

Characterization of ZnO Nanotip Array by Aqueous Solution Deposition under UV Illumination

Ming-Kwei Lee, Yi-Fan Lin

Chung Yuan Christian University, Department of Electronic Engineering
200 Chung-Pei Rd., Chung-Li, 32023, Taiwan, R.O.C.
mkleec@cycu.edu.tw; g10276005@cycu.edu.tw

Zheng-Shiun Lee, Yung-Chin Chu

National Sun Yat-sen University, Department of Electrical Engineering
70 Lianhai Rd., Kaohsiung, 80424, Taiwan, R.O.C.
shiun56789@gmail.com; m013010004@student.nsysu.edu.tw

Abstract- The ZnO nanotip array was synthesized on a sputtered ZnO buffer layer/glass by aqueous solution deposition with precursors of zinc nitrate and ammonia. The growth rate of ZnO nanotips can be much enhanced by ultraviolet light illumination. The growth rate has 1.38 and 1.86 times enhancement under 1 and 2 times UV light illumination, respectively. The quality of ZnO nanotip can be improved by the thermal treatment in N₂.

Keywords: Aqueous solution deposition, Nanotip array, Ultraviolet light, Zinc Oxide.

1. Introduction

ZnO is a promising material for optoelectronic devices from its wide direct band gap of 3.37 eV and high exciton binding energy of 60 mV at room temperature as shown by Pearton et al. (2005). Due to these properties, ZnO possesses a potential as UV detector as shown by Huang et al. (2001), solar cell as shown by Lee et al. (2008), gas sensor as shown by Wan et al. (2004) and field-effect transistor as shown by Chang et al. (2006). ZnO nanostructure can be synthesized via various methods including: (1) anodic alumina membrane (AAM), (2) vapor-liquid-solid process, (3) sputter deposition, (4) metal organic chemical vapor deposition (MOCVD), (5) aqueous solution deposition (ASD). Among these methods, the ASD as shown by Govender et al. (2002) has many advantages from the viewpoints of simple process, low cost, low growth temperature, selective growth and unlimited growth area. However, the growth rate of ZnO nanotip array is quite low, usually 350 nm/hr. For the deposition of semiconductor materials, ultraviolet (UV) illumination can enhance the growth rate as shown by Yeh et al. (1992). In this study, the characteristics of ZnO nanotip array prepared by ASD and illuminated by ultraviolet light were investigated.

2. Experimental

For the growth of ASD-ZnO nanotip array, a ZnO seed layer was prepared by RF sputtering with a ZnO target of 99.99% purity on the glass substrate. The flow rate of argon was kept at 35 sccm and the RF power was kept at 60W during the sputtering. The aqueous solutions of 0.02 M zinc nitrate (Zn(NO₃)₂) 80 ml and 15.4 M ammonium hydroxide (NH₄OH) 3 ml were used as precursors for the growth of ZnO nanotip array at 70°C. Under ultraviolet light illumination, the sputtered ZnO/glass substrate in the solution was 3 cm away from the solution surface, which was 20 cm away from the UV lamp. The UV lamp has a strong wavelength peak at 253.7 nm and the intensity is 0.96 mW/cm². In order to prevent ZnO precipitates falling on the substrate, the substrate was held upside down in the solution. The thermal annealing was used to improve the quality of ZnO nanotip array in N₂. The morphology of the ZnO nanotip array was observed by field-emission scanning electron microscopy (FE-SEM). The

optical property was characterized by micro-photoluminescence (Micro-PL). The bonding characterization was examined by Fourier-transform infrared spectroscopy (FTIR).

3. Results and Discussion

The SEM top and cross-sectional views of ZnO nanotip array prepared under dark (ASD-ZnO) and UV illumination (UV-ASD-ZnO) were shown in Fig. 1, in which the growth time is 2 hrs and the growth temperature is kept at 70°C. The thickness of sputtered seed layer is kept at 50 nm. The lengths of ASD-ZnO, 1xUV-ASD-ZnO and 2xUV-ASD-ZnO nanotip array are about 728, 1006 and 1359 nm as shown in Fig. 1(a), 1(b) and 1(c), respectively. The growth rate can be much enhanced to about 1.38 and 1.86 times under 1 and 2 times UV illumination. Figure 2 shows the lengths of ASD-ZnO, 1xUV-ASD-ZnO and 2xUV-ASD-ZnO nanotip arrays as a function of growth time.

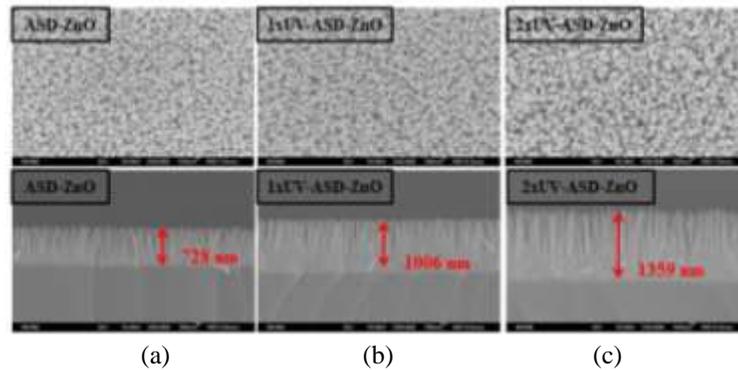


Fig. 1. Top and cross-section views of (a) ASD-ZnO and (b) 1xUV-ASD-ZnO and (c) 2xUV-ASD-ZnO nanotip arrays on sputtered ZnO seed layer/glass.

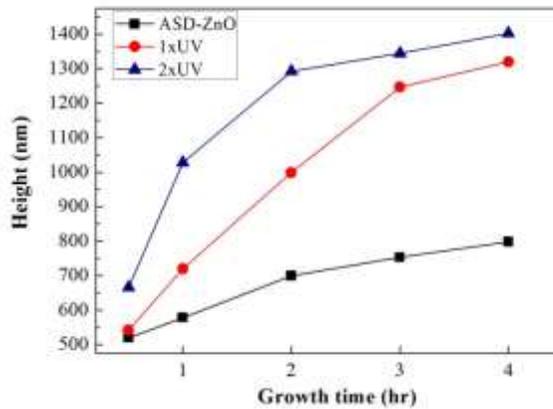
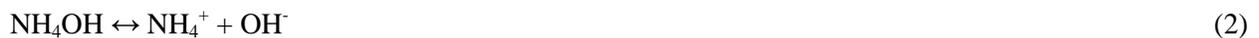


Fig. 2. Lengths of ASD-ZnO and UV-ASD-ZnO nanotip arrays as a function of growth time.

Basically, the length of ASD-ZnO nanotip array increases linearly with the growth time and then saturates due to the exhaust of precursors. The linear region is shortened with the intensity of UV illumination. The chemical reactions for the ASD-ZnO growth are as follows as shown by Wang et al. (2004):





In the ZnO growth process, the OH^- from NH_4OH shown in Eq. (2) reacts with Zn^{2+} from $\text{Zn(NO}_3)_2$ shown in Eq. (1) to form Zn(OH)_2 shown in Eq. (3). The Zn(OH)_2 dehydrates and subsequently produces ZnO and H_2O shown in Eq. (4) and (5). Under UV illumination, holes generated in ZnO by photoexcitation diffuse to the surface and can enhance the decomposition of ammonia and hence increase the concentration of OH^- . Thus, Eq. (3) will be shifted toward right to increase Zn(OH)_2 concentration and enhance the growth rate of ZnO. Figure 3 shows the corresponding FTIR spectra of the as-grown ASD-ZnO and 2×UV-ASD-ZnO nanotip arrays. The band at 520 cm^{-1} is assigned to zinc oxide as shown by Tang et al. (2006). The broad band in the range of $3260\text{--}3600\text{ cm}^{-1}$ is assigned to hydrogen-bonded OH groups as shown by Jin et al. (2000). The broad band of $3260\text{--}3600\text{ cm}^{-1}$ of 2×UV-ASD-ZnO is much stronger than that of ASD-ZnO. It supports that higher concentration of OH^- is contained in ASD-ZnO nanotip arrays under UV illumination.

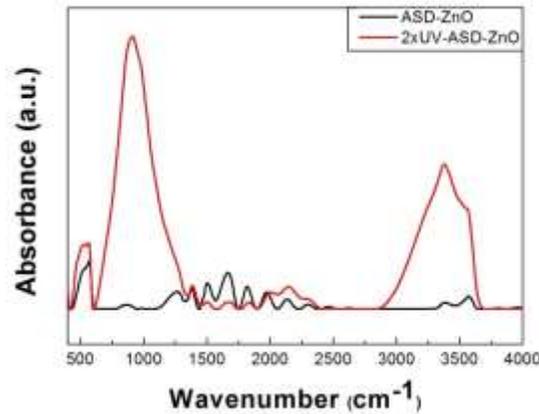


Fig. 3. FTIR spectra of as-grown ASD-ZnO and 2×UV-ASD-ZnO.

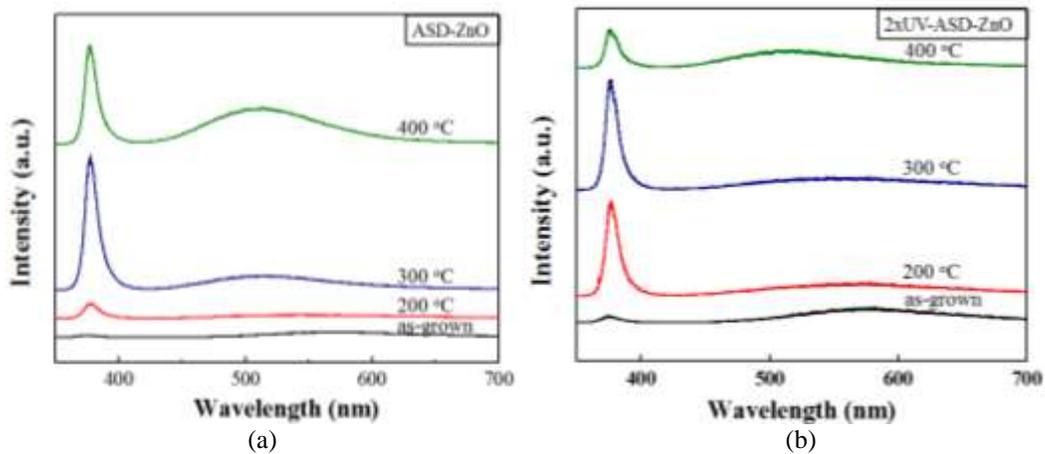


Fig. 4. Micro-PL spectra of (a) ASD-ZnO and (b) 2×UV-ASD-ZnO nanotip array annealed in N_2 for 1 hr at various temperature.

Figure 4 shows the micro-PL spectra of the as-grown and thermally annealed ASD-ZnO and 2×UV-ASD-ZnO nanotip arrays for 1 hr in N₂ ambient at room temperature. The PL of the as-grown ASD-ZnO nanotip array shows a very weak band edge emission centered at 375 nm as shown by Yang et al. (2006) and a green emission at about 580 nm as shown by Yang et al. (2006), which may be from O-vacancy as shown by Yang et al. (2006) and Zhu et al. (2008), Zn-vacancy as shown by Yang et al. (2006) and Zhu et al. (2008), interstitial Zn as shown by Yang et al. (2006) and Zhu et al. (2008), donor-acceptor pairs, and surface states. The band edge emission increases and the deep level emission decreases with the annealing temperature due to the crystalline rearrangement and the O-vacancy decrease which may be from the decomposition of OH⁻ to O²⁻. The strongest band edge emission of ASD-ZnO is at 300°C and it decays at higher annealing temperature due to oxygen outgas. The band edge and broad band emissions of 2×UV-ASD-ZnO annealed at 200°C are stronger than those of ASD-ZnO maybe from high concentration of OH⁻ under UV illumination. The strongest band edge emission of 2×UV-ASD-ZnO is also at 300°C.

4. Conclusion

The ZnO nanotip arrays with the length of 0.8 μm and the diameter ranged from 60~100 nm were obtained by ASD method under UV illumination at 70 °C for 5 hr, in which 0.02 M zinc nitrate 80 ml and 15.4 M ammonia 3 ml aqueous solutions were used. The nanotip array growth under UV illumination shows faster growth rate and the optical quality is improved after thermal annealing at 300°C in N₂ ambient.

Acknowledgements

The authors would like to thank the National Science Council of Republic of China for their support under contract No. 101-2221-E-033-080-MY3.

References

- Chang P.C., Fan Z., Chien C.J., Stichtenoth D., Ronning C., Lu J.G. (2006). High-performance ZnO nanowire field effect transistors. *Appl. Phys. Lett.*, 89, 133113.
- Govender K., Boyle D.S., O'Brien P., Binks D., West D., Coleman D. (2002). Room-Temperature Lasing Observed from ZnO Nanocolumns Grown by Aqueous Solution Deposition. *Adv. Mater.*, 14, 1221-1224.
- Huang M.H., Mao S., Feick H., Yan H., Wu Y., Kind H., Weber E., Russo R., Yang P. (2001). Room-Temperature Ultraviolet Nanowire Nanolasers. *Science*, 292, 1897-1899.
- Jin B.J., Bae S.H., Lee S.Y., Im S. (2000). Effects of native defects on optical and electrical properties of ZnO prepared by pulsed laser deposition. *Mater. Sci. Eng. B*, 71, 301-305.
- Lee Y.J., Ruby D.S., Peters D.W., McKenzie B.B., Hsu J.W.P. (2008). ZnO Nanostructures as Efficient Antireflection Layers in Solar Cells. *Nano Lett.*, 8, 1501-1505.
- Pearnton S.J., Norton D.P., Ip K., Heo Y.W., Steiner T. (2005). Recent progress in processing and properties of ZnO. *Progress in Materials Science*, 50, 293-340.
- Tang E., Cheng G., Pang X., Ma X., Xing F. (2006). Synthesis of nano-ZnO/poly(methyl methacrylate) composite microsphere through emulsion polymerization and its UV-shielding property. *Colloid Polym. Sci.*, 284, 422-428.
- Wan Q., Li Q.H., Chen Y.J., Wang T.H., He X.L., Li J.P., Lin C.L. (2004). Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors. *Appl. Phys. Lett.*, 84, 3654.
- Wang Z., Qian X.F., Yin J., Zhu Z.K. (2004). Aqueous solution fabrication of large-scale arrayed obelisk-like zinc oxide nanorods with high efficiency. *Journal of Solid State Chemistry*, 177, 2144-2149.
- Yang Y., Yan H., Fu Z., Yang B., Zuo J. (2006). Correlation between 577cm⁻¹ Raman scattering and green emission in ZnO ordered nanostructures. *Appl. Phys. Lett.*, 88, 191909.
- Yeh M.Y., Hu C.C., Lin G.L., Lee M.K. (1992). ZnSe growth by laser-enhanced metal-organic chemical vapour deposition. *Thin Solid Films*, 215, 142-146.

Zhu B.L., Zhao X.Z., Xu S., Su F.H., Li G.H., Wu X.G., Wu J., Wu R., Liu J. (2008). Oxygen Pressure Dependences of Structure and Properties of ZnO Films Deposited on Amorphous Glass Substrates by Pulsed Laser Deposition. *Jpn. J. Appl. Phys.*, 47, 2225-2229.