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Chemical manipulation of hydrogen induced high p-type and n-type conductivity in Ga_2O_3

Md Minhazul Islam^{1,2}, Maciej Oskar Liedke³, David Winarski^{1,2}, Maik Butterling³,
Andreas Wagner³, Peter Hosemann⁴, Yongqiang Wang⁵, Blas Uberuaga⁵ & Farida A. Selim^{1,2*}

Advancement of optoelectronic and high-power devices is tied to the development of wide band gap materials with excellent transport properties. However, bipolar doping (n-type and p-type doping) and realizing high carrier density while maintaining good mobility have been big challenges in wide band gap materials. Here P-type and n-type conductivity was introduced in $\beta\text{-Ga}_2\text{O}_3$, an ultra-wide band gap oxide, by controlling hydrogen incorporation in the lattice without further doping. Hydrogen induced a 9-order of magnitude increase of n-type conductivity with donor ionization energy of 20 meV and resistivity of $10^{-4} \Omega\cdot\text{cm}$. The conductivity was switched to p-type with acceptor ionization energy of 42 meV by altering hydrogen incorporation in the lattice. Density functional theory calculations were used to examine hydrogen location in the Ga_2O_3 lattice and identified a new donor type as the source of this remarkable n-type conductivity. Positron annihilation spectroscopy measurements confirm this finding and the interpretation of the experimental results. This work illustrates a new approach that allows a tunable and reversible way of modifying the conductivity of semiconductors and it is expected to have profound implications on semiconductor field. At the same time, it demonstrates for the first time p-type and remarkable n-type conductivity in Ga_2O_3 which should usher in the development of Ga_2O_3 devices and advance optoelectronics and high-power devices.

A wide band gap energy has become a key parameter for the future development of high-power transistors and optoelectronic devices¹ and wide band gap oxides, such as ZnO , have been shown to exhibit excellent characteristics². However, their deployment in many applications has been hindered due to the lack of conductivity control or the difficulty of realizing high carrier density with good mobility. Bipolar doping (realizing both n-type and p-type) is one of the big challenges in wide band gap materials but it is crucial for most devices^{2,3}. Further, substitutional doping of elements, the common method to provide charge carriers, often causes disorder, suppressing carrier mobility and there is always a trade-off between increasing the maximum attainable carrier density and maintaining good mobility in oxides. In this work, we report how to induce p-type and n-type conductivity in an ultra-wide band gap oxide (Ga_2O_3) through controlling hydrogen (H) incorporation in the lattice without further substitutional doping and demonstrate a sheet carrier density of 10^{16} cm^{-2} with electron mobility $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature leading to $10^{-4} \Omega\cdot\text{cm}$ resistivity. Such high electron density and good mobility is remarkable for oxide semiconductors. We identify a new donor concept behind this remarkable conductivity. While recent works reported room temperature electron mobility of $153 \text{ cm}^2/(\text{Vs})^4$, $130 \text{ cm}^2/(\text{Vs})^5$, and $176 \text{ cm}^2/(\text{Vs})^6$ for unintentionally doped $\beta\text{-Ga}_2\text{O}_3$ grown by different techniques, the carrier concentrations were significantly low ($<10^{17} \text{ cm}^{-3}$) in these reports. The same trend is true for Si and Ge doped Ga_2O_3 ⁷ where the carrier concentrations are often low for $100 \text{ cm}^2/(\text{Vs})$ electron mobility. For p-type conductivity we report a hole density of 10^{15} cm^{-2} , but with very low hole mobility less than $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is expected from the flat valence band of Ga_2O_3 .

The study was carried out on $\beta\text{-Ga}_2\text{O}_3$, as it is emerging as a promising material for high power devices due to its large band gap ($\sim 4.5\text{--}5 \text{ eV}$) and high breakdown field of 8 MV/cm . It is receiving significant attention in the scientific community as a potential candidate for a wide range of applications^{8–13}. $\beta\text{-Ga}_2\text{O}_3$ is the most stable polymorph of the Ga_2O_3 phases, with a monoclinic crystal structure of space group $C2/m$ ¹¹. It behaves as an

¹Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio, 43403, USA. ²Department of Physics and Astronomy, Bowling Green State University, Bowling Green, Ohio, 43403, USA. ³Institute of Radiation Physics, Helmholtz-Center Dresden-Rossendorf, Dresden, 01328, Germany. ⁴Department of Nuclear Engineering, University of California at Berkeley, Berkeley, CA, 94720, USA. ⁵Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico, 87545, USA. *email: faselim@bgsu.edu

insulator in its defect free crystalline form. As of today, only one type of conductivity (n-type) has been achieved by doping β -Ga₂O₃ with Sn, Ge or Si during growth^{14–17}. With respect to p-type conductivity, there has not been any significant success. Only deep acceptors (with activation energy > 1 eV) for undoped and doped samples have been reported where acceptor ionization was critically low at room temperature^{18,19}.

Hydrogen is known to have a strong influence on the electrical conductivity of semiconductors²⁰. In β -Ga₂O₃, monoatomic H has a low formation energy and can occupy both interstitial and substitutional sites to act as a shallow donor²¹. The complex crystal structure of β -Ga₂O₃ allows for the formation of many configurations where interstitial hydrogen (H_i^+) forms a bond with oxygen, creating electronic states which are close in energy. According to J. Varley et al.¹³, H_i acts as a shallow donor, although not stable and substitutional hydrogen, H_O , has low formation energy only under oxygen poor condition. Despite these theoretical predictions on the possibility of n-type conductivity due to H-incorporation in various locations, there has not been any report on significant experimental success. In this work, we generate H-donors and H-acceptors in Ga₂O₃ by controlling H incorporation on cation vacancy sites, not as H_i or H_O . A cation vacancy is an electrical compensating acceptor in semiconductors including β -Ga₂O₃²². Although cation vacancies have high formation energy in some oxide semiconductors (e.g. SnO₂, In₂O₃), previous first principle calculations showed that their formation energy is significantly lower in β -Ga₂O₃ and hence a high probability of H-decorated V_{Ga} formation can be achieved after incorporating H into the crystal^{22,23}.

It is necessary to understand the interaction of H₂ with the surface of metal-oxide semiconductors to gain insight on the process of H-incorporation into the crystal. H-incorporation into the crystals at high temperature occurs in two steps. At first, H₂ dissociates and becomes attached to the surface, then diffuses into the bulk crystal. Depending on the nature of the materials, H₂ can follow either homolytic or heterolytic dissociation pathways. In case of homolytic cleavage, H₂ molecule dissociates to form two H-atoms that become attached to the oxygen on the crystal surface. On the other hand, H₂ dissociates to form a proton and a hydride during heterolytic cleavage where the proton and hydride become attached to the oxygen and metal atoms respectively. The redox capacity of metals determines the type of dissociation that is most likely to occur. Density functional theory (DFT) predicts that H₂ tends to dissociate heterolytically on nonreducible oxide (e.g. MgO, γ -Al₂O₃) surfaces while following a homolytic pathway on reducible oxide (e.g. CeO₂) surfaces²⁴. β -Ga₂O₃ was found to be nonreducible via DFT²⁵. Therefore, it is most likely that H₂ follows heterolytic dissociation as shown in Fig. 1a. The adsorbed proton and hydride diffuse into the bulk crystal at high temperatures. The proton is attracted toward the negatively charged V_{Ga} while the hydride is attracted toward the positively charged or neutral V_O , as shown in Fig. 1b.

Results and Discussions

Electrical parameters of the samples measured by Hall measurement system are shown in Table 1. The details of the measurements are given in the method section. Table 1 shows that the as-grown samples were highly resistive, but after H₂ diffusion they showed an increase in carrier density and p-type conductivity. H₂ diffusion at 700 °C for 1 hr led to unstable conductivity that decays with time (Table 1a). However, H₂ diffusion at 950 °C for 2 hrs led to a greater increase in carrier density and stable p-type conductivity over time (Table 1b). Sheet carrier density of 10^{15} cm^{-2} was achieved but hole mobility lower than $1 \text{ cm}^2/\text{Vs}$ was measured which is expected due to the flat band nature of valence band made of predominately O 2p states. Other procedures were carried out to incorporate H₂ into different sites in the undoped β -Ga₂O₃. One sample was annealed in O₂ flow and another was annealed with Ga in a closed ampoule at 950 °C for 2 hrs. This process should fill up the respective (anion or cation) vacancies. After that, hydrogen was diffused into the crystals at 580 torr in a closed ampoule at 950 °C for 2 hrs. O₂-annealing followed by H₂ diffusion led to high n-type conductivity (stable over time) and remarkable sheet carrier density of about 10^{16} cm^{-2} with electron mobility $100 \text{ cm}^2/\text{Vs}$ (Table 1c). The thickness of the conductive layer where H diffuses in is 500 nm as revealed from depth resolved positron measurements in Fig. 2a. This indicates a remarkable conductivity of $10^{-4} \Omega \cdot \text{cm}$. The sample exhibits 9-orders of magnitude increase in conductivity and 10-orders of magnitude increase in carrier density. In contrast, annealing in Ga followed by H₂ diffusion did not lead to a significant increase in conductivity (Table 1c). Both sole H-diffusion and H-diffusion after O₂-anneal treatments were carried out on other as-grown undoped Ga₂O₃ samples and led to the same results. Samples preserved their p-type or n-type conductivity with no decay or negligible decay after months. The hole sheet number was measured after several months and found to be very $9.4 \times 10^{14} \text{ cm}^{-2}$ (initial sheet hole number was $1.2 \times 10^{15} \text{ cm}^{-2}$); after that the carrier concentration seems to be very stable with time with no further decay. The electron sheet number is stable at 10^{16} cm^{-2} . As the samples have been processed at very high temperatures, we expect that further processing at high temperature would not be a problem. It is also expected that the samples should sustain high voltage owing to the wide band gap of Ga₂O₃. However we have not built a device to test their stability under high voltage, future studies for further device development are necessary and would be highly valuable.

Figure 3 shows the temperature dependence of sheet resistance and sheet number of the p-type and n-type Ga₂O₃ samples, signifying the ionization of carrier regions followed by extrinsic semiconductor behavior at higher temperatures. Intrinsic semiconductor behavior cannot occur at room temperature as band to band transitions are not possible in Ga₂O₃ at this temperature because of the ultra-wide band gap. It is noteworthy to mention that the freeze out regions for the two samples are consistent with the donor/acceptor ionization energy calculated by thermally stimulated luminescence technique presented in later section. It is useful to compare these current measurements by the recent work by Ekaterina et al.¹⁸ who performed temperature dependent Hall-effect measurements for deep acceptors in unintentionally doped β -Ga₂O₃ with ionization energy more than 1 eV, their measurements showed that the activation region is in the range of 300–650 K consistent with deep acceptors. Figure 3 here shows that the activation occurs for donor and acceptor at significantly lower temperatures, which confirms the shallow nature of the induced donor and acceptor states. Figure 3d shows the electron mobility behavior with temperature.

Figure 1. Schematic diagrams showing hydrogen incorporation in β - Ga_2O_3 (a) hydrogen molecules coming in contact with the surface at elevated temperature and dissociating heterolytically. The electron cloud of H_2 is attracted toward gallium while the proton is attracted toward oxygen. (b) The proton and hydride ion are attached to oxygen and gallium atoms, respectively, on the crystal surface and diffuse through the bulk crystal at high temperatures. The proton is attracted toward the negatively charged gallium vacancy. (c) Ga vacancy decorated with four hydrogen as predicted from DFT calculations providing stable donor state (d) Ga vacancy decorated with two hydrogen as predicted from DFT calculations providing stable acceptor state.

The realization of p-type and n-type conductivity after H_2 diffusion can be explained as follows. Since the n-type conductivity of the samples was realized after filling up oxygen vacancies and since we know that H-interstitials which act as shallow donors are not stable in Ga_2O_3 ¹³, we attribute the origin of n- and p-type conductivity to hydrogen decorated gallium vacancies, $V_{\text{Ga-H}}$. A Ga-vacancy acts as a deep acceptor with -3 charge state (V_{Ga}^{3-}). During the diffusion of hydrogen into the crystal, the surface adsorbed proton (Fig. 1a,b) becomes attracted toward the (V_{Ga}^{3-}) where it stabilizes the negative charge and, therefore, lowers the acceptor state. This results in H-decorated Ga-vacancy ($V_{\text{Ga-2H}}^{1-}$) (as represented in Fig. 1c) and p-type conductivity. At lower temperatures (e.g. 700 °C), protons are less likely to diffuse deep inside the bulk crystal. This results in a decrease in conductivity over time due to the reverse diffusion at room temperature. However, the high p-type conductivity persists over time and becomes stable for the sample exposed to H_2 at higher temperature and for a longer period of time due to the diffusion of H^+ deeper into the crystal.

The sample that is exposed to the H_2 after filling up V_{O} (after annealing in O_2) showed high n-type conductivity. In this case, more H are diffused into the V_{Ga} due to the absence/reduction of V_{O} leading to the formation of ($V_{\text{Ga-4H}}^{1+}$) as represented in Fig. 1d, which acts as a donor. That is, the absence of V_{O} in this case means that the only available traps for H are V_{Ga} , which thus become filled to a greater extent. The contribution of n-type conductivity from H_i or H_c is not prominent as filling up V_{Ga} followed by H-diffusion shows a negligible increase in carrier concentration. Moreover, it confirms that the H-decorated V_{Ga} are primarily responsible for the induced n-conductivity in the samples. It should be also noted that oxygen vacancies are confirmed by now to be deep donors in Ga_2O_3 and not source of conductivity¹³.

Density functional theory was used to examine H-incorporation into a Ga-vacancy. The details of the calculation are given in the method section. The results are presented in Table 2. The binding energy of one H^+ ion to the Ga-vacancy is -4.4 eV. The DFT calculations reveal that, as N (the number of H ions) increases, at least up to

sample number	sample	sheet number (cm ⁻²)	sheet resistance (ohm/cm ²)
(a) H₂ diffusion took place in a closed ampoule at 700 °C and 580 torr for one hour			
1	undoped β-Ga ₂ O ₃ single crystal	7.00E + 06	1.940E + 8
2	annealed in H ₂	5.45E + 10 (P-type)	1.480E + 5
3	annealed in H ₂ (after 4 days)	3.44E + 06	7.330E + 8
4	annealed in H ₂ (2nd time)	1.54E + 15 (P-type)	4.060E + 1
5	annealed in H ₂ (2nd time, after 4days)	3.24E + 06	2.360E + 8
(b) H₂ diffusion took place in a closed ampoule at 950 °C and 580 torr for two hours			
a	undoped β-Ga ₂ O ₃ single crystal	5.67E + 06	3.151E + 7
b	annealed in H ₂ (immediately after annealing)	1.20E + 15 (p-type)	1.288E + 1
c	annealed in H ₂ (4 days after annealing)	1.35E + 15 (p-type)	4.126E + 1
(c) samples annealed in different environments at 950 °C for two hours followed by H₂ diffusion at the same temperature and pressure (580 torr)			
1 or a	as-grown undoped β-Ga ₂ O ₃ single crystal	5.67E + 06	3.15E + 7
2	annealed in O ₂	2.87E + 06	1.99E + 9
3	annealed in O ₂ followed by annealed in H ₂	6.14E + 16 (n-type)	6.21E + 0
b	annealed in Ga followed by annealed in H ₂	1.55E + 10	2.59E + 5

Table 1. Transport properties of Ga₂O₃ samples measured at room temperature, the thickness of the conductive layer for p-type and n-type is 500 nm measured by depth resolved DBPAS.

$N = 4$, the reaction remains exothermic, though the strength of the binding, per H atom, decreases. The energy gained by adding the 4th H⁺ ion is only -0.8 eV, much less than the -4.4 eV gained by adding the 1st H⁺ ion. If the trend persisted, this suggests that no more than 4 H⁺ ions can be favorably accommodated into V_{Ga} . Thus, these calculations indicate that a single V_{Ga} can accommodate up to 4 H⁺ ions, changing the net charge of the complex from 3- (when $N = 0$) to 1+ (when $N = 4$), and confirm that $(V_{Ga}-4H)^{1+}$ (Fig. 1d) is more favorable than H_i^{+} . These calculations verified our interpretation of the electrical transport measurements that $(V_{Ga}-4H)^{1+}$ is the dominant donor in the treated highly conductive n-type sample. This cation vacancy filled with the relevant numbers of H⁺ represents a new type of donor that does not create disorder in the lattice suppressing electron mobility as in the case of standard dopants on substitutional or interstitial sites.

Low temperature thermally stimulated luminescence spectroscopy was performed on the samples to reveal the shallow donor/acceptor levels. At low temperatures, shallow donor/acceptor level can be provided with carriers by optical injection that get trapped at respective levels. These carriers can be released by thermal excitation that reveals valuable information about the shallow donor/acceptor levels. The details of the experiments can be found in the method section and in the text and Supplementary Figure 1 in the Supplementary Information file. Figure 4a displays the TSL emission for as-grown, p-type and n-type H₂ treated Ga₂O₃. The as-grown sample shows no peak corresponding to shallow levels. Each of the other two samples shows a peak at low temperature indicating the formation of shallow level. The peak formed at 107 K in the p-type H₂-anneal sample (red curve in Fig. 4a) is associated with the formation of shallow acceptors with ionization energy of 42 meV, calculated using the simplified model of TL developed by Randal and Williams^{26–28}. The ionization energy of the donor, emerging after O₂-annealing followed by H₂-diffusion (green curve in Fig. 4a), was also calculated by the initial rise method from the peak at 111 K and found to be 20 meV. Figure 4b,c shows the corresponding flat band diagram and corresponding donor and acceptor state. The details of the calculation of donor/acceptor ionization energy is provided in the text and Supplementary Figure 2 in the Supplementary Information.

To further understand the effect of H-incorporation and confirm our interpretation of the origin of conductivity, we carried out Positron Annihilation Spectroscopy (PAS) measurements. The details of the experiments and data analysis are given in the method section. Positron Annihilation Spectroscopy is a powerful technique to investigate cation vacancy type defects²⁹. It has also been established as an effective tool to probe the incorporation of hydrogen in cation vacancies as partial or complete passivation of vacancies by hydrogen strongly impact positron trapping^{30–32}. We have performed Positron Annihilation Lifetime Spectroscopy (PALS) and Doppler Broadening of Positron Annihilation Spectroscopy (DBPAS), two varieties of Positron Annihilation Spectroscopy that gives valuable information about the electronic environments in cation vacancy sites. Figure 2a presents the defect parameters S and W (defined in Fig. 2) as a function of depth for the two treated samples. The large values of S at the very beginning of the two curves are common in all DBPAS measurements, indicating the formation of positronium at the surface. The graph shows a large difference between the two samples only in the first 500 nm (where H diffuses in) with lower S values and higher W values for the sample annealed in O₂ followed by H₂, which exhibits high n-type conductivity. The decrease in S -parameter is an indication for the suppression of positron trapping at cation or neutral vacancies. Thus, these measurements confirm the decrease of negatively charged and neutral vacancies in the O₂-annealed followed by H₂-diffusion sample. This must be due to filling of Ga-vacancies with more than three H-ions leading to a positive charge state and the formation

Figure 2. (a) Defect parameters S and W measured by Doppler Broadening of Positron Annihilation Spectroscopy (DBPAS) as a function of penetration depth, S and W are defined as the fraction of positrons annihilating with valence and core electrons respectively. The lower x-axis represents the positron energies and the upper x-axis represents the penetration depth. The graph shows that H₂ diffuses about 500 nm in the crystal. Positron Annihilation Lifetime Spectroscopy (PALS) data of (b) as-grown and (c) annealed in H₂ (950 °C for 2 hours) (d) annealed in O₂ followed by H₂ (950 °C for 2 hours) samples. E_p = Positron implantation energy, Z_{mean} = positron implantation depth, τ = positron lifetime, I = intensity of lifetime component, the graphs (b, c, and d) show the two positron lifetime components and their intensities in each sample. τ₁ is related to the positrons annihilate in the bulk and τ₂ is related to the positrons annihilate in the defect sites. τ₂ has significantly decreased after H₂ diffusion (graph c) because of the change of the charge state of the defect center (V_{Ga}-2H)⁻¹. After O₂ + H₂ annealing, the contribution of τ₂ is almost zero because the (V_{Ga}-4H)⁺¹ center has positive charge state and does not trap positrons.

of a shallow donor as indicated by the immense increase in n-type conductivity. This (H-V_{Ga})¹⁺ complex has a positive charge state and cannot trap positrons, leading to the substantial decrease in S-parameter. On the other hand, sole H₂-diffusion leads to partial filling of V_{Ga} with hydrogen maintaining a negative charge state and leading to shallow acceptors, which imparts p-type conductivity. This (H-V_{Ga})¹⁻ complex is still an active positron trap which leads to a higher S-value.

Depth resolved measurements of PALS revealed two major positron lifetime components for each sample (example of PALS spectra measured for the p-type and n-type samples is given in Supplementary Figure 3 in the Supplementary Information file). Figure 2b–d show the lifetime components and their intensity as a function of depth for the as-grown sample, and the H₂ diffused, and O₂-annealed followed by H₂-diffused samples. A distinctive difference can be seen in the intensity and magnitude of the positron lifetime components among the three samples. The large second lifetime component τ₂ indicates the presence of V_{Ga}-related defects with negative charge states. For as-grown Ga₂O₃, τ₂ is about 470 ps with about 25 to 30% intensity across the sample depth (Fig. 2b). After H₂-anneal, τ₂ was reduced to ~320 ps indicating partial filling of V_{Ga} related defects with hydrogen while its intensity was reduced to about 13% (Fig. 2c) due to the decrease of positron trapping at these vacancies as result of less negativity. After annealing in O₂ followed by H₂-diffusion, almost all positrons annihilate with lifetimes close to the bulk lifetime (Fig. 2d)³³. The intensity of τ₂ was reduced to about less than 1% indicating almost complete absence of positron trapping at defects providing strong evidence for filling up V_{Ga} related defects with

Figure 3. Temperature dependent transport properties of the n-type and p-type H_2 treated Ga_2O_3 samples. (a) sheet resistance, (b) sheet number, (c) sheet number logarithm plotted as a function of $1000/T$. (d) The dependence of n-type mobility on temperature. The mobility was found to be $100 \text{ cm}^2/\text{VS}$ at room temperature; it was normalized to the highest value at low temperature because of the noise in the cryostat system.

N	Net charge of the H- V_{Ga} complex	Binding energy (eV)	Binding energy per H (eV)	Binding energy of extra H (eV)
1	-2	-4.4	-4.4	-4.4
2	-1	-7.5	-3.7	-3.1
3	0	-9.4	-3.1	-1.9
4	+1	-10.2	-2.6	-0.8

Table 2. Binding energy of H^+ ions to a Ga vacancy.

H_2 transforming them into donors with a positive charge state, which cannot trap positrons. Thus, DBPAS and PALS measurements explicitly confirm our interpretation for the origin of n-type and p-type conductivity.

Precise doping and carrier control is important to realize $\beta\text{-Ga}_2\text{O}_3$ based bipolar devices^{34,35}. In this work, we found that the best way to control the number of H in V_{Ga} is to remove V_{O} and keep H_2 pressure the same. By doing this, we can increase the number of H incorporating in the V_{Ga} . Here, the number of H resides in the V_{Ga} is governed by the thermodynamic stability of the complex and the availability of hydrogen atoms. However, the number of H incorporated in the V_{Ga} can also be controlled by adjusting H_2 pressure. A detail study of the effect of hydrogen pressure on the type and concentration of carriers would be of great interest to further develop different processes for H incorporation.

Conclusions

In summary, by controlling H-incorporation in the lattice, we have demonstrated the development of stable p-type and n-type Ga_2O_3 , which is expected to significantly advance optoelectronics and high-power devices. In the meantime, we illustrated a potential simple method for tuning and switching the conductivity of semiconductors between p-type and n-type with the realization of remarkable high carrier density and good mobility in wide band gap oxides, which is a significant challenge by common substitutional doping methods. A concept for new donor type as cation vacancy filled with the relevant numbers of H^+ was introduced and found to be behind the remarkable n-type conductivity. This new donor type does not create disorder in the lattice, which often suppresses carrier mobility in the case of standard doping.

Figure 4. Thermally stimulated luminescence emission (a) of the samples annealed at 950 °C for two hours in different environments and the as-grown sample. Data points for annealed samples were normalized from 0 to 1. Data points for as-grown sample were normalized from 0 to 0.5 to minimize noise (no glow peak). Peaks were fitted with a Gaussian function. The two peaks appeared at low temperature after H₂ diffusion, and after O- anneal followed by H-diffusion are associated with the induced shallow acceptor and shallow donor in the samples respectively and they were used for calculating the ionization energies. The flat band diagrams showing donor and acceptor states of the samples after direct hydrogen diffusion (b) and hydrogen diffusion after filling up oxygen vacancies (c).

Methods

Hydrogen incorporation process. High quality β -Ga₂O₃ samples grown by Edge-defined Film-fed Growth (EFG) method were obtained from Tamura Inc., Japan. A number of undoped highly resistive samples (5 mm × 5 mm × 0.5 mm) were selected and placed in a quartz ampoule with one open end that was connected to a vacuum pump to pump the air out and evacuate the ampoule. After that, the tube was filled with H₂ gas at 580 torr pressure. After filling the tube with hydrogen, the open end was properly sealed. The ampoule was placed in an oven where temperature can be precisely controlled. The temperature was increased in two steps up to the desired value and H₂ was allowed to diffuse into the crystal for 1 or 2 hours. A few other samples of same dimensions were first annealed in oxygen flow at 950 °C and then hydrogen following the same procedure, while others were annealed first with gallium, then hydrogen following the same procedure.

Hall-effect measurements. Van der Pauw Hall-effect measurements were performed to determine the electrical transport properties of the samples. The measurements were carried out from 30 K to room temperature (298 K) and at constant magnetic field of 9300 G. Four indium contacts were made in a square arrangement on the surface of each sample and carefully adjusted to keep the contacts as small as possible. Current-voltage linearity was checked every time to make sure that the contacts were good and resistivity does not vary more than 10% between different contact points. Temperature dependent measurements of the carrier concentration were carried out from 30 K or below to room temperature using a closed cycle cryostat.

Computational analysis. Density functional theory, as implemented in the Vienna ab-initio Simulation Package (VASP)^{36,37}, was used to examine H-incorporation into a Ga-vacancy. These calculations were performed on a $1 \times 4 \times 2$ supercell of β -Ga₂O₃, containing a total of 160 atoms in the defect-free structure. A Γ -centered $2 \times 2 \times 2$ Monkhorst-Pack k-point mesh³⁸ was used to sample the Brillouin zone. The energy cutoff for the plane-waves was 400 eV. Pseudopotentials based on the projector augmented wave method³⁹ and the Perdew, Burke, and Ernzerhof (PBE)⁴⁰ generalized gradient approximation (GGA) exchange-correlation functional (which should be good enough for our purpose here) were used. Calculations were continued until the maximum component of the force on any atom was less than 0.02 eV/angstrom, with one exception (the charged Ga-vacancy), where such a tight convergence was not possible. In this case, the maximum force was 0.024 eV/angstrom. Both monopole corrections (using a calculated dielectric constant of 4.16, which is a bit higher but similar to previously reported

values)⁴¹ and an alignment correction were applied to the energies. Instead of averaging the potential to perform the alignment correction, we simply shifted the density of states such that the deepest state in the material aligned across different structures, which has been shown to give similar corrections⁴². In any case, the magnitude of this correction was no greater than 0.1 eV.

A V_{Ga} was created by removing a tetrahedrally-coordinated Ga ion from the cell, as this vacancy structure has been identified as being more favorable⁴³. A net charge of -3 was imposed on the structure. H^+ ions with a charge of $+1$ were inserted into the resulting vacancy structure (leaving the total number of electrons in the system constant but reducing the net charge of the cell). The resulting binding energy for each configuration was computed via the following relationship:

$$E_b = E([V_{\text{Ga}}\text{NH}]^{(-3+N)}) + E(\text{Bulk Ga}_2\text{O}_3)E(V_{\text{Ga}}^{3-}) - NE(\text{H}^+) \quad (1)$$

where $E([V_{\text{Ga}}\text{NH}]^{(-3+N)})$ is the energy of the system with the Ga vacancy filled with $N\text{H}^+$ ions, $E(\text{Bulk Ga}_2\text{O}_3)$ is the energy of defect-free $\beta\text{-Ga}_2\text{O}_3$, $E(V_{\text{Ga}}^{3-})$ is the energy of the isolated Ga vacancy in a 3- charge state, and $E(\text{H}^+)$ is the energy of an isolated $1 + \text{H}$ interstitial. With this definition, a negative energy indicates an exothermic or favorable reaction. We did not perform a systematic search for the lowest energy H interstitial position but performed multiple minimizations where the H was randomly displaced to find a reasonable structure. The structure found here, in which the H^+ ion is bonded to one of the three-fold coordinated oxygen ions, is similar to that described by Varley *et al.*¹³.

Thermal stimulated luminescence spectroscopy (TSL). Thermal stimulated luminescence (TSL) spectroscopy^{26–28,44–46} was performed on the samples to calculate the donor and acceptor ionization energies⁴⁵. The measurements were performed using an in-house built spectrometer^{26,47}, from -190°C to 25°C . The samples were first placed in a dark compartment and irradiated with UV light at -190°C for 30 min. After irradiation, the temperature of the samples was set to increase at constant rate ($60^\circ\text{C}/\text{min}$) and the emission spectra were recorded from 200 to 800 nm at every 5 seconds. The glow curves which represent the emission intensity as a function of temperature were constructed from the integration of emission over wavelengths at each temperature.

Positron annihilation spectroscopy. We carried out positron annihilation spectroscopy (PAS), which is a well-established technique to detect and characterize cation vacancies in semiconductors and oxides^{48,49}. Both Doppler Broadening of Positron Annihilation Spectroscopy (DBPAS) and Positron Annihilation Lifetime Spectroscopy (PALS) were employed. DBPAS measurements were carried out using a mono-energetic variable energy positron beam at Helmholtz-Zentrum Dresden-Rossendorf (HZDR) facility in Dresden, Germany⁵⁰. Positrons are emitted from an intense ^{22}Na source and a tungsten moderator and accelerated to discrete energy values E_p in the range of $E_p = 0.05\text{--}35\text{ keV}$. Such positron implantation energy, E_p , allows penetrating up to about $1.8\text{ }\mu\text{m}$ in Ga_2O_3 . Doppler broadened spectra representing positron annihilation distribution for each E_p were acquired using a single high-purity germanium detector with energy resolution of $1.09 \pm 0.01\text{ keV}$ at 511 keV and the S and W parameters (defined in the caption of Fig. 2) were calculated from the peak. PALS has been established as the most effective method to probe cation vacancy related defects, distinguishing between their types and providing information about their concentrations⁴⁹. PALS was performed at the Mono-energetic Positron Spectroscopy (MePS) pulsed beam, which is the end station of the radiation source ELBE (Electron Linac for beams with high Brilliance and low Emittance) at HZDR facility in Dresden Germany⁵⁰. The lifetime spectrum was measured at each positron energy E_p up to 16 keV with a time resolution of 205 ps . All lifetime spectra contained at least 5×10^6 counts and were analyzed as a sum of time-dependent exponential decays, $N(t) = \sum_i I_i/\tau_i \exp(-t/\tau_i)$ convoluted with the Gaussian's functions describing the spectrometer timing resolution, using the PALSfit fitting software⁵¹. Depth-resolved measurements of PALS revealed two major positron lifetime components for each sample.

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References

- Higashiwaki, M., Sasaki, K., Kuramata, A., Masui, T. & Yamakoshi, S. Gallium oxide (Ga_2O_3) metal-semiconductor field-effect transistors on single-crystal $\beta\text{-Ga}_2\text{O}_3$ (010) substrates. *Appl. Phys. Lett.* **100**, 013504 (2012).
- Selim, F., Weber, M., Solodovnikov, D. & Lynn, K. Nature of native defects in ZnO . *Phys. Rev. Lett.* **99**, 085502 (2007).
- Ogo, Y. *et al.* p-channel thin-film transistor using p-type oxide semiconductor, SnO . *Appl. Phys. Lett.* **93**, 032113 (2008).
- Oishi, T., Koga, Y., Harada, K. & Kasu, M. High-mobility $\beta\text{-Ga}_2\text{O}_3$ (201) single crystals grown by edge-defined film-fed growth method and their Schottky barrier diodes with Ni contact. *Appl. Phys. Express* **8**, 031101 (2015).
- Irmscher, K., Galazka, Z., Pietsch, M., Uecker, R. & Fornari, R. Electrical properties of $\beta\text{-Ga}_2\text{O}_3$ single crystals grown by the Czochralski method. *J. Appl. Phys.* **110**, 063720 (2011).
- Zhang, Y. *et al.* MOCVD grown epitaxial $\beta\text{-Ga}_2\text{O}_3$ thin film with an electron mobility of $176\text{ cm}^2/\text{Vs}$ at room temperature. *APL Mater.* **7**, 022506 (2018).
- Neal, A. T. *et al.* Donors and deep acceptors in $\beta\text{-Ga}_2\text{O}_3$. *Appl. Phys. Lett.* **113**, 062101 (2018).
- Mastro, M. A. *et al.* Perspective-Opportunities and Future Directions for Ga_2O_3 . *ECS J. Solid. State Sci. Technol.* **6**, 356 (2017).
- Higashiwaki, M. & Jessen, G. H. The dawn of gallium oxide microelectronics. *Appl. Phys. Lett.* **112**, 060401 (2018).
- Pearton, S. J. *et al.* Perspective: Ga_2O_3 for ultra-high power rectifiers and MOSFETs. *Appl. Phys. Rev.* **5**, 011301 (2018).
- Geller, S. Crystal Structure of $\beta\text{-Ga}_2\text{O}_3$. *J. Chem. Phys.* **33**, 676 (1960).
- Hajnal, Z. *et al.* Role of oxygen vacancy defect states in the n-type conduction of $\beta\text{-Ga}_2\text{O}_3$. *J. Appl. Phys.* **86**, 3792 (1999).
- Varley, J., Weber, J., Janotti, A. & Van de Walle, C. Oxygen vacancies and donor impurities in $\beta\text{-Ga}_2\text{O}_3$. *Appl. Phys. Lett.* **97**, 142106 (2010).
- Ueda, N., Hosono, H., Waseda, R. & Kawazoe, H. Synthesis and control of conductivity of ultraviolet transmitting $\beta\text{-Ga}_2\text{O}_3$ single crystals. *Appl. Phys. Lett.* **70**, 3561 (1997).

15. Villora, E. G., Shimamura, K., Yoshikawa, Y., Ujiie, T. & Aoki, K. Electrical conductivity and carrier concentration control in β -Ga₂O₃ by Si doping. *Appl. Phys. Lett.* **92**, 202120 (2008).
16. Sasaki, K., Higashiwaki, M., Kuramata, A., Masui, T. & Yamakoshi, S. Si-ion implantation doping in β -Ga₂O₃ and its application to fabrication of low-resistance ohmic contacts. *Appl. Phys. Express* **6**, 086502 (2013).
17. Feng, Z., A U Bhuiyan, A. F. M., Karim, M. R. & Zhao, H. MOCVD homoepitaxy of Si-doped (010) β -Ga₂O₃ thin films with superior transport properties. *Appl. Phys. Lett.* **114**, 250601 (2019).
18. Chikoidze, E. *et al.* P-type β -gallium oxide: A new perspective for power and optoelectronic devices. *Mater. Today Phys.* **3**, 118–126 (2017).
19. Qian, Y. P. *et al.* Mg-doped p-type β -Ga₂O₃ thin film for solar-blind ultraviolet photodetector. *Mater. Lett.* **209**, 558–561 (2017).
20. McCluskey, M., Tarun, M. & Teklemichael, S. Hydrogen in oxide semiconductors. *J. Mat. Res.* **27**, 17 (2012).
21. Janotti, A. & Van de Walle, C. G. Hydrogen multicentre bonds. *Nat. Mater.* **6**, 44 (2007).
22. Korhonen, E. *et al.* Electrical compensation by Ga vacancies in Ga₂O₃ thin films. *Appl. Phys. Lett.* **106**, 242103 (2015).
23. Weiser, P., Stavola, M., Fowler, W., Qin, Y. & Pearton, S. Structure and vibrational properties of the dominant O-H center in β -Ga₂O₃. *Appl. Phys. Lett.* **112**, 232104 (2018).
24. Garcia-Melchor, M. & Lopez, N. Homolytic Products from Heterolytic Paths in H₂ Dissociation on Metal Oxides: The Example of CeO₂. *J. Phys. Chem. C* **118**, 20 (2014).
25. Helali, Z., Jedidi, A., Syzgantseva, O. A., Calatayud, M. & Minot, C. Scaling reducibility of metal oxides. *Theoret. Chem. Acc.: Theory, Computation, Modeling*. Springer Verl. **136**(9), 100 (2017).
26. Mackay, D. T., Varney, C. R., Buscher, J. & Selim, F. A. Study of exciton dynamics in garnets by low temperature thermoluminescence. *J. Appl. Phys.* **112**, 023522 (2012).
27. Islam, M. M., Rana, D., Hernandez, A., Haseman, M. & Selim, F. A. Study of trap levels in β -Ga₂O₃ by thermoluminescence spectroscopy. *J. Appl. Phys.* **125**, 055701 (2019).
28. Mahesh, K., Weng, P. & Furetta, C. Thermoluminescence in solids and its applications. Nuclear Technology, Kent, England, (1989).
29. Weber, M. H., Selim, F. A., Solodovnikov, D. & Lynn, K. G. Defect engineering of ZnO. *Appl. Surf. Sci.* **255**, 68 (2008).
30. Selim, F. A. *et al.* Positron lifetime measurements of hydrogen passivation of cation vacancies in yttrium aluminum oxide garnets. *Phys. Rev. B* **88**, 174102 (2013).
31. Huang, L. J., Lau, W. M., Simpson, P. J. & Schultz, P. J. Depth profiling of hydrogen passivation of boron in Si(100). *Phys. Rev. B* **46**, 4086–4091 (1992).
32. Winarski, D. J. *et al.* Induced conductivity in sol-gel ZnO films by passivation or elimination of Zn vacancies. *AIP Adv.* **6**, 095004 (2016).
33. Ting, W. Y., Kitai, A. H. & Mascher, P. Crystallization phenomena in β -Ga₂O₃ investigated by positron annihilation spectroscopy and X-ray diffraction analysis. *Mater. Sci. Eng., B* **91**, 541 (2002).
34. Zhang, F. *et al.* Toward controlling the carrier density of Si doped Ga₂O₃ films by pulsed laser deposition. *Appl. Phys. Lett.* **109**, 102105 (2016).
35. Sasaki, K., Higashiwaki, M., Kuramata, A., Masui, T. & Yamakoshi, S. Si-Ion Implantation Doping in β -Ga₂O₃ and Its Application to Fabrication of Low-Resistance Ohmic Contacts. *Appl. Phys. Express* **6**, 086502 (2013).
36. Kresse, G. & Furthmüller, J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169 (1996).
37. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758 (1999).
38. Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **13**, 5188 (1976).
39. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953 (1994).
40. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865 (1996).
41. Sturm, C., Furthmüller, J., Bechstedt, F., Schmidt-Grund, R. & Grundmann, M. Dielectric tensor of monoclinic Ga₂O₃ single crystals in the spectral range 0.5–8.5 eV. *Appl. Mat.* **3**, 106106 (2015).
42. Yadav, S. K., Uberuaga, B. P., Nikl, M., Jiang, C. & Stanek, C. R. Band-Gap and Band-Edge Engineering of Multicomponent Garnet Scintillators from First Principles. *Phys. Rev. Appl.* **4**, 054012 (2015).
43. Varley, J. B., Peelaers, H. & Janotti, A. and Van de Walle, C.G. Hydrogenated cation vacancies in semiconducting oxides. *J. Phys.: Condens. Matter* **23**, 334212 (2011).
44. Varney, C. R., Mackay, D. T., Pratt, A., Reda, S. M. & Selim, F. A. Energy levels of exciton traps in yttrium aluminum garnet single crystals. *J. Appl. Phys.* **111**, 063505 (2012).
45. Ji, J., Boatner, L. A. & Selim, F. A. Donor characterization in ZnO by thermally stimulated luminescence. *Appl. Phys. Lett.* **105**, 041102 (2014).
46. Reda, S. M., Varney, C. R. & Selim, F. A. Radio-luminescence and absence of trapping defects in Nd-doped YAG single crystals. *Results Phys.* **2**, 123 (2012).
47. Selim, F. A., Khamehchi, A., Winarski, D. & Agarwal, S. Synthesis and characterization of Ce:YAG nano-phosphors and ceramics. *Optical Mater. Express* **6**, 3704 (2016).
48. Krause-Rehberg, R. & Leipner, H. S. Positron Annihilation in Semiconductors. Springer-Verlag (1999).
49. Selim, F. A. *et al.* Generation and characterization of point defects in SrTiO₃ and Y₃Al₅O₁₃. *Results Phys.* **5**, 28 (2015).
50. Wagner, A., Butterling, M., Liedke, M. O., Potzger, K. & Krause-Rehberg, R. AIP Confer. Pro. **1970**, 040003 (2018).
51. Olsen, J. V., Kirkegaard, P., Pedersen, N. J. & Eldrup, M. PALSfit: A new program for the evaluation of positron lifetime spectra. *Phys. Status Solidi C* **4**, 4004 (2007).

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Author contributions

F.A. Selim, B.P. Uberuaga and M.M. Islam wrote the manuscript. F.A. Selim designed the experiments and interpreted the results. M. M. Islam carried out most of the experiments except PAS, analyzed the data, prepared the graphs and calculated the ionization energies. B.P. Uberuaga performed the computational analysis. M.O. Liedke, M. Butterling, and A. Wagner performed PAS experiments. D. Winarski contributed in preparing and measuring samples. Y. Wang and P. Hosemann contributed in the analysis discussion and revised the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to F.A.S.

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