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Growth of ZnO Nanorod Film on Glass Substrate by Nitric Acid Assisted Aqueous Solution Deposition

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Abstract - In this paper, the growth of ZnO nanorod film transformed from ZnO nanorod array on glass substrate was investigated. ZnO seed layer was first prepared on substrate by RF sputtering. Zinc nitrate and hexamethylenetetramine were used as precursors for the growth of ZnO nanorod array on glass substrate at 50 ^{o}C. The aqueous solution was assisted with the incorporation of nitric acid to increase the growth rate and the grain size of ZnO nanorod. With the growth time, ZnO nanorod film is gradually transformed from ZnO nanorod array.

***Keywords*:** ZnO, nanorod, film, glass, ASD

1. Introduction

ZnO is a promising material for electronic devices from its wide direct band gap of 3.37 eV and high exciton binding energy of 60 meV at room temperature and has been extensively studied because of its potential applications in various fields, such as gas sensors, solar cells, photodetectors, light emitting diodes, field effect transistors, and etc [1-5]. The preparation of high quality ZnO film is a fundamental work for those applications. There are many techniques for the preparation of ZnO films, such as pulsed laser deposition [6], chemical vapor deposition [7], spray pyrolysis [8], sol–gel process [9] and etc.

The aqueous solution deposition (ASD) has many advantages, for example very low growth temperature, unlimited growth area, cheap and simple process, and suitable for mass production. Recently, the ASD method was used for the growth of single crystalline ZnO nanorod array with excellent optical characteristics on various substrates [10], [11]. It is expected that high quality ZnO nanorod film can be transformed from single crystalline nanorod array by extending the growth time.

Generally, the glass substrate for ASD-ZnO film has many advantages such as transparent and low cost, but the growth rate is quite low and the transformation into film is difficult on amorphous glass substrate. Nitric acid (HNO3) is a strong acid and can modulate the concentrations of Zn2+ ions and hence control the ZnO growth. In this report, the characteristics of ZnO nanorod film transformed from ZnO nanorod array on glass substrate by HNO3 assisted ASD were investigated.

2. Experimental

ZnO nanorod array was grown on glass substrate with a sputtered ZnO seed layer by aqueous solution deposition. A ZnO seed layer with the thickness of about 100 nm was prepared by RF sputtering on glass substrate. ZnO with the purity of 99.99% was used as the target. The argon flow rate and the RF power were kept at 35 sccm and 60 W, respectively. The aqueous solutions of 0.1 M zinc nitrate ($Zn(NO_3)_2$) 30 ml and 0.1 M hexamethylenetetramine ($C_6H_{12}N_4$, HMT) 30 ml were used as precursors for the growth of ZnO nanorod arrays at 50 °C. In order to prevent the ZnO precipitates falling on the substrate, the substrate was held upside down to avoid ZnO precipitates falling on ZnO nanorod array. For HNO_3 assisted ASD-ZnO growth, 0.05 M HNO_3 1 ml was used. The preparation conditions for ZnO nanorod film are the same as those

for ZnO nanorod array except longer growth time. The electron mobility was examined by Van der Pauw Hall measurement.

3. Result and discussion

The morphology of ZnO nanorod film was observed by field-emission scanning electron microscopy (FE-SEM). Figure 1 (a) and (b) show SEM top views of ASD-ZnO nanorod films grown on glass substrates for 12 and 36 hrs at 50°C. A continuous and smooth film is hard to be obtained and it is not suitable for TFT fabrication.

Figure 2 (a) and (b) show the SEM top views of HNO3 assisted ASD-ZnO nanorod films grown on glass substrates for the growth time of 12 and 36 hrs at 50°C with the incorporation of 0.05 M HNO3 1 ml, respectively. We can observe that the diameter of ZnO nanorod is increased and the ZnO nanorod film transformed from ZnO nanorod array is apparently improved on ZnO sputtered glass substrate.

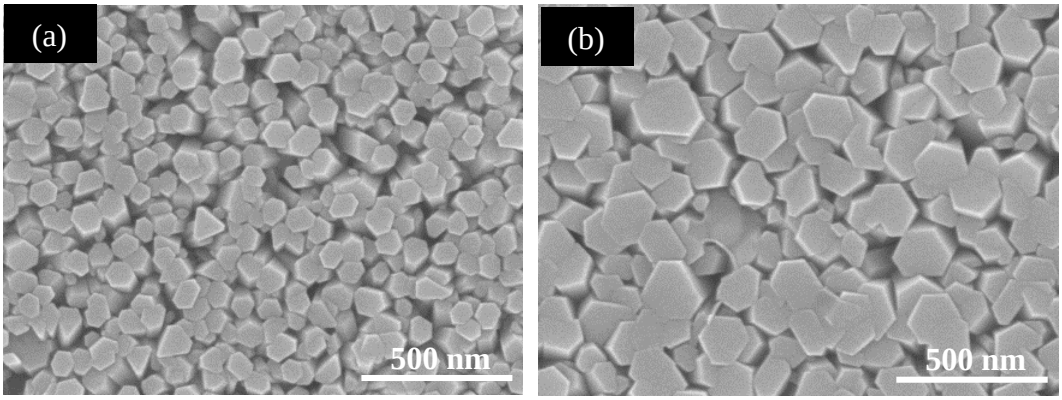

Fig. 1: Top views of ASD-ZnO nanorod films grown on glass substrates for (a) 12 and (b) 36 hrs at 50°C.

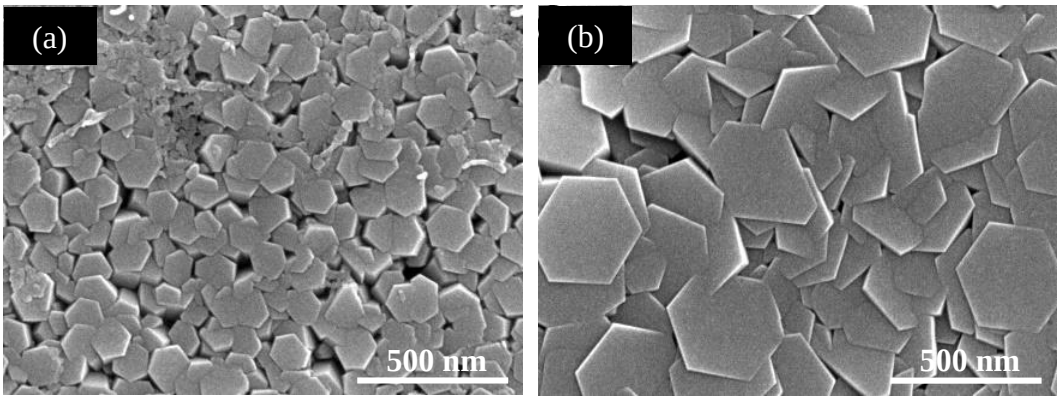

Fig. 2: Top views of HNO_3 assisted ASD-ZnO nanorod films grown on glass substrates for (a) 12 and (b) 36 hrs at 50°C.

Figure 3 shows the grain size as a function of the growth time for conventional and HNO3 assisted ASD-ZnO nanorod films. The growth rate of HNO3 assisted ASD-ZnO nanorod film is much enhanced. It could be strongly associated by Zn2+ from HNO3 incorporation [12]. Moreover, the HNO3 assisted ASD-ZnO nanorod film exhibits electron Hall mobility of 1.25 cm2/V-s for the growth time of 12 hrs and 2 cm2/V-s for the growth time of 36 hrs.

Figure 4 shows micro-PL spectra of ASD-ZnO nanorod films grown at 50 °C for 36 hrs with the incorporation of HNO3 before and after thermal annealing in N2O at 300°C for 1 hr. The PL spectrum of as-grown ZnO nanorod film has two main emission peaks. The peak at 380 nm (3.26 eV) is from the near-bandgap emission and the broadband emission centered at about 580 nm is associated with impurities or intrinsic defects [11]. After thermal annealing, the near-bandgap emission increases and the broadband emission decreases from OH out-gassing and crystalline improvement.

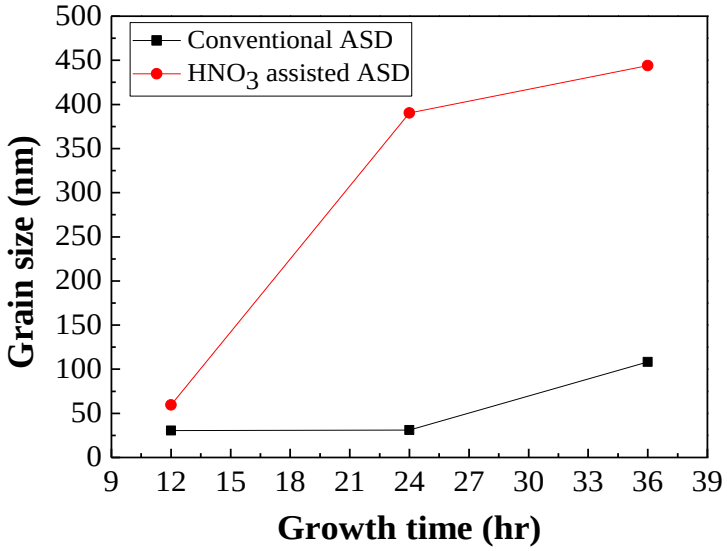

Fig. 3: Grain sizes of conventional and HNO_3 assisted ASD-ZnO nanorod films as a function of the growth time.

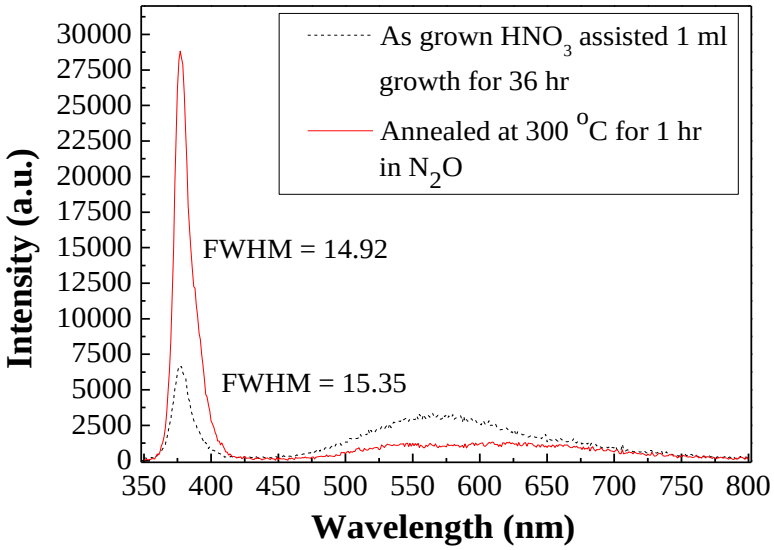

Fig. 4: Micro-PL spectra of as-grown and thermal annealed HNO_3 assisted ASD-ZnO nanorod films grown for 36 hrs.

4. Conclusion

In this report, the growth of ZnO nanorod film transformed from ZnO nanorod array on glass substrate was investigated. Zinc nitrate and HMT were used as precursors for the growth of ZnO nanorod array at 50 ^{o}C. Nitric acid plays an important role for the improvement of ZnO nanorod film quality. The quality of ZnO nanorod film can be improved by thermal annealing in N_2O ambient. The electron mobility of ZnO nanorod film on glass substrate can reach 2 cm^2/V-s examined by Van der Pauw Hall measurement.

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