Materials Science in Semiconductor Processing 172 (2024) 108040

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Synthesis and properties of β-Ga_2O_3 nanowires and nanosheets on doped GaS:Mn substrates

Veaceslav Sprincean [a], Haoyi Qiu [b], Oleg Lupan [b,c,d,*], Tim Tjardts [e], Deik Petersen [b], Salih Veziroglu [e], Rainer Adelung [b], Mihail Caraman [a]

[a] Faculty of Physics and Engineering, Moldova State University, 60 Alexei Mateevici str., MD-2009, Chisinau, Republic of Moldova
[b] Functional Nanomaterials, Faculty of Engineering, Institute for Materials Science, Kiel University, Kaiserstr, 2, D-24143, Kiel, Germany
[c] Center for Nanotechnology and Nanosensors, Department of Microelectronics and Biomedical Engineering, Technical University of Moldova, 168, Stefan cel Mare Av., MD-2004, Chisinau, Republic of Moldova
[d] Department of Physics, University of Central Florida, Orlando, FL, 32816-2385, USA
[e] Chair for Multicomponent Materials, Institute for Materials Science, Kiel University, Kaiserstr, 2, D-24143, Kiel, Germany

ARTICLE INFO

Keywords:
Gallium oxide
Gallium sulfide
Manganese
Nanowires
Nanosheets
Doping

ABSTRACT

In this work, the synthesis, morphology, optical and luminescence properties of Mn-doped β-Ga_2O_3 (Ga_2O_3:Mn) nanowires/nanosheets on Mn-doped GaS (GaS:Mn) substrate are studied. The aim was to obtain structures of semiconductors with layers of nanoformations (nanowires, nanosheets) from a wide energy band semiconductor such as β-Ga_2O_3 and to determine their characteristic properties. For the base material, Mn-doped GaS lamellae were chosen, which are optically transparent in the spectral region where the optical properties of Mn^{2+} and Mn^{3+} ions are manifested. Through thermal annealing, single-crystalline β-GaS plates doped with 1.3 atomic percent (at.%) of manganese (Mn) are exposed to an atmosphere enriched with H_2O vapor at a temperature of 800 °C for 6 h. As a result, the surface of these plates is covered with a composite layer consisting of crystallites of α-Ga_2S_3:Mn and β-GaS:Mn planar junctions. This composite exhibits a direct band gap of 2.88 eV and an indirect band gap of 2.55 eV corresponding to the β-GaS:Mn crystallites. Upon further increasing the temperature during thermal annealing to 850 °C and 920 °C, the surface of the β-GaS:Mn samples transform into a layer of β-Ga_2O_3:Mn nanowires/nanosheets with a band gap of 4.5 eV. Its intense green-orange photoluminescence is caused by electronic transitions within the Mn^{2+} ion.

1. Introduction

In recent years, wide bandgap semiconductors have received considerable research attention due to their unique physical properties and potential applications in various electronic devices [1]. Among these semiconductors, compounds such as GaN, $Al_xGa_{1-x}N$, and oxide semiconductors like TiO_2, ZnO, $MgZn_{1-x}O$, and Ga_2O_3 (especially monoclinic β-Ga_2O_3) have attracted particular interest due to their application in ultraviolet radiation photo-detectors (UVB and UVC), power electronic devices, and of UV radiation sources [2–5]. The range of applications of these materials is expanding with the transition from massive bulk single crystals to micro- and nano-crystallites [6,7]. Gallium oxide (β-Ga_2O_3) is a *n*-type semiconductor with a direct bandgap of about 4.4–4.9 eV and a monoclinic crystal lattice. The high-temperature stability of β-Ga_2O_3 can be achieved by doping with chemical elements such as Zn and Sn [8,9]. As a result, it is considered a promising material for use in UV optoelectronics, acting as a photocatalyst for the decomposition of organic pollutants and water, and functioning as a sensor for toxic gases at high temperatures [10–12].

One of the basic parameters that determine the applicability of this material in electronic devices is the critical (breakdown) electric field. For undoped β-Ga_2O_3, the critical electric field is about 8 MV/cm, while for β-Ga_2O_3 doped with Zn, this parameter reaches the value of 13.2 MV/cm. In addition, β-Ga_2O_3:Zn in nanosheets exhibits intense photoluminescence in the green region [13] and shows high sensitivity as a photo-detector in the UVC region, with response reaching up to 210 A/W at a wavelength of 232 nm [14].

Nanostructured undoped and doped β-Ga_2O_3 grown on substrates such as Si, GaN, GaAs, Al_2O_3, and other oxide semiconductors such as TiO_2 and ZnO play an important role in the development of electronic

* Corresponding author. Functional Nanomaterials, Faculty of Engineering, Institute for Materials Science, Kiel University, Kaiserstr, 2, D-24143, Kiel, Germany.
E-mail address: ollu@tf.uni-kiel.de (O. Lupan).

https://doi.org/10.1016/j.mssp.2023.108040
Received 4 July 2023; Received in revised form 18 November 2023; Accepted 3 December 2023
Available online 21 December 2023

devices, UV radiation receivers and sources, gas sensors, and photocatalysts [14–17]. It has been shown that the manganese (Mn) dopant induces impurity bands near the band edge, resulting in the decrease of the band gap of the Ga_2O_3 [18].

Considering that GaS:Mn is an optically transparent material in the region where the luminescent transitions of Mn^{2+} and Mn^{3+} ions are manifested, thus also obtaining intense luminescence in the green-orange region. A thorough knowledge of the basic structural, optical and vibrational properties of Mn-doped β-Ga_2O_3/GaS:Mn is crucial, since information on cost-efficient and simple technological approaches and structure is still lacking. Mn - doped composites as β-Ga_2O_3/GaS:Mn are extremely important for fundamental research, as well as for developing new devices, e.g. various applications including optoelectronic sensors, non-toxic biomedical imaging, energy down-conversion in nanostructured solar cells, nonlinear optical applications, optoelectronic devices, e.g., high-power laser radiation sensors. Recent structures demonstrate that Mn-doped β-Ga_2O_3 thin films as well as nanostructured layers are promising materials in light sources in the visible region of the spectrum under electron beam excitation and photon excitation in the UV region.

In this work, the synthesis and morphology of Mn-doped β-Ga_2O_3 (Ga_2O_3:Mn) nanowires/nanosheets on Mn-doped GaS (GaS:Mn) substrates are investigated. Furthermore, the composition as well as the optical and luminescence properties of Mn-doped β-Ga_2O_3 nanowires/nanosheets on a GaS:Mn substrate are investigated in detail.

References

[1] J.Y. Tsao, S. Chowdhury, M.A. Hollis, D. Jena, N.M. Johnson, K.A. Jones, R. J. Kaplar, S. Rajan, C.G. Van de Walle, E. Bellotti, C.L. Chua, R. Collazo, M. E. Coltrin, J.A. Cooper, K.R. Evans, S. Graham, T.A. Grotjohn, E.R. Heller, M. Higashiwaki, M.S. Islam, P.W. Juodawlkis, M.A. Khan, A.D. Koehler, J.H. Leach, U.K. Mishra, R.J. Nemanich, R.C.N. Pilawa-Podgurski, J.B. Shealy, Z. Sitar, M. J. Tadjer, A.F. Witulski, M. Wraback, J.A. Simmons, Ultrawide-bandgap semiconductors: research opportunities and challenges, Adv. Electron. Mater. 4 (2018), https://doi.org/10.1002/aelm.201600501.

[2] J. Zhang, J. Shi, D.-C. Qi, L. Chen, K.H.L. Zhang, Recent progress on the electronic structure, defect, and doping properties of Ga 2 O 3, Apl. Mater. 8 (2020), 020906, https://doi.org/10.1063/1.5142999.

[3] T.F. Weng, M.S. Ho, C. Sivakumar, B. Balraj, P.F. Chung, VLS growth of pure and Au decorated β-Ga2O3 nanowires for room temperature CO gas sensor and resistive memory applications, Appl. Surf. Sci. 533 (2020), https://doi.org/10.1016/j.apsusc.2020.147476.

[4] M. Baldini, Z. Galazka, G. Wagner, Recent progress in the growth of β-Ga2O3 for power electronics applications, Mater. Sci. Semicond. Process. 78 (2018) 132–146, https://doi.org/10.1016/j.mssp.2017.10.040.

[5] S.J. Pearton, J. Yang, P.H. Cary, F. Ren, J. Kim, M.J. Tadjer, M.A. Mastro, A review of Ga2O3 materials, processing, and devices, Appl. Phys. Rev. 5 (2018), https://doi.org/10.1063/1.5006941.

[6] S. Elafandi, Z. Ahmadi, N. Azam, M. Mahjouri-Samani, Gas-phase formation of highly luminescent 2D GaSe nanoparticle ensembles in a nonequilibrium laser ablation process, Nanomaterials 10 (2020), https://doi.org/10.3390/nano10050908.

[7] G. Chen, L. Zhang, L. Li, F. Cheng, X. Fu, J. Li, R. Pan, W. Cao, A.S. Chan, G. N. Panin, J. Wan, H. Zhang, C. Liu, GaSe layered nanorods formed by liquid phase exfoliation for resistive switching memory applications, J. Alloys Compd. (2020) 823, https://doi.org/10.1016/j.jallcom.2020.153697.

[8] E. Chikoidze, T. Tchelidze, C. Sartel, Z. Chi, R. Kabouche, I. Madaci, C. Rubio, H. Mohamed, V. Sallet, F. Medjdoub, A. Perez-Tomas, Y. Dumont, Ultra-high critical electric field of 13.2 MV/cm for Zn-doped p-type β-Ga2O3, Mater. Today Phys. 15 (2020), https://doi.org/10.1016/j.mtphys.2020.100263.

[9] M. Zervos, A. Othonos, V. Gianneta, A. Travlos, A.G. Nassiopoulou, Sn doped β-Ga2O3 and β-Ga2S3 nanowires with red emission for solar energy spectral shifting, J. Appl. Phys. 118 (2015), https://doi.org/10.1063/1.4935633.

[10] M. Ogita, K. Higo, Y. Nakanishi, Y. Hatanaka, Ga2O3 thin film for oxygen sensor at high temperature, Appl. Surf. Sci. 175–176 (2001) 721–725, https://doi.org/10.1016/S0169-4332(01)00080-0.

[11] R. Ito, M. Akatsuka, A. Ozawa, Y. Kato, Y. Kawaguchi, M. Yamamoto, T. Tanabe, T. Yoshida, Photocatalytic activity of Ga 2 O 3 supported on Al 2 O 3 for water splitting and CO 2 reduction, ACS Omega 4 (2019) 5451–5458, https://doi.org/10.1021/acsomega.9b00048.

[12] B. Alhalaili, R. Vidu, M.S. Islam, The growth of Ga2O3 nanowires on silicon for ultraviolet photodetector, Sensors (2019) 19, https://doi.org/10.3390/s19235301.

[13] J. Jiang, J. Zhang, Z. Song, Influence of Zn doping on the morphology and luminescence of Ga2O3 low-dimensional nanostructures, J. Lumin. 221 (2020), https://doi.org/10.1016/j.jlumin.2020.117048.

[14] F. Alema, B. Hertog, O. Ledyaev, D. Volovik, G. Thoma, R. Miller, A. Osinsky, P. Mukhopadhyay, S. Bakhshi, H. Ali, W.V. Schoenfeld, Solar blind photodetector

based on epitaxial zinc doped Ga2O3 thin film, Physica Status Solidi (A) Appli. Mater. Sci. (2017) 214, https://doi.org/10.1002/pssa.201600688.

[15] G. Gundiah, A. Govindaraj, C.N.R. Rao, Nanowires, nanobelts and related nanostructures of Ga2O3, Chem. Phys. Lett. 351 (2002) 189–194, https://doi.org/10.1016/S0009-2614(01)01372-0.

[16] S. Kumar, S. Dhara, R. Agarwal, R. Singh, Study of photoconduction properties of CVD grown β-Ga2O3 nanowires, J. Alloys Compd. 683 (2016) 143–148, https://doi.org/10.1016/j.jallcom.2016.05.079.

[17] B. Zhao, F. Wang, H. Chen, Y. Wang, M. Jiang, X. Fang, D. Zhao, Solar-Blind avalanche photodetector based on single ZnO-Ga2O3 core-shell microwire, Nano Lett. 15 (2015) 3988–3993, https://doi.org/10.1021/acs.nanolett.5b00906.

[18] X. Wang, R. Quhe, Y. Zhi, Z. Liu, Y. Huang, X. Dai, Y. Tang, Z. Wu, W. Tang, The electronic structure and magnetic property of the Mn doped β-Ga2O3, Superlattice. Microst. 125 (2019) 330–337, https://doi.org/10.1016/j.spmi.2018.12.001.

[19] I. Goronovskii, Y.P. Nazarenko, E. Nekryach, Concise Handbook of Chemistry, 1987.

[20] Y. Huang, Z. Liu, J. Wang, Y. Zhi, D. Guo, X. Wang, X. Wang, Z. Chen, P. Li, W. Tang, The effect of Mn dopant on structural and optoelectronic properties of γ-Ga 2 O 3 thin film photodetectors, ECS J. Solid State Sci. Technol. 9 (2020), 055010, https://doi.org/10.1149/2162-8777/ab9ab3.

[21] Z. Chen, X. Wang, K. Saito, T. Tanaka, M. Nishio, Q. Guo, The impact of growth temperature on the structural and optical properties of catalyst-Free β-Ga2O3 nanostructures, Mater. Res. Express 3 (2016), https://doi.org/10.1088/2053-1591/3/2/025003.

[22] E. Filippo, M. Siciliano, A. Genga, G. Micocci, A. Tepore, T. Siciliano, Single crystalline β-Ga2O3 nanowires synthesized by thermal oxidation of GaSe layer, Mater. Res. Bull. 48 (2013) 1741–1744, https://doi.org/10.1016/j.materresbull.2012.08.083.

[23] S.Y. Lee, H.C. Kang, Synthesis and characterization of β-Ga2O3 nanowires on amorphous substrates using radio-frequency powder sputtering, J. Cryst. Growth 412 (2015) 25–30, https://doi.org/10.1016/j.jcrysgro.2014.11.030.

[24] S. Okayama, K. Kanaya, Penetration and energy-loss theory of electrons in solid targets, J. Phys. D Appl. Phys. 5 (1972) 43.

[25] C. Jastrzebski, K. Olkowska, D.J. Jastrzebski, M. Wierzbicki, W. Gebicki, S. Podsiadlo, Raman scattering studies on very thin layers of gallium sulfide (GaS) as a function of sample thickness and temperature, J. Phys. Condens. Matter 31 (2019), https://doi.org/10.1088/1361-648X/aaf53b.

[26] C.H. Ho, M.H. Lin, Y.P. Wang, Y.S. Huang, Synthesis of In2S3 and Ga2S3 crystals for oxygen sensing and UV photodetection, Sensor Actuator Phys. 245 (2016) 119–126, https://doi.org/10.1016/j.sna.2016.05.003.

[27] D. Dohy, G. Lucazeau, Valence force field and Raman spectra of β Ga2O3, J. Mol. Struct. 79 (1982) 419–422, https://doi.org/10.1016/0022-2860(82)85094-1.

[28] O.A. Balitskii, V.P. Savchyn, P.V. Savchyn, Thermal oxidation of indium and gallium sulphides, Phys. B Condens. Matter 355 (2005) 365–369, https://doi.org/10.1016/j.physb.2004.11.033.

[29] S.I. Boldish, W.B. White, Optical band gaps of selected ternary sulfide minerals, Am. Mineral. 83 (1998) 865–871, https://doi.org/10.2138/am-1998-7-818.

[30] J.I. Pankove, Optical Processes in Semiconductors, 1971.

[31] K.A. Kokh, Z.M. Huang, J.G. Huang, Y.Q. Gao, B. Uralbekov, J. Panomarev, I. N. Lapin, V.A. Svetlichnyi, G.V. Lanskii, Y.M. Andreev, Study of Ga2S3 crystals grown from melt and PbCl2 flux, Mater. Res. Bull. 84 (2016) 462–467, https://doi.org/10.1016/j.materresbull.2016.08.046.

[32] H.F. Liu, K.K.A. Antwi, N.L. Yakovlev, H.R. Tan, L.T. Ong, S.J. Chua, D.Z. Chi, Synthesis and phase evolutions in layered structure of Ga2S 3 semiconductor thin films on epiready GaAs (111) substrates, ACS Appl. Mater. Interfaces 6 (2014) 3501–3507, https://doi.org/10.1021/am4056535.

[33] M. Isik, E. Tugay, N. Gasanly, Optical properties of GaS crystals: combined study of temperature-dependent band gap energy and oscillator parameters, Indian J. Pure Appl. Phys. 55 (2017) 583–588.

[34] Z. Galazka, S. Ganschow, K. Irmscher, D. Klimm, M. Albrecht, R. Schewski, M. Pietsch, T. Schulz, A. Dittmar, A. Kwasniewski, R. Grueneberg, S. Bin Anooz, A. Popp, U. Juda, I.M. Hanke, T. Schroeder, M. Bickermann, Bulk single crystals of β-Ga2O3 and Ga-based spinels as ultra-wide bandgap transparent semiconducting oxides, Prog. Cryst. Growth Char. Mater. 67 (2021), https://doi.org/10.1016/j.pcrysgrow.2020.100511.

[35] J.X. Chen, X.X. Li, J.J. Tao, H.Y. Cui, W. Huang, Z.G. Ji, Q.L. Sai, C.T. Xia, H.L. Lu, D.W. Zhang, Fabrication of a Nb-doped β-Ga2O3 nanobelt field-effect transistor and its low-temperature behavior, ACS Appl. Mater. Interfaces 12 (2020) 8437–8445, https://doi.org/10.1021/acsami.9b20499.

[36] M. Fang, W. Zhao, F. Li, D. Zhu, S. Han, W. Xu, W. Liu, P. Cao, M. Fang, Y. Lu, Fast response solar-blind photodetector with a quasi-zener tunneling effect based on amorphous in-doped Ga2O3 thin films, Sensors (2020) 20, https://doi.org/10.3390/s20010129.

[37] F. Du, D. Yang, Y. Sun, Y. Jiao, F. Teng, H. Fan, Electrospun Zn-doped Ga2O3 nanofibers and their application in photodegrading rhodamine B dye, Ceram. Int. 47 (2021) 4963–4971, https://doi.org/10.1016/j.ceramint.2020.10.072.

[38] D. Guo, Z. Wu, Y. An, X. Li, X. Guo, X. Chu, C. Sun, M. Lei, L. Li, L. Cao, P. Li, W. Tang, Room temperature ferromagnetism in (Ga 1−x Mn x) 2 O 3 epitaxial thin films, J. Mater. Chem. C 3 (2015) 1830–1834, https://doi.org/10.1039/C4TC02833C.

[39] S. Shigetomi, T. Ikari, Radiative transitions of layered semiconductor GaS doped with P, J. Lumin. 118 (2006) 106–110, https://doi.org/10.1016/j.jlumin.2005.08.002.

[40] S. Shigetomi, T. Ikari, Radiative centers in layered semiconductor GaS doped with Zn, J. Lumin. 113 (2005) 137–142, https://doi.org/10.1016/j.jlumin.2004.09.116.

[41] S. Shigetomi, K. Sakai, T. Ikari, Photoluminescence of layered semiconductor GaS doped with Mn, Physica Status Solidi (B) Basic Res. 241 (2004) 2607–2612, https://doi.org/10.1002/pssb.200402044.

[42] T. Ahamad, S.M. Alshehri, Green synthesis and characterization of gallium(III) sulphide (α-Ga_2S_3) nanoparicles at room temperature, Nano Hybrids 6 (2014) 37–46. https://doi.org/10.4028/www.scientific.net/nh.6.37.

[43] J.S. Lee, Y.H. Won, H.N. Kim, C.D. Kim, W.T. Kim, Photoluminescence of Ga2S3 and Ga2S3: Mn single crystals, Solid State Commun. 97 (1996) 1101–1104, https://doi.org/10.1016/0038-1098(95)00728-8.

[44] Y.P. Song, P.W. Wang, X.Y. Xu, Z. Wang, G.H. Li, D.P. Yu, Magnetism and photoluminescence in manganese-gallium oxide nanowires with monoclinic and spinel structures, Phys. E Low-dimens. Syst. Nanostruct. 31 (2006) 67–71, https://doi.org/10.1016/j.physe.2005.09.003.