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# HYDROGEN INCORPORATION INTO III-V NITRIDES DURING PROCESSING

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## ABSTRACT

Hydrogen is readily incorporated into GaN and related alloys during wet and dry etching, chemical vapor deposition of dielectric overlayers, boiling in water and other process steps, in addition to its effects during MOCVD or MOMBE growth. The hydrogen is bound at defects or impurities and passivates their electrical activity. Reactivation occurs at 450-550°C, but evolution from the crystal requires much higher temperatures ( $\geq$ 800°C).

## INTRODUCTION

Hydrogen plays an important role in semiconductors, passivating the electrical activity of shallow and deep level impurities [1]. Unintentional incorporation of hydrogen can therefore lead to uncontrolled variations in conductivity of a semiconductor, and this effect has been observed for virtually all group IV, III-V and II-VI materials. The properties of hydrogen in group III nitrides and their alloys are attracting much recent attention because of the discovery that post-growth annealing is required to attain high conductivity [2]. This problem will be especially evident in materials grown using $NH_3$ as the nitrogen precursor, but past studies in other III-V semiconductors have shown that metalorganics such as trimethylgallium $Ga(CH_3)_3$ can also produce significant hydrogen incorporation [3].

For photonic devices such as light-emitting diodes or heterostructure diode lasers. we will also need to understand the effect of hydrogen in ternary and qurternary nitrides, because these will comprise the active or cladding layers.

In this paper we report on the incorporation of hydrogen into GaN, InN, AlN and their alloys during intentional exposure to hydrogen-containing plasmas, and also during various processing steps such as wet etching, dry etching, and boiling in water. We find extensive indiffusion of hydrogen in all of these cases.

## EXPERIMENTAL

Samples of the binary and ternary nitrides up to ~2μm thick were grown on $Al_2O_3$, Si or GaAs substrates at 500-700°C in an Intevac Gas-Source Gen II system [4]. Triethylgallium, trimethylindium and dimethylethylamine alane were transported by He carrier gas and an Electron Cyclotron Resonance (ECR) source operating at 2.45 Ghz and 200W forward power was used to provide the $N_2$ flux. The epitaxial layers contained both cubic and hexagonal phases, and were defective single crystals. The major structural imperfections present were microtwins and stacking faults. The GaN and AlN were resistive, the InN was strongly n-type ($\sim 5\times10^{20}cm^{-3}$, depending on the In content), while the InGaN and InAlN were also n-type ($10^{18}$-$10^{20}$ $cm^{-3}$) Some of the material was contacted with alloyed HgIn eutectic (400°C, 60sec) in a Van der Pauw pattern, while other sections were left blank. Hall measurements were used to detect changes in conductivity, while Secondary Ion Mass Spectrometry(SIMS) was carried out using a $Cs^+$ ion beam.

## RESULTS AND DISCUSSION

By analogy with the models for neutral hydrogen-dopant complexes in other III-V semiconductors [1]. Figure 1 shows schematic representations of the likely configurations in GaN. For donor dopants, Figure 1(a) and (b), the hydrogen occupies an anti-bonding position either attached to the dopant in the case of group IV donors or attached to the Ga neighbour in the case of a group VI donor. For acceptor dopants, Figure 1(c) and (d), the hydrogen is at a bond-centered site, bonded predominantly either to the acceptor or a N neighbour, respectively, depending on whether the acceptor is from column IV or II of the Periodic Table. Upon annealing at > 400°C the hydrogen is dissociated from the complex, leading to reactivation of the dopant. The hydrogen does not leave the crystal at this temperature but probably associates with other hydrogen atoms to form molecules and larger clusters. At much higher temperatures ( > 800°C) these clusters are evolved from the sample.

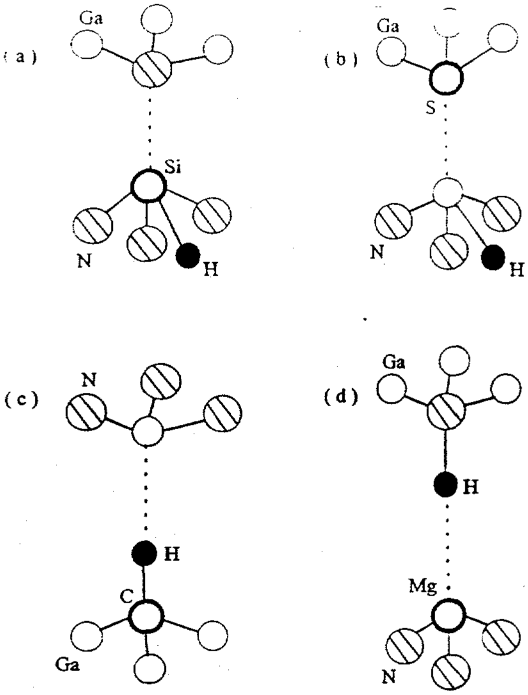

Figure 1. Schematic representation of hydrogen-dopant complexes in GaN.

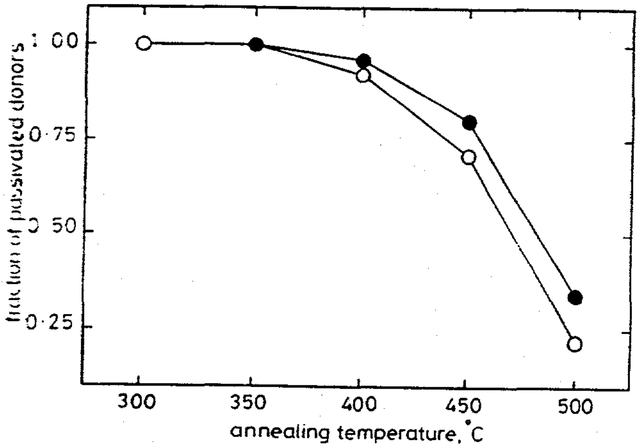

Figure 2. Fraction of passivated donors remaining in InAlN or InGaN after deuteration at 250°C and subsequent annealing at different demperatures.

We exposed the ternary samples to an ECR D2 plasma for 30 min at 250°C. Figure 2 shows the fraction of passivated donors remaining in both InAlN and InAlGaN as a function of post-hydrogenation annealing temperature. Both samples displayed a decrease in carrier concentration of approximately an order of magnitude after hydrogen plasma exposure, consistent with previous reports [5]. On subsequent annealing the passivated donors begin to reacivate around 400°C, and by 500°C 78% of the lost carriers were restored in InAlN and 66% in the InAlGaN. The reactivation of the donors was fit to the relation[1].

$$\frac{N_o}{N} = 1\text{-exp}\left[-tv\exp(E_d/kT)\right]$$

where No/N is the fraction of passivated centres reactivated by annealing at temperature T for time *t*, v is the attempt frequency (assumed to be $10^{14}s^{-1}$) and $E_d$ is the activation energy for reactivation. The recovery of the donor activity occured over a slightly broader temperature range than generally observed for other passivated dopants in binary semiconductors, and is consistent with the presence of a Gaussian distribution of activation energies [1]. This may be due to nitrogen vacancies with different numbers of specific group III neighbours surrounding them (i.e., 2 In and 2 Al against 1 In and 3 Al). Assuming a Gaussian distribution of activation energies, we obtained values for $E_d$ around 2.4eV, with a full width at half maximum of ~0.3eV. The fact that reactivation of these donors occurs around 500°C means that the apparent thermal stability is similar to that of passivated Mg acceptors in GaN.

SIMS profiles of deuterium in InAlN for as-hydrogenated plus subsequent 900°C annealing treatments are shown in Figure 3. The deuterium concentration ($\sim 10^{21}cm^{-3}$) throughout the epitaxial layer thickness, well in excess of the doping concentration. The sites to which this deuterium is bonded are at present unclear, but presumably involve the structural defects in the material. Annealing up to 800°C did not measurably alter the deuterium profile, whereas annealing at 900°C reduced the plateau concentration to $\sim 5 \times 10^{18}cm^{-3}$. This is similar to the behaviour in the component binaries reported previously [6].

Samples were also boilded in $D_2O$ at ~100°C for 30mins. Figure 4 shows that extensive deuterium incorporation occured under these conditions in both GaN and InN (each grown on a GaAs substrate). A GaN sample exposed to an etching solution of KOH:$D_2O$ at 85°C, which we have found will selectively wet etch AlN, also showed incorporation of

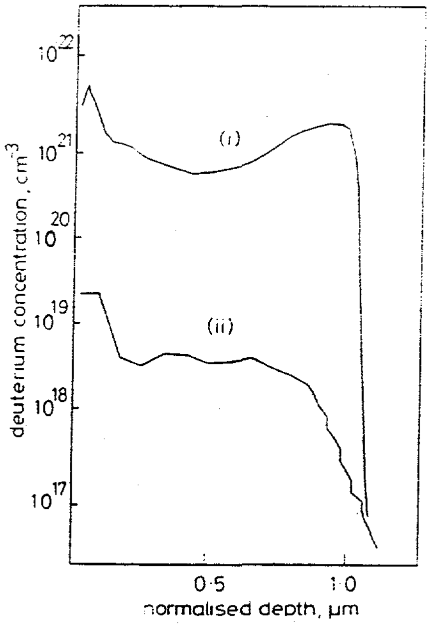

Figure 3. SIMS profiles of deuterium in InAlN exposed to $D_2$ plasma for 0.5h at 250°C and subsequent annealing at different temperatures

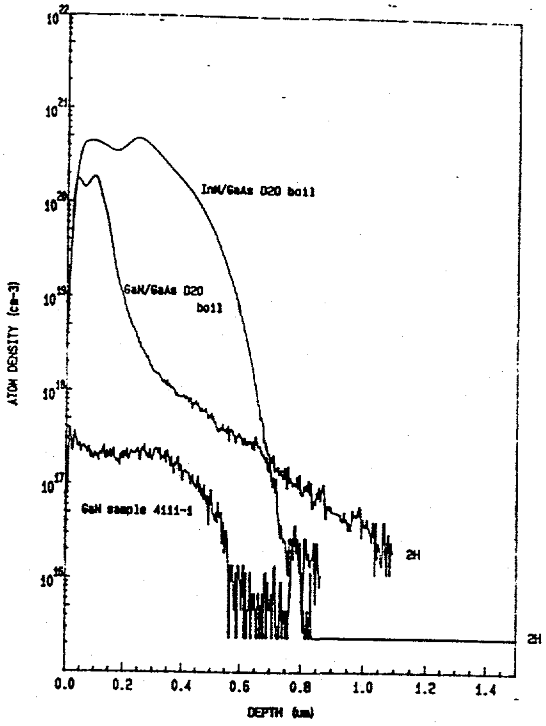

Figure 4. SIMS profiles of deuterium in GaN or InN samples after boiling in $D_2O$ or etching in KOH:$D_2O$ (sample 4111-1).

shown for InN in Figure 5 and for AlN in Figure 6. The diffusion coefficient of deuterium is $>10^{-11}cm^2/s$ at 170°C in both materials. based on a simple $(Dt)^{1/2}$ calcuration. Similar results were obtained for GaN. The $Cl_2/CH_4/D_2/Ar$ chemistry provides rapid, non-selective dry etching of all of the nitrides. but one should be aware of possible hydrogen passivation effects [7].

For the ternary, materials we observed a strong dependence of incorporation depth on the In content, as shown for $In_XGa_{1-X}N$ in Figure 7. This may be related to the fact that the residual background n-type doping falls off rapidly as the In content is decreased, and therefore there are fewer trapping sites to impede diffusion of the deuterium. Extensive deuterium indiffusion was also observed for InAlN exposed to an ECR $Cl_2/CH_4/D_2/Ar$ plasma for 40sec. at 170°C. as shown in Figure 8.

## SUMMARY AND CONCLUSIONS

Hydrogen is found to readily diffuse into the binary and ternary nitrides at temperatures in the range 65-250°C. These are typical process temperatures for fabrication steps such as wet and dry etching, dielectric deposition, sintering of contacts, boiling in solvents and baking of resists. The hydrogen forms electrically neutral complexes with dopants, defects and impurities in the epitaxial nitride films. Reactivation occurs at 450-550°C, and the hydrogen is removed at temperatures $\geq$ 800°C.

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### DISCLAIMER

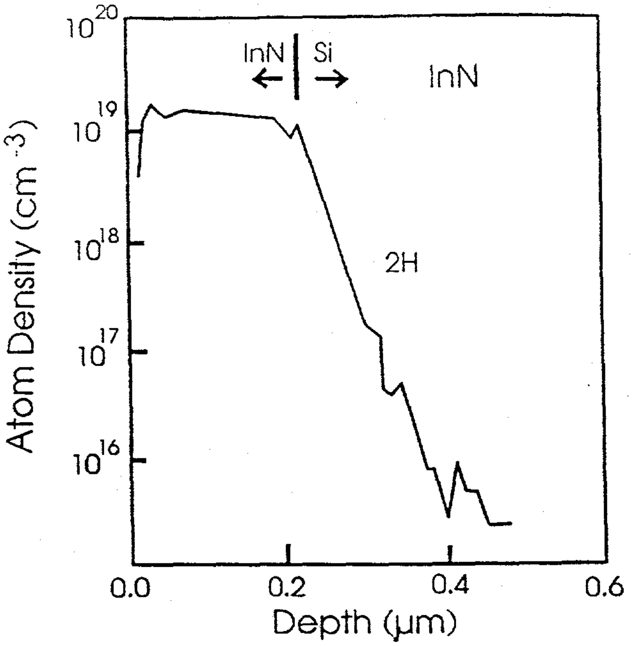

Figure5. SIMS profile of deuterium in InN/Si sample after a short etch in a $Cl_2/CH_4/H_2/D_2$ ECR plasma.

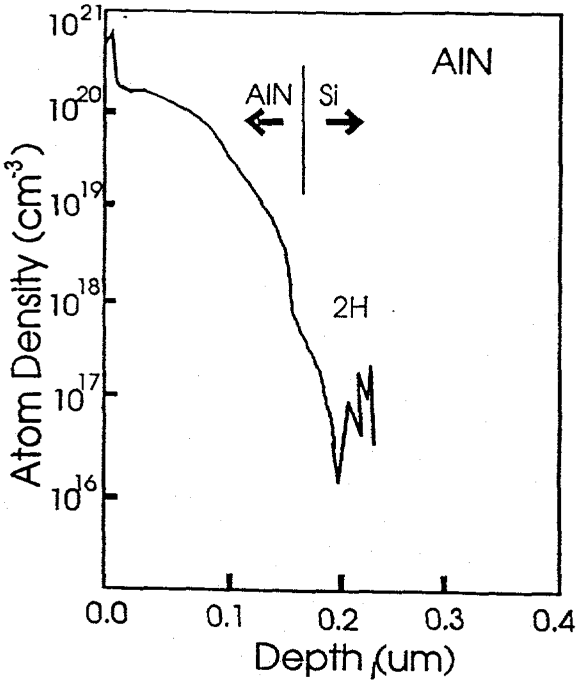

Figure6. SIMS profile of deuterium in AlN/Si sample after a short etch in a $Cl_2/CH_4/H_2/D_2$ ECR plasma.

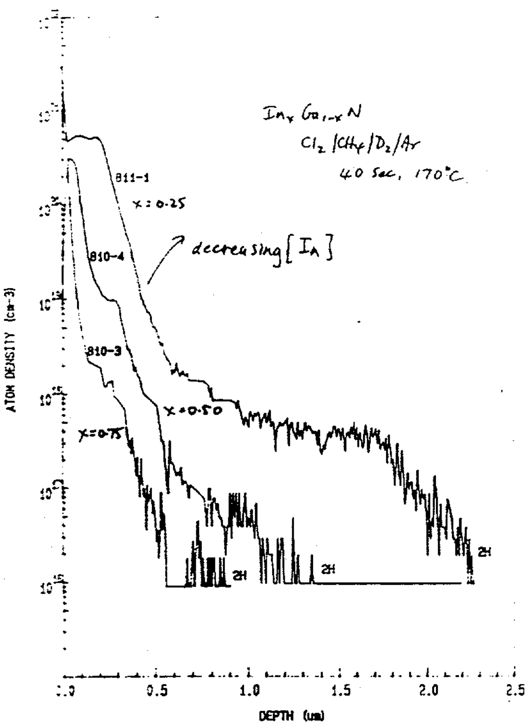

Figure7. SIMS profile of deuterium in $In_XGa_{1-X}N/Si$ sample after a 40 sec. etch in $Cl_2/CH_4/H_2/D_2$ at 170°C.

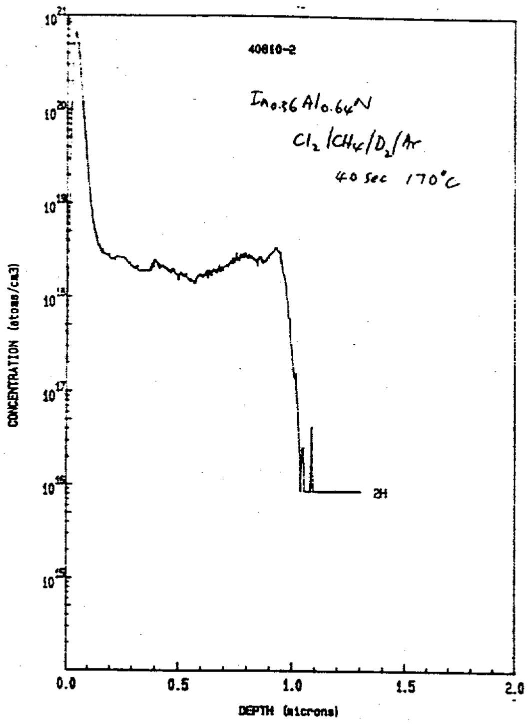

Figure8. SIMS profile of deuterium in In0.36Al0.64N after a 40 sec. etch in $Cl_2/CH_4/H_2/D_2$ at 170°C.

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