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Structural and optical properties of pulsed-laser deposited crystalline β -Ga₂O₃ thin films on silicon

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Crystalline β -Ga₂O₃ thin films on (100)- and (111)-oriented Si substrates are produced by pulsed laser deposition. The as-deposited thin films are demonstrated to be polycrystalline and contain a slight deficit of oxygen atoms as measured by X-ray diffraction spectroscopy and Rutherford backscattering spectrometry, respectively. The crystallographic orientation of the Si substrate is found to play no role on the ultimate properties of the films. A direct optical band gap of 4.8 eV is determined by temperature-dependent photoluminescence excitation. Temperature-dependent photoluminescence excitation spectra reveal the existence of a deep acceptor level of around 1.1 eV with respect to the valence band related to self-trapped holes. We experimentally demonstrate that point defects in O-poor β -Ga₂O₃ thin films act as deep donors and the optical transitions are found to take place via recombination of electrons from one of the intrinsic deep donor levels with self-trapped holes located at 1.1 eV above the valence band. The 3.17 eV-ultraviolet photoluminescence is proven to be related to self-trapped holes in a small polaron state between two O(II)-s sites, whereas the two blue (2.98 eV, 2.72 eV) and the green (2.39 eV) luminescence bands are mainly originated from gallium-oxygen vacancy pairs in the (1-) charge state, gallium vacancies in the (2-) charge state and neutral oxygen interstitials, respectively.

Keywords: β -Ga₂O₃ thin film on silicon, pulsed laser deposition, substrate orientation, photoluminescence

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1. Introduction

Gallium oxide (Ga_2O_3) lies in the focus of present-day investigations of the so-called ultra-wide band gap semiconductor materials (viz. band gaps wider than 3.4 eV, GaN) [1]. Among the five known crystalline Ga_2O_3 polymorphs labeled as α -, β -, γ -, δ -, and ϵ - Ga_2O_3 , the thermodynamically stable monoclinic β - Ga_2O_3 phase with a melting point of 1795°C [2] is the most investigated because of its wide 4.8-eV band gap and high 8-MV/cm breakdown electric field [3, 4]. These unique properties make β - Ga_2O_3 a promising prospect for UV optoelectronic devices and high-power electronic applications [5, 6].

Monoclinic β - Ga_2O_3 belongs to the space group 12 ($C2/m$) and its unit cell consists of two inequivalent Ga sites and three inequivalent O sites. Ga(I) and Ga(II) ions are located at distorted tetrahedral and octahedral sites, respectively. O(I) and O(II) are threefold coordinated, while O(III) is fourfold coordinated [7]. This leads to a strong anisotropy of the electrical, magnetic, optical and thermal properties. The lattice parameters are $a = 12.2140(3)$ Å, $b = 3.0371(9)$ Å, $c = 5.7981(9)$ Å, $\beta = 103.83(2)$ Å[8], and the unit cell possesses two facile cleavage planes parallel to the (100) and (001) planes, which can be used for the mechanical exfoliation-based synthesis of two-dimensional β - Ga_2O_3 [9].

The growth of β - Ga_2O_3 thin films can be performed using either physical or chemical vapor deposition methods. Several approaches such as electron-beam evaporation [10], atomic layer deposition [11], low-pressure chemical vapor deposition [12], ultrasonic spray pyrolysis [13], sol-gel [14], high-frequency sputtering [15] and pulsed laser deposition (PLD) [16] are typically used. The properties of the resulting films depend on the processing conditions, namely deposition rate, base pressure, growth temperature,

annealing conditions, among others. The substrate plays also a crucial role on the ultimate crystalline quality of β -Ga₂O₃ thin films. Traditionally, c-plane (0001) sapphire is the substrate of choice because of its hardness, chemical stability, broad range of optical transparency and resistance to high temperatures and pressures [17]. However, little attention has been paid to the use of Si substrates despite its ubiquity in the semiconductor industry. Some attempts have so far been reported on the growth of β -Ga₂O₃ on either (100) or (111) Si substrates using atomic layer deposition [11, 18, 19, 20], metal organic chemical vapor deposition [21] and spin coating methods [22]. In all the reported works, the as-grown Ga₂O₃ thin films have resulted to be amorphous irrespective of the fabrication methods and the growth conditions. A post-annealing treatment at temperatures in the range of 500-900°C has shown to be required to achieve crystalline Ga₂O₃ thin films with the desirable β -phase.

Alternatively, the development and optimization of β -Ga₂O₃ depend on the possibility of correlating fabrication parameters with defect concentration and its energy. It has recently been reported that unintentionally doped (010) β -Ga₂O₃ reveals a rich spectrum of defect states throughout the band gap which largely define bulk recombination behavior in devices [23]. One of the most powerful techniques for the investigation of point defects in semiconductors is photoluminescence (PL). It can detect point defects with both shallow and deep energy levels, charge states, and many other parameters. As-grown single-crystalline bulk β -Ga₂O₃ usually exhibits three room-temperature PL bands centered at around 3.40 eV (UV), 2.95 eV (blue), and 2.48 eV (green) which have been reported to be related to electron recombination with a self-trapped hole [24], donor-acceptor-pair transition [25] and donor-acceptor-pair transition involving an unintentionally introduced

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3 impurity center such as Si or Sn [26], respectively. More recently, however, theoretical
4 calculations suggest that each of the observed PL bands can unambiguously be
5 explained by electron recombination with a hole trapped in one of the intrinsic point
6 defects [27].
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13 In the present work, the development of crystalline β -Ga₂O₃ thin films on either (100)-
14 or (111)-oriented Si substrates using pulsed laser deposition is demonstrated. The
15 crystallographic orientation of the Si substrate is found to play no role on the ultimate
16 properties of the films. The correlation between the structural and the optical properties
17 is reported. Based on this correlation and temperature-dependent PL measurements, a
18 model for the defect-related PL bands in O-poor β -Ga₂O₃ is proposed. This model
19 consists of the recombination of electrons from one of the intrinsic deep donor levels with
20 self-trapped holes located at 1.1 eV above the valence band.
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32 **2. Experimental details**

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35 β -Ga₂O₃ thin films were grown on (100)- and (111)-oriented Si substrates by PLD. A
36 30-mm-diameter and 5-mm-thick highly pure (99.999%) ceramic Ga₂O₃ target from
37 American Elements company was used. The Ga₂O₃ target to Si substrate distance was
38 70 mm. The substrate temperature during deposition was fixed at 800°C. The deposition
39 chamber was pumped down to a base pressure of 2.67×10^{-9} mbar. Subsequently, a
40 working pressure of oxygen of 3.91×10^{-2} mbar was introduced. A 248-nm KrF excimer
41 laser with a repetition rate of 10 Hz, 4500 pulses and an energy density of 2.4 J/cm² was
42 used to deposit about 200-nm thick β -Ga₂O₃ thin films.
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3 The crystalline structure of the films was investigated by X-ray diffraction analyses
4 (XRD) using a Brucker D8 advance diffractometer with a Cu-target source. The setup
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6 uses a Bragg-Brentano-geometry with a graphite secondary monochromator and a
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8 scintillator.
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13 Spectroscopic ellipsometry (SE) was used to determine the thickness (d) and refractive
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15 index dispersion of the pulsed laser deposited β -Ga₂O₃ films. The measurements were
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17 made using a Woollam M-2000 spectroscopic ellipsometer operating in the energy range
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19 of 1-4 eV with a step size of 0.02 eV at a fixed-angle illumination-detection geometry. The
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21 ellipsometry data modelling and analysis was performed using commercially available
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23 WVASE32 software.
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27 The thickness and composition of the thin films were determined by Rutherford
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29 backscattering spectrometry (RBS) using the 1.7 MeV He⁺ beam of the Rossendorf van
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31 de Graff accelerator at a scattering angle of 170°. SIMNRA software [28] was employed
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33 to simulate the experimental RBS data.
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37 A 5 μ m x 5 μ m surface of the samples was inspected by atomic force microscopy
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39 (AFM). Tapping mode imaging was implemented in ambient air leading to topographical
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41 images of the samples. Gwyddion software was used for visualization and analysis of the
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43 experimental data.
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47 The optical properties in the as-deposited β -Ga₂O₃ thin films were investigated by
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49 temperature-dependent PL and photoluminescence excitation (PLE). The measurements
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51 were made using a xenon lamp coupled to a monochromator for the selective PL
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53 excitation. The emitted PL light from the sample was guided through a set of lenses to a
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3 Jobin Yvon Triax 320 monochromator and then recorded by a Hamamatsu Si
4 photomultiplier. A lock-in amplifier synchronized to an optical chopper at 20 Hz was
5 employed to enhance the signal-to-noise ratio. A closed-cycle helium gas cooling system
6 was used to perform the temperature-dependent measurements in the temperature range
7 of 15–300K.
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14 15 **3. Results and Discussion**

16 17 **3.1. Structural properties**

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20 XRD patterns of the as-deposited Ga₂O₃ thin films on (100) and (111) Si substrates are
21 shown in figure 1. Several diffraction peaks indexed to Ga₂O₃ are identified. This reveals
22 the polycrystalline nature of as-deposited Ga₂O₃ thin films on both (100) and (111) Si.
23 Among the identified peaks, the three peaks indexed to (-201), (-402), and (-603) planes
24 indicate the presence of the β phase in the as-deposited Ga₂O₃ samples on both (100)-
25 and (111)-oriented Si substrates. The (-603) peak indexed to Ga₂O₃ deposited on (111)
26 Si was found to be overlapped by the (222) peak belonging to the (111) plane family. As
27 a result of contamination from the sample holder, additional diffraction peaks indexed to
28 WL α and WL β are observed. In addition, the average crystal size (D_p) for the β -
29 Ga₂O₃//Si(100) and β -Ga₂O₃//Si(111) thin films was determined to be (33 \pm 3) nm and (32
30 \pm 3) nm, respectively, as calculated by the Scherrer's formula [29]:
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$$46 \quad D_p = K\lambda / (B \cos \theta) \quad (1)$$

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49 where K stands for the Scherrer constant, λ is the X-ray wavelength (1.54056 Å), B is the
50 full width at half maximum of an XRD peak and θ is the XRD peak position (one half of 2
51 θ). This suggests that the average crystal size of the as-deposited β -Ga₂O₃ thin films is
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not affected by the crystallographic orientation of the Si substrate. The average crystal size of the as-deposited β -Ga₂O₃ thin films on both (100)- and (111)-oriented Si substrates was found to be three and a half times larger than that of β -Ga₂O₃ deposited on (111) Si by plasma-enhanced atomic layer deposition followed by rapid thermal annealing at 800°C [19].

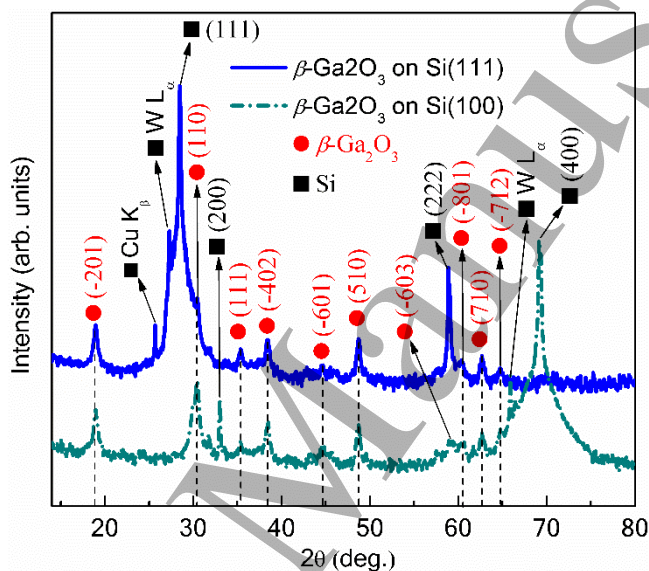


Figure 1. XRD patterns of as-deposited β -Ga₂O₃ thin films on (100)- and (111)-oriented Si substrates.

The composition and the thickness of samples were quantitatively determined by RBS. The backscattering spectra of β -Ga₂O₃ thin films deposited on (100)- and (111)-oriented Si are illustrated in figure 2(a) and (b), respectively. The measured height and width of the backscattered Ga signal, which is the heaviest element present in the oxide film, can be used to determine the concentration of Ga and the thickness of the thin films by using SIMNRA code. Figures 2(a) and (b) show the good agreement between the simulated RBS spectra from SIMNRA (solid red lines) and the experimental RBS spectra for both

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3 thin films (open black circles correspond to β -Ga₂O₃//Si(100), while open black squares
4 correspond to β -Ga₂O₃//Si(111)). The resulting thickness for β -Ga₂O₃//Si(100) and β -
5 Ga₂O₃//Si(111) was found to be (208 ± 5) nm and (200 ± 5) nm, respectively. Likewise,
6
7 the elemental composition of these β -Ga₂O₃ films was determined to be Ga:41 atom %
8 and O:59 atom %, leading to an O/Ga ratio of 1.43 in both cases (see Table. 1). This is
9
10 slightly lower compared to the theoretical ratio of 1.50 (Ga:40 atom % and O:60 atom %).
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12 These results indicate that these β -Ga₂O₃ thin films suffer from a deficit of oxygen atoms.
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14 Theoretical calculations have recently shown that the formation of O vacancies, neutral
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16 O interstitials, Ga vacancies, and Ga-O divacancies are the predominant defects in O-
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18 poor β -Ga₂O₃ films [27]. This kind of O-poor β -Ga₂O₃ thin films are reported to be one of
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20 the materials of choice for gas sensors at high temperature [30].
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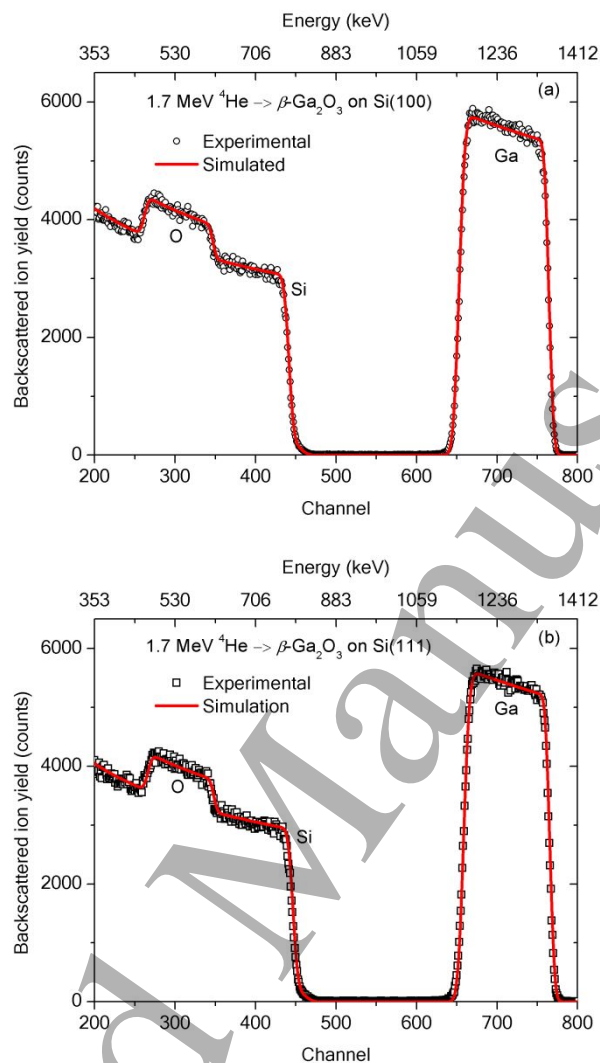


Figure 2. RBS spectra of the as-deposited β -Ga₂O₃ thin films on (100) and (111) Si substrates (a) and (b), respectively. Both the experimental and the simulated curves are shown.

Thickness and refractive index of the thin films were determined by SE. An optical model with a layer stack consisting of a Si substrate and a Ga₂O₃ film was employed. An extra layer on top of the Ga₂O₃ film accounting for the surface roughness was considered to properly fit the experimental data. The following empirical Cauchy dispersion model for the refractive index was used [31]:

$$n = 1.9044 + 0.01096/\lambda^2 + 0.000587/\lambda^4 \quad (2),$$

where λ is the wavelength in μm .

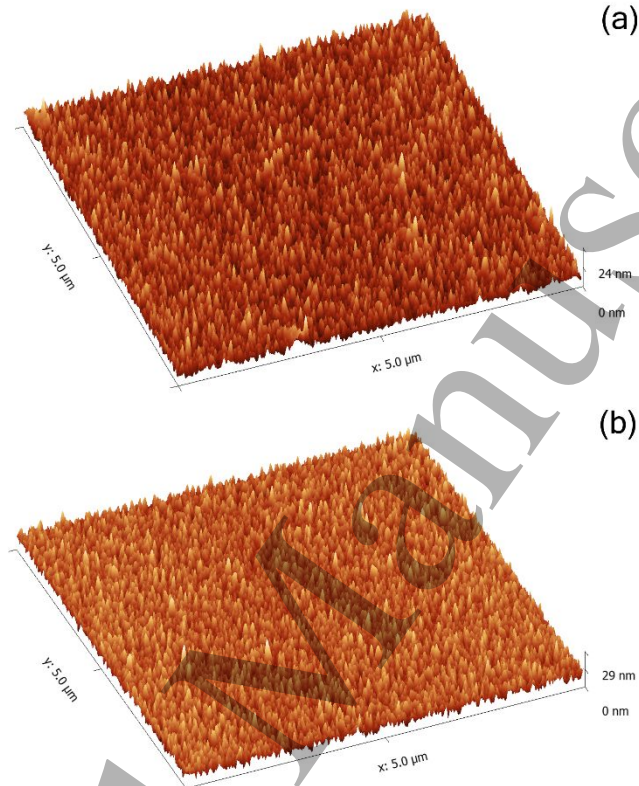


Figure 3. Topographical AFM images of the as-deposited $\beta\text{-Ga}_2\text{O}_3$ thin films on (100) and (111) Si substrates (a) and (b), respectively.

Topographical AFM images reveal no significant differences in terms of surface roughness between the as-deposited $\beta\text{-Ga}_2\text{O}_3$ thin films on (100)- and (111)-oriented Si substrates (Figure 3). The mean surface roughness for $\beta\text{-Ga}_2\text{O}_3$ thin films deposited on (100)- and (111)-oriented Si substrates is found to be (2.8 ± 0.3) nm and (3.2 ± 0.3) nm, respectively. This indicates smooth surfaces in both samples.

Table 1 summarizes the deduced film thickness and surface roughness of both as-deposited β -Ga₂O₃ thin films. The film thicknesses determined by SE are in accordance with those estimated by RBS measurements. This confirms the validity of the SE modelling.

Table. 1. Atomic composition, film thickness, surface roughness and average crystal size (D_p) of as-deposited β -Ga₂O₃ thin films on (100)- and (111)-oriented Si substrates as deduced by XRD, RBS, SE and AFM experiments.

sample	O(%)	Ga(%)	O/Ga ratio	d(nm) RBS	d(nm) SE	surface roughness (nm)	D_p (nm)
β -Ga ₂ O ₃ //Si (100)	59	41	1.43	208±5	215±3	2.8±0.3	33±3
β -Ga ₂ O ₃ //Si (111)	59	41	1.43	200±5	206±3	3.2±0.3	32±3

3.2. Optical properties

To correlate the microstructure with the optical properties, temperature-dependent PLE and PL experiments are performed. β -Ga₂O₃ thin films deposited on either (100)- or (111)-oriented Si substrates show a room-temperature broad PL band centered at around 2.39 eV under 4.80 eV excitation, which spans from 1.85 eV to 3.50 eV (Figure 4(a)). This room-temperature broad emission band is composed of two Gaussian bands centered at 2.42 eV and 2.15 eV, respectively (Figure 4(b)). The 2.42-eV green emission is attributed to neutral oxygen interstitials [32], whereas the red luminescence peaked at 2.15 eV is ascribed to neutral oxygen vacancies [27]. Recently, the formation energy of neutral

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3 oxygen vacancies has theoretically been predicted to be lower than that of gallium
4 vacancies, neutral oxygen interstitials and Ga-O divacancies in O-poor β -Ga₂O₃ [27].
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8 The spectral line shape changes as a function of temperature under 4.8-eV excitation
9 as seen in figure 4(c). A new PL peak centered at around 3.10 eV arises at 200 K and its
10 intensity predominates at 15 K. Two well-resolved peaks in the PLE spectra for the 3.10
11 eV peak are found to be centered at 4.8 eV and 3.7 eV (Figure 4(c)). The intensity of
12 these two peaks increases as the temperature decreases. The 4.8-eV PLE peak is in well
13 agreement with the reported band gap of β -Ga₂O₃ [33]. Alternatively, the 3.7-eV PLE
14 band is attributed to self-trapped holes in a small polaron state since this defect-related
15 energy level comes from O(I) sites, which has the lowest formation energy among the
16 other intrinsic defects in O-poor β -Ga₂O₃ layers [27]. No differences in terms of the PL
17 spectral line shape in the range of the investigated temperatures are observed when
18 using either 4.8 eV or 3.7 eV excitation energies (not shown). This indicates that electrons
19 are promoted to the conduction band from either the valence band (4.8 eV excitation) or
20 from a well-defined acceptor level located at around 1.1 eV with respect to the valence
21 band (3.7 eV excitation). Next, electrons de-excite non-radiatively from the conduction
22 band to one of the deep donor levels. Thus, the defect-related PL takes place by the
23 recombination of electrons located at deep donors with self-trapped holes located at 1.1
24 eV above the valence band.
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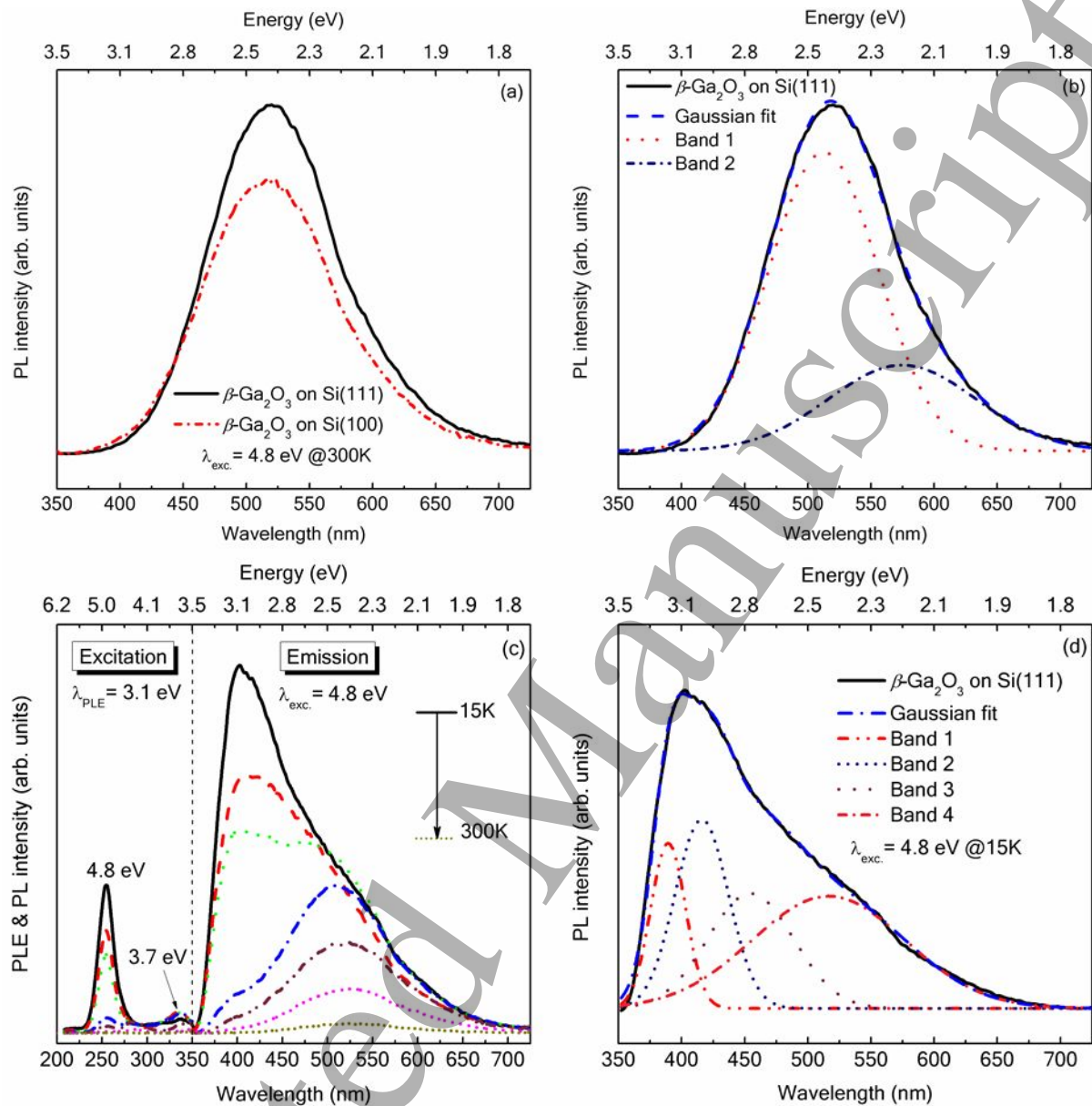


Figure 4. (a) Room-temperature PL spectra of as-deposited β -Ga₂O₃ thin films on (100)- and (111)-oriented Si substrates. (b) Room-temperature deconvoluted PL spectrum of as-deposited β -Ga₂O₃ thin films on (111)-oriented Si. (c) Temperature-dependent PLE and PL spectra of as-deposited β -Ga₂O₃ thin films on (111)-oriented Si. (d) Deconvoluted PL spectrum at 15 K of as-deposited β -Ga₂O₃ thin films on (111)-oriented Si.

To further elucidate the origin of the defect-related PL, the PL spectrum at 15 K under 4.8 eV excitation was deconvoluted into four Gaussian bands centered at 3.17 eV, 2.98 eV, 2.72 eV and 2.39 eV (Figure 4(d)). The optical transitions leading to the defect-related PL bands are summarized in figure 5. The UV-blue band at around 3.17 eV comes from the recombination of electrons with self-trapped holes in a small polaron state between two O(II)-s sites [27, 32, 34]. The two blue bands at around 2.98 eV and 2.72 eV are thought to be related to gallium and oxygen vacancy pairs in the (1-) charge state and gallium vacancies in the (2-) charge state, respectively. This is in agreement with theoretical calculations [27] and temperature-dependent cathodoluminescence investigations [31]. Alternatively, the green band peaking at around 2.39 eV is ascribed to neutral oxygen interstitials originated by the splitting with O(I) [27, 32].

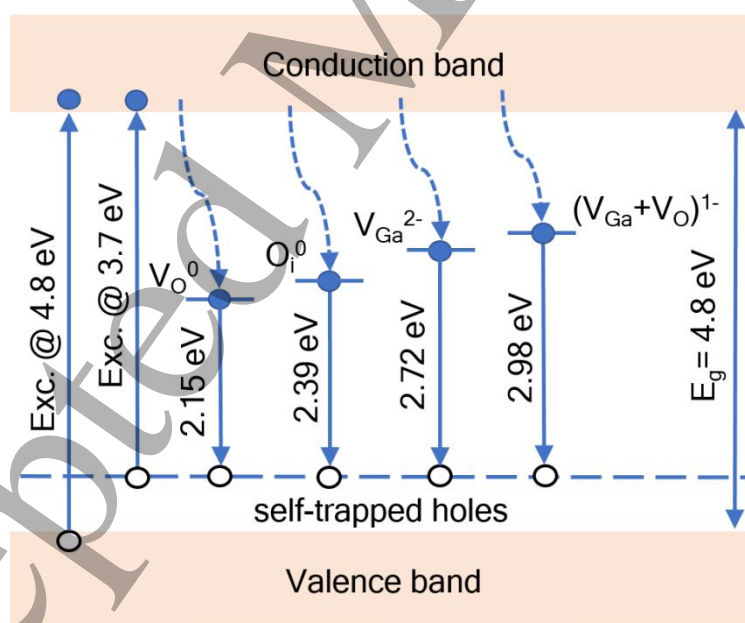


Figure 5. Sketch of the band diagram involving the PL mechanism associated to the different emission bands in crystalline β -Ga₂O₃ thin films under 3.7 eV and 4.8 eV excitation. Filled circles denote electrons and empty circles denote holes. Curvy arrows

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3 correspond to the non-radiative process of an electron from the conduction band to the
4 specific deep level.
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7 8 **4. Conclusions** 9

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11 In summary, the development of crystalline β -Ga₂O₃ thin films on either (100)- or (111)-
12 oriented Si substrates by PLD has been demonstrated. The resulting films have been
13 determined to be polycrystalline with a deficit of oxygen atoms. No differences in terms
14 of the structural and the optical properties of the films with the crystallographic orientation
15 of the Si substrate have been found. From the industrial standpoint, this might lead to
16 more flexibility for the fabrication of β -Ga₂O₃-based devices using either 100- or 111-
17 oriented Si substrates. A direct optical band gap of 4.8 eV has been determined by
18 temperature-dependent PLE measurements. The sub-band gap PL excitation at 3.7 eV
19 of β -Ga₂O₃ films has been correlated with a deep acceptor level located at around 1.1 eV
20 with respect to the valence band, originating from self-trapped holes. Four defect-related
21 PL bands in the range of 3.17 eV-2.39 eV have been observed at 15 K and ascribed to
22 the recombination of electrons from one of the intrinsic deep levels with self-trapped holes
23 located at 1.1 eV above the valence band.
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41 **Acknowledgments** 42

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45 acknowledged. Y.B. would like to thank the Alexander-von-Humboldt foundation for
46 providing a postdoctoral fellowship. The authors also thank Ilona Skorupa for her
47 assistance with the pulsed laser deposition setup.
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