



Temperature and doping concentration dependence of the energy band gap in β -Ga₂O₃ thin films grown on sapphire

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Abstract: This paper presents the effects of temperature and n-type doping concentration on the energy band gap of β -Ga₂O₃ thin films grown on c-plane sapphire substrates by low pressure chemical vapor deposition (LPCVD). The β -Ga₂O₃ thin films were grown using high purity gallium (Ga) and oxygen (O₂) as precursors, and Si as the n-type dopant. The transmission electron microscopy (TEM) diffraction pattern showed that the thin films are single crystals that have a monoclinic crystal structure. The dependence of the energy band gap on temperature and n-type doping concentration have been experimentally determined from photoluminescence excitation (PLE) and absorbance spectra. The PLE spectra were measured in the temperature range of 77–298 K. The results indicate that both temperature and carrier concentration play important roles in determining the energy band gap of β -Ga₂O₃ thin films. The optical gap increased with the electron concentration for $n_e \leq 2.52 \times 10^{18} \text{ cm}^{-3}$, which is due to the dominant Burstein-Moss (BM) shift. The sudden decrease in the energy gap at a doping concentration of $6.23 \times 10^{18} - 3.05 \times 10^{19} \text{ cm}^{-3}$ is consistent with the theoretical prediction of Mott criterion for Ga₂O₃ semiconductor-metal transition. The energy band gap shrinks with an increasing temperature from 77 to 298 K.

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References and links

1. S. Kumar, C. Tessarek, G. Sarau, S. Christiansen, and R. Singh, "Self-Catalytic Growth of β -Ga₂O₃ Nanostructures by Chemical Vapor Deposition," *Adv. Eng. Mater.* **17**(5), 709–715 (2015).
2. T. Kawaharamura, G. T. Dang, and M. Furuta, "Successful growth of conductive highly crystalline Sn-doped α -Ga₂O₃ thin films by fine-channel mist chemical vapor deposition," *Jpn. J. Appl. Phys.* **51**, 040207 (2012).
3. H. Nishinaka, D. Tahara, S. Morimoto, and M. Yoshimoto, "Epitaxial growth of α -Ga₂O₃ thin films on a-, m-, and r-plane sapphire substrates by mist chemical vapor deposition using α -Fe₂O₃ buffer layers," *Mater. Lett.* **205**, 28–31 (2017).
4. N. A. Moser, J. P. Mccandless, A. Crespo, K. D. Leedy, A. J. Green, E. R. Heller, K. D. Chabak, N. Peixoto, and G. H. Jessen, "High pulsed current density β -Ga₂O₃ MOSFETs verified by an analytical model corrected for interface charge," *Appl. Phys. Lett.* **110**(14), 143505 (2017).
5. M. H. Wong, Y. Nakata, A. Kuramata, S. Yamakoshi, and M. Higashiwaki, "Enhancement-mode Ga₂O₃ MOSFETs with Si-ion-implanted source and drain," *Appl. Phys. Express* **10**(4), 041101 (2017).
6. K. Konishi, K. Goto, H. Murakami, Y. Kumagai, A. Kuramata, S. Yamakoshi, and M. Higashiwaki, "1-kV vertical Ga₂O₃ field-plated Schottky barrier diodes," *Appl. Phys. Lett.* **110**(10), 103506 (2017).
7. X. Zhao, W. Cui, Z. Wu, D. Guo, P. Li, Y. An, L. Li, and W. Tang, "Growth and Characterization of Sn Doped β -Ga₂O₃ Thin Films and Enhanced Performance in a Solar-Blind Photodetector," *J. Electron. Mater.* **46**(4), 2366–2372 (2017).
8. S. Nakagomi, T.-A. Sato, Y. Takahashi, and Y. Kokubun, "Deep ultraviolet photodiodes based on the β -Ga₂O₃/GaN heterojunction," *Sens. Actuators A Phys.* **232**, 208–213 (2015).

9. S. Ahn, F. Ren, S. Oh, Y. Jung, J. Kim, M. A. Mastro, J. K. Hite, C. R. Eddy, Jr., and S. J. Pearton, "Elevated temperature performance of Si-implanted solar-blind β -Ga₂O₃ photodetectors," *J. Vac. Sci. Technol. B* **34**(4), 041207 (2016).
10. T. Oishi, Y. Koga, K. Harada, and M. Kasu, "High-mobility β -Ga₂O₃ (-201) single crystals grown by edge-defined film-fed growth method and their Schottky barrier diodes with Ni contact," *Appl. Phys. Express* **8**(3), 031101 (2015).
11. E. G. Villora, K. Shimamura, Y. Yoshikawa, K. Aoki, and N. Ichinose, "Large-size β -Ga₂O₃ single crystals and wafers," *J. Cryst. Growth* **270**(3-4), 420–426 (2004).
12. Y. Tomm, P. Reiche, D. Klimm, and T. Fukuda, "Czochralski grown Ga₂O₃ crystals," *J. Cryst. Growth* **220**(4), 510–514 (2000).
13. H. Okumura, M. Kita, K. Sasaki, A. Kuramata, M. Higashiwaki, and J. S. Speck, "Systematic investigation of the growth rate of β -Ga₂O₃ (010) by plasma-assisted molecular beam epitaxy," *Appl. Phys. Express* **7**(9), 095501 (2014).
14. M. Baldini, M. Albrecht, A. Fiedler, K. Irmscher, D. Klimm, R. Schewski, and G. Wagner, "Semiconducting Sn-doped β -Ga₂O₃ homoepitaxial layers grown by metal organic vapour-phase epitaxy," *J. Mater. Sci.* **51**(7), 3650–3656 (2016).
15. Y. Oshima, E. G. Villora, and K. Shimamura, "Quasi-heteroepitaxial growth of β -Ga₂O₃ on off-angled sapphire (0001) substrates by halide vapor phase epitaxy," *J. Cryst. Growth* **410**, 53–58 (2015).
16. S. Rafique, L. Han, A. T. Neal, S. Mou, M. J. Tadjer, R. H. French, and H. Zhao, "Heteroepitaxy of N-type β -Ga₂O₃ thin films on sapphire substrate by low pressure chemical vapor deposition," *Appl. Phys. Lett.* **109**(13), 132103 (2016).
17. S. Rafique, L. Han, M. J. Tadjer, J. A. Freitas, Jr., N. A. Mahadik, and H. Zhao, "Homoepitaxial growth of β -Ga₂O₃ thin films by low pressure chemical vapor deposition," *Appl. Phys. Lett.* **108**(18), 182105 (2016).
18. S. Rafique, L. Han, and H. Zhao, "Synthesis of wide bandgap Ga₂O₃ (E_g ~ 4.6–4.7 eV) thin films on sapphire by low pressure chemical vapor deposition," *Phys. Status Solidi., A Appl. Mater. Sci.* **213**(4), 1002–1009 (2016).
19. D. Guo, Z. Wu, P. Li, Y. An, H. Liu, X. Guo, H. Yan, G. Wang, C. Sun, L. Li, and W. Tang, "Fabrication of β -Ga₂O₃ thin films and solar-blind photodetectors by laser MBE technology," *Opt. Mater. Express* **4**(5), 1067 (2014).
20. D. Guo, H. Liu, P. Li, Z. Wu, S. Wang, C. Cui, C. Li, and W. Tang, "Zero-Power-Consumption Solar-Blind Photodetector Based on β -Ga₂O₃/NSTO Heterojunction," *ACS Appl. Mater. Interfaces* **9**(2), 1619–1628 (2017).
21. C.-Y. Huang, R.-H. Horng, D.-S. Wu, L.-W. Tu, and H.-S. Kao, "Thermal annealing effect on material characterizations of β -Ga₂O₃ epilayer grown by metal organic chemical vapor deposition," *Appl. Phys. Lett.* **102**(1), 011119 (2013).
22. H. He, M. A. Blanco, and R. Pandey, "Electronic and thermodynamic properties of β -Ga₂O₃," *Appl. Phys. Lett.* **88**(26), 261904 (2006).
23. J. B. Varley, J. R. Weber, A. Janotti, and C. G. Van De Walle, "Oxygen vacancies and donor impurities in β -Ga₂O₃," *Appl. Phys. Lett.* **97**(14), 142106 (2010).
24. F. B. Zhang, K. Saito, T. Tanaka, M. Nishio, and Q. X. Guo, "Structural and optical properties of Ga₂O₃ films on sapphire substrates by pulsed laser deposition," *J. Cryst. Growth* **387**, 96–100 (2014).
25. K. N. Shinde, S. J. Dhoble, H. C. Swart, and K. Park, *Phosphate Phosphors for Solid-State Lighting* (Springer, 2012), Chap. 2.
26. B. Monemar, "Fundamental energy gap of GaN from photoluminescence excitation spectra," *Phys. Rev. B* **10**(2), 676–681 (1974).
27. B. Monemar, "Fundamental energy gaps of AlAs and AlP from photoluminescence excitation spectra," *Phys. Rev. B* **8**(12), 5711–5718 (1973).
28. Y. Tokida and S. Adachi, "Photoluminescent Properties of Eu³⁺ in Ga₂O₃:Cr³⁺ Films Prepared by Metal Organic Deposition," *Jpn. J. Appl. Phys.* **52**(10R), 101102 (2013).
29. P. Gollakota, A. Dhawan, P. Wellenius, L. M. Lunardi, J. F. Muth, Y. N. Saripalli, H. Y. Peng, and H. O. Everitt, "Optical characterization of Eu-doped β -Ga₂O₃ thin films," *Appl. Phys. Lett.* **88**(22), 221906 (2006).
30. Q. Guo and A. Yoshida, "Temperature dependence of band gap change in InN and AlN," *Jpn. J. Appl. Phys.* **33**(Part 1, No. 5A), 2453–2456 (1994).
31. S. K. V. Farahani, V. M. Sanjose, J. Z. Perez, C. F. Mcconville, and T. D. Veal, "Temperature dependence of the direct bandgap and transport properties of CdO," *Appl. Phys. Lett.* **102**(2), 022102 (2013).
32. K. Shimamura, E. G. Villora, T. Ujiie, and K. Aoki, "Excitation and photoluminescence of pure and Si-doped β -Ga₂O₃ single crystals," *Appl. Phys. Lett.* **92**(20), 201914 (2008).
33. K. Yamaguchi, "First principles study on electronic structure of β -Ga₂O₃," *Solid State Commun.* **131**(12), 739–744 (2004).
34. T. Onuma, S. Saito, K. Sasaki, T. Masui, T. Yamaguchi, T. Honda, and M. Higashiwaki, "Valence band ordering in β -Ga₂O₃ studied by polarized transmittance and reflectance spectroscopy," *Jpn. J. Appl. Phys.* **54**(11), 112601 (2015).
35. Y. P. Varshni, "Temperature dependence of the energy gap in semiconductors," *Physica* **34**(1), 149–154 (1967).
36. H. Y. Fan, "Temperature dependence of the energy gap in semiconductors," *Phys. Rev.* **82**(6), 900–905 (1951).
37. K. P. O'Donnell and X. Chen, "Temperature dependence of semiconductor band gaps," *Appl. Phys. Lett.* **58**(25), 2924–2926 (1991).

38. T. Onuma, S. Saito, K. Sasaki, K. Goto, T. Masui, T. Yamaguchi, T. Honda, A. Kuramata, and M. Higashiwaki, "Temperature-dependent exciton resonance energies and their correlation with IR-active optical phonon modes in β -Ga₂O₃ single crystals," *Appl. Phys. Lett.* **108**(10), 101904 (2016).
39. S. Arab, M. Yao, C. Zhou, P. D. Dapkus, and S. B. Cronin, "Doping concentration dependence of the photoluminescence spectra of n-type GaAs nanowires," *Appl. Phys. Lett.* **108**(18), 182106 (2016).
40. Z. M. Gibbs, A. D. Lalonde, and G. J. Snyder, "Optical band gap and the Burstein-Moss effect in iodine doped PbTe using diffuse reflectance infrared Fourier transform spectroscopy," *New J. Phys.* **15**(7), 075020 (2013).
41. T. L. Tansley and C. P. Foley, "Optical band gap of indium nitride," *J. Appl. Phys.* **59**(9), 3241–3244 (1986).
42. J. G. Lu, S. Fujita, T. Kawaharamura, H. Nishinaka, Y. Kamada, T. Ohshima, Z. Z. Ye, Y. J. Zeng, Y. Z. Zhang, L. P. Zhu, H. P. He, and B. H. Zhao, "Carrier concentration dependence of band gap shift in n-type ZnO: Al films," *J. Appl. Phys.* **101**(8), 083705 (2007).
43. A. Walsh, J. L. F. Da Silva, and S.-H. Wei, "Origins of band-gap renormalization in degenerately doped semiconductors," *Phys. Rev. B* **78**(7), 075211 (2008).
44. E. Chikoidze, H. J. Von Bardeleben, K. Akaiwa, E. Shigematsu, K. Kaneko, S. Fujita, and Y. Dumont, "Electrical, optical, and magnetic properties of Sn doped α -Ga₂O₃ thin films," *J. Appl. Phys.* **120**(2), 025109 (2016).
45. R. J. Van Overstraeten and R. P. Mertens, "Heavy doping effects in silicon," *Solid-State Electron.* **30**(11), 1077–1087 (1987).
46. J. W. Slotboom and H. C. De Graaff, "Measurements of bandgap narrowing in Si bipolar transistors," *Solid-State Electron.* **19**(10), 857–862 (1976).

1. Introduction

Ultrawide bandgap (UWBG) gallium oxide (Ga₂O₃) represents an emerging semiconductor material with excellent chemical and thermal stability up to 1400 °C [1]. It exists in five different polymorphs: α , β , γ , δ and ϵ [2]. Different phases of Ga₂O₃ exhibit different band gap. Based on the polymorphs, it has an energy band gap of 4.4–5.3 eV [2, 3], much higher than that of the GaN (3.4 eV) and 4H-SiC (3.2 eV). It exhibits high transparency in the deep ultraviolet (DUV) and visible wavelength region due to its very large band gap and has a transmittance of over 80% in the UV region. The monoclinic β -phase Ga₂O₃ represents the thermodynamically stable crystal among the known five phases (α , β , γ , δ , ϵ). The breakdown field of β -Ga₂O₃ is estimated to be 6–8 MV/cm [4], which is about two–three times larger than that of 4H-SiC and GaN. These unique properties make β -Ga₂O₃ a promising candidate for high power electronic devices [4–6] and solar blind photodetectors applications [7–9]. More advantageously, single crystal β -Ga₂O₃ substrates can be synthesized by scalable and low cost melting based growth techniques such as edge-defined film-fed growth (EFG) [10], floating zone (FZ) [11] and Czochralski [12] methods. For β -Ga₂O₃ thin film growth, both molecular beam epitaxy (MBE) [13] and metal organic vapor phase epitaxy (MOVPE) [14] have been demonstrated to produce high quality and controllable doping films but with relatively slow growth rates (2–10 nm/min). Halide vapor phase epitaxy (HVPE) using chloride precursors was demonstrated to grow β -Ga₂O₃ films with fast growth rates (>5 μ m/hr) [15]. Recently, we have developed a low pressure chemical vapor deposition (LPCVD) method to grow high quality β -Ga₂O₃ thin films on both native β -Ga₂O₃ and c-sapphire substrates with controllable n-type doping and fast growth rates [16–18]. Besides the aforementioned growth techniques, β -Ga₂O₃ thin films growth have also been reported by laser MBE [19], radio frequency magnetron sputtering [20] and metal organic chemical vapor deposition (MOCVD) [21]. Nevertheless, the fundamental physical properties of β -Ga₂O₃ thin films have not been well studied or understood yet due to the limited availability of high quality epi-films.

Theory predicted that β -Ga₂O₃ is an indirect band gap semiconductor but the indirect gap is only 30–40 meV smaller than the direct band gap [22, 23]. There has been no experimental confirmation yet on the indirect band gap transition for β -Ga₂O₃ thin films. In this work, we presented a study on the direct band gap of β -Ga₂O₃ thin films as a function of temperature and n-type doping concentration. The shift in the band gap was experimentally determined from photoluminescence excitation (PLE) in the temperature range of 77–298 K and room temperature absorbance spectra.

2. Experimental section

C-plane (0001) sapphire was used as the growth substrate, which was cleaned following standard solvent cleaning procedure, and rinsed by de-ionized water and dried with nitrogen flow prior to growth. High purity gallium (Ga) and oxygen (O_2) gas were used as the sources for gallium and oxygen, respectively. Argon (Ar) was used as the carrier gas. The LPCVD growths of β - Ga_2O_3 thin films on sapphire substrates were carried out at 900 °C for 1 hour. $SiCl_4$ was used as the n-type dopant source.

The film growth rate, crystal orientation and optical properties of the heteroepitaxial β - Ga_2O_3 thin films were characterized by using field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), PLE and absorbance spectroscopy. FESEM images were taken with Helios 650. High resolution transmission electron microscopy (HRTEM) images and selected-area electron diffraction (SAED) were taken using a FEI Tecnai F30 at 300 kV. The PLE spectra were measured using a continuous Xenon lamp source. The room temperature doping concentrations were measured with HMS 3000 Hall measurement system. The absorbance spectra were taken with Cary 6000i UV-VIS-spectrophotometer in the spectral range from 188 to 1800 nm at an 8° angle of incidence.

3. Results and discussions

To accurately determine the growth rate of β - Ga_2O_3 thin films grown on sapphire substrates, cross-sectional SEM was conducted. Figure 1 shows the cross-sectional FESEM image of the focused ion beam (FIB) prepared β - Ga_2O_3 TEM sample grown on c-sapphire substrate. The β - Ga_2O_3 thin film was grown at 900 °C for 1 hour having a Si doping concentration of $2.5 \times 10^{18} \text{ cm}^{-3}$. From this image, the thickness of the thin film was estimated to be 6 μm , which corresponds to a growth rate of 6 $\mu\text{m/hr}$. Cross-sectional SEM characterization on samples with various doping concentrations (not shown) have been performed, which did not show obvious dependence of film growth rate on doping concentration. It is worthwhile to mention that this growth rate is much higher than the growth rates of the β - Ga_2O_3 thin films grown by MBE, pulsed laser deposition (PLD), or current MOVPE technologies. Some reported growth rates of β - Ga_2O_3 thin films synthesized by MBE, MOCVD and PLD are 0.13 $\mu\text{m/hr}$ [13], 0.33 $\mu\text{m/hr}$ [14] and 0.22 $\mu\text{m/hr}$ [24], respectively.

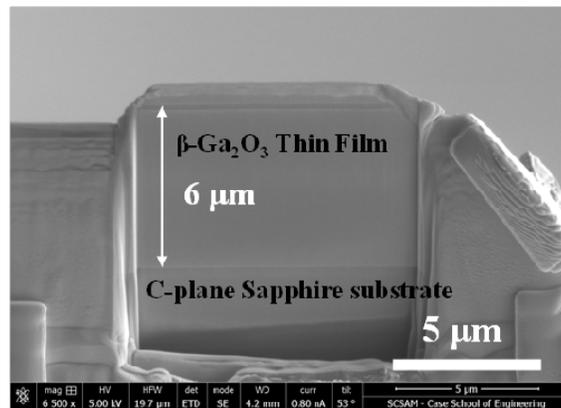


Fig. 1. Cross sectional FESEM image of TEM sample prepared by FIB. The sample was prepared from a β - Ga_2O_3 heteroepitaxial layer (6 μm) grown on c-plane sapphire substrate for 1 hour.

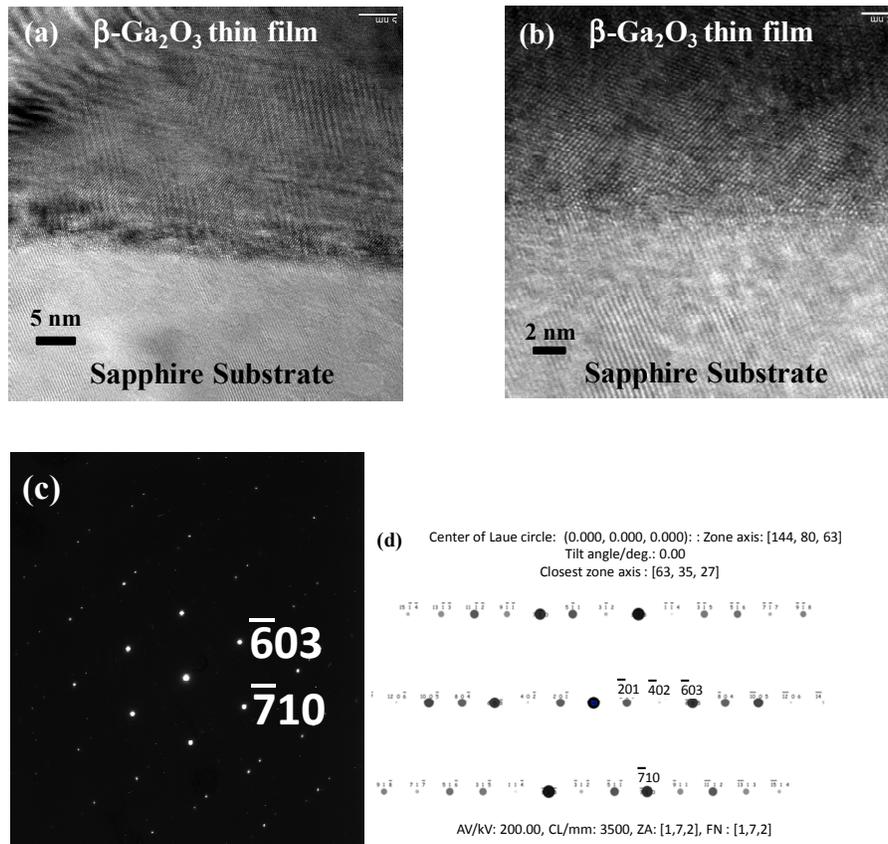


Fig. 2. (a-b) HRTEM images of β - Ga_2O_3 heteroepitaxial layer showing the lattice fringes. (c) SAED pattern of β - Ga_2O_3 layer taken along $[172]$ zone axis. (d) SAED pattern of β - Ga_2O_3 layer generated by JEMS.

The crystal quality and interfacial structure of the β - Ga_2O_3 heteroepitaxial thin film was investigated with HRTEM as well as the SAED pattern. Figure 2(a) and 2(b) show the HRTEM images of the heteroepitaxial layer. The lattice fringes of both the β - Ga_2O_3 layer and the substrate are clearly visible in the images. The interface between the β - Ga_2O_3 thin film and c-plane sapphire substrate is not as sharp which can be due to the lattice and crystal symmetry mismatch. The characterization and understanding of defects present in the β - Ga_2O_3 layer are subject of future studies. Figure 2(c) shows the SAED pattern of the heteroepitaxial layer, which confirms that the grown thin film is single crystalline monoclinic β - Ga_2O_3 . This result corroborates our conclusion from X-ray diffraction (XRD) measurement; details of which had been reported in our previous paper [16]. From XRD measurement, only (-201) and higher order diffraction peaks of β - Ga_2O_3 were observed, indicating that the as-grown thin films are phase pure with $[-201]$ as the growth orientation. To identify the zone axis and the Miller indices of the diffraction spots present in the pattern, several diffraction patterns of monoclinic β - Ga_2O_3 along different zone axes were generated using JEMS (a commercialized software package). Such a diffraction pattern is shown in Fig. 2(d). This pattern taken along $[172]$ zone axis matched with the diffraction pattern of Fig. 2(c). By comparing the two patterns together with X-ray diffraction measurement, we confirmed that the (-201) plane is the growth orientation of the β - Ga_2O_3 thin film grown on c-plane sapphire.

To study the temperature dependence of the optical band gap of $\beta\text{-Ga}_2\text{O}_3$ thin films, PLE spectra were collected at different temperatures ranging from 77 K up to 298 K. PLE is a method of obtaining information about the structure of the absorption edge [25]. In PLE, the emission wavelength remains fixed and the excitation energy is varied to see all the energy states contribution to the luminescence of the selected emission wavelength. In this method, crystals of arbitrary thickness and geometry can be used, unlike the transmission absorption measurements. Accurate results for absorption edge structures and fundamental transitions have previously been obtained for III-V and III-nitride compounds [26, 27]. PLE has also been used to identify the absorption edge of $\beta\text{-Ga}_2\text{O}_3$ thin films grown by metal organic deposition [28] and pulsed laser deposition [29]. It is still difficult to observe near band edge emission peak in the standard PL measurements, and the reason for which is still unclear. Figure 3(a) plots the PLE spectra of a Si-doped $\beta\text{-Ga}_2\text{O}_3$ thin film with a doping concentration of $2.5 \times 10^{18} \text{ cm}^{-3}$. Note that the temperature dependent PLE measurements were performed on unintentionally doped $\beta\text{-Ga}_2\text{O}_3$ thin films grown by the same method, which shows a very similar trend. The PLE spectra were collected at an emission wavelength of $\lambda_{\text{emission}} = 415 \text{ nm}$. Note that relatively broad band edge absorptions were observed at different temperatures, which could be due to the impurities and defects that exist in the heteroepitaxially grown films. With the comparison of the band gap values extracted from the absorbance measurements, the PLE peak values are identified as the optical band gap in the band gap temperature dependence analysis. The PLE peaks redshifted with increasing temperature from 257 nm ($T = 77\text{K}$) to 266.4 nm ($T = 298\text{K}$). This corresponds to a band gap narrowing from 4.82 eV to 4.65 eV as the temperature increases from 77K to 298K. Such dependence of band gap on temperature has been reported for other semiconductor materials [30, 31]. Note that the PLE peak intensity reduced and the peak was broadened with the increase of temperature. At higher temperatures, the carriers have sufficient energy to be excited to the non-radiative recombination centers. As a result, the intensity of the PLE peak reduces. In addition, the electron-phonon interaction increases with increasing temperature. This leads to a broadening of the PLE peaks and the overlapping of bands with close energies. We measured the temperature dependence PLE properties of the intrinsic thin films as well as thin films with intentional doping concentrations (not shown). We did not observe obvious PLE peak intensity reduction or peak broadening dependence on the doping concentration that are discussed here. In this paper, temperature dependence of direct absorption edge had been measured. In monoclinic crystal structure, valence band splitting occurs under the influence of crystal field [32, 33]. Polarized lights can be used to selectively excite various transitions from valence bands to conduction band minimum (CBM) [32, 34]. For our PLE measurements, unpolarized light was used as the excitation source. Therefore, the measured band gap values correspond to the narrowest direct band gap of $\beta\text{-Ga}_2\text{O}_3$. This conclusion is also supported from the absorption spectra measurements shown in Fig. 4. The estimated band gaps reported in this paper also match with the previous reported values [22, 23].

Figure 3(b) summarizes the dependence of the PLE peak positions as a function of temperature for Si-doped $\beta\text{-Ga}_2\text{O}_3$ thin films with doping concentration $n = 2.5 \times 10^{18} \text{ cm}^{-3}$. From Fig. 3(b), the energy band gap shrinks as the increase of temperature. The shrinkage of energy band gap with increasing temperature occurs mainly due to two contributing factors: (i) Thermal dilation of crystal lattice which reduces the overlap between the electron wave functions of neighboring atoms; and (ii) Electron-phonon interaction at finite temperature which changes the bond energy of the electron. At moderate temperature, lattice phonons are excited in large numbers. They influence the electron bonding energy through various orders of electron-phonon interactions. The change of bonding energy in turn alters the optical band gap [35–37]. It has been reported previously that the major contribution for the temperature dependence of the bandgap comes from the electron-phonon interaction [35]. However, for quantitative analysis of the thermal expansion of $\beta\text{-Ga}_2\text{O}_3$ in the studied temperature range,

temperature dependent X-ray diffraction measurement needs to be conducted which is part of our future studies on this material.

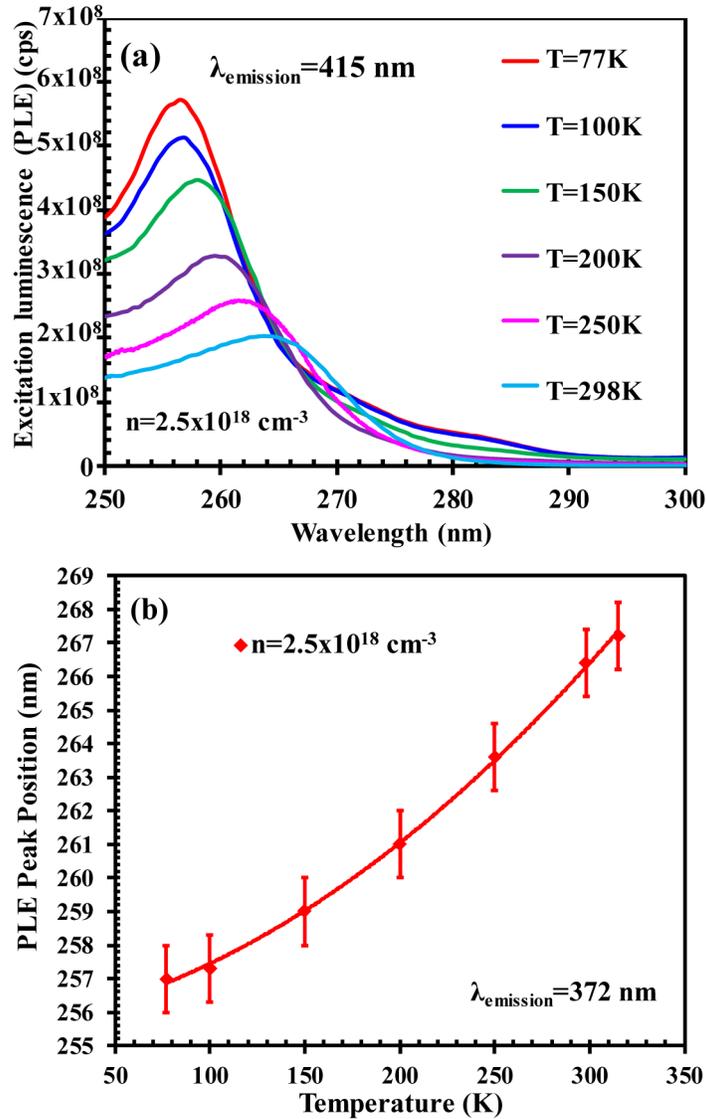


Fig. 3. (a) Photoluminescence excitation spectra measured at different temperatures (77-298 K) for a Si-doped β -Ga₂O₃ thin film with doping concentration of $2.5 \times 10^{18} \text{ cm}^{-3}$. (b) PLE peak positions as a function of temperature for the same Si-doped β -Ga₂O₃ thin film.

To determine the Varshni parameters for the temperature dependence of β -Ga₂O₃ band gap, the band gap vs temperature curve was fitted using the Varshni equation [35]:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{\beta + T} \quad (1)$$

where $E_g(0)$ is the bandgap value at 0 K, α and β are Varshni parameters. From the fitting curve, the Varshni parameters governing the temperature variations of the energy band gap of β -Ga₂O₃ are extracted to be $\alpha = 4.45 \times 10^{-3} \text{ eV/K}$ and $\beta = 2000 \text{ K}$. Temperature dependence of the band gap of β -Ga₂O₃ has been reported previously for Mg doped (010) and

unintentionally doped (001) single crystal commercial substrates [38]. The Varshni parameters reported in this work are expected to be different since the growth methods of these materials are different and therefore affecting the material quality as well as the optical properties.

Optical absorbance spectroscopy was used to study the effects of doping concentration on the optical band gap of $\beta\text{-Ga}_2\text{O}_3$ thin films grown on double-side polished c-sapphire substrates. Absorbance measurement is an accurate method to estimate the optical band gap of the semiconductor materials [39, 40]. For our absorbance measurements, the samples were loaded at the center of an integrating sphere. The integrating sphere collected the signals and then calibrated them with the reference signal. All the thin films used for the measurements have similar thicknesses and same crystal orientations. The doping concentration, mobility and resistivity of the thin films were measured by Hall measurements using van der Pauw method. The Hall mobility varied in the range between $\sim 12\text{-}42\text{ cm}^2/\text{V}\cdot\text{s}$ depending on the carrier concentration [16]. The sample with the highest mobility has a Hall resistivity of $1.11 \times 10^{-1}\ \Omega\cdot\text{cm}$. Note that the electron Hall mobility strongly depends on the sample growth condition. Further optimization of the growth condition will improve the material quality as well as the electron Hall mobility. The background doping concentration for an unintentionally doped $\beta\text{-Ga}_2\text{O}_3$ film grown on c-sapphire substrate was measured at $3 \times 10^{16}\text{ cm}^{-3}$. Figure 4(a) plots the optical absorbance spectra of Si-doped $\beta\text{-Ga}_2\text{O}_3$ thin films with various carrier concentrations ranging from high- 10^{16} to high- 10^{19} cm^{-3} . The optical band gaps of the thin films were estimated from Tauc plots shown in the inset of Fig. 4(a). For carrier concentration up to $2.52 \times 10^{18}\text{ cm}^{-3}$, the band gap increased from $\sim 4.69\text{ eV}$ to $\sim 4.716\text{ eV}$. The widening in band gap with increasing doping concentration is due to the dominant Burstein-Moss (BM) band-filling effect for a doped semiconductor [39, 41, 42]. In the case of a doped n-type semiconductor, states near the conduction band edge have a nonzero occupancy. As a result, the photon energy required for excitation across a direct band gap becomes higher which results in an increase in the optical band gap. In general, both BM Fermi-band filling effect (bandgap widening) and many-body bandgap renormalization effect (band gap narrowing) competitively affect the optical bandgap of semiconductor materials with relatively heavy doping. The bandgap narrowing effect was considered due to the mutual exchange and Coulomb interactions between the added free electrons in the conduction band and electron-impurity scattering [43]. Therefore, the measured optical band gap is a result of the competing BM effect and band gap renormalization effect.

For the thin films with doping concentrations ranging in $6.23 \times 10^{18} - 3.05 \times 10^{19}\text{ cm}^{-3}$, the band gaps suddenly reduced to $\sim 4.7\text{-}4.68\text{ eV}$. The sudden decrease of the band gap can be due to the Mott semiconductor-metal transition. We did not observe obvious peaks in the absorbance spectra that corresponds to bound exciton states. This could be due to the existence of defects in the heteroepitaxially grown $\beta\text{-Ga}_2\text{O}_3$ thin films which results in the broadening of the absorbance spectra. Recently, the Mott semiconductor-metal transition is calculated to occur at carrier concentration of $n_c \sim 4 \times 10^{18}\text{ cm}^{-3}$ for Ga_2O_3 [44]. According to the theoretical prediction, the onset of the Mott semiconductor-metal transition can occur in the range between n_c to $10 n_c$ [42]. The experimental observation of the sudden decrease of band gap in our LPCVD grown $\beta\text{-Ga}_2\text{O}_3$ thin film ($6.23 \times 10^{18} - 3.05 \times 10^{19}\text{ cm}^{-3}$) is in agreement with the theoretical prediction. Above this critical concentration range, the overall band gap increased again for a thin film with a doping concentration of $n > 7.23 \times 10^{19}\text{ cm}^{-3}$, which is due to the competing BM effect and band gap renormalization effect. Band gap narrowing can also occur due to the random impurity distribution in a heavily doped material [45]. This random distribution causes fluctuation of the electrostatic potential which in turn results in a tailing of both the conduction and valence band. Such narrowing of band gap can be determined by electrical measurements [46].

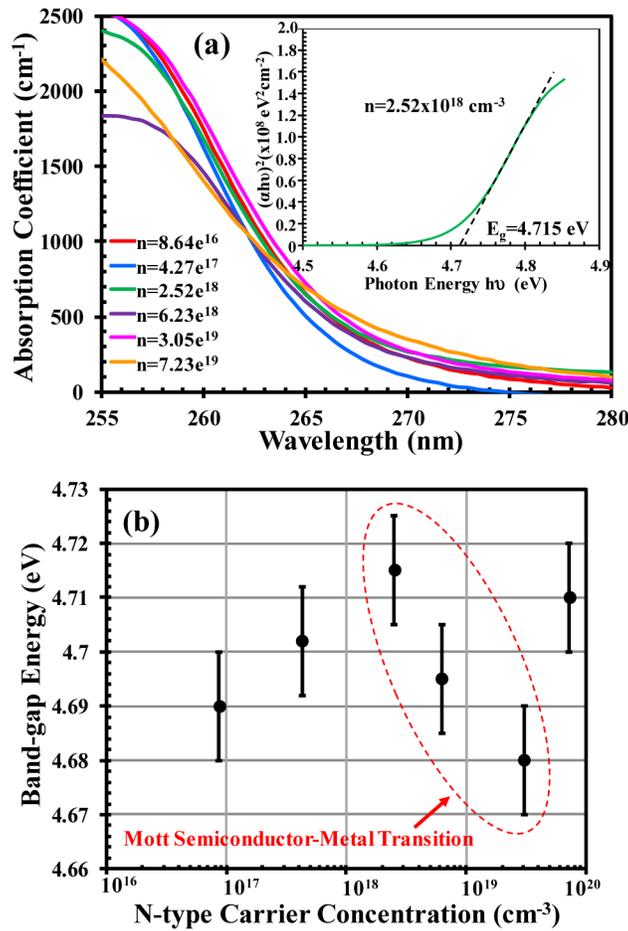


Fig. 4. (a) Optical absorbance spectra of Si-doped β -Ga₂O₃ thin films with different doping concentrations. (Inset: Tauc plot of a β -Ga₂O₃ thin film with carrier concentration of $2.52 \times 10^{18} \text{ cm}^{-3}$); (b) Band gap energy as a function of n-type carrier concentration for Si-doped β -Ga₂O₃ thin films.

4. Conclusion

In summary, the temperature and doping concentration dependence of the direct optical band gap were studied for Si-doped β -Ga₂O₃ thin films grown via LPCVD. The crystal orientation and epitaxial relationship of β -Ga₂O₃ thin films on c-plane sapphire substrate were established by TEM measurement. The band gap of β -Ga₂O₃ shrinks as temperature increases. The band gap extracted from the absorbance measurement increases with doping concentration for $n_c \leq 2.52 \times 10^{18} \text{ cm}^{-3}$ due to the dominant Burstein-Moss shift. The sudden decrease in energy gap occurs at $6.23 \times 10^{18} - 3.05 \times 10^{19} \text{ cm}^{-3}$ is consistent with the predicted onset of semiconductor-metal transition for Ga₂O₃. The understanding of such fundamental physical properties of β -Ga₂O₃ thin films are critical for future device applications.

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