Epitaxial ZnO on p-Si and its MSM Structure Photoconductive Ultraviolet Detector

Wen’an Zhong1, Jianfeng Liu1, Yu Zhao1, Quanlin Zhang1, Yijun Zhao1 and Yuchao Wang1*
1 Xichang Satellite Launch Center, Xichang, Sichuan, 615000, China
2 Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-Sen University, Guangzhou, Guangdong, 510000, China;
*Corresponding author’s e-mail: wangyuchao321@yeah.net

Abstract. In this work, a plasma-assisted molecular-beam epitaxy (PA-MBE) was used to prepare high-quality ZnO thin films on p-type silicon substrates. Be/BeO composite buffer layers were designed to improve the crystal quality of ZnO thin films. Based on the ZnO thin films, we fabricated interdigitated electrode MSM structure photoconductive UV detector by lithography, electron beam evaporation and other traditional semiconductor processes. In addition, dark current, spectral response of the UV detector were measured by responsivity testing system to explore the application of ZnO based UV detectors.

1. Introduction
ZnO is a direct wide bandgap semiconductor. It has advantages of large bandgap of 3.37eV at room temperature, high binding energy of exciton up to 60 meV, abundant reservation and so on. Many researchers have focused on ZnO since the realization of stimulated emission of ZnO films at room temperature by optical pumping in 1997. Research areas of ZnO including the growth of ZnO material, band gap engineering, the p-type doping, light emitting diode (LED), laser, detectors are performed in decades[1-10]. R.B.Lal et al. studied the conductivity of ZnO irradiated by ultraviolet light [11]. Since then, studies of ZnO photoconductive ultraviolet detector have increasingly been reported. In 1985, the German Institute of Semiconductor Electronics invented the use of special electrode shapes to improve the performance of the device, which was known as the Interdigital electrode with a well-known transverse structure. Their "back-to-back" double Schottky barrier makes the dark current 3-5 orders of magnitude smaller than that of the photoconductive detector of the same material, and the response time is much faster. As a result, the finger-shaped electrode has been imitated on a large scale in the subsequent detector process. In 2001, S. Liang et al. from Rutgers University reported that ZnO photoconductive ultraviolet detectors were fabricated with circular electrodes[12]. The two electrodes formed Schottky contact by Ag plating and ohmic contact by Al plating, respectively. Under 1 V bias, the dark current of Ag-ZnO-Al is 0.1 nA and the dark current of Al-ZnO-Al is 10 uA. It can be seen that Schottky contact can effectively reduce the dark current of the device. It also fabricated an Inter-finger electrode with a length of 180 um, a width of 10 um and an interval of 10 um, irradiated by the 368 nm light with power of 0.1 uW. At 5V reverse bias, the dark current of the Ag-ZnO-Ag device is 1 nA and the photoelectric responsivity is 1.5 A/W. The response time is: rise time of 12 ns, decade time of 50 ns. In 2007, K.W. Liu from Changchun Optical Machinery Institute grew...
high-quality ZnO on silicon substrated and fabricated a gold-plated Interdigital electrode to form ohmic contact[13]. The photoconductive detector was working under the irradiation wavelength of 350 nm (5 uW) at reverse bias 3 V. The dark current of the device is 250 nA and the photocurrent is 300 uA. Therefore, the photoelectric responsivity is 60 A / W, the response rise time is 20 ns and the decade time is 10 us when illumination and 5 V reverse bias are used. In addition to the methods of MBE or MOCVD, there are others who grow ZnO on Si and SiO$_2$ substrates by sol-gel and magnetron sputtering. These methods are relatively cheap and can greatly reduce the cost[14-23].

2. Epitaxial growth of ZnO material

(1) The silicon we selected in this experiment is low resistance and high hole concentration p-Si (111). The arrangement of atomic silicon on the (111) plane is hexagonal, which contributes to the epitaxy of BeO and ZnO, which both have the same hexagonal arrangement. Since the surface of silicon substrate is likely to be oxidized by air during its production and use in this experiment, the substrate was immersed in 1% hydrofluoric acid HF for 15 minutes before the substrate was put into MBE chamber to remove the SiO$_2$ oxide layer on the surface. If other materials are epitaxial on the substrate, it is easy to cause the irregular arrangement of atoms in the epitaxial layer, thus affecting the quality of the film. Rinse clean the p-Si substrate soaked by HF with deionized water, and then blow dry with nitrogen. Then dry in the blast oven.

(2) Growth pretreatment. Similarly, the silicon substrate is dried by a magnetic push rod and fed into the MBE growth chamber. The temperature is 120 °C and the time is 10 minutes in the high vacuum growth chamber in order to remove the residual H$_2$O on the surface of the silicon substrate. After pretreatment, the substrate was moved to the growth stage.

(3) The growth temperature of Be layer is $T_{sub}=200$ °C, the Be source temperature is $T_{Be}=1100$ °C, and the growth time is 1 h. The BeO in the experimental Be/BeO buffer layer is grown in two ways: the first is to oxidize the Be directly, the oxygen flow rate is 1sccm, the RF power is 350 W, the substrate temperature is $T_{sub}=200$ °C, and the growth time is 30 s. The second one is BeO, substrate temperature is $T_{sub}=500$ °C, the Be source temperature is $T_{Be}=1100$ °C, the oxygen flow rate is 1 sccm, the RF power is 350 W, and the growth time is 3 min. The BeO, substrate temperature is $T_{sub}=500$ °C, the Be source temperature is $T_{Be}=1100$ °C and the RF power is 350 W. The growth temperature of the two layers of ZnO buffer layer is 500 °C, 550 °C, Zn source temperature is $T_{Zn}=320$ °C, 330 °C, oxygen source flow rate is 1 sccm, 1.6 sccm, RF power is 350 W, 380 W, growth time is 3 min, respectively, 5 min. ZnO thin films were grown at $T_{sub}=650$ °C. The Zn source temperature was $T_{Zn}=340$ °C, the oxygen flow rate was 2.4 sccm, the RF power was 400 W, and the growth time was 4 h.

![Figure 1. Buffer layer design of material growth](image_url)
samples in a mode of ω-θ scanning. It can be seen from the graph that the ZnO diffraction peak of SZ01, SZ02, SZ03 weakens in turn, and the width of the diffraction peak increases in turn. These results indicate the crystal quality of the three samples decrease as the oxidation time increases. The PL spectra of these samples are shown in Figure 3. Similar with the results from XRD, the ZnO emission peaks of the three samples in the spectra are weakened sequentially, and the ZnO peaks are broadened in varying degrees, and the defect packets of SZ02, SZ03 in the 450 nm~700 nm segment are also very large. The results show that there are many intrinsic defects in these two samples. The results of XRD and PL spectra of these samples show that the oxidation effect of BeO layer is better than that of BeO grown by oxygen source and beryllium source at the same time, and the oxidation time for Be should not be too long, so that the ZnO epitaxial film obtained is better than that of BeO film grown by oxygen source and beryllium source at the same time.

Figure 2. XRD patterns of ZnO thin films

Figure 3. Photoluminescence spectra of ZnO thin films

3. ZnO-based ultraviolet detector
Based on these samples, MSM photoconductive ultraviolet detectors were fabricated by photolithography and evaporation, and measured their dark current in the order of $10^{-7} \sim 10^{-8}$ A at 1 V bias. At 1 V bias, we tested their photoresponse with a home-built light response test system. From the following diagram, we can see that the photoresponse of SZ01 samples with good crystal quality of ZnO is the largest, and then of SZ02. The lowest photoresponse intensity is SZ03. The results show
that the crystal quality and defect density of ZnO thin films affect the photoresponse current of the device because the photogenerated carriers can be eliminated by these defects.

![Figure 4](image-url)

**Figure 4.** The responsivity of ZnO UV detectors

### 4. Conclusion

In this paper, we use molecular beam epitaxy (MBE), insert BeO buffer layer on P-Si substrate to grow ZnO single crystal thin films. Due to the excellent buffer layer, ZnO thin films’ crystal qualities are very good. Based on the ZnO single crystal materials, the interdigital Ultraviolet detector was fabricated by MSM structure. At 1 V voltage, the responsivity of the ZnO single crystal detector at 360 nm is 0.0504 A/W, and the dark current reaches the order of 10⁻⁸. Our research provide a specific path to realize high performance UV photodetectors.

**Acknowledgement:**

This work was supported by National Key Basic Research Program of China (No. 2011CB302000), National Natural Science Foundation of China (No. 51232009 & No. 51202299) and the Fundamental Research Funds for the Central Universities (No. 11lgpy16).

**References**

[1] Tang Z K, Wong G K L, Yu P, et al. Room-temperature ultraviolet laser emission from self-assembled ZnO microcrystallite thin films. Appl Phys Lett, 1998, 72 (25): 3270.

[2] Sun H D, Makino T, Tuan N T, et al. Stimulated emission induced by exciton-exciton scattering in ZnO/ZnMgO multiquantum wells up to room temperature. Appl Phys Lett, 2000, 77 (26): 4250-4252.

[3] Will UV Lasers Beat the Blues? . Science, 1997, 276 (5314): 895.

[4] Bagnall D M, Chen Y F, Zhu Z, et al. Optically pumped lasing of ZnO at room temperature. Appl Phys Lett, 1997, 70 (17): 2230.

[5] P. Zu Z K T, G. K. L. Wong. Ultraviolet spontaneous and stimulated emissions from ZnO microcrystallite thin films at room temperature. Solid State Commun, 1997, 103 (8): 459-463.

[6] A. Tsukazaki A O, T. Onuma Repeated temperature modulation epitaxy for p- type doping and light- emitting diode based on ZnO. Nature Materials, 2005, 4 (1): 42-46.

[7] Su, L. , Zhu, Y. , Zhang, Q. , Chen, M. , Ji, X. , & Wu, T. , et al. (2013). Solar-blind wurtzite mgzno alloy films stabilized by be doping. Journal of Physics D: Applied Physics, 46(24), 245103.
[8] Su, L., Yuan, Z., Zhang, Q., Chen, M., Wu, T., & Gui, X., et al. (2013). Structure and optical properties of ternary alloy bezno and quaternary alloy bemgzno films growth by molecular beam epitaxy. Applied Surface Science, 274(5), 341-344.
[9] Su, L., Yuan, Z., Chen, M., Zhang, Q., Su, Y., & Xu, J., et al. (2013). Temperature-dependent structural relaxation of bezno alloys. Applied Physics Letters, 103(7), 2230.
[10] Su, L., Yuan, Z., Xu, X., Chen, H., Tang, Z., & Fang, X. (2018). Back-to-back symmetric schottky type uva photodetector based on ternary alloy BeZnO. Journal of Materials Chemistry C, 6(29), 7776-7782.
[11] Lal R and Arnett G. Effect of Ultra-violet Irradiation on the Electrical Conductivity of Zinc Oxide Single Crystals. 1965:
[12] S. Liang H S, Y. Liu,Z. Huo,Y.Lu, H. Shen. ZnO Schottky ultraviolet photodetectors. J Cryst Growth, 2001, 225: 110-113.
[13] Liu K W, Ma J G, Zhang J Y, et al. Ultraviolet photoconductive detector with high visible rejection and fast photoresponse based on ZnO thin film. Solid State Electron, 2007, 51 (5): 757-761.
[14] Xu Z Q, Deng H, Xie J, et al. Ultraviolet photoconductive detector based on Al doped ZnO films prepared by sol-gel method. Appl Surf Sci, 2006, 253 (2): 476-479.
[15] Jiang D Y, Shen D Z, Liu K W, et al. Effect of post annealing on the band gap of MgZn1-xO thin films. Semicond Sci Tech, 2008, 23 (3):
[16] Xu Z, Deng H, Xie J, et al. Photoconductive UV detectors based on ZnO films prepared by sol-gel method. J Sol-Gel Sci Techn, 2005, 36 (2): 223-226.
[17] Bi Z, Zhang J, Bian X, et al. A high-performance ultraviolet photoconductive detector based on a ZnO film grown by RF sputtering. J Electron Mater, 2008, 37 (5): 760-763.
[18] Zhao Y M, Zhang J Y, Jiang D Y, et al. Ultraviolet Photodetector Based on a MgZnO Film Grown by Radio-Frequency Magnetron Sputtering. Acs Appl Mater Inter, 2009, 1 (11): 2428-2430.
[19] Su, L., Yuan, Z., Zhang, Q., Chen, M., Wu, T., & Gui, X., et al. (2013). Structure and optical properties of ternary alloy bezno and quaternary alloy bemgzno films growth by molecular beam epitaxy. Applied Surface Science, 274(5), 341-344.
[20] Su, L., Chen, H., Xu, X., & Fang, X. (2017). Novel bezno based self-powered dual-color uv photodetector realized via a one-step fabrication method. Laser & Photonics Reviews, 11(6), 1700222.
[21] Wang, Y., Wu, T., Chen, M., Su, L., Zhang, Q., & Yuan, L., et al. (2014). Well-controlled wet etching of zinc oxide films using hydrogen peroxide solution. Applied Surface Science, 292(4), 34-38.
[22] Wang, Y. C., Su, L. X., Zhao, Y., Liu, J. F., Shen, Z. C., & Feng, Y. H., et al. (2017). Resonant raman scattering study of beznx1–xO thin films grown on sapphire by molecular beam epitaxy. International Journal of Modern Physics B, 31(16-19), 1744067.
[23] Yu-Chao, W., Tian-Zhun, W. U., Long-Xing, S. U., Quan-Lin, Z., Ming-Ming, C., & Zi-Kang, T.(2013). Luminescence characteristics of high-quality zno and bezno films. Chinese Journal of Luminescence, 34(8), 1035-1039.