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Thermal Stability Of Hydrogen In Lialo2 And Ligao2

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Thermal stability of hydrogen in LiAlO₂ and LiGaO₂

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Hydrogen as ²H has been incorporated into LiAlO₂ and LiGaO₂ by both ion implantation and by exposure to a plasma at 250 °C. In the implanted samples, approximately 50% of the hydrogen is lost from the surface during annealing at 500 °C for 20 min, and essentially all is gone by 700 °C. This hydrogen retention is considerably less than for other materials that are being used as substrates for III-nitride epilayer growth, such as SiC and sapphire. The indiffusion of ²H from a plasma is much faster for LiAlO₂ with an apparent diffusivity at 250 °C of $\sim 10^{-13}$ cm² s⁻¹, approximately two orders of magnitude larger than for LiGaO₂. Hydrogen outdiffusion from LiAlO₂ or LiGaO₂ substrates during III-nitride epitaxy should not be a significant problem; the hydrogen should have left these materials at temperatures less than epitaxial layer growth temperatures. © 1996 American Institute of Physics. [S0003-6951(96)04451-8]

Lithium aluminate (LiAlO₂) and lithium gallate (LiGaO₂) single crystals are attracting attention as substrates for epitaxial growth of GaN and other III-nitrides.¹ Pulsed operation of GaN/InGaN blue laser diodes has been reported for films grown on *c*-axis sapphire where facets were formed by dry etching,² and on *a*-plane sapphire where facets were formed by cleaving.³ The lattice mismatch for GaN grown on sapphire is 13.6%, which produces columnar growth in most cases, with defect densities in the 10⁹ and 10¹⁰ cm⁻² ranges.⁴ GaN has also been grown on 3C-SiC (3.1% mismatch)⁴⁻⁷ and on ZnO (2.2% mismatch)⁸ substrates, both of which have cubic symmetry and are easily cleaved. The largest bulk GaN crystals that are currently available are typically 5×10 mm², produced by high pressure solution growth (20 kbar at ~ 1600 °C),⁹ LiAlO₂ and LiGaO₂ have oriented *a*-axis lattice constants of 0.3134 and 0.3186 nm, respectively, which translates into mismatches with GaN of -1.5% for LiAlO₂ and +0.2% for LiGaO₂. Initial studies of growth of III-nitride epilayers on these oxide substrates have shown excellent results for deposition temperatures below 900 °C.¹⁰ At higher temperatures, surface degradation is apparent under some conditions, especially when hydrogen is present in the growth ambient. Because NH₃ is the most commonly used source of nitrogen for metalorganic chemical vapor deposition, and metalorganics such as (CH₃)₃Ga produce hydrogen during decomposition, it is clearly important to understand the thermal behavior and stability of hydrogen in LiAlO₂ and LiGaO₂.

In this letter, we report on measurements of hydrogen incorporation in both LiAlO₂ and LiGaO₂ during ²H plasma treatment and about the thermal stability of implanted hydrogen (as ²H). In the latter case, outdiffusion begins at about 500 °C and is completed by about 700 °C, whereas in sapphire, temperatures up to 1000 °C have little effect on im-

planted ²H depth distributions. High densities of hydrogen ($>10^{20}$ cm⁻³ in LiAlO₂ and 10^{19} cm⁻³ in LiGaO₂) are incorporated during plasma exposure at 250 °C.

Undoped crystals were grown using the Czochralski technique, with diameter 1.5 in., and orientation (100), for both materials. Hall measurements showed high resistivity ($>10^8$ Ω cm) as expected for such wide band gap materials (~ 6 eV). Wafers were polished on one side using a combination of mechanical and chemical treatments. To facilitate measurements of hydrogen incorporation and thermal stability, we introduced the ²H isotope of hydrogen [which can be detected with better sensitivity using secondary ion mass spectrometry (SIMS) than for ¹H], by two different methods. In the first method, ²H ions were implanted at 100 keV to a fluence of 2×10^{15} cm⁻². Sections of this sample were substantially annealed at temperatures up to 700 °C for 10 min, and SIMS depth profiling was performed for each temperature. In the second method, pieces were exposed to electron cyclotron resonance (ECR) ²H plasmas for 1 h at 250 °C. The microwave power was 750 W, and the process pressure was 10 mTorr. SIMS measurements were again carried out before and after a subsequent anneal at 500 °C for 1 min under N₂.

Depth profiles of ²H for as-implanted and annealed LiAlO₂ and LiGaO₂ are shown in Figs. 1(a) and 1(b), respectively. In the as-implanted samples, the ²H peak density is greater in LiAlO₂, and the distribution is broader in LiGaO₂, because of the greater mass of Ga compared with Al. Annealing at temperatures greater than about 350 °C causes a reduction in the peak density of ²H in both materials. Note that the implanted profiles do not show diffusion broadening as is seen for doped semiconductors in which hydrogen can attach to donor or acceptor impurities to form

FIG. 1. SIMS profile of ^2H implanted in LiAlO_2 (a) and LiGaO_2 (b) crystals before and after annealing.

stable neutral complexes.¹¹ It appears that in LiAlO_2 and LiGaO_2 , hydrogen is basically lost from the crystals during thermal annealing, with the remaining hydrogen at each temperature decorating the residual crystal damage (caused by the implantation). This is an issue of potential concern because residual hydrogen in the oxide substrates could be readily transferred to GaN epitaxial films during device processing steps, such as contact alloying, implant activation, or

FIG. 2. SIMS profiles of ^2H implanted in sapphire (Al_2O_3) before and after annealing.

implant isolation annealing. However, as seen below, this may be less of an issue than in other potential substrates for GaN epitaxial growth.

Implanted ^2H is much less thermally stable in LiAlO_2 and LiGaO_2 than in sapphire. A wafer of sapphire was implanted with ^2H at the same time as the other materials and annealed at the same temperatures as the others. The SIMS profiles for ^2H before and after annealing up to 950 °C for 10 min are shown in Fig. 2 for sapphire (crystalline Al_2O_3). No measurable change is caused by such anneals. In Fig. 3, we have plotted the percentage of implanted ^2H that remains in LiGaO_2 , LiAlO_2 , Al_2O_3 , SiC, GaN, AlN, and GaAs after various thermal treatments, based on the data given here and

FIG. 3. Percentage of implanted ^2H remaining in various crystalline materials after 10 min anneals at various temperatures.

FIG. 4. SIMS profiles of ^2H in plasma-exposed LiAlO_2 (left) and LiGaO_2 (right) crystals, as-treated and after annealing for 1 min at 500°C .

on that reported previously for the nitrides^{12,13} and for GaAs.¹¹ These materials are all potential substrates for III-nitride epitaxy. Clearly the LiAlO_2 and LiGaO_2 fall at the lower end of the thermal stability range for H retention, which is an advantage because there will be lower levels of residual H after a high temperature growth step. The ^2H is presumably in random positions following implantation, and in semiconductors, it moves to regions of strain (defects or impurities) during annealing. The observation that H is not retained at high temperatures in the oxide materials is at least an indication that they are free of large densities of defects or impurities, otherwise one would expect to observe plateaus forming in the ^2H depth profiles at certain annealing temperatures, as for GaAs.¹¹ It might also be considered that it is better to employ substrates such as alumina and SiC which have extremely high stabilities for hydrogen retention, to prevent diffusion of hydrogen into overlying GaN epilayers. This is a valid viewpoint, although our feeling is that it is better to simply eliminate the hydrogen rather than retain the potential for possible future problems with it.

The fact that ^2H is so mobile in LiAlO_2 and LiGaO_2 at relatively low temperatures is clear from the data in Fig. 4, in which are shown the ^2H profiles after exposure to a ^2H plasma for 1 h at 250°C . Based on a simple $(4Dt)^{1/2}$ calculation for the diffusion distance, we can estimate diffusivities

of $\sim 1.1 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ in LiAlO_2 , and $\sim 1.7 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ for LiGaO_2 . The values are approximately one and three orders of magnitude, respectively, lower than in GaAs at the same temperature.¹¹ We note that annealing at 500°C again reduces the ^2H density in LiAlO_2 (whereas there is little change in LiGaO_2) without causing significant diffusional broadening of the profiles. The ^2H appears to have been lost from the surface. The incorporation depth in LiGaO_2 is so shallow that the indiffusion of ^2H may be controlled by trapping on defects created by plasma exposure. Clearly however the permeation is significantly slower than in LiAlO_2 .

In summary, hydrogen is found to diffuse readily in LiAlO_2 and LiGaO_2 at temperatures as low as 250°C . Out-diffusion begins at less than 400°C , and is complete by 700°C in both materials. The temperatures at which hydrogen is retained are much lower than for SiC, Al_2O_3 , GaN, and AlN.

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