J Mater Sci: Mater Electron (2014) 25:3629–3632
DOI 10.1007/s10854-014-2066-0

Growth characteristics and device properties of MOD derived β-Ga_2O_3 films

Pei Guo · Jie Xiong · Xiaohui Zhao · Tuo Sheng · Chao Yue · Bowan Tao · Xingzhao Liu

Received: 23 April 2014 / Accepted: 1 June 2014 / Published online: 10 June 2014
© Springer Science+Business Media New York 2014

Abstract β-Ga_2O_3 films prepared by metal organic deposition (MOD) on (000*l*) sapphire substrates, have been developed for ultraviolet photodectors. The structural, surface, optical properties of MOD derived β-Ga_2O_3 films depending on growth temperatures were investigated. As growth temperature increased, the crystallinity of β-Ga_2O_3 films enhanced, crystallite size and surface roughness increased. The optical band gap of β-Ga_2O_3 films maintained within 4.8–4.9 eV at different growth temperatures. Metal–semiconductor–metal ultraviolet photodetectors based on MOD derived β-Ga_2O_3 films were successfully fabricated, demonstrating the responsivity of 0.76 A/W at 20 V and the upper limits of the rise and decay time of 50 and 30 ms, respectively, indicating a promising low-cost approach for Ga_2O_3-base photoelectronics applications.

1 Introduction

Monoclinic structure β-Ga_2O_3, a wide and direct band gap semiconductor, has been identified as a promising material for photoelectronics devices, such as gas sensors, flat-panel displays, phosphors, and transparent electronic devices [1, 2]. β-Ga_2O_3 is also an important candidate for deep ultraviolet (DUV) photodetectors [3, 4] responding to solar-blind wavelength (200–280 nm), which would be potentially applied in flame detectors, missile plume sensors, ozone holes monitors and fire control. Several successful techniques have been developed for the growth of hetero-epitaxial Ga_2O_3 films including metal-organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) [5–9]. However, their disadvantages such as high cost, low deposition rates and complex technological processes have become the obstacle to mass production of Ga_2O_3-based devices. The alternative cost-effective ways for high-performance β-Ga_2O_3 films including electron beam evaporation [10], sputtering [11] and chemical solution deposition, could significantly boost its industrialization and applications, however, so far, no related results of the resultant devices were reported.

Metal organic deposition (MOD) method was developed for decades and widely applied in electronic thin films deposition for its potential large scale production accessibility and low cost. As one kind of chemical solution method, compared with traditional sol–gel method, the composition of the precursor in MOD method keeps constant with the starting materials without any hydrolysis and condensation, which enables better control of the quality of the precursor solution and as a result better quality of films [12, 13]. In this paper, we report β-Ga_2O_3 films firstly prepared by MOD method on (000*l*) sapphire substrates, and their use in the metal–semiconductor–metal (MSM) structure ultraviolet photodetectors. The influences of growth temperature on the crystalline quality, crystallite size, surface roughness and optical band gap of MOD derived β-Ga_2O_3 films were investigated in detail. A preliminary result of ultraviolet photodetectors was presented.

2 Experimental details

Gallium acetylacetonate was used as the starting material, and dissolved in the formic acid at room temperature.

P. Guo · J. Xiong (✉) · X. Zhao · T. Sheng · C. Yue · B. Tao · X. Liu (✉)
State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, People's Republic of China
e-mail: jiexiong@uestc.edu.cn

X. Liu
e-mail: xzliu@uestc.edu.cn

www.spm.com.cn

Homogeneous and stable precursor solution was achieved with the gallium acetylacetonate concentration of 0.2 M. Sapphire substrates (5 × 5 mm) were ultrasonic cleaned in acetone, alcohol and deionized water separately before the precursor film deposition. The precursor films were spin coated with the spin speed of 2,500 rpm for 40 s, then baked at 80 °C in air for 5 min to evaporate the solvent. The sample was directly pushed into a 300 °C furnace in order to achieve high heating rate to reduce Ga loss according to the decomposition characteristic of gallium acetylacetonate [14], and stayed for 10 min to decompose organic component in films. Finally the decomposed amorphous films were crystallized at different growth temperature from 850 to 1,250 °C in air for 1 h. Due to large lattice mismatch between β-Ga_2O_3 and c-Al_2O_3, the thickness of a single-coated Ga_2O_3 films was controlled at 23.8 nm. This procedure was repeated 21 times to achieve the film thickness of 500 nm. For the fabrication of MSM photodetector device, 200 nm Ti film (used as the contact metal) and 20 nm Al film (used as the electrode metal) were deposited in turn onto the sample by electron beam evaporation, followed by a rapid thermal annealing (RTA) at 500 °C for 5 min. The interdigitated contact electrodes were fabricated through standard photolithography and wet etching. The interdigitated patterns on the shadow mask were 0.013 mm^2 in area, with the same finger width and interspacing of 3 µm and the length of 96 µm, and the total numbers of fingers were 40.

The structural properties of the β-Ga_2O_3 films were characterized using X-ray diffractometer (XRD, Bede D1) with Cu Kα radiation. The surface morphology was examined by Atomic Force Microscopy (AFM, CSPM 5500). The optical properties were evaluated using ultraviolet–visible transmission spectroscopy (UV2100). The time-dependent photoresponse characteristics of the MSM photodetector were measured on a Cascade probe table by Agilent 4155B semiconductor parameter analyzer, the light source was a 3 W mercury lamp of 254 nm with a shutter, the light intensity was 13 µW/cm^2.

3 Results and discussion

Figure 1 shows XRD $\theta - 2\theta$ scans of the β-Ga_2O_3 films prepared at various growth temperatures. When the temperature was lower than 950 °C, only Al_2O_3 (000l) peaks from the substrate were detected, indicating an amorphous or microcrystalline structure of the films. As the temperature was over 1,050 °C, obvious ($\bar{2}$01), ($\bar{4}$02), ($\bar{6}$03) peaks of monoclinic phase β-Ga_2O_3 were observed, indicating that β-Ga_2O_3 films was oriented along ($\bar{2}$01) direction. It is noted that the ($\bar{2}$01) peak intensity increased with the increasing temperature, in other words, the crystallinity of the β-Ga_2O_3 films was improved. Other β-Ga_2O_3 peaks such as ($\bar{4}$01), (002) or ($\bar{2}$02), (401) appeared at 1,250 °C, indicating a polycrystalline structure.

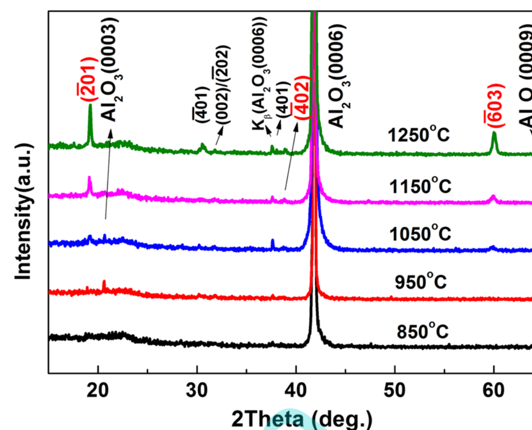

Fig. 1 XRD $\theta - 2\theta$ scans of the β-Ga_2O_3 films prepared at different growth temperatures

The crystallite size of β-Ga_2O_3 films can be estimated by the Scherrer Eq. [15]:

$$D = 0.9\lambda/(\beta\cos\theta) \quad (1)$$

where D, λ, β and θ were the crystallite size, the X-ray wavelength (0.15418 nm), the full width at half maximum ($FWHM$) value of the ($\bar{2}$01) diffraction peak, and the Bragg diffraction angle of the XRD spectra, respectively. Calculated crystallite size of films crystallized at 1,050, 1,150, 1,250 °C were 19.95, 26.78, 34.01 nm, respectively, showing that crystallite size increased with increasing growth temperature.

The AFM images (3 × 3 µm) and line scans of β-Ga_2O_3 films prepared with different growth temperatures were illustrated in Fig. 2. The root-mean-square (RMS) roughness of β-Ga_2O_3 films prepared at 1,150, 1,250 °C were 6.84 nm, 7.88 nm, respectively, indicating that the surface roughness was increased with the increasing temperature. The linear height profiles of β-Ga_2O_3 films, as shown the beneath top-view images, confirmed that rougher surface was obtained at higher temperature. The dependence of surface morphology on growth temperature was in according to that of crystallite size, attributing to surface grain coalescence and growth at higher temperature.

The optical band gap of β-Ga_2O_3 is a key parameter for photoelectronic applications, which can be evaluated from transmission spectra. The optical transmission spectra of β-Ga_2O_3 films showed an absorption edge of around 250 nm and the transmittance was above 60 % in the wavelength region above the absorption edge. Figure 3 shows $(\alpha h\nu)^2$ vs $h\nu$ plots, where α and $h\nu$ were the absorption coefficient

www.som.com.cn

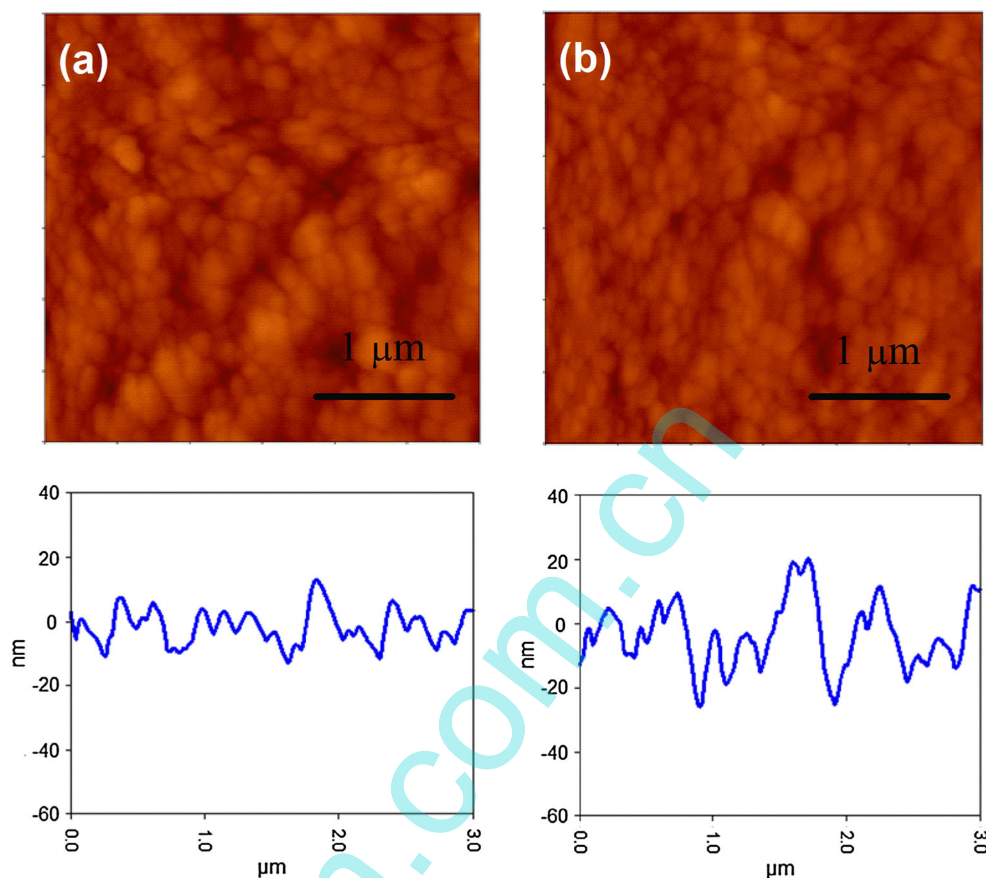

Fig. 2 AFM 3 × 3 μm images and line scans of the β-Ga_2O_3 films prepared at various temperatures: **a** 1,150 °C, **b** 1,250 °C

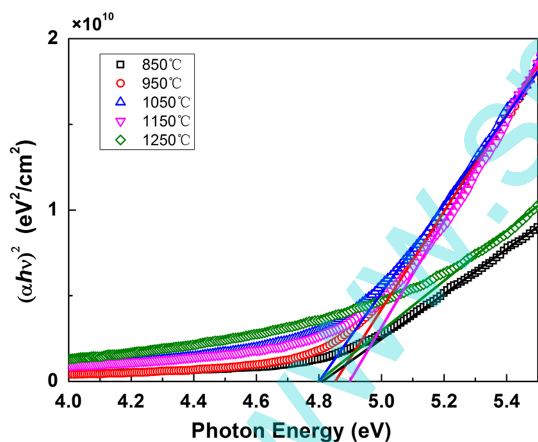

Fig. 3 Square of absorption coefficient as a function of photon energy for the β-Ga_2O_3 films prepared at various growth temperatures

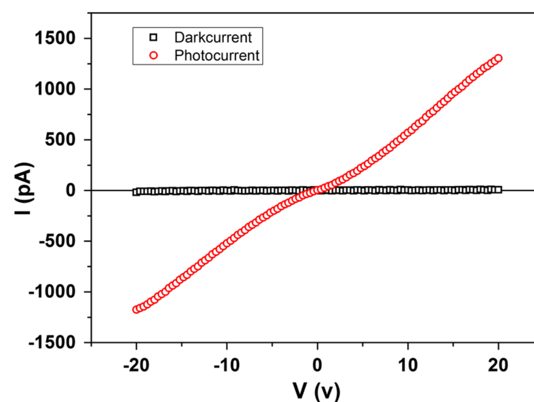

Fig. 4 *I-V* curves of MOD prepared β-Ga_2O_3 ultraviolet photodetector with and without 254 nm light illumination

and photon energy, respectively. As a direct band gap material of β-Ga_2O_3, the optical band gap was obtained from the intersection of the straight line and horizontal axis [16]. The optical band gap maintained within 4.8–4.9 eV at various growth temperatures, which was consistent with the generally acknowledged band gap of Ga_2O_3. In contrast with Kokubun's result [5] that the optical band gap increased with enhanced heat-treatment temperature, which were primarily attributed to the variety of lattice constants, 21-times spin-coated films were fully relaxed, and therefore, the lattices and optical band gap indicated almost constant, as proved by the XRD results in the Fig. 1.

Metal–semiconductor–metal structure ultraviolet photodetectors were fabricated to testify the film quality. The representative *I–V* curves of MOD derived β-Ga_2O_3 ultraviolet photodetector was shown in Fig. 4. The responsivity obtained from the *I–V* curves was 0.76 A/W at 20 V,

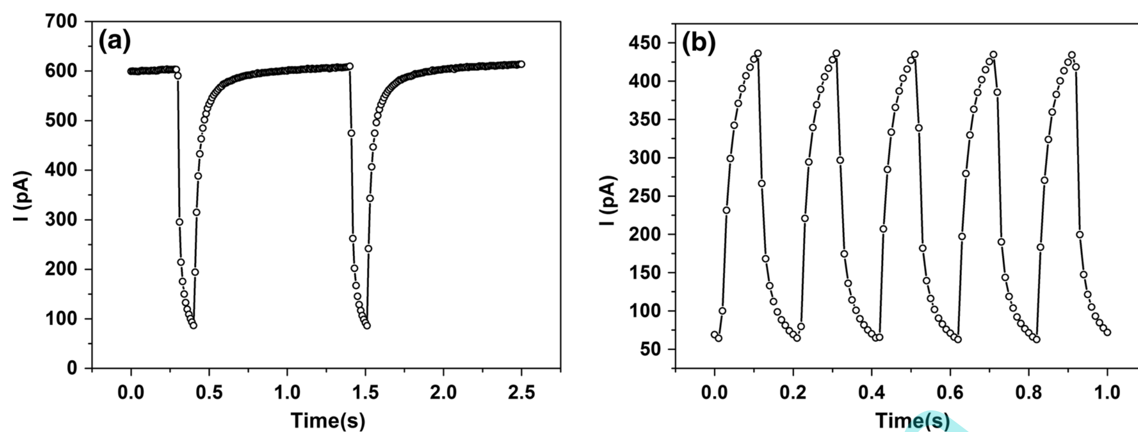

Fig. 5 Time-dependent photoresponse of MOD prepared β-Ga_2O_3 ultraviolet photodetector: **a** the open time of the UV light was 1 s and the close time was 0.1 s; **b** both the open time and close time of the UV light was 0.1 s

according to the definition formula $R = I_p/PS$, where $I_p = I_{il} - I_d$, in which I_{il}, I_d, P, S were photocurrent, dark current, light intensity, photosensitive area, respectively.

The time-dependent photoresponse of MOD derived β-Ga_2O_3 ultraviolet photodetector was shown in Fig. 5. Figure 5a shows a stabilized photocurrent of approximately 600 pA with a long turn-on light time (1 s), and Fig. 5b shows quick photoresponse of MOD derived β-Ga_2O_3 ultraviolet photodetector with both turn-on and turn-off light time of 0.1 s. Signal collection interval of 10 ms was applied in both tests. According to the definition of photoresponse time [17] [the decay time, τ_d (or rise time, τ_r)], defined as the time in which the photocurrent drops from 90 to 10 % (or increases from 10 to 90 %) of its maximum value), the upper limits of the rise time τ_r and decay time τ_d were 50 and 30 ms, respectively. The preliminary results of ultraviolet photodetectors demonstrate a low-cost approach for Ga_2O_3-base photoelectronics applications.

4 Conclusion

β-Ga_2O_3 thin films were prepared on (000l) sapphire substrates at 850–1,250 °C by MOD method. XRD results confirmed that ($\bar{2}$01) oriented β-Ga_2O_3 polycrystalline films were formed above 1,050 °C. With increasing growth temperature, the crystallinity of β-Ga_2O_3 films enhanced, crystallite size and surface roughness increased. The optical band gap of β-Ga_2O_3 films maintained within 4.8–4.9 eV at different growth temperatures. MSM ultraviolet photodetectors based on MOD prepared thin films were fabricated, demonstrating responsivity of 0.76 A/W at 20 V and the upper limits of the rise and decay time of 50 and 30 ms, respectively. These results provide a potentially low-cost alternative for Ga_2O_3-base photoelectronics devices.

References

1. J.B. Varley, J.R. Weber, A. Janotti, C.G. Van de Walle, Appl. Phys. Lett. **97**, 142106 (2010)
2. P.D.C. King, I. McKenzie, T.D. Veal, Appl. Phys. Lett. **96**, 062110 (2010)
3. R. Suzuki, S. Nakagomi, Y. Kokubun, N. Arai, S. Ohira, Appl. Phys. Lett. **94**, 222102 (2009)
4. T. Oshima, T. Okuno, N. Arai, N. Suzuki, S. Ohira, S. Fujita, Appl. Phys. Express **1**, 011202 (2008)
5. Y. Kokubun, K. Miura, F. Endo, S. Nakagomi, Appl. Phys. Lett. **90**, 031912 (2007)
6. T. Oshima, T. Okuno, S. Fujita, Jpn. J. Appl. Phys. **46**, 7217 (2007)
7. P. Feng, J.Y. Zhang, Q.H. Li, T.H. Wang, Appl. Phys. Lett. **88**, 153107 (2006)
8. Y.B. Li, T. Tokizono, M.Y. Liao, M. Zhong, Y. Koide, I. Yamada et al., Adv. Funct. Mater. **20**, 3972 (2010)
9. D.S. Wuu, S.L. Ou, R.H. Horng, P. Ravadgar, T.Y. Wang, H.Y. Lee, Proc. SPIE **8263**, 826317 (2012)
10. Y. Cheng, K. Yang, Y. Peng, Y. Yin, J.X. Chen, H.W. Liang et al., J. Mater. Sci. Mater. Electron. **24**, 5122 (2013)
11. J.H. Kim, K.H. Yoon, J. Mater. Sci. Mater. Electron. **20**, 879 (2009)
12. R.W. Schwartz, Chem. Mater. **9**, 2325 (1997)
13. M.S. Bhuiyan, M. Paranthaman, K. Salama, Supercond. Sci. Technol. **19**, R1 (2006)
14. K. Al-Khamis, Z.A. Al-Othman, Prog. React. Kinet. Mech. **35**, 187 (2010)
15. W.T. Lim, C.H. Lee, Thin Solid Films **353**, 12 (1999)
16. K. Prabakar, S. Venkatachalam, Y.L. Jeyachandran, Sa.K. Narayandass, D. Mangalaraj, Mater. Sci. Eng. B **107**, 99 (2004)
17. E. Monroy, F. Omnes, F. Calle, Semicond. Sci. Technol. **18**, R33 (2003)

www.som.com.cn