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Correlation between blue luminescence intensity and resistivity in β-Ga_2O_3 single crystals

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Temperature-dependent cathodoluminescence spectra were measured from (001) unintentionally doped, (100) Si-doped, and (010) Mg-doped β-Ga_2O_3 substrates prepared by either the floating zone growth or edge-defined film-fed growth methods. Although β-Ga_2O_3 is expected to be an indirect bandgap material, direct Γ-Γ transitions were found to be dominant in the optical transmittance spectra. The substrates exhibited no near-band-edge emission and instead exhibited ultraviolet luminescence, blue luminescence (BL), and green luminescence bands. Since the BL intensity strongly depended on the resistivity in the crystals, there was evidence of a correlation between the BL intensity and formation energy of oxygen vacancies. *© 2013 AIP Publishing LLC*.
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Monoclinic β-Ga_2O_3 has a wide bandgap-energy (E_g) of 4.8–4.9 eV, and it has attracted much attention because of its potential use in UV transparent electrodes,[1] photo detectors,[2,3] and field-effect transistors (FETs).[4] The biggest advantage of this material is the availability of low-cost, large-size single-crystalline substrates grown by the melt-growth method.[5] Vertical current injection has been demonstrated in nitride-based blue light-emitting diodes fabricated on these substrates.[6] Single-crystalline β-Ga_2O_3 has superior material properties for high-power and high-voltage FETs, owing to its high breakdown electric field of 8 MV/cm.[4,7] This has made β-Ga_2O_3 a promising material for future low-cost and environmentally friendly devices.

Despite its superior material properties, the complexity of the optical processes in β-Ga_2O_3 has so far restricted its application to deep-UV light emitters. The pioneering studies on its optical characteristics analyzed single crystals grown by the Verneuil method.[8–11] Since then, polarized optical measurements have been made on single crystals grown by the Verneuil method,[9,11] halide vapor phase epitaxy,[12] and melt-growth method.[13] Because GaO_6 octahedral and GaO_4 tetrahedral chains are aligned along the b-axis of a base-centered monoclinic structure with the space group symmetry of C_{2h}^3 (C2/m), the optical and electrical properties are anisotropic parallel and perpendicular to the chains.[9,11–13] The emission spectra do not typically exhibit near-band-edge (NBE) emissions; instead, the emission bands are distinguished by three different emission bands, abbreviated as UV luminescence (UV),[9,14] blue luminescence (BL),[10,11,14] and green luminescence (GL) bands.[15] The UV band is generally impurity independent,[9] and experimental[9] and theoretical[16] studies have assigned it to recombination of free electrons and self-trapped holes (STHs). The BL band has been attributed to donor-acceptor-pair (DAP) transitions involving deep donors and acceptors.[10,11] Possible donors are intrinsic point defects such as oxygen vacancies (V_O) and interstitial Ga (Ga_i),[10,11] and possible acceptors are Ga vacancies (V_{Ga}), V_O-V_{Ga} complexes,[10,11] and Mg acceptors (Mg_{Ga}) for Mg-doped crystals. However, further investigation will be needed to correlate the emissions with the point defects.

In this letter, the temperature-dependent cathodoluminescence (CL) spectra of β-Ga_2O_3 crystals are presented, and the emission properties are discussed. It will be shown that there is a correlation between the BL intensity and resistivity in β-Ga_2O_3 crystals.

A (001) unintentionally doped (undoped) colorless substrate was grown with the floating zone (FZ) growth method.[5] The substrate exhibited n-type conductivity due to unintentional Si doping. The Hall-effect measurement yielded the carrier concentration $n = 7.7 \times 10^{16}\,cm^{-3}$ and the Hall electron mobility $\mu_H = 172\ cm^2/(Vs)$ at room temperature. The resistivity ρ is given by $\rho = 1/(qn\mu_H)$, where q is the electron charge. The ρ of $4.7 \times 10^{-1}\ \Omega\cdot cm$ is shown by the closed triangle as a function of n in Fig. 1. An (100) Si-doped bluish substrate was grown using the edge-defined film-fed growth (EFG) method. Values of $n = 4.9 \times 10^{18}\,cm^{-3}$, $\mu_H = 93\,cm^2/(Vs)$, and $\rho = 1.4 \times 10^{-2}\ \Omega\cdot cm$ were obtained at room temperature (see the closed square in Fig. 1). For comparison, ρ of (010) Si-doped substrates[7] is shown by the open circles in Fig. 1. Note that ρ of the present (001) undoped and (100) Si-doped substrates exhibited similar dependency on n with those of the reported (010) Si-doped substrates. In contrast, the

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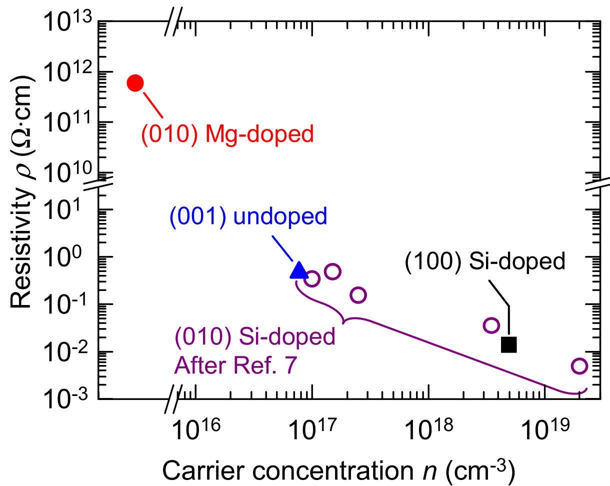

FIG. 1. Resistivity ρ of (001) undoped (closed triangle), (100) Si-doped (closed square), and (010) Mg-doped (closed circle) β-Ga_2O_3 substrates. Values for (010) Si-doped substrates[7] (open circles) are shown for comparison.

(010) Mg-doped colorless substrate grown by the FZ growth method[5] exhibited a semi-insulating behavior, and a ρ of 6×10^{11} Ω·cm was obtained with a Mg concentration of 4×10^{18}–$2 \times 10^{19}\,\mathrm{cm}^{-3}$ (see the closed circle in Fig. 1). Optical transmittance spectra were measured at room temperature using a Xe lamp. The CL was excited by an electron beam operated at 20 kV with a filament current of 1.8 A. It was detected using an optical fiber and a Hamamatsu C7473 multichannel analyzer. Back-thinned charge coupled device image sensors were used to make simultaneous measurements of wavelengths from 200 to 950 nm with a wavelength resolution of 2 nm. Details of the CL setup can be found elsewhere.[17]

As shown in Fig. 2, the optical transmittance spectra at room temperature exhibited distinct shoulders at 4.6–4.7 eV for the (001) undoped and (100) Si-doped substrates. According to theoretical calculations,[18–20] the conduction band maximum is isotropic and the effective electron mass near it is extremely light. On the other hand, the valence bands are almost flat, and the effective hole mass is heavy in

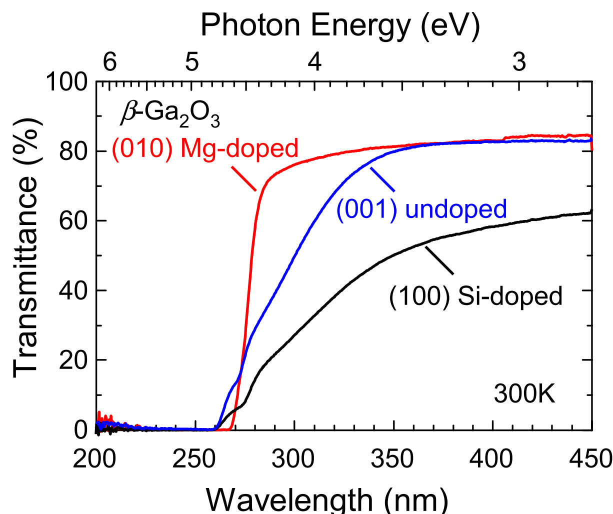

FIG. 2. Room-temperature optical transmittance spectra of (001) undoped, (100) Si-doped, and (010) Mg-doped β-Ga_2O_3 substrates.

them. The calculations predict that β-Ga_2O_3 has an indirect bandgap. However, the dipole matrix element of the indirect transition is calculated to be an order of magnitude smaller than those of the direct Γ-Γ transitions.[20] Thus, the direct transitions should be dominant in the optical transmittance spectra, and the shoulders attributed to the transition from the valence band with Γ_1^- symmetry to the conduction band with Γ_1^+ symmetry having an electric field vector E parallel to the b-axis ($E//b$).[13,18] Because of this, no shoulder appears in the spectrum for the (010) Mg-doped substrate. The rapid decrease in the transmittance spectra at 4.4–4.6 eV is attributed to the transition from the valence band with Γ_2^- symmetry to the conduction band having E perpendicular to the b-axis ($E \perp b$).[13,18]

The temperature-dependent CL spectra are summarized in Fig. 3. None of the samples exhibited NBE emissions, and the UV, BL, and GL bands appeared at 3.2–3.6, 2.8–3.0, and 2.4 eV, respectively. The UV bands at 3.6, 3.4, and 3.2 eV

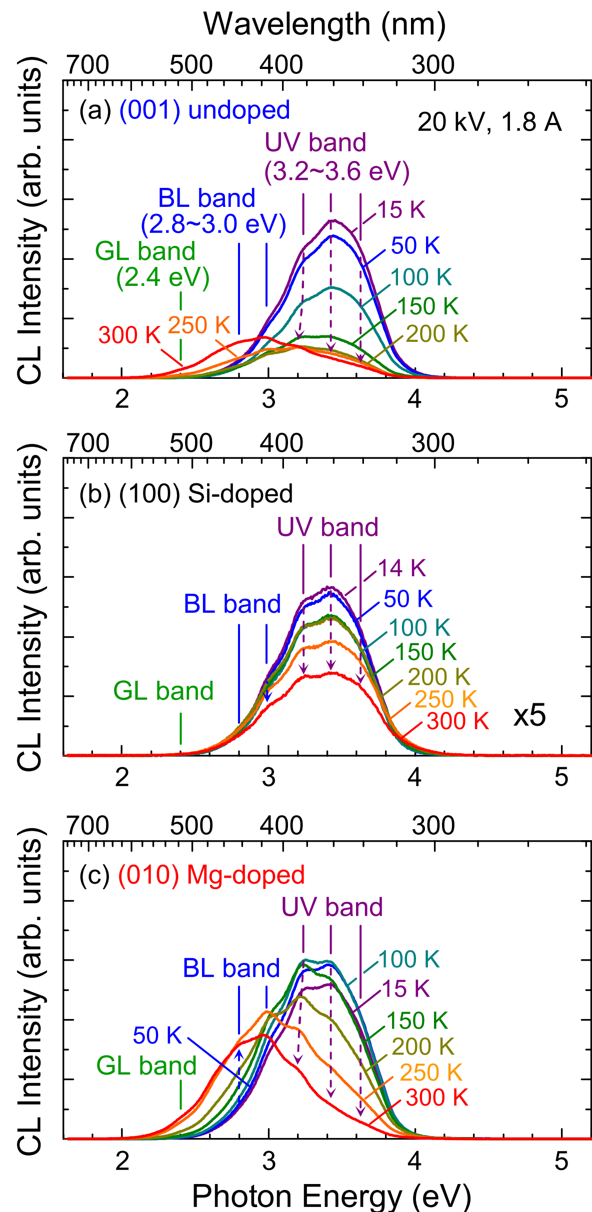

FIG. 3. Temperature-dependent CL spectra of (a) (001) undoped, (b) (100) Si-doped, and (c) (010) Mg-doped β-Ga_2O_3 substrates. Spectral intensities for the (100) Si-doped substrate were multiplied by 5 for ease of viewing.

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were dominant at 15 K in the case of the (001) undoped substrate [see Fig. 3(a)]. Their intensities decreased as the temperature increased, and the BL bands at 3.0 and 2.8 eV and the GL band at 2.4 eV became dominant at 300 K. The peak positions were almost temperature independent, and they were also independent of the doped impurities, as follows. In the case of the (100) Si-doped substrate, the CL intensities were relatively low, the UV bands were dominant, and the BL and GL bands were suppressed at all measured temperatures. In the case of the (010) Mg-doped substrate, the UV bands were dominant at 15 K, and the BL and GL bands were enhanced at 300 K. The UV bands were impurity independent, as has been observed in the spectra for Verneuil-grown crystals.[9] Thus, the present results are evidence of the proposed emission mechanism, i.e., recombination of free electrons and STHs.[9,16] Note that STHs were originally discovered in alkali halides.[21] Referred to as *V*-centers, these STHs trap holes in a local electric field induced by small displacements of oxygen atoms. STHs might contribute to the so-called polaron behavior of hole conductivity. Further study will be necessary to clarify these phenomena.

In contrast to the above impurity independent behavior, the BL intensity exhibited an impurity dependency at 300 K (see Fig. 3): the Si-doped substrate was the lowest intensity, the undoped substrate was in the middle, and the Mg-doped substrate had the highest intensity. The BL band has been attributed to a DAP transition involving deep donors and acceptors.[10,11] Possible donors are V_O and Ga_i,[10,11] and possible acceptors are V_{Ga} and/or the V_O-V_{Ga} complex[10,11] and Mg_{Ga} for the Mg-doped substrate. It has been theoretically shown[20] that V_O acts as a deep donor with an ionization energy of more than 1 eV. The formation energies of charged defects and impurities depend sensitively on the position of the Fermi level (E_F), where E_F is referenced with respect to the valence band maximum, i.e., $E_F = 0$ at the valence band maximum and $E_F = E_g$ at the conduction band minimum. In the case of V_O, the formation energy decreases when E_F moves towards the valence band maximum.[20] Since the Mg-doped substrate exhibited a high ρ of 6×10^{11} Ω·cm (see the closed circle in Fig. 1), the Fermi level would shift toward the valence band maximum, resulting in a decrease in the formation energy. In contrast, by reflecting the decrease in ρ, the formation energy would increase for the Si-doped substrate (see the closed square in Fig. 1). Therefore, the increase in ρ would induce a simultaneous increase in the V_O concentration and BL intensity.

In summary, temperature-dependent CL spectra were measured for (001) undoped, (100) Si-doped, and (010) Mg-doped β-Ga_2O_3 substrates prepared by the FZ growth or EFG methods. Although β-Ga_2O_3 was expected to be an indirect bandgap material, the direct Γ-Γ transitions were found to be dominant in the optical transmittance spectra. The substrates exhibited no NBE emission. The UV band was attributed to recombination of free electrons and STHs. The BL intensity depended on the doped impurities, and there was a correlation between the intensity and the formation energy of V_O.

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