Thermal Stability of Implanted or Plasma Exposed Deuterium in Single Crystal Ga$_2$O$_3$

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The thermal stability and migration of both ion implanted (100 keV, 10^{15} cm^{-2}) or plasma diffused (100–270°C for 0.5h) D in single-crystal β-Ga$_2$O$_3$ was examined as a function of post-implantation annealing temperature (450–650°C for the implanted samples, 400–500°C for the plasma diffused samples) by Secondary Ion Mass Spectrometry. In the as-implanted condition, the profiles show a peak deuterium concentration of $\sim$3.1 x 10^{15} cm^{-3} at a depth of $\sim$0.85 μm for our dose and energy conditions. Subsequent annealing causes outdiffusion of D from the Ga$_2$O$_3$ with the remaining deuterium migrating toward the surface and decorating the residual implant damage. After annealing at 650°C, only 12% of the original dose is retained within the Ga$_2$O$_3$. This loss of deuterium in the implanted samples was modelled with using the FLOOPS code, and showed good agreement with experiment and an activation energy of 1.35 eV for the rate constant. The plasma treated samples showed deuterium incorporated to a depth of $\sim$0.67 μm for plasma exposure at 270°C, corresponding to an estimated deuterium diffusivity of 6.4 x 10^{-13} cm^2/s at this temperature.

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Hydrogen plays an important role in many oxides and contributes to the n-type conductivity of several of them, including ZnO, SnO$_2$ and In$_2$O$_3$. In the first two of these materials, H trapped at an oxygen vacancy is the dominant shallow donor, while interstitial H$^+$ is found to be the dominant H-related shallow donor in In$_2$O$_3$. It is well known that atomic hydrogen can passivate virtually all impurities in semiconductors like Si, GaAs and GaN through formation of neutral dopant-hydrogen complexes. In most semiconductors, hydrogen is a negative-U center, so in p-type material, hydrogen is a compensating acceptor and therefore in these materials hydrogen always counteracts the prevailing conductivity. However, different behavior has been found for conducting oxides.

We found previously that hydrogen diffuses rapidly in ZnO, producing incorporation depths of almost 30 μm for a 0.5 h exposure of bulk, single crystal ZnO to a 3-H plasma. The incorporation depths are much larger than in other wide bandgap semiconductors such as GaN, where a similar process leads to incorporation depths of less than 1 μm. Hydrogen was found to be a shallow donor in ZnO and to play a significant role in the background n-type conductivity. Similarly, the role played by hydrogen impurities in the conductivity of indium oxide (In$_2$O$_3$) was initially controversial. Some studies, based on the effect of oxygen partial pressure in growth or annealing environments, argued that oxygen vacancies were the cause of the prevailing conductivity. However, both theoretical and experimental work found that hydrogen centers can be important shallow donors in this material. Muon-spin-resonance experiments found that implanted muons, whose properties mimic those of hydrogen, form shallow donors in In$_2$O$_3$. In$_2$O$_3$ thin films containing hydrogen show n-type conductivity with high mobility. Theory predicted that interstitial hydrogen (H$^+$) and hydrogen trapped at an oxygen vacancy (H$_2^0$) were shallow donors giving rise to n-type conductivity or compensating acceptors in In$_2$O$_3$. Annealing of In$_2$O$_3$ crystals in an H$_2$ or D$_2$ ambient at 500°C produces a thin conducting layer near the surface with thickness $\sim$0.06 mm and with a carrier concentration of $1.6 \times 10^{19}$ cm$^{-3}$. An OH vibrational line at 3306 cm$^{-1}$ was assigned to the interstitial H shallow-donor center that is responsible for the hydrogen-related conductivity. The corresponding D$_2$ center had an OD line at 2464 cm$^{-1}$. The H$_2$ center was stable up to $\approx$500°C. Investigations of hydrogen shallow-donor centers in ZnO and SnO$_2$ found that H$_2$ is only marginally stable at room temperature in these materials and H$_2$ is a more thermally stable donor that dominates the n-type conductivity of hydrogenated samples of these materials stored at room temperature. The conductivity produced by the thermal treatment of In$_2$O$_3$ in hydrogen can be explained primarily by a thermally stable H$_2$ center, consistent with theoretical predictions that H$_2$ has a higher formation energy. Recently, Ga$_2$O$_3$ has attracted attention for its potential applications in power electronics, high temperature gas sensing and also for solar blind photodetectors. Ga$_2$O$_3$ remains transparent well into the ultraviolet (UV) part of the spectrum, allowing its use as a transparent conducting oxide in this region. With a direct bandgap of $\approx$4.9 eV, Ga$_2$O$_3$ has a very high theoretical breakdown electric field ($\approx$8 MV/cm), making it of interest for high power electronics. The Baliga figure-of-merit is almost four times higher for Ga$_2$O$_3$ compared to GaN. Experimental breakdown field values have reached 3.8 MV/cm in Ga$_2$O$_3$ and these are already higher than the bulk critical field strengths of GaN and SiC. As control of crystal growth processes improves, it is clear that the experimental values will move even closer to the theoretical maximum. Different types of diode rectifiers and transistors have been reported, including metal-semiconductor field-effect transistors (MESFETs), depletion-mode metal-oxide-semiconductor field-effect transistors (MOSFETs) and Schottky diodes fabricated on either bulk or thin film β-Ga$_2$O$_3$. In- implanted or plasma exposed hydrogen in this material. Ion implantation of Si or Sn has been used to create n-type layers in Ga$_2$O$_3$, but little is known about the characteristics of ion implanted or plasma exposed hydrogen in this material. Ion implantation of hydrogen could be used for inter-device electrical isolation, while the incorporation of hydrogen during processes like plasma-enhanced chemical vapor deposition (PECVD) of dielectrics on the Ga$_2$O$_3$ is of interest for its effect on near-surface conductivity. There is particular interest in the properties of hydrogen in Ga$_2$O$_3$, because of the predictions from density functional theory and total energy calculations that it should be a shallow donor. The generally observed...
n-type conductivity, therefore, may at least be explained by the presence of residual hydrogen from the growth ambient, rather than to native defects such as Ga interstitials or O vacancies. In some oxides, oxygen vacancies may even be deep donors. There is some experimental support for the fact that hydrogen may be a shallow donor in Ga$_2$O$_3$ from experiments on its muonium counterpart and from electron paramagnetic resonance, with an expected donor ionization energy of 15–30 meV. Muonium is a light isotope analog of hydrogen that often can shed light on the expected behavior of hydrogen in semiconductors.

In this paper we report on an investigation into the thermal stability and redistribution of both implanted and plasma introduced deuterium in single-crystal, bulk Ga$_2$O$_3$ as a function of post-process annealing temperature. The temperatures at which implanted hydrogen is evolved from the Ga$_2$O$_3$ are fairly similar to those reported previously for ZnO. The deuterium is used to provide high detection sensitivity during Secondary Ion Mass Spectrometry (SIMS) profiling.

**Experimental**

The starting sample was a bulk β-phase Ga$_2$O$_3$ single crystal with (-201) surface orientation (Sojitz Machinery Corporation, Japan) grown by the edge-defined film-fed growth method. Hall effect measurements showed the sample was unintentionally n-type with an electron concentration of $\sim 3 \times 10^{17}$ cm$^{-3}$. Sections from these wafers were implanted with $^2$H$^+$ ions. During implantation, samples were tilted by $\sim 7^\circ$ relative to the incident ion beam to minimize channeling. The $^2$H$^+$ implantation was performed at an energy of 100 keV to a dose of $10^{13}$ cm$^{-2}$. Some of the samples were then annealed for 5 mins at 500–600 $^\circ$C under flowing O$_2$ in a Solaris 100 rapid thermal processing furnace (Surface Science Integration, Goodyear, AZ) with the samples in a face-to-face configuration. The annealing temperatures were chosen based on past experience with implanted deuterium in ZnO and also that the melting temperature of Ga$_2$O$_3$ is 1725 $^\circ$C and we would expect a fairly high temperature is needed to obtain migration of the implanted deuterium. The plasma exposed samples were treated for 30 mins at 100, 200 and 270 $^\circ$C in a 0.5 Torr, 13.56 MHz discharge. Sections of the 200 $^\circ$C treated sample were then annealed for 5 min at either 500 or 600 $^\circ$C under flowing O$_2$ to measure the thermal stability of the deuterium introduced into the Ga$_2$O$_3$ by plasma exposure. All of the samples were examined by SIMS. The latter was performed in a Camera system using a Cs$^+$ ion beam with 14.5 keV energy and 24$^\circ$ incident angle.

**Results and Discussion**

Figure 1 shows the SIMS profiles of implanted $^2$H before and after annealing at 650 $^\circ$C. The as-implanted profile shows a peak deuterium concentration of $\sim 3.1 \times 10^{19}$ cm$^{-3}$ at a depth of $\sim 0.85$ μm concentration, in good agreement with the values predicted by the SRIM code. The annealing produces an evolution of $^2$H out of the Ga$_2$O$_3$ crystal, with the remaining deuterium atoms decorating the residual implant damage. The thermal stability of the implanted $^2$H is fairly similar to that in ZnO, but lower than in GaN, where temperatures of $\sim$900 $^\circ$C are needed to remove deuterium to below the detection limit ($\sim 3 \times 10^{15}$ cm$^{-3}$) of SIMS. As discussed earlier, hydrogen in ZnO is different from conventional semiconductors in that both interstitial and substitutional hydrogen are shallow donors and it typically substitutes on the oxygen site, forming a multicenter bond with the neighboring Zn atoms and contributing to the n-type conductivity. The role of hydrogen in Ga$_2$O$_3$ is less clear, though some theoretical calculations suggest it can also occupy either interstitial or substitutional sites where it also acts as a shallow donor.

Figure 2 shows the percentage of $^2$H remaining in the Ga$_2$O$_3$ as a function of annealing temperature (5 min anneals). The closed squares are experimental data, while the open squares are predictions from the FLOOPS simulation.

**Figure 2.** Percentage of retained $^2$H implanted into Ga$_2$O$_3$ (100 keV, $10^{15}$ cm$^{-2}$) as a function of annealing temperature (5 min anneals). The closed squares are experimental data, while the open squares are predictions from the FLOOPS simulation.
in ZnO. It is likely that hydrogen isotopes must diffuse as an interstitial, with little trapping by the lattice elements or by defects or impurities. The position of $^{2}\text{H}$ in the lattice after immobilization has not yet been determined experimentally, but from theory the lowest energy state for $^{2}\text{H}$ is forming an O-H bond with three-fold coordinated oxygen, but there were many configurations close in energy.\textsuperscript{36}

Using a simple estimate of the diffusivity $D$, from $D = X^2/4t$, and where $X$ is taken to be the distance at which $^{2}\text{H}$ concentration has fallen to the background concentration of $10^{-15}$ cm$^{-3}$ in Figure 4, we can estimate the value as $6.4 \times 10^{-13}$ cm$^2$/Vs. This is about three orders of magnitude lower than in ZnO. Note that the absolute diffusivities of $^1\text{H}$ would be $\sim 40\%$ larger because of the relationship for diffusivities of isotopes, i.e.\textsuperscript{44}

$$
D_{^2\text{H}} = \frac{M_{^1\text{H}}}{M_{^2\text{H}}} \times D_{^1\text{H}}^{1/2}
$$

We do note that our plasma-exposed samples showed an increase in surface conductivity. With a donor nature for hydrogen, but at this stage we cannot exclude plasma-induced surface effects that might also change the near-surface conductivity.

Figure 3. Simulated fractions of implanted $^2\text{H}$ remaining as a function of anneal time for three different anneal temperatures.

Figure 4. SIMS profiles of $^2\text{H}$ in Ga$_2$O$_3$ exposed to a deuterium plasma at 270°C for 30 mins.

Conclusions

In conclusion, the thermal stability of deuterium introduced by direct ion implantation or by plasma exposure in Ga$_2$O$_3$ has been examined. Annealing at 650°C removes $90\%$ of the implanted deuterium and this is accurately simulated using a model of interstitial diffusion and trapping at residual implant damage. Incorporation of deuterium in the Ga$_2$O$_3$ for plasma exposure at 270°C occurred to a depth of $\sim 0.68$ μm, corresponding to a diffusion coefficient of $6.4 \times 10^{-13}$ cm$^2$/Vs.

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References

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