ELSEVIER

Journal of Alloys and Compounds 389 (2005) 177–181

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Influence of postdeposition annealing on the properties of Ga_2O_3 films on SiO_2 substrates

Hyoun Woo Kim*, Nam Ho Kim

School of Materials Science and Engineering, Inha University, Incheon 402-751, Korea

Received 7 January 2004; accepted 20 May 2004

Abstract

We have investigated the structural and optical properties of annealed gallium oxide (Ga_2O_3) film in the range of 750–1050 °C, which had been grown on SiO_2 substrates by the metal organic chemical vapor deposition (MOCVD) technique. We revealed that postdeposition annealing of amorphous Ga_2O_3 generated grains in β-Ga_2O_3 phase. While photoluminescence spectra of as-deposited Ga_2O_3 films showed strong blue–green (BG) and ultraviolet (UV) emission, postdeposition annealing at high temperatures resulted in appearance of a longer wavelength UV band and a new green band.

PACS: 81.15Gh; 68.55Jk

Keywords: Thin films; Chemical synthesis; X-ray diffraction; Luminescence

1. Introduction

Since metal oxides exist in a variety of compositions and crystal structures and their property vary widely from insulators to superconductors, metal oxide thin films are finding rapidly growing applications in advanced technologies. Especially, gallium oxide (Ga_2O_3) crystals have recently attracted considerable attention as materials for the new generation of optoelectronic devices [1–5], since the crystals are transparent in a wide range of ultraviolet (UV) down to 280 nm and they are potentially electro-conductive. These characteristics originate from their band gaps of about 4.8 eV and n-type conductivity. Additionally, Ga_2O_3 has been considered as one of the most promising materials as a metal oxide gas sensor [6–8], due to its n-type semiconductor property and its stability in the high temperature range over 600 °C [9].

Although various techniques have been employed to prepare the Ga_2O_3 films [10–18], metal organic chemical vapor deposition (MOCVD) method offers more flexible approach to the growth of metal oxides. Additionally, this method has several other advantages of producing uniform, pure, reproducible, adherent, and good step-coverage films. In spite of their several advantages, there are only few reports on the growth of Ga_2O_3 thin films by the MOCVD techniques and the precursors of $Ga(hfac)_3$, $Ga[OCH(CF_3)_2]_3{}^{\bullet}HNMe_2$, $[Ga(\mu\text{-O-t-Bu})(O\text{-t-Bu})_2]_2$ and $Ga(O^iPr)_3$ have been investigated [19–22].

In the present work, we have deposited the Ga_2O_3 thin films on SiO_2 substrates at a temperature of 550 °C, using a conventional precursor of trimethylgallium (TMGa). With an expectation of transforming Ga_2O_3 films to its stable β-phase, we have annealed the Ga_2O_3 thin films at temperatures in the range of 750–1050 °C and have investigated the effect of annealing on the structural properties of Ga_2O_3 thin films, by comparing the annealed films to the as-grown films, using scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), and atomic force microscopy (AFM). We also have studied the optical properties of the as-deposited and annealed Ga_2O_3 films using room temperature photoluminescence (PL).

* Corresponding author. Tel.: +82 32 860 7544; fax: +82 32 862 5546.
E-mail address: hwkim@inha.ac.kr (H.W. Kim).

0925-8388/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.05.082

2. Experimental

The Ga_2O_3 films were deposited on SiO_2 substrates, which were prepared by depositing a 60-nm-thick SiO_2 layer on Si(1 0 0) substrate thermally. The substrate was cleaned in acetone for 10 min, in HF (20:1) for 1 min and then rinsed in deionized water for 1 min before loading into the system. A schematic diagram of the MOCVD system used in this experiment is described in Fig. 1. TMGa and O_2 were used as sources. High-purity Ar passed through the TMGa bubbler, which had been maintained at the temperature of −5 °C, and delivered the TMGa vapor to the reactor. The Ga_2O_3 film was synthesized by supplying O_2 and Ar carrier gases with the flow rate of 30 standard cubic centimeters per min (sccm) and 30 sccm, and the reaction temperature was set to 550 °C. Thermal annealing after the growth was done in air ambient for 1 h. The annealing temperatures were varied between 700 and 1050 °C.

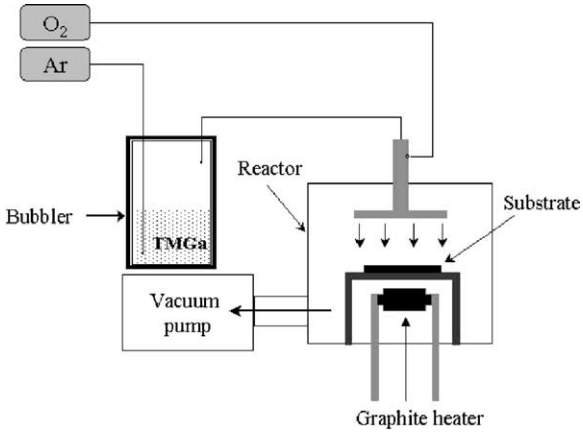

Fig. 1. Schematic illustration of the MOCVD reactor.

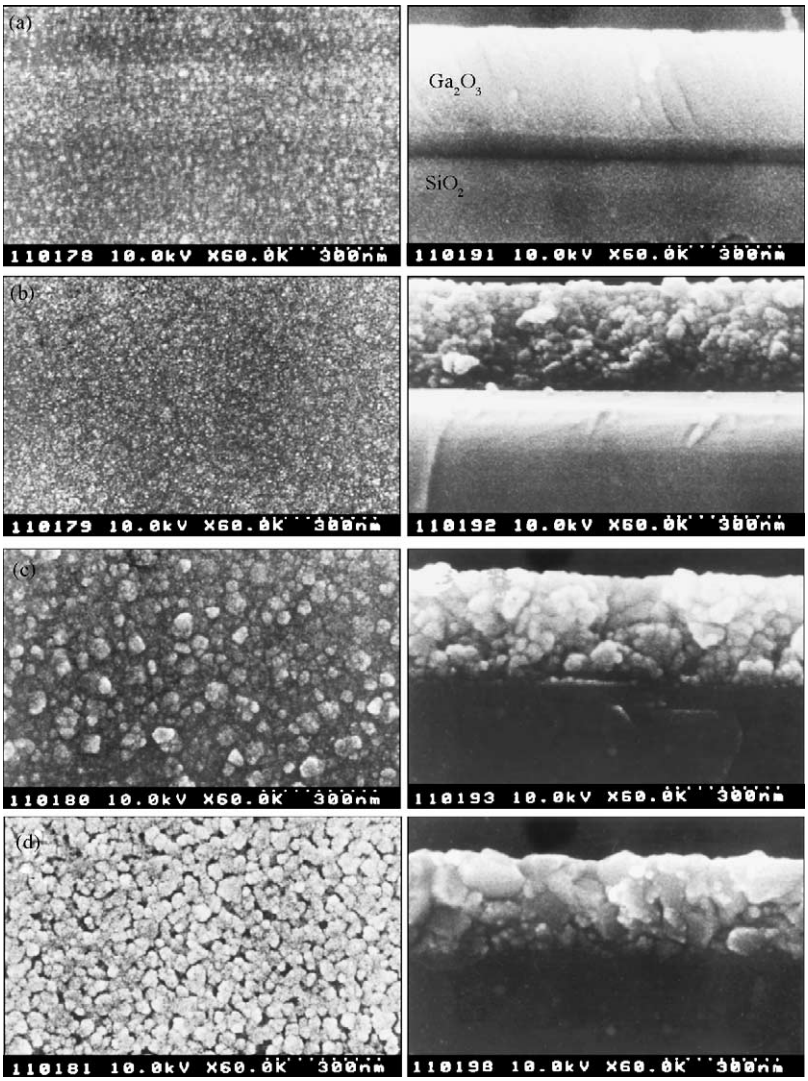

Fig. 2. Plain-view SEM images (left: plain-view images, right: cross-sectional images) of (a) as-deposited, (b) 750 °C-annealed, (b) 900 °C-annealed, and (c) 1050 °C-annealed Ga_2O_3 thin films.

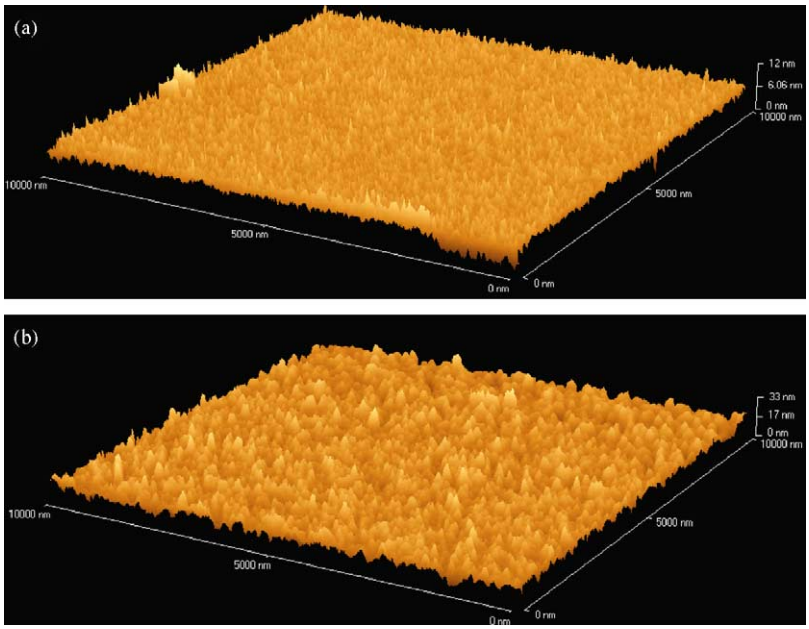

Fig. 3. AFM images of (a) as-deposited and (b) 1050 °C-annealed Ga_2O_3 thin films.

The structural characteristics of the films were analyzed by XRD (Philips, CM20T, 200 kV) using Cu Kα1 radiation (λ = 0.154056 nm) and SEM (Hitachi S-4200). The surface roughness was measured by using an AFM (Nanoscope III, Digital Instruments) with a scan size of 10 μm × 10 μm. PL measurements were carried out at room temperature with a Shimadzu fluorescence spectrophotometer (RF-5301PC). The excitation light was the monochromatic light from a xenon short arc lamp with a wavelength of λ = 250 nm.

3. Results and discussion

Fig. 2a–d show the SEM images of Ga_2O_3 thin films, respectively, which are as-deposited, 750 °C-annealed, 900 °C-annealed, and 1050 °C-annealed. Plain-view SEM images indicate that by the thermal annealing process at 900–1050 °C, the microstructure tends to change into the grain-like structures. The cross-sectional SEM images also indicate that although no clear grain boundaries are found inside the as-grown Ga_2O_3 thin films, the grain-like structure appears by the thermal annealing. Furthermore, the size of the grain-like structure becomes larger with increasing the annealing temperature in the range of 900–1050 °C.

In order to investigate the surface roughness of the Ga_2O_3 films grown on SiO_2 substrates, we have performed an AFM analysis. Fig. 3a and b show the AFM topographies representing the surface morphology of as-deposited and 1050 °C-annealed Ga_2O_3 film, respectively, indicating that the grain-like structures are clearly observed on top of the Ga_2O_3 film after the thermal annealing. The root-mean-square (RMS) surface roughnesses of the as-deposited and 1050 °C-annealed Ga_2O_3 films, respectively, are 0.89 and

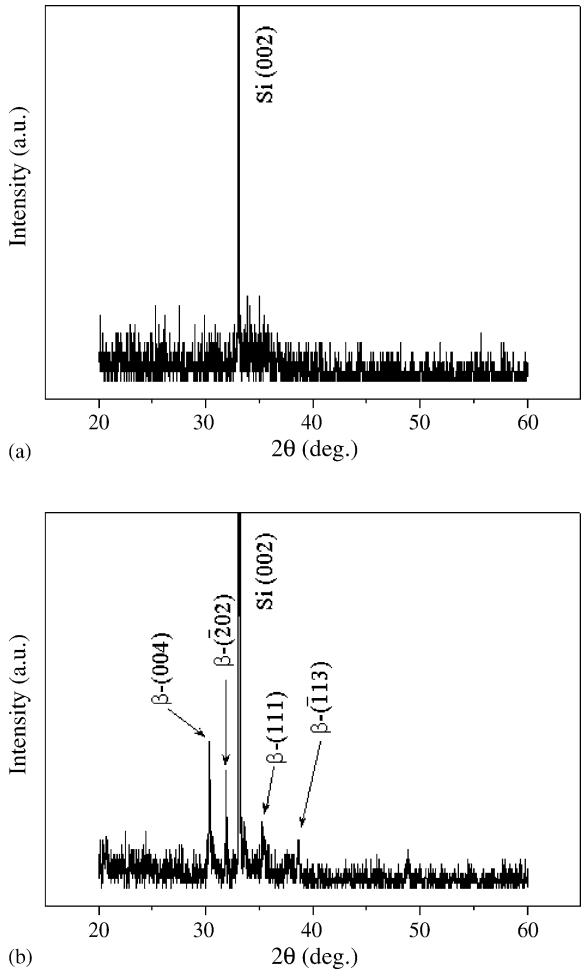

Fig. 4. XRD patterns of the (a) as-deposited and (b) 1050 °C-annealed Ga_2O_3 thin films.

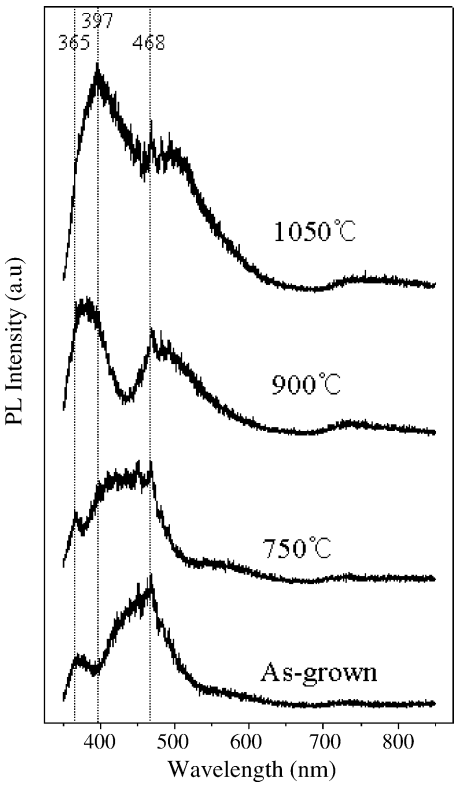

Fig. 5. Room temperature PL spectra of as-deposited and annealed Ga_2O_3 films at temperatures in the range of 750–1050 °C.

3.56 nm, indicating that the surface of annealed Ga_2O_3 film is more rough than that of the as-deposited Ga_2O_3 film. We surmise that the surface becomes rougher due to the appearance of grains on top of the films, and thus the AFM images agree with the SEM images.

In order to investigate the effect of thermal annealing on the crystallinity of Ga_2O_3 thin film, we have performed an XRD analysis on the as-deposited and 1050 °C-annealed samples. Fig. 4a shows the XRD diffraction pattern of the as-deposited Ga_2O_3 films. Due to the absence of a distingushiable Ga_2O_3 diffraction peak, we suppose that the Ga_2O_3 films have an amorphous structure. Fig. 4b shows the diffraction pattern of the 1050 °C-annealed Ga_2O_3 films, indicating that the lines observed in this diffractogram are found to coincide with (0 0 4), ($\bar{2}$ 0 2), (1 1 1), and ($\bar{1}$ 1 3) peak of monoclinic β-Ga_2O_3 obtained from the Joint Committee on Powder Diffraction Standards (JCPDS) card (No. 43-1012). The stable β-Ga_2O_3 phase is known to have a monoclinic structure [23]. The existence of the β-Ga_2O_3 peaks indicates the production of β-Ga_2O_3 grains on SiO_2 substrates by the thermal annealing at a sufficiently high temperature.

Fig. 5 shows the PL spectra of as-deposited and annealed Ga_2O_3 films in the range of 750–1050 °C, which are recorded at room temperature (300 K). The dominant emissions from as-deposited films are bands located at a wavelength of around 468 nm (2.656 eV) and 365 nm (3.405 eV), respectively, in the blue–green (BG) spectral region and in the ultraviolet (UV) spectral region. UV luminescence of Ga_2O_3 has been reported to be attributed to an intrinsic transition, due to the recombination of a self-trapped exciton [24]. PL spectra from the Ga_2O_3 films show a strong dependency on the postdeposition annealing. The peak intensity in the UV region shifts to longer wavelengths, which has distinguishable peaks at 397 nm with the annealing at 1050 °C. The peak wavelength change of the PL by the thermal annealing is not clearly understood at this time.

Postdeposition annealing also causes dramatic change in PL band, as shown in Fig. 5, indicating that a strong and broad emission in the green light range appears with the thermal annealing at a high temperature of 900–1050 °C. Since the formation of gallium vacancies enhances green emission [25], we surmise that annealing of Ga_2O_3 films on SiO_2 substrates at high temperatures of 900–1050 °C is in favor of the gallium vacancies, contributing to the appearance of green emission. Further systematic study is necessary in order to reveal the mechanism of the observed emissions.

4. Conclusions

We have prepared the Ga_2O_3 films on SiO_2 substrate by a reaction of a TMGa and O_2 mixture and have investigated the effects of postdeposition annealing. The SEM images indicate that grain-like structures appears by the thermal annealing and the AFM images reveals that the RMS surface roughness increase by the thermal annealing. The XRD data indicate that even though the as-deposited Ga_2O_3 films turns out to be amorphous, the β-Ga_2O_3 phases appear by the thermal annealing. PL spectra of the as-deposited Ga_2O_3 films reveal the dominant emission in the BG and UV regions. Annealing at higher temperature results in the shift of UV band to the longer wavelength region and appearance of a broad green emission band, in addition to the existing BG emission band.

Acknowledgements

This work was supported by grant no. R05-2001-000-00843-0 from the Basic Research Program of the Korea Science and Engineering Foundation.

References

[1] M. Fleischer, H. Meixner, Sens. Actuators B 26 (1995) 81–84.
[2] L.P. Sosman, T. Abritta, O. Nakamura, M.M.F. D'aguiar Neto, J. Mater. Sci. Lett. 14 (1995) 19.
[3] T. Miyata, T. Nakatani, T. Minami, J. Lumin. 87–89 (2000) 1183.
[4] M. Passlack, E.F. Schubert, W.S. Hobson, M. Hong, N. Moriya, S.N. Chu, K. Konstadinis, J.P. Mannaerts, M.L. Schnoes, G.J. Zydzik, J. Appl. Phys. 77 (1995) 686.
[5] K.L. Chopra, S. Major, D.K. Pandya, Thin Solid Films 102 (1983) 1.

[6] M. Fleischer, W. Hanrieder, H. Meixner, Thin Solid Films 190 (1990) 93.
[7] M. Fleischer, H. Meixner, Sens. Actuators B 5 (1991) 115.
[8] F. Reti, M. Fleischer, H. Meixner, J. Giber, Sens. Actuators B 18–19 (1994) 573.
[9] T. Harwig, J. Schoonman, J. Solid State Chem. 23 (1978) 205.
[10] Y. Li, A. Trinchi, W. Wlodarski, K. Galatsis, K. Kalantar-zadeh, Sens. Actuators B 93 (2003) 431.
[11] A.C. Lang, M. Fleischer, H. Meixner, Sens. Actuators B 66 (2000) 80.
[12] P.P. Macri, S. Enzo, G. Sberveglieri, S. Groppelli, C. Perego, Appl. Surf. Sci. 65/66 (1993) 277.
[13] M. Ogita, K. Higo, Y. Nakanishi, Y. Hatanaka, Appl. Surf. Sci. 175/176 (2000) 721.
[14] M. Orita, H. Hiramatsu, H. Ohta, M. Hirano, H. Hosono, Thin Solid Films 411 (2002) 134.
[15] C. Huang, A. Ludviksson, R.M. Martin, Surf. Sci. 265 (1992) 314.
[16] R. Franchy, M. Eumann, G. Schmitz, Surf. Sci. 470 (2001) 337.
[17] R. Franchy, Surf. Sci. Rep. 38 (2000) 195.
[18] P. Chen, R. Zhang, X.F. Xu, Y.G. Zhou, Z.Z. Chen, S.Y. Xie, W.P. Li, Y.D. Zhang, Appl. Phys. A 71 (2000) 191.
[19] G.A. Battiston, R. Gerbasi, M. Porchia, R. Bertoncello, F. Caccavale, Thin Solid Films 279 (1996) 115.
[20] L. Miinea, S. Suh, S.G. Bott, J.-R. Liu, W.-K. Chu, D.M. Hoffman, J. Mater. Chem. 9 (1999) 929.
[21] M. Valet, D.M. Hoffman, Chem. Mater. 13 (2001) 2135.
[22] D.H. Kim, S.H. Yoo, T.-M. Chung, K.-S. An, H.-S. Yoo, Y. Kim, Bull. Korean Chem. Soc. 23 (2002) 225.
[23] Y. Jeliazova, R. Franchy, Surf. Sci. 527 (2003) 57.
[24] E.G. Villora, K. Hatanaka, H. Odaka, T. Sugawara, T. Miura, H. Fukumura, T. Fukuda, Solid State Commun. 127 (2003) 385.
[25] T. Harwig, G.J. Wubs, G.J. Dirksen, Solid State Commun. 18 (1976) 1223.