Photoluminescence polarization characteristics of self-trapped excitons in an undoped $\beta$-Ga$_2$O$_3$ single crystal

Suguru Yamaoka, Yusuke Mikuni, and Masaaki Nakayama

Department of Applied Physics, Graduate School of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

nakayama@a-phys.eng.osaka-cu.ac.jp

Abstract. We have investigated the photoluminescence (PL) polarization characteristics of the self-trapped exciton (STE) in an undoped $\beta$-Ga$_2$O$_3$ single crystal at 77 K under three-photon excitation. From analysis of the polarization characteristics, we found that the STE PL is polarized almost parallel to the $a$-axis. The STE-PL polarization corresponds to the orientation of the self-trapped hole which was investigated in previous works using an electron-paramagnetic-resonance experiment and a first-principles calculation.

1. Introduction

Since $\beta$-Ga$_2$O$_3$ is one of wide-gap group-III semiconductor oxides, the band gap of which is $\sim$4.7 eV [1], much attention has been paid to high-power field-effect transistors [2] and optoelectronic devices in a deep ultraviolet region [3-5]. The crystal structure of $\beta$-Ga$_2$O$_3$ is monoclinic with the lattice parameters of $a=1.223$ nm, $b=0.304$ nm, $c=0.580$ nm, and the angle between the $a$- and $c$-axes, $\beta=103.7^\circ$ [6]. Figure 1 shows the unit cell of the crystal structure of $\beta$-Ga$_2$O$_3$. The unit cell consists of two types of gallium-atom site, Ga(I) and Ga(II), and three types of oxygen-atom site, O(I), O(II), and O(III). This crystal structure will be considered in the discussion of this paper. In our previous work [7], it was confirmed from analysis of the temperature dependence of the Urbach tail that a broad photoluminescence (PL) band, the peak energy of which is $\sim$3.35 eV, is attributed to the self-trapped exciton (STE). In alkali halides, which are typical materials for the investigation of the STE, it was reported that the STE PL has a polarization nature [8,9]; however, the polarization characteristics in $\beta$-Ga$_2$O$_3$ have not been revealed until now.

In the present work, we have investigated the PL polarization characteristics of the STE in an undoped $\beta$-Ga$_2$O$_3$ single crystal at 77 K under three-photon excitation. The PL polarization was clearly observed. It was found that the PL band of the STE is polarized almost parallel to the $a$-axis. We discuss the PL polarization characteristics of the STE, comparing with the orientation of the self-trapped hole (STH) which was investigated by an electron paramagnetic resonance (EPR) experiment [10] and a first-principles calculation [11].

2. Experimental details

The sample used was a (010)-oriented undoped $\beta$-Ga$_2$O$_3$ single crystal with a thickness of 0.60 mm grown by an edge-defined film-fed growth method at Tamura Corporation. In the PL measurements, the excitation light source was a mode-locked Ti:sapphire laser with a pulse duration of 110 fs and a repetition rate of 76 MHz. The energy of the fundamental laser light was 1.72 eV for the three-photon
excitation to avoid influence of defects and impurities around the surface on the PL properties because the sample is transparent to the excitation light. In other words, the three-photon excitation enabled us to observe the intrinsic properties of the STE. The excitation fluence was $\sim 1.4 \text{ mJ/cm}^2$ in the PL polarization measurement. Figure 2 shows the schematic diagram of the experimental setup for the measurement of the PL polarization of the STE. The incident angle of the excitation light was normal to the sample surface along the $b$-axis [010] and the PL from the sample was detected at the parallel and perpendicular directions to the excitation light, which are labelled the direction A and B in Fig. 2, respectively. In the measurement at the direction A (B), we obtained the PL polarization in the $ac$-plane (the plane perpendicular to the $ac$-plane). Thus, the PL polarization was determined in three dimensions. A band-pass filter was used to cut off the excitation laser light. The band-pass filter distorted the PL spectrum because of its absorption property; however, the spectrum distortion did not affect the PL polarization characteristics owing to the fact that the STE PL is a single band. The PL spectra were detected with a cooled charge-coupled device attached to a single monochromator with a resolution of 1.5 nm. All the optical measurements were performed at 77 K because only a liquid nitrogen cryostat was available in our experimental equipment to detect the PL both in the direction A and in the direction B.

3. Results and discussion

Figure 3 shows the PL spectrum at 77 K of the $\beta$-Ga$_2$O$_3$ single crystal in a back scattering configuration without the band-pass filter. A broad PL band peaking at 3.37 eV is attributed to the STE [7]. Because the STH in $\beta$-Ga$_2$O$_3$ is thermally stable in the temperature region lower than 90 K [10], the STE, which consists of the STH and an electron, is also stable at 77 K. The inset in Fig. 3 shows the integrated PL intensity as a function of excitation fluence. It is evident from the fitted line that the integrated PL intensity exhibits the cubic dependence on the excitation fluence, which demonstrates the occurrence of the three-photon excitation.

Figure 4(a) shows the polarization-angle dependence of the integrated PL intensity of the STE band detected at the direction A shown in Fig. 2 at 77 K, where the open circles indicate the experimental results. The inset shows the PL spectra of the STE at various polarizer angles for the reference of the polarization property. The polarization characteristics of the STE exhibit a typical cosine law; therefore, the following equation was used to analyze the experimental result:

\[
I_{\text{PL}}(\theta) = I_0 \cos^2(\theta - \theta_{\text{pol}}) + I_{\text{offset}},
\]

(1)

where $\theta$ and $\theta_{\text{pol}}$ indicate the polarization angle and polarization angle of the STE PL, respectively, and $I_{\text{offset}}$ is the non-polarized PL intensity. The solid curve indicates the fitted result. We found that the polarization angle of the STE PL at the direction A is $\theta_{\text{pol},A}=138^\circ$. The degree of polarization (DOP), which is defined as $\text{DOP}=(I_{\text{max}}-I_{\text{min}})/(I_{\text{max}}+I_{\text{min}})=I_0/(I_0+2I_{\text{offset}})$, was evaluated to be 0.61, where $I_{\text{max}}$ and
$I_{\text{min}}$ are the maximum and minimum PL intensities, respectively. The polarization angle $\theta_{\text{pol},A}$ is almost parallel to the $a$-axis corresponding to $\theta = 180^\circ - 49.9^\circ = 130.1^\circ$ at the direction A as shown in Fig. 2. Thus, the STE PL is clearly polarized. The non-polarized PL component corresponding to $I_{\text{off}}$ seems to be due to the random orientation originating from the hopping motion of the STEs. Figure 4(b) shows the polarization-angle dependence of the integrated PL intensity of the STE band detected at the direction B shown in Fig. 2 at 77 K, where the open circles and solid curve indicate the experimental results and fitted result using Eq. (1). The inset shows the PL spectra of the STE at various polarizer angles. The polarization angle and DOP of the STE PL at the direction B were estimated to be $\theta_{\text{pol},B} = 10^\circ$ and 0.53, respectively. The polarization angle of $\theta_{\text{pol},B} = 10^\circ$ corresponds to that the PL polarization of the STE is inclined by $10^\circ$ relative to the $ac$-plane. These results indicate that the polarization in three dimensions of the STE PL is almost parallel to the $a$-axis.

Hereafter, we discuss the PL polarization characteristics of the STE, comparing with the orientation of the STH that is the core of the STE. The hole in $\beta$-Ga$_2$O$_3$ is on a single O$^-$ site with its $2p^5$ configuration ($2p_x^22p_y^22p_z$) [10]. Kananen et al. found from the EPR experiment for $\beta$-Ga$_2$O$_3$ that the STH is localized in a nonbonding O 2p orbital which is approximately along the $a$-axis [10]. This result indicates that the STH is localized at the O(I) in Fig. 1 because only the nonbonding O(I) 2p orbital is oriented nearly along the $a$-axis. This STH nature is consistent with the theoretical study of

Figure 3. PL spectrum at 77 K of the $\beta$-Ga$_2$O$_3$ single crystal. The inset shows the integrated PL intensity as a function of excitation fluence ($F$). The solid line indicates the fitted result: $I_{\text{PL}} \propto F^{3.1}$.

Figure 4. Polarization-angle dependence of the integrated PL intensity of the STE band at 77 K detected at the (a) direction A and (b) direction B, which are defined in Fig. 2, where the open circles and solid curve indicate the experimental results and fitted result using Eq. (1). The inset shows the PL spectra of the STE at various polarizer angles.
the STH in $\beta$-Ga$_2$O$_3$ based on hybrid functional calculations [11]. Thus, the STE-PL polarization almost along the $a$-axis corresponds to the orientation of the STH which was reported in Refs. [10,11]. In alkali halides, the polarization of the singlet (triplet) STE is parallel (perpendicular) to the orientation of the STH [8,9]. Consequently, the fact that the STE-PL polarization is parallel to the orientation of the STH suggests that the STE has a singlet nature. In our previous work [12], we confirmed that the STE-PL decay profile exhibits a fast component with a decay time of ~80 ns corresponding to the singlet characteristics.

4. Conclusion
We clearly observed the PL polarization characteristics of the STE in an undoped $\beta$-Ga$_2$O$_3$ single crystal at 77 K under three-photon excitation. Analyzing the PL polarization characteristics of the STE, we confirmed that the STE PL is polarized almost parallel to the $a$-axis, which is consistent with the STH orientation investigated by the EPR experiment and the first-principles calculation. This fact suggests that the STE has a singlet nature.

References
[1] Onuma T, Saito S, Sasaki K, Masui T, Yamaguchi T, Honda T and Higashiwaki M 2015 Jpn. J. Appl. Phys. 54 112601
[2] Higashiwaki M, Sasaki K, Kuramata A, Masui T and Yamakoshi S 2012 Appl. Phys. Lett. 100 013504
[3] Ueda N, Hosono H, Waseda R and Kawazoe H 1997 Appl. Phys. Lett. 70 3561
[4] Muhammed M M, Roldan M A, Yamashita Y, Sahonta S-L, Ajia I A, Iizuka K, Kuramata A, Humphreys C J and Roqan I S 2016 Sci. Rep. 6 29747
[5] Guo D, Wu Z, Li P, An Y, Liu H, Guo X, Yan H, Wang G, Sun C, Li L and Tang W 2014 Opt. Mater. Express 4 1067
[6] Geller S 1960 J. Chem. Phys. 33 676
[7] Yamaoka S and Nakayama M 2016 Phys. Status Solidi C 13 93
[8] Pellaux J P, Iida T, von der Weid J P and Aegerter M A 1980 J. Phys. C: Solid State Phys. 13 1009
[9] Purdy A E, Murray R B, Song K S and Stoneham A M 1977 Phys. Rev. B 15 2170
[10] Kananen B E, Giles N C, Halliburton L E, Foundos G K, Chang K B and Stevens K T 2017 J. Appl. Phys. 122 215703
[11] Varley J B, Janotti A, Franchini C and Van de Walle C G 2012 Phys. Rev. B 85 081109(R)
[12] Yamaoka S, Furukawa Y and Nakayama M 2017 Phys. Rev. B 95 094304