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ABSTRACT

Si is an n-type dopant in Ga_2O_3 that can be intentionally or unintentionally introduced. The results of Secondary Ion Mass Spectrometry, Hall effect, and infrared absorption experiments show that the hydrogen plasma exposure of Si-doped Ga_2O_3 leads to the formation of complexes containing Si and H and the passivation of n-type conductivity. The Si-H (D) complex gives rise to an O-H (D) vibrational line at 3477.6 (2577.8) cm^{-1} and is shown to contain a single H (or D) atom. The direction of the transition moment of this defect has been investigated to provide structure-sensitive information. Theory suggests possible structures for an OH-Si complex that is consistent with its observed vibrational properties.

β-Ga_2O_3 is attracting much recent attention as an ultra-wide bandgap semiconductor that shows great promise for high-power, deep UV, and extreme environment applications.[1–6] Hydrogen can give rise to n-type conductivity in a variety of transparent conducting oxides,[7–9] and β-Ga_2O_3 is no exception where several hydrogen centers have been reported to be shallow donors.[10,11] Therefore, it seems counterintuitive that hydrogen plasma exposure could introduce H into Ga_2O_3 that passivates the Si_{Ga} center that is also a shallow donor.[10,12,13] Nonetheless, it has been recently reported that hydrogen plasma exposure compensates or passivates Si_{Ga} shallow donors in micrometer-thick layers of Ga_2O_3 grown by hydride-vapor-phase epitaxy and that these effects are anisotropic.[14–16] In the present work, the introduction of hydrogen into a Si-doped layer by hydrogen plasma exposure has been investigated by Secondary Ion Mass Spectrometry (SIMS) and vibrational spectroscopy.[17,18] We show that H (and D) form complexes with Si_{Ga} in Ga_2O_3 leading to its passivation.

There is a growing body of information about H in Ga_2O_3 and its interactions with other defects that affect conductivity.[11,13,19–27] The $V_{Ga(1)}$ center in Ga_2O_3 gives rise to a deep triple acceptor and has shifted configurations that have low formation energies.[28–32] Theory and positron annihilation spectroscopy suggest that V_{Ga} deep acceptors compensate n-type shallow donors.[28,33,34] $V_{Ga(1)}$-nH complexes are predicted to have even lower formation energies than $V_{Ga(1)}$ and also act as deep acceptors that could compensate shallow donors.[22,28] The $V_{Ga(1)}$-2H center has been found to be the dominant hydrogen-containing center in undoped Ga_2O_3 hydrogenated either by annealing in an H_2 ambient or by the implantation of protons.[19–21] (There are two shifted configurations of $V_{Ga(1)}$ that can trap H atoms.[22,28,29] The shifted configuration of $V_{Ga(1)}$ predicted by Kyrtsos *et al.*[29] is the hydrogen trap that gives rise to the most stable $V_{Ga(1)}$-2H center that has been observed by vibrational spectroscopy.[19] The implantation of protons into Ga_2O_3 has been found to give rise to a resistive layer whose defects are suggested to interact with the implanted H upon annealing to restore the layer's conductivity.[23] Another recent study reports that the controlled introduction of H into Ga_2O_3 can give rise to both n-type and p-type behaviors.[11]

Samples for our studies were prepared from Ga_2O_3 epitaxial layers that were purchased from Novel Crystal Technology and had been grown by molecular-beam-epitaxy to be 0.5 μm thick and doped with Si to a concentration of 2×10^{18} cm^{-3}. The (010) semi-insulating Ga_2O_3 substrate was doped with Fe. Samples were treated in H- or D-plasmas for 60 min at a nominal temperature of 250 °C and were characterized with Hall effect measurements and SIMS (EAG Laboratories). Detection limits for SIMS for Si and D were reported to be 5×10^{15} and 3×10^{15} cm^{-3}, respectively.[35]

IR absorption spectra were measured with a Nicolet iS50 Fourier transform infrared spectrometer equipped with a CaF_2 beam splitter and an InSb detector. The probing light was incident normal to the face of the sample, and the polarization was analyzed with a wire grid polarizer that was placed after the sample. Samples were cooled to

77 K for our measurements with a Helitran continuous-flow cryostat. Annealing treatments to probe the thermal stabilities of defects were performed in a tube furnace with a flowing Ar ambient.

Following a treatment in a D-plasma, a Ga_2O_3 sample was characterized by SIMS. Results for the concentration profiles of Si and D are shown in Fig. 1. The depth profile for Si shows a concentration of $[Si] = 3 \times 10^{18}\,cm^{-3}$ for the 0.5 μm-thick epitaxial layer. The D profile shows a plateau with a concentration $[D] > 5 \times 10^{18}\,cm^{-3}$ throughout most of the thickness of the Si-doped epilayer. The D concentration then drops to near $4 \times 10^{17}\,cm^{-3}$ beyond a depth of 0.5 μm, i.e., in the Fe-doped semi-insulating substrate. The formation of a plateau in the D-profile that follows the dopant concentration profile is typical of the compensation or passivation of the dopant impurity in the layer.[36] Similar profiles were observed by Polyakov *et al.*[15] for Si-doped Ga_2O_3 layers ($n \approx 10^{17}\,cm^{-3}$) treated in a "harsh" D-plasma.

Prior to treatment in an H-plasma, Hall measurements found a carrier concentration of $3.0 \times 10^{18}\,cm^{-3}$, a resistivity of $2.9 \times 10^{-2}\,\Omega$ cm, and a mobility of 70 cm^2/V s for our Ga_2O_3:Si epitaxial sample. Following a treatment in an H-plasma, the carrier concentration was reduced to $1.2 \times 10^{18}\,cm^{-3}$ and the resistivity and mobility were increased to $5.4 \times 10^{-2}\,\Omega$ cm and 96 cm^2/V s, respectively. These results for the decrease in the electrical activity of the n-dopant in the layer along with an increase in the Hall mobility provides further evidence for the compensation and/or passivation of Si_{Ga} by hydrogen.

Infrared absorption spectra are shown in Figs. 2 for Ga_2O_3:Si epilayers treated in D and H plasmas. [The D spectrum (c) was measured for a piece of the same D-treated sample whose SIMS profiles are shown in Fig. 1.] The frequencies of the O-D (O-H) lines are 2577.8 (3477.6) and 2584.6 (3489.8) cm^{-1}. These two lines have also been observed in bulk Ga_2O_3 samples annealed in at a D_2 ambient but have different relative intensities in the different samples, indicating that they arise from different defects. The line at 2577.8 (3477.6) cm^1 is stronger for the Si-doped epilayer shown here, while the line at 2584.6 (3489.8.) cm^{-1} is stronger for a deuterated bulk substrate deliberately doped with Fe (inset to Fig. 2). Both Si and Fe are adventitious impurities in Ga_2O_3 with typical concentrations near $10^{17}\,cm^{-3}$ (see, for example, Refs. 37 and 38), and the substrate for our Si-doped epitaxial

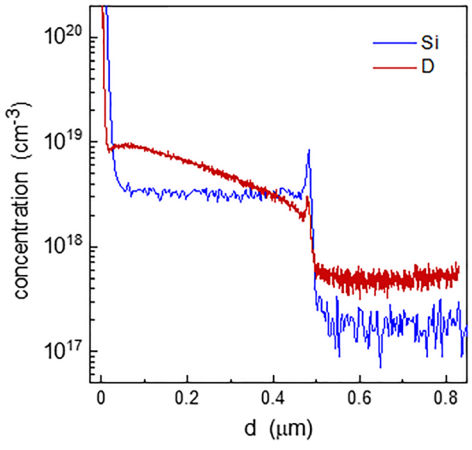

FIG. 1. SIMS profiles for Si and D in a Si-doped Ga_2O_3 epitaxial layer grown by MBE that was subsequently treated in a D-plasma.

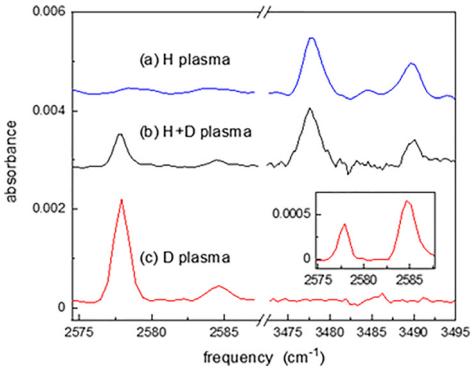

FIG. 2. IR spectra (77 K) of Si-doped Ga_2O_3 epitaxial layers treated for 30 min (250 °C) in (a) an H plasma, (b) a plasma containing H and D, and (c) a D plasma. The inset shows a spectrum for an Fe-doped Ga_2O_3 substrate annealed in a D_2 ambient at 1000 °C.

layer is intentionally doped with Fe so it is not surprising that we see hydrogen centers associated with both of these impurities in our samples. We assign the 2577.8 and 3477.6 cm^1 lines to Si-D and Si-H complexes, respectively, because they are dominant in spectra for samples deliberately doped with Si. We assign the 2584.6 and 3489.8 cm^{-1} lines to Fe-D and Fe-H complexes because they are dominant in spectra for samples deliberately doped with Fe. The appearance of distinct lines associated with Si and Fe in Ga_2O_3 indicates the close proximity of these impurities to the vibrating H (or D) atom and is consistent with the formation of passivated complexes rather than a compensation process for which the impurity atom and H could be more distant. In the following, we focus on the lines at 2577.8 and 3477.6 cm^1 and the hydrogen passivation of the Si donor in Ga_2O_3. Investigations of the Fe-D (H) complex are in progress in our laboratory.

Equation (1) yields an estimate of the concentration, N, of Si-D centers in our samples from the integrated absorbance for the IR line at 2577.8 cm^{-1} shown in the lower spectrum in Fig. 2 and a calibration determined in Ref. 24 (an effective charge of q = 0.47e) for O-D centers in Ga_2O_3. This equation[17] is written in CGS units to be consistent with the absorption coefficient and frequency $\overline{\nu}$ in units cm^{-1}. Here, m is the mass of the oscillating impurity, n is the refractive index, c is the speed of light, and l is the thickness of the absorbing layer.

$$N = \left(2.303\, m\, n\, c^2 / l\, \pi\, q^2\right) \int A(\overline{\nu})\, d\overline{\nu}. \quad (1)$$

The concentration of Si-D centers in the 0.5 μm Si-doped epitaxial layer treated in a D_2 plasma is estimated to be $3.8 \times 10^{18}\,cm^{-3}$. We take the agreement of this result with the concentration of Si in the epitaxial layer determined by SIMS and Hall effect to be fortuitous, given that the errors in defect concentrations calculated from IR intensities can easily be a factor of 2 or more. Nonetheless, this result shows that the intensity of the 2577.8 cm^{-1} IR line reported here is consistent with most or a significant fraction of the Si in the epitaxial layer being involved in the defect giving rise to that line and provides further support for the assignment of the 2577.8 cm^{-1} line to a Si-D complex.

O-H and O-D centers containing one or two H or D atoms have been observed in Ga_2O_3 by others.[19,25,26] Centers that contain two H or D atoms can be identified from the characteristic IR spectra that

occur for samples that contain both H and D where a fraction of the defects that are produced contain both H and D atoms. Spectrum (b) in Fig. 2 was measured for a sample treated in a plasma that contained both H and D and shows both the O-H and O-D lines at 3477.6 and 2577.8 cm^{-1}, respectively, in the same sample with a relative intensity of 4:1. When spectrum (b) in Fig. 2 for the sample containing both H and D is compared with spectra (a) and (c) in the same figure, there is no sign of a line splitting, broadening, or shift that would be characteristic of a defect that contained both hydrogen isotopes. These results are consistent with Si-H and Si-D complexes that contain a single H or D atom.

The results of annealing experiments that probe the thermal stabilities of the 2577.8 and 2584.6 cm^{-1} lines due to Si-D and Fe-D complexes are shown in Fig. 3. IR absorbance spectra were measured for a sample initially treated in a D_2 plasma and then subsequently annealed (30 min) at successively higher temperatures. Spectra were measured for two polarization angles, one near the maximum for the 2577.8 cm^{-1} absorption and the second at 90° with respect to this angle.

Both the 2577.8 and 2584.6 cm^{-1} lines were produced by the plasma treatment. Upon annealing at 100 °C, the 2577.8 cm^{-1} line increased in intensity by 70%, suggesting that a portion of the D introduced by the plasma treatment remained present in a form available to interact with impurities in the sample. (D_2 and D_O centers are candidates for a form of D produced by a D-plasma treatment that does not give rise to an observable O-D vibrational mode.) The 2577.8 cm^{-1} line is annealed away at 400 °C. As the 2577.8 cm^{-1} line decreased in strength at 350 °C, the intensity of the 2584.6 cm^{-1} increased before it finally disappeared at 450 °C. The different annealing behaviors of the 2577.8 and 2584.6 cm^{-1} lines confirm that they arise from two different defects.

When the 2577.8 and 2584.6 cm^{-1} lines are completely annealed away at 450 °C, the 2546.4 cm^{-1} line assigned previously to the $V_{Ga(1)}$-2D complex appears for the polarization direction oriented 90° with respect to the direction giving strong absorption for the 2577.8 and 2584.6 cm^{-1} lines. These results confirm that the 2577.8 and 2584.6 cm^{-1} lines have transition moment directions in the a-c plane roughly perpendicular to that of the $V_{Ga(1)}$-2D center whose transition moment is ≈15° clockwise from the [102] direction.[39]

The directions of the transition moments for O-H (O-D) centers in Ga_2O_3 provide structure-sensitive information about the defects. There are two types of Si–D complexes whose O-D transition

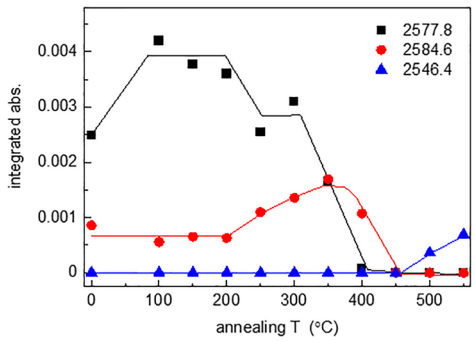

FIG. 3. Annealing behavior of a Si-doped Ga_2O_3 epitaxial layer treated in a D_2 plasma whose spectrum prior to annealing is shown in Fig. 2(c). The lines are drawn to guide the eye.

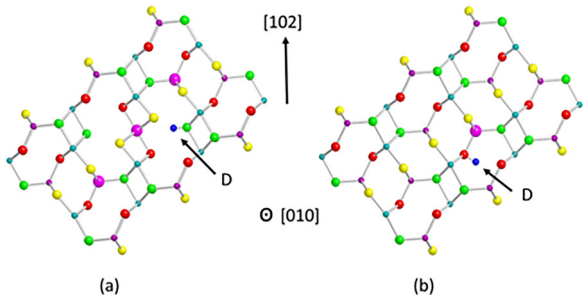

FIG. 4. Possible structures of the defect associated with the 2577.8 O-D line. (a) shifted Ga(1) vacancy with a trapped D and three candidate Si substitutional sites. (b) D trapped next to a Si substituted for a Ga(1). The inequivalent atomic sites are color coded as follows: Ga(1), purple; Ga(2), dark green; O(1), red; O(2), yellow, O(3), light green; and Si, pink. These figures were constructed using MOLDRAW[41] and POV-Ray.[42]

moments within the a-c plane could approximately satisfy the observed O-D moment direction for the 2577.8 cm^{-1} line. Fig. 4(a) shows a Ga(1) vacancy shifted as predicted by Varley *et al.*[28] A single H is trapped at an unsaturated O(3), while three potential sites for a Si substituted for a Ga(1) are shown. We have theoretically investigated this situation using the CRYSTAL17 code[40] with computational parameters used in previous calculations[19–22] and find only small variations of the transition moment direction from that perpendicular to the (–201) plane. This direction is then ≈75° from the ≈15° moment for the $V_{Ga(1)}$-2D center.

Figure 4(b) shows a H trapped at an O(1) site next to a Si that is substituted for a Ga(1). Our calculations find that in this case the transition moment direction is ≈125° clockwise from the [102] direction. It is, thus, ≈110° from the transition moment for the $V_{Ga(1)}$-2D center.

Our O-H (O-D) spectra and their polarization dependence are consistent with both of the structures shown in Fig. 4 and do not allow us to rule out either of these possible assignments for the 2577.8 cm^{-1} line.

In conclusion, the introduction of H into Si doped Ga_2O_3 leads to the formation of an OH-Si complex and a reduction of n-type conductivity. Theory suggests possible structures for an OH-Si complex that are consistent with the observed vibrational properties.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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