) results, the growth of the highest quality film with hall mobility of 175cm^2/Vs and low carrier concentration down to 10^{13}cm^{-2} orders was achieved at 70°C and molarity of 40mM.

1. Introduction

Since several decades ago, zinc oxide (ZnO) has been successfully applied in ultraviolet (UV) optoelectronic devices, sensors, solar cells, etc., due to its unique properties such as wide direct bandgap energy (3.37eV), large exciton binding energy (60meV), good thermal stability and good transparency [1]. Due to the lack of low-cost lattice-matched-epitaxy substrate, the growth of ZnO thin film is commonly done on a-plane sapphire or SiC substrates [2]. Many efforts have been made previously to achieve good ZnO films and it seems to show that the effects of seed/buffer layer either homo or hetero, and the deposition method are very prominent. For example, Tampo et al. reported the effect of utilizing MgO as a buffer layer in order to increase heterostructures hall mobility by increasing Mg concentration [3]. As a result, high hall mobility of 250cm^2/Vs at RT and low sheet carrier concentration of 1 x 10^{13}cm^{-2} was achieved.

In this paper, we report the growth of ZnO film on CVD grown ZnO seed by hydrothermal process. The effects of growth temperature and molarity on the morphology, crystallinity, optical and electrical properties were investigated.

2. Experimental Procedure

CVD grown ZnO seed layer on a-plane sapphire with thicknesses ranging from 1.0 to 3.0µm was applied as the substrate. The substrate was placed facing downwards in the middle of teflon-made holder inside a glass beaker containing an equimolar solution of zinc nitrate dehydrate ($Zn(NO_3)_2 \cdot 6H_20$) and hexamethylenetetramine (HMTA) dissolved in 100ml of deionized (DI) water. The molarities of solutions were set to 2, 20, 30 and 40mM, while the growth temperatures were set to 70, 80 and 90°C. The growth time was carried out for 3 hours after the temperature of the aqueous solution reached the set temperatures, i.e. 70-90°C. Finally, the sample was taken out from the aqueous solution and immersed into DI water to remove any residue on the substrate.

3. Results and Discussion

Field emission scanning electron microscope (FESEM) was used to characterize the surface morphology of ZnO seed layer and ZnO film. Fig. 1(a) shows the top and cross-sectional FESEM images of CVD grown ZnO seed. The surface is relatively smooth with a roughness in root-mean-square (RMS) value of 12nm. Fig. 1(b)-(d) show the surface and cross-sectional morphologies of the grown ZnO film at growth temperatures of 70, 80 and 90°C, respectively with molarity of 40mM. The surface shows the hexagonal shape morphologies where the size of hexagonal shape increases with molarities. However, the hexagonal shape morphology was confirmed to disappear at 90°C with molarity of 40mM. The thicknesses of the grown ZnO film were also found to significantly increase with temperatures and molarities. Here, the thicknesses of film were about 0.20, 0.30 and 0.81µm for samples grown at 70, 80 and 90°C, respectively, with molarity of 40mM. It is speculated that due to the smooth surface of the ZnO seed layer, the grown structures seem to be promoted in horizontal direction rather than vertical direction. That is the reason why the resulted structures were in the form of thin films.

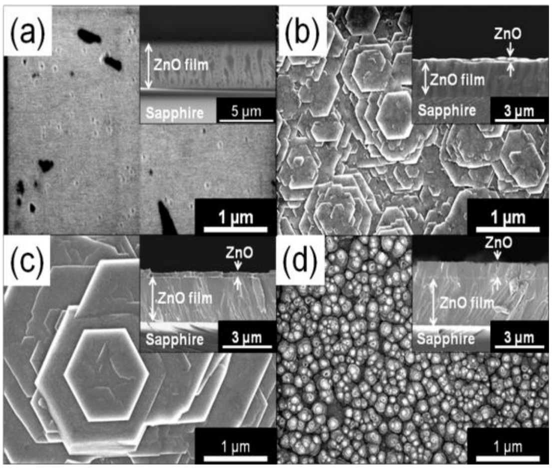

Fig. 1 FESEM top view and cross sectional images of (a) CVD grown ZnO seed, (b) ZnO film (70°C), (c) ZnO film (80°C) and (d) ZnO film (90°C).

The 2θ XRD spectra of CVD grown ZnO seed and hydrothermally grown ZnO film at 70°C was shown in Fig. 2(a). All samples grown at other temperatures and molarities show relatively strong peaks intensity around 34.51° to 34.71° and 37.5° to 37.7° which correspond to ZnO (0002) orientation and a-plane sapphire were observed, respectively. This simply indicates that the growth orientation is along c-axis. Fig. 2(b) shows the measured FWHM of 2θ spectra of samples grown at different molarities as a function of temperatures. Here, the FWHM values of 2θ spectra of ZnO seed were around 0.233° (841 arcsec). It clearly shows that the smallest FWHM value of 2θ was achieved at 70°C and molarity of 40mM, which are around 0.103° (371 arcsec). This indicates that the grown film shows considerably good crystallinity [4].

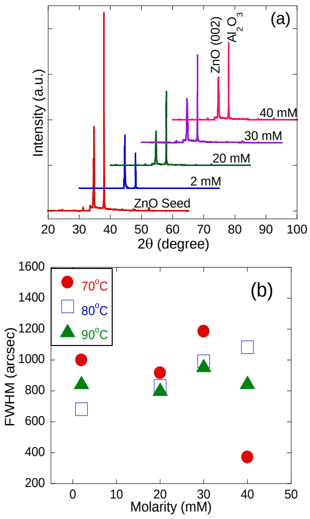

Fig. 2 (a) 2θ scan spectra, and (b) FWHM value as a function of molarity.

The room temperature (RT) PL spectra of ZnO film grown at 70°C with different molarities are shown in Fig 3. Two distinct peaks correspond to near-band-edge (NBE) emission peak and green emission (GE) peak were observed in all samples. The relative RT PL intensity ratio of NBE to GE (I_{NBE}/I_{GE}) was obviously increased with molarities with highest I_{NBE}/I_{GE} value of 1.17 was observed at sample grown at 40mM. This indicates fewer structural defects in the films [5].

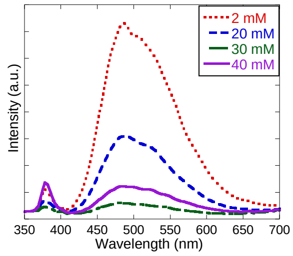

Fig. 3 PL spectra of ZnO film grown at 70°C.

Hall effect measurement was performed to investigate the hall mobility and carrier concentration. It is noted that the initial hall mobility of CVD grown ZnO seed were around 35 to 118cm^2/Vs. After the hydrothermal process, all films show the increment in their hall mobilities ranging from 60 to 175cm^2/Vs or from 20 to 285%. The mobility of films grown at 40mM was found to be in the range of 137-175cm^2/Vs regardless of growth temperatures. Meanwhile, the sheet carrier concentrations measured on ZnO film was confirmed to be around 3.69-7.73 x 10^{13}cm^{-2}. It was observed that, the highest mobility of 175cm^2/Vs was obtained for film grown at 70°C and 40mM with increment equivalent to 68%. This may due to its morphology of smooth flat surface stacking hexagonal shaped end facets disc and thinner compare to others. It is also supported by lowest FWHM value and highest hall mobility achieved at this condition.

4. Conclusions

A relatively high carrier mobility and low carrier concentration of hydrothermally grown ZnO film on pre-deposited ZnO seed on sapphire was achieved. The results demonstrate the promising route to grow ZnO crystals with good crystallinity together with excellent mobility and low carrier concentration.

Acknowledgements

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