

O-H centers in β -Ga₂O₃ with a Ga(1) vacancy at their core

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ABSTRACT

β -Ga₂O₃ is an ultrawide bandgap semiconductor that shows promise for high-power, deep-UV, and extreme environment applications. Hydrogen can affect the conductivity of β -Ga₂O₃ through the introduction of shallow donors and the passivation of deep acceptors. This work is a study of the interaction of H with V_{Ga} deep acceptors as well as other impurities in β -Ga₂O₃ by IR spectroscopy and complementary theory.

Keywords: Ga₂O₃, hydrogen, vibrational spectroscopy

Hydrogen in transparent conducting oxides (TCOs) forms shallow donors and passivates deep acceptors, and through these mechanisms, has a strong effect on conductivity.^{1,2} In β -Ga₂O₃, H has also been found to impact electrical properties.³⁻⁵ Interstitial H (H_i) and H at an oxygen vacancy (H_O) have been predicted to be shallow donors, similar to the situation for other common TCOs.⁶ The gallium vacancy (V_{Ga}) in β -Ga₂O₃ was predicted to be a triple acceptor with low formation energy, and its importance for the compensation of n-type doping was noted.⁷ The V_{Ga}-H complex was predicted to have lower formation energy than the bare vacancy.

Recent studies of hydrogen impurities in β -Ga₂O₃ have found that the dominant O-H center is a complex of H with a Ga(1) vacancy.^{8,9} β -Ga₂O₃ has two inequivalent Ga sites with the Ga(1) site being 4-fold coordinated and the Ga(2) site 6-fold coordinated.^{10,11} *Split configurations* of V_{Ga1} are also predicted to have lower energy than an unshifted vacancy by ~ 1 eV.^{7,12,13} An unshifted vacancy is shown in Fig. 1(a). Three split configurations of V_{Ga} are possible.^{12,13} The configurations labeled “b” and “c” are shown in Figs. 1(b) and 1(c).

Positron annihilation measurements have found the V_{Ga} defect to be abundant in β -Ga₂O₃ with a concentration of 10^{18} cm⁻³ or more.^{16,17} Split configurations of V_{Ga} have been observed by electron paramagnetic resonance (EPR)^{18,19} and scanning transmission electron microscopy (STEM).²⁰

A complex of the shifted Ga(1) vacancy with H was identified in early experiments by vibrational spectroscopy and its interpretation by theory.⁸ Different configurations of the split Ga vacancy have been found to be effective traps for H and its ²H isotope, deuterium.^{9,21} This paper is a survey of the vibrational properties^{22,23} of O-H and O-D complexes in β -Ga₂O₃ that have a Ga(1) vacancy at their core.^{8,9,21} (We focus on O-D in this paper because, in infrared-absorption experiments, O-D can be detected with higher signal to noise ratio than O-H.)

Most samples for our experiments were purchased from the Tamura Corp. H and D were introduced by sealing β -Ga₂O₃ samples in quartz ampoules in an H₂ or D₂ ambient.²⁴ These ampoules were typically annealed at 900°C for several hours and then cooled to room temperature by quenching in sand. Infrared absorption experiments were performed with a Nicolet iS50 FTIR spectrometer equipped with a liquid-N₂ cooled InSb detector and a CaF₂ beam splitter.

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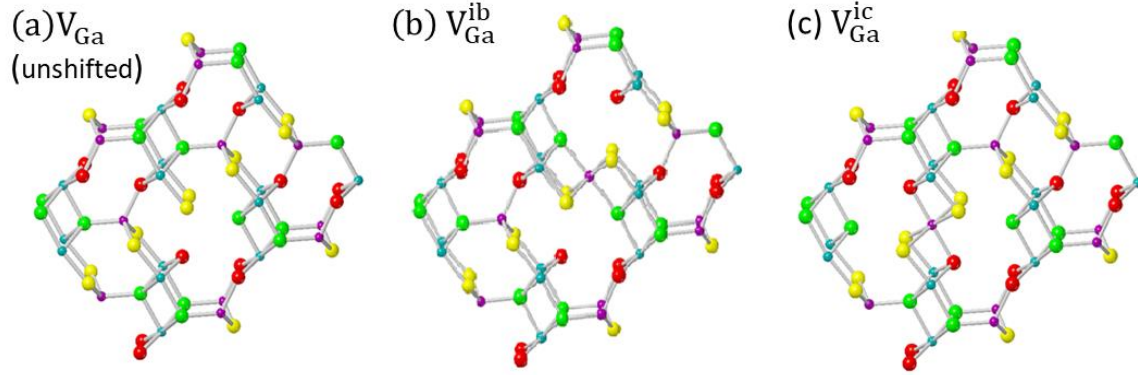


Figure 1. (a) Unshifted Ga(1) vacancy. (b) Split vacancy configuration V_{Ga}^{ib} suggested by Kyrtos et al.¹² (c) Split vacancy configuration V_{Ga}^{ic} suggested by Varley et al.^{7,13} The inequivalent atomic sites are color coded as follows: Ga(1), purple; Ga(2), dark green; O(1), red; O(2), yellow, O(3), light green. These figures and others showing models in this paper were constructed using MOLDRAW and POV-Ray.^{14,15}

Figure 2(a) shows an infrared absorption spectrum for the dominant O-D center in β -Ga₂O₃ that was produced by annealing a sample in a D₂ ambient at high temperature.⁸ The O-D line at 2546.4 cm⁻¹ is strongly polarized along the [102] direction and shows no absorption for the polarization with electric vector $E//[010]$. The corresponding O-H line at 3437.0 cm⁻¹ has also been observed to confirm the assignment to D and H vibrational modes.

Figure 2(b) shows that when a sample that contains both the D and H isotopes of hydrogen is prepared (by annealing in an ambient that contains both H₂ and D₂), a new line appears at 2547.1 cm⁻¹. The corresponding O-H line is at 3438.2 cm⁻¹. The appearance of these additional lines is a signature of a defect that contains two identical H or D atoms.^{8,9}

A defect that contains two identical D (or H) atoms will have antisymmetric and symmetric stretching modes.²² The symmetric mode is forbidden and is not seen in our spectra. The additional new line in the spectrum shown in Fig. 2(b) arises from a defect that contains both an H atom and a D atom. The O-D and O-H oscillators of the defect become dynamically decoupled because of the large difference in their isotopic masses, giving rise to a new line that lies midway between the antisymmetric and symmetric modes.²²

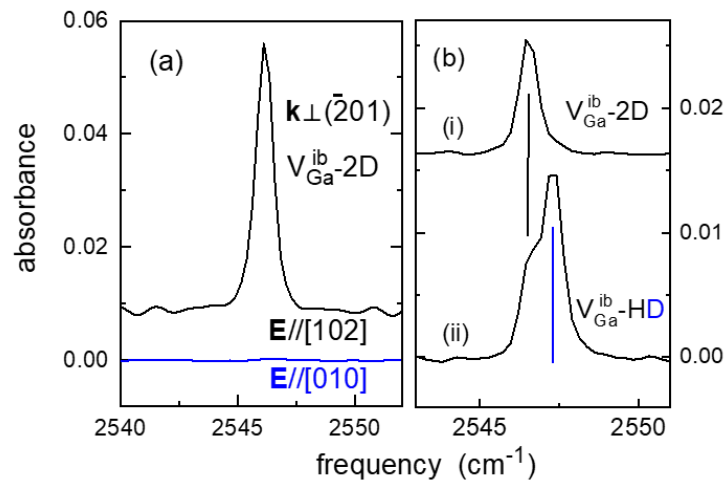


Figure 2. (a) IR absorption spectrum [77 K, propagation direction $k \perp (\bar{2}01)$] for the dominant O-D line at 2546 cm⁻¹. (a) This sample was annealed in a D₂ ambient at 900°C for 6 h and then subsequently annealed at 600°C in an inert ambient to produce the $V_{Ga}^{ib} - 2D$ complex.

(b) Spectrum (i) shows the O-D stretching mode for a β -Ga₂O₃ sample annealed in D₂ alone. The spectrum labeled (ii) is for a sample annealed in a mixture of H₂ and D₂.

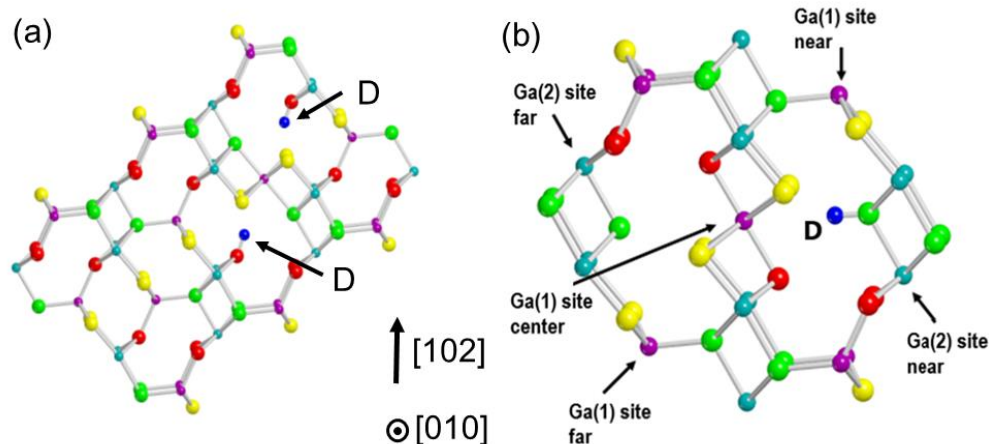


Figure 3. (a) Structure of the $V_{Ga}^{ib} - 2D$ complex that gives rise to the 2546 cm^{-1} line in β -Ga₂O₃. (b) Structure for OD-impurity complexes. A shifted Ga(1) vacancy with a trapped D and candidate substitutional Ga sites for a metal impurity is shown. The color code is the same as was used in Fig. 1.

Theory has identified the $V_{Ga}^{ib} - 2D$ defect structure shown in Fig. 3(a) that has vibrational properties consistent with the 2546.4 cm^{-1} line seen by experiment.⁸ Furthermore, a more complete study of the polarization properties of the $V_{Ga}^{ic} - 2D$ center yielded results that are consistent with the O-D bond angles predicted by theory, providing a further confirmation of this assignment.^{21,25}

Subsequent infrared absorption experiments have discovered more than a dozen different O-H and O-D centers.²⁶ Fig. 4, for example, shows polarized IR spectra and their evolution upon annealing for an Fe-doped β -Ga₂O₃ sample grown by the Czochralski method. This sample had been deuterated by an anneal in a D₂ ambient at 900°C.

β -Ga₂O₃ contains a variety of unintentional impurities and intentional dopants that can form OD-impurity complexes. Si and Fe, for example, are both adventitious impurities^{27,28} and intentional dopants. Si doping is used to produce n-type material²⁹ and Fe is used to make β -Ga₂O₃ semi-insulating³⁰. Additional impurities that are deep acceptors have been

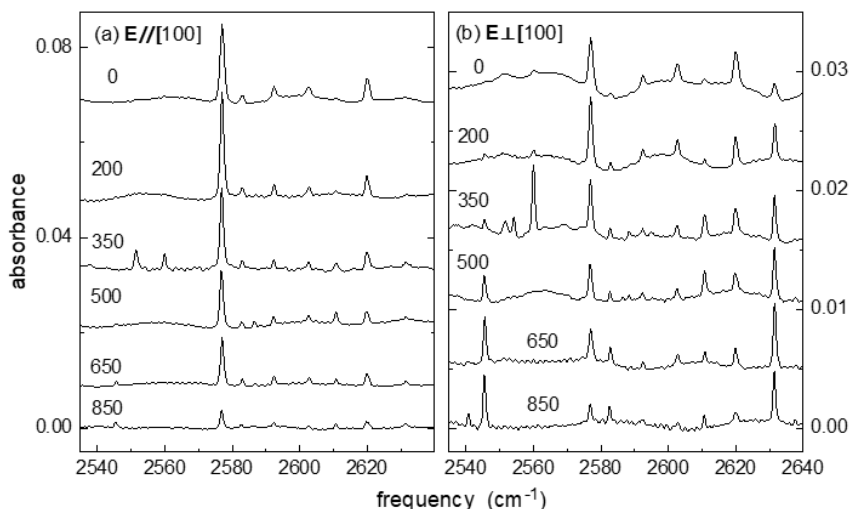


Figure 4. Panels (a) and (b) show polarized IR absorption spectra (77 K) for a (010) β -Ga₂O₃ boule grown by the Czochralski method (at Synoptics) that had been doped with Fe. This sample was annealed in a D₂ ambient at 900°C to introduce D and was then sequentially annealed at the temperatures shown (°C) in a flowing Ar ambient.

investigated as alternatives to Fe to make β -Ga₂O₃ semi-insulating.³¹⁻³³ These impurities form complexes with H and D. Assignments have been suggested for a few OD-impurity (OH-impurity) centers in β -Ga₂O₃ based on the dominant impurities present in the samples.³¹⁻³⁴ A selection of these assignments is listed in Table I. It can be seen that several of the lines assigned to OD-impurity complexes have similar vibrational frequencies. It has also been found that these lines have similar temperature dependences and polarization properties.²¹

These similar vibrational properties suggest a family of defect complexes with similar structures. Fig. 3(b) shows a defect model suggested by theory with a D atom trapped by a split vacancy with the “c” configuration.²¹ Sites are also shown for an additional substitutional impurity that would perturb this core structure to give rise to different defects with properties dominated by the defect’s $V_{\text{Ga}}^{\text{ic}} - \text{D}$ core. While we have focused on $V_{\text{Ga}} - \text{D}$ centers that contain additional impurities, defects with additional native defects are also candidates for the many OD vibrational lines that have been seen by experiment.

While much progress has been made with the identification of hydrogen centers in β -Ga₂O₃ by vibrational spectroscopy and theory, many questions have not been answered. The mechanisms for defect reactions involving the O-D (and O-H) centers that occur upon annealing remain unknown.²⁶ Defects such as interstitial H and H at an oxygen vacancy have been predicted to be shallow donors in β -Ga₂O₃,⁶ similar to their behavior in other TCOs, but have not been identified by experiment. H₂ molecules provide a reservoir of H in TCOs such as ZnO;^{35,36} is H₂ important in β -Ga₂O₃? Furthermore, additional hydrogen centers have been seen in β -Ga₂O₃ by other experimental techniques such as DLTS^{37,38} whose relationship to O-H centers seen by vibrational spectroscopy remains unknown.

Hydrogen plays an important, multi-faceted role in determining the electrical properties of β -Ga₂O₃. Much exciting work remains to be done before its fundamental properties will be fully revealed and understood.

Table I. OD-stretching frequencies of a selection of OD-impurity complexes in β -Ga₂O₃.

defect	OD-Si	OD-Fe	OD-Mg	OD-Zn	OD-Ca
ω_{D}	2579.1	2585.8	2586.3	2582.9	2556
Ref.	21,34	21,34	21,31	33	32

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