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Photoluminescence mapping of laser-damaged β-Ga_2O_3

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Abstract

Photoluminescence (PL) mapping was utilized to investigate damage in β-Ga_2O_3 epilayers induced by 1064 nm laser pulses. The intensity and position of the intrinsic UV band were determined and plotted as a false-color image. Two types of damage were identified: circular damage and damage cracks. Circular damage shows lower UV PL intensity than the surrounding material with color centers in a "halo" around the damaged region. Damage cracks are aligned with the *a* and *c* axes and show higher PL intensity than undamaged material. Defects in the as-grown material were revealed by shifts in the UV band energy.

Keywords: semiconducting, oxide, laser-induced reaction

Introduction

Monoclinic gallium oxide (β-Ga_2O_3) is an ultrawide bandgap (~4.6 eV) semiconductor with potential applications as an active material in high-power, high-voltage devices. Understanding and controlling defects is important to optimize performance and reliability. This is especially true in harsh environments that involve energetic particles, high-intensity lasers, or extreme temperatures. The high hardness and anisotropy of β-Ga_2O_3 make the crystal susceptible to crack formation when subjected to mechanical or thermal stress.[1]

High energy electron irradiation affects the electronic properties of β-Ga_2O_3 through the formation of point defects.[2] The optical emission intensity of Cr^{3+} impurities, for example, is strongly affected by the Fermi level changes introduced by irradiation by high-energy electrons[3] or protons.[4] The effect of high-intensity laser pulses on ultrawide bandgap semiconductors, however, is less well understood. Characterizing damage caused by laser irradiation is essential for applications such as high-power lasers,[5] photoconductive switches,[6,7] and beam shaping systems.[8] Optically addressable light valves (OALVs), which mask selected portions of a high-intensity laser beam, must be designed to withstand large irradiances.[9]

Prior work on wide bandgap semiconductors found that damage in GaN epilayers originates at the GaN/sapphire interface.[10] The damage process appears to be initiated by absorption and heating of nanoscale defects,[11] although an identification of the specific defects is lacking. In the present work, photoluminescence (PL) mapping was utilized to investigate damage in β-Ga_2O_3 induced by intense laser pulses. By using a deep-UV excitation source, we obtain images with high spatial resolution that reveal several different types of damage.

Materials and Methods

Room-temperature measurements were performed on β-Ga_2O_3 thin films that were grown on (010) β-Ga_2O_3 substrates by metalorganic vapor phase epitaxy (MOCVD). Five samples with different thicknesses and Si doping levels were grown. Thicknesses, Si doping levels (intended), and free-electron densities measured by Hall-effect are listed in Table 1. Substrates were double-side polished 10 × 15 mm^2 (010) oriented Fe-doped Ga_2O_3 crystals acquired from Novel Crystal Technology (NCT), Japan. The β-Ga_2O_3 epitaxial films were grown using an Agnitron Agilis 100 vertical quartz tube reactor with TEGa (triethylgallium) and ultra-high purity O_2 gases as precursors, diluted silane (SiH_4) as the Si source for doping, and Ar as the carrier gas. All the films were grown at a growth temperature of 600 °C and a growth rate of ~6 nm/min. Further details on the substrate preparation and MOCVD growth can be found in Refs. 12 and 13.

Table 1. β-Ga_2O_3 epilayer parameters, damage thresholds, and percentage of damaged regions that contain cracks.

Sample No.	Thickness (nm)	Si doping (cm^{-3})	Electron density (cm^{-3})	Damage threshold (J/cm^2)	Damage cracks
AB220608-3	500	5×10^{19}	6.1×10^{19}	10	9%
AB220609-1	500	5×10^{18}	8.1×10^{18}	10	29%
AB220609-2	500	5×10^{17}	3.1×10^{17}	9	26%
AB220609-3	100	5×10^{18}	3.7×10^{18}	12	96%
AB220609-4	1000	5×10^{18}	3.6×10^{18}	7	47%

Laser-induced damage testing[14] based on the S-on-1 testing protocol (ISO-21254-2 standard) was performed by Spica Technologies, Inc.[15] Specific sites on a sample were exposed to 1064 nm laser pulses with 3 ns pulse width, 515±2 μm spot diameter ($1/e^2$), 5 Hz rep rate, and random polarization. The fluence was varied from 2 to 25 J/cm^2 per pulse. Each site was irradiated with 200 pulses of a given fluence. Damage was identified by plasma detection, increased He-Ne laser scatter, and visual inspection under a 150× microscope.

PL/Raman mapping was performed with a Klar Mini Pro confocal microscope with a scanning XY stage. Step sizes of 2-4 μm were chosen; smaller step sizes were not required given the relatively large sizes of the features. The laser was focused on the sample surface to a diffraction-limited spot. Focus was maintained throughout the scan by the acquisition software. PL spectra were acquired with a 266 nm pulsed laser (1.0 ns width, 10 kHz, 0.5 μJ energy) and an optical density (OD) 0.7 filter to prevent further laser damage. Because the monoclinic structure of β-Ga_2O_3 is anisotropic, the absorption of band-edge 266 nm (4.66 eV) photons is polarization dependent.[16] The reflective objectives used in this study are not polarization preserving,[17] however, so rotating the sample did not have a significant effect on the PL signal. Raman spectra, which also contained visible PL bands, were taken using a 532 nm continuous wave laser (~37 mW delivered to the sample).

Integration times for the PL and Raman spectra acquisition were 40 ms and 500 ms per spatial point, respectively. For the PL measurements, a 40× reflective objective with numerical aperture (NA) of 0.5 and working distance (WD) of 7.8 mm was used, resulting in a diffraction-limited 266 nm laser spot 0.65 μm in diameter. For the Raman measurements, we used a 50× refractive objective (0.75 NA, 1 mm WD), for a focused spot diameter of 0.87 μm.

Results

A summary of laser-induced damage testing results is shown in Fig. 1. The damage threshold is defined as the maximum pulse fluence that resulted in no damage for a set of 10 sites (the least fluence failure criterion). With this definition, the samples tested showed damage thresholds around 10 J/cm^2, in agreement with prior work.[18] The thinnest sample (100 nm) had the highest threshold, 12 J/cm^2, while the thickest sample (1000 nm) had the lowest threshold at 7 J/cm^2 (Table 1).

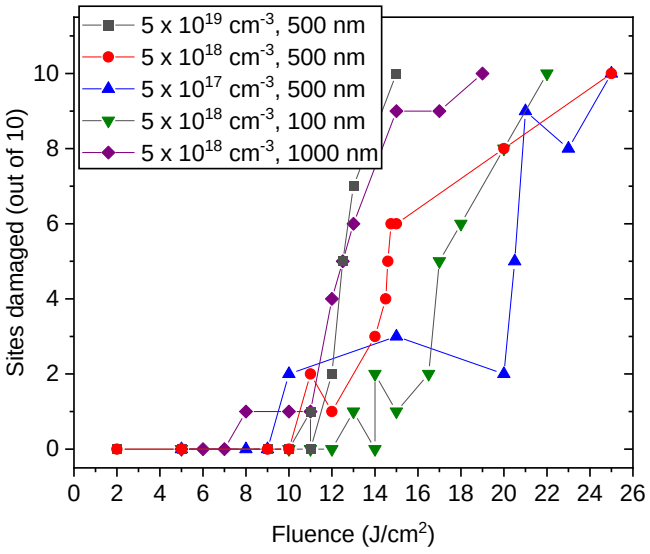

Fig. 1. Laser induced damage results for five MOCVD-grown β-Ga_2O_3 thin films. Si doping levels and epilayer thicknesses are listed.

A representative PL spectrum is shown in Fig. 2(a). The spectrum is dominated by a broad UV band centered at ~3.3 eV, which is due to recombination of an electron with a self-trapped hole.[19,20] Spectra were collected from a grid of (x,y) points on the sample surface by Raster-scanning the sample.The UV band was fit with a bi-gaussian function, which is a gaussian with different widths on the left and right side. Each fit yielded the intensity (peak height), peak

position (eV), and widths of the bi-gaussian function. The intensity and position are plotted in false-color images.

From the PL maps, we identified two major classes of damage, *circular damage* and *damage cracks*. Examples of these features are shown in Fig. 2(b) for the 100 nm-thick sample. The circular damage regions have a diameter of ~300 μm and ringlike variations inside. The defects for the 1000-μm thick sample appeared more disordered, with less well-defined ring structures, than for the thinner samples (see supplemental data). For all samples, the circular damage exhibits lower PL intensity than the surrounding, undamaged material. Laser-irradiated regions were separated by ~0.5 mm. The damaged regions showed differences in PL intensity but no significant changes in the PL peak shape or position.

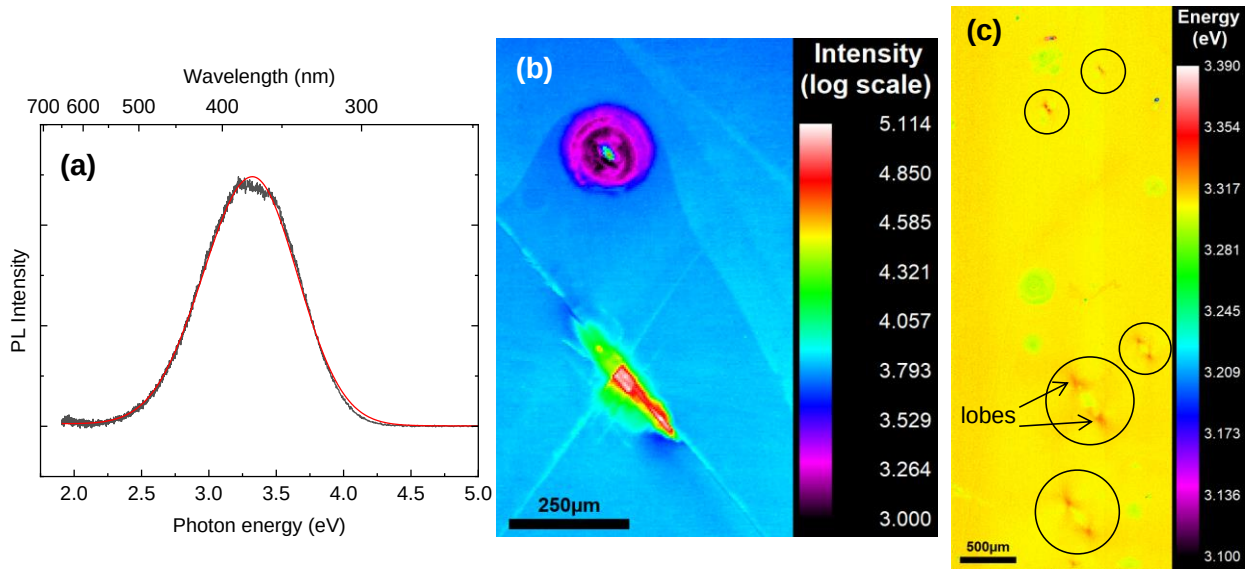

Fig. 2. (a) PL spectrum of β-Ga_2O_3 (266 nm excitation) with a fit shown in red. (b) PL map of the intensity of the UV band for a damaged sample (AB220609-3). A circular damage center, with a small crack in the center, is near the top. Below that, a damage crack is shown.(c) PL map of the energy of the UV band for a damaged sample (AB220609-2). Defects in the as-grown epilayer, unrelated to laser-induced damage, are circled.

Damage cracks are clearly aligned along the crystallographic *a* and *c* axes [Fig. 2(b)], which correspond to the cleavage planes for monoclinic β-Ga_2O_3.[21] Unlike circular damage, the region around the damage cracks emits more brightly than the undamaged material. The enhanced PL could be due to residual strain that confines photogenerated electrons to the crack region via a local reduction in the conduction-band energy.[22] In addition to "pure" damage cracks, circular damage regions were observed with cracks in the center. An example of this is shown in Fig. 2(b), where the high-intensity PL in the center of the circular damage arises from a small crack. To quantify these results, the percentage of damage centers that contain at least one crack is listed in Table 1. Notably, the 100-nm thick sample shows a much greater tendency to form damage cracks than for the thicker samples. This is also the sample with the largest damage threshold.

Figure 3 shows a Raman map for the 500-nm thick sample doped with 5×10^{18} cm^{-3} Si donors. The Raman peaks did not show any significant changes in the damaged region and no evidence for a different phase (e.g., γ-Ga_2O_3) was uncovered. The intensities of the Raman peaks were only slightly affected by the damage. However, the depth of field of the confocal Raman measurement (~10 μm) is such that the signal is dominated by the substrate rather than the epilayer.

At the high-energy end of the Raman spectrum, the tail of Cr^{3+} PL is observed. More interestingly, a broad visible emission (~600 nm, 2.1 eV) is observed in a "halo" around the circular damage. Overlaying the PL and Raman images shows that the halo is clearly outside the damaged region. While the origin of this feature is not known, the halo could be related to interstitial atoms that were created in the damaged region and pushed into the surrounding

material. Repeated scanning with the 532 nm laser caused the halo PL intensity to drop, suggesting relatively unstable defects consistent with interstitials.

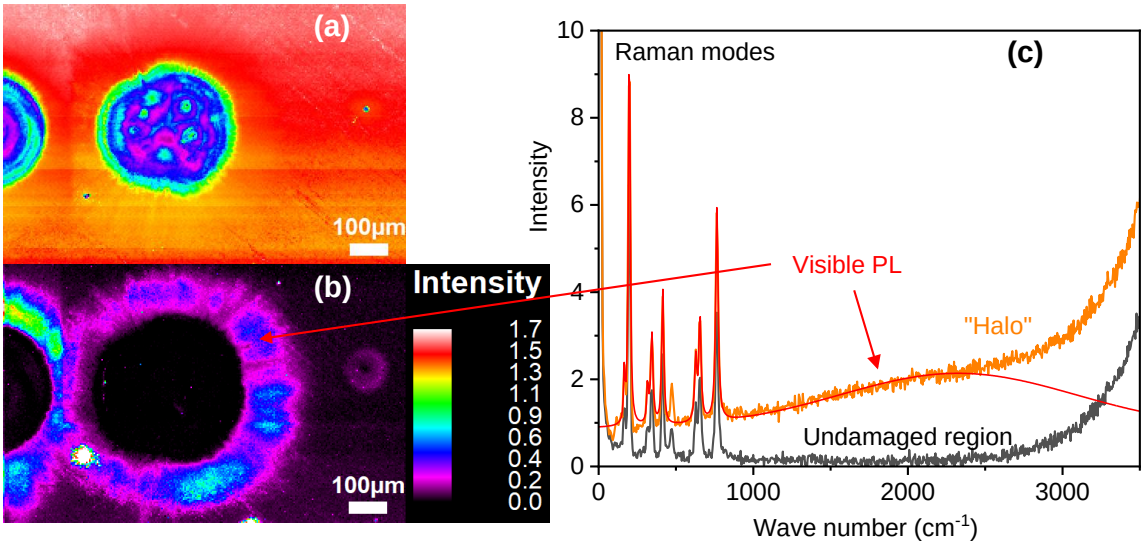

Fig. 3. PL and Raman spectra of β-Ga_2O_3 (sample AB220609-1). (a) Intensity of the UV PL band under 266 nm excitation. (b) Intensity of the visible PL band observed in Raman spectra, 532 nm excitation. (c) Raman spectra of the halo and undamaged regions.

Additional insight can be gleaned from examining subtle variations in the peak center. Maps of the peak energy (eV) reveal defects with two "lobes" in which the PL peak is shifted to higher energy [Fig. 2(c)]. From the false-color image in Fig. 2(c), the PL energy in the lobes (red) is ~0.05 eV higher than the unperturbed material (yellow). These features are consistent with a strain field around a dislocation core,[23] which in turn affects the bandgap energy via deformation potentials.[24] The lobed defects are present in the as-grown sample and do not appear to be the result of laser damage. They are distinct from the "sympetalous defects" observed by Cooke et al.,[25] which were ascribed to inverted, polycrystalline pyramids in the thin film. Sympetalous defects result in significant changes in PL intensity. For the lobed defects observed

here, however, the PL intensity is not modified – the defects can only be observed through the *shift* in PL energy. The defects could not be observed in a wide-field microscope, unpolarized or with a cross-polarized geometry, presumably due to the small magnitude of the strain.

Conclusions

From deep-UV (266 nm) PL mapping, we identified two main damage region types in β-Ga_2O_3 epilayers, which we refer to as circular damage and damage cracks. The former damage type is reminiscent of conchoidal fracture patterns observed in brittle solids such as glass.[26] A halo of color centers (under 532 nm excitation) is observed around the circular damage. Inside the circular damage, the UV PL intensity was diminished. Damage cracks, on the other hand, are straight and aligned along the *a* and *c* axes of the monoclinic crystal. The region around the cracks shows enhanced PL intensity, perhaps due to strain-induced carrier confinement. Hybrids of the two – circular damage regions that contain one or more cracks – were also observed. The thinnest sample (100 nm) had the highest damage threshold, 12 J/cm^2, while the thickest sample (1000 nm) had the lowest threshold at 7 J/cm^2. By plotting the UV band energy, defects were identified that are tentatively assigned to threading dislocations, which shift the UV band via the strain field.

Conflict of Interest

J.H. is an employee of Klar Scientific and M.D.M. owns equity in the company.

Data availability statement

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information.

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Author contributions

All authors contributed to the study conception and design. Semiconductor growth was performed by Arkka Bhattacharyya and Sriram Krishnamoorthy. Data collection and analysis were performed by Jesse Huso, Matthew D. McCluskey, and Clint D. Frye. The first draft of the manuscript was written by Matthew McCluskey and all authors contributed to the manuscript. All authors read and approved the final manuscript.

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