

Hydrogen incorporation, diffusivity and evolution in bulk ZnO

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Abstract

Hydrogen is readily incorporated into bulk, single-crystal ZnO during exposure to plasmas at moderate (100–300°C) temperatures. Incorporation depths of >25 μm were obtained in 0.5 h at 300°C, producing a diffusivity of $\sim 8 \times 10^{-10}$ cm²/V s at this temperature. The activation energy for diffusion is 0.17 ± 0.12 eV, indicating an interstitial mechanism. Subsequent annealing at 500–600 °C is sufficient to evolve all of the hydrogen out of the ZnO, at least to the sensitivity of Secondary Ion Mass Spectrometry ($< 5 \times 10^{15}$ cm⁻³). The thermal stability of hydrogen retention is slightly greater when the hydrogen is incorporated by direct implantation relative to plasma exposure, due to trapping at residual damage.

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1. Introduction

There has been considerable recent attention paid to the properties of hydrogen in ZnO and related oxides [1–17]. The primary interest comes from the prediction that interstitial atomic hydrogen will introduce a shallow donor state in ZnO [1–4], which is supported by some experimental data for its muonium counterpart [5,6], from electron paramagnetic resonance of bulk single-crystals [7] and from the fact that hydrogen can lead to electron conduction in other wide bandgap oxides such as SnO [18]. It is clear that the presence of hydrogen in the growth on processing ambient can significantly affect the electrical and optical properties of ZnO [8–17], but

there is little systematic data available on its diffusivity and thermal stability when introduced by different methods.

In this paper we report on an investigation on the diffusion of hydrogen in ZnO during exposure to ²H plasmas, a comparison of the thermal stability of hydrogen incorporated by either direct implantation or by plasma exposure and finally on changes in the electrical and optical properties of the ZnO or a result of hydrogen incorporation. The hydrogen is found to diffuse very rapidly even at temperatures of 100 °C, but can be evolved from the ZnO by subsequent annealing under N₂ at ≤ 600 °C.

2. Experimental

Bulk wurtzite (0001) ZnO crystals from Eagle-Picher (grade I quality) were used in all cases. The

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samples were nominally undoped with as-received n-type carrier concentrations of $\sim 10^{17} \text{ cm}^{-3}$ and a room temperature mobility of $190 \text{ cm}^2/\text{Vs}$. The samples were exposed to ^2H plasmas at temperatures of $100\text{--}300^\circ\text{C}$ in a Plasma Therm 720 series reactor operating at 900 mTorr with 50 W of 13.56 MHz power. Some of these samples were subsequently annealed at temperatures up to 600°C under flowing N_2 ambients for 5 min. We also implanted 100 keV ^2H on ^1H ions at doses of $10^{15}\text{--}10^{16} \text{ cm}^{-2}$ and then used secondary ion mass spectrometry (SIMS) measurements to obtain the hydrogen or deuterium profiles as a function of post-implant annealing temperature [19]. The electrical properties of some of the samples were examined by electrochemical capacitance–voltage ($C\text{--}V$) measurements using a 0.2 M NaOH/0.1 M EDTA electrolyte as the rectifying contact. Finally, optical properties were measured using photoluminescence (PL) spectroscopy at variable temperatures, with a He–Cd laser as the excitation source.

3. Results and discussion

Fig. 1 shows SIMS profiles of ^2H in plasma exposed ZnO, for different sample temperatures during the plasma treatment. The profiles follow those expected for diffusion from a constant or semi-infinite source, i.e.

$$C(x, t) = C_0 \operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}}\right)$$

where $C(x, t)$ is the concentration at a distance x for diffusion time t , C_0 is the solid solubility and D is the diffusivity of ^2H in ZnO [20]. The incorporation depths of ^2H are very large compared to those in GaN or GaAs under similar conditions, where depths of $1\text{--}2 \mu\text{m}$ are

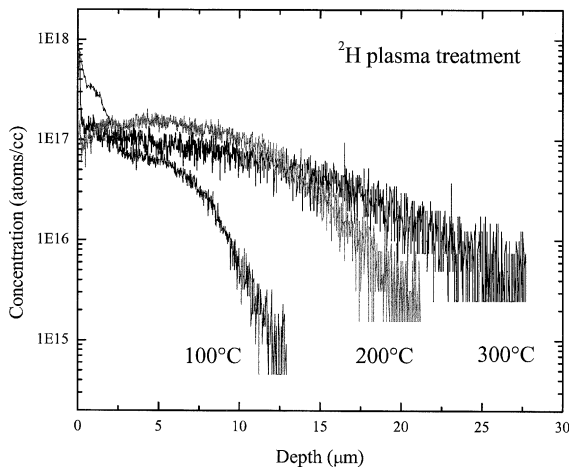


Fig. 1. SIMS profiles of ^2H in ZnO exposed to deuterium plasmas for 0.5 h at different temperatures.

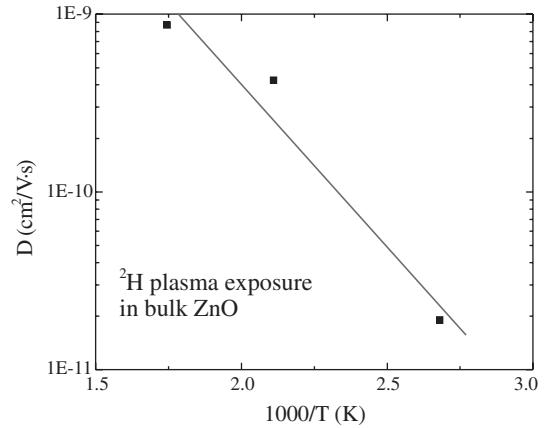


Fig. 2. Arrhenius plot of diffusivity for ^2H in ZnO.

observed [21,22]. It is clear that hydrogen must diffuse as an interstitial, with little trapping by the lattice elements or by defects or impurities. The position of H in the lattice after immobilization has not yet been determined experimentally, but from theory the lowest energy states for H^+ is at a bond-centered position forming an O–H bond, while for H_2 the anti-bonding Zn site is most stable [1].

Using a simple estimate of the diffusivity D , from $D = X^2/4t$, and where X is taken to be the distance at which ^2H concentration has fallen to $5 \times 10^{15} \text{ cm}^{-3}$ in Fig. 1, we can estimate the activation energy for diffusion from the data shown in Arrhenius form in Fig. 2. The extracted activation energy, E_a , is $0.17 \pm 12 \text{ eV}$ for ^2H in ZnO. Note that the absolute diffusivities of ^1H would be $\sim 40\%$ larger because of the relationship for diffusivities of isotopes, i.e. [20].

$$\frac{D_{1\text{H}}}{D_{2\text{H}}} = \left(\frac{M_{2\text{H}}}{M_{1\text{H}}}\right)^{1/2}$$

The small activation energy is consistent with the notion that the atomic hydrogen diffuses in interstitial form.

Fig. 3 shows SIMS profiles of a ZnO sample exposed to a ^2H plasma of 0.5 h at 200°C , then annealed for 5 min under N_2 at different temperatures. There is significant loss of ^2H even after a short anneal at 400°C , with virtually all of it evolved out of the crystal by 500°C . This is in sharp contrast to ^2H in GaN, where much higher temperatures ($\geq 800^\circ\text{C}$) are needed to evolve the deuterium out of the sample [21,22].

To compare this data to the thermal stability of ^2H incorporated by direct implantation [17], Fig. 4 shows the percentage of ^2H remaining (measured by SIMS) as a function of annealing temperature for incorporation by either plasma exposure or implantation. The ^2H is slightly more thermally stable in the latter case, most likely due to trapping at residual damage in the ZnO

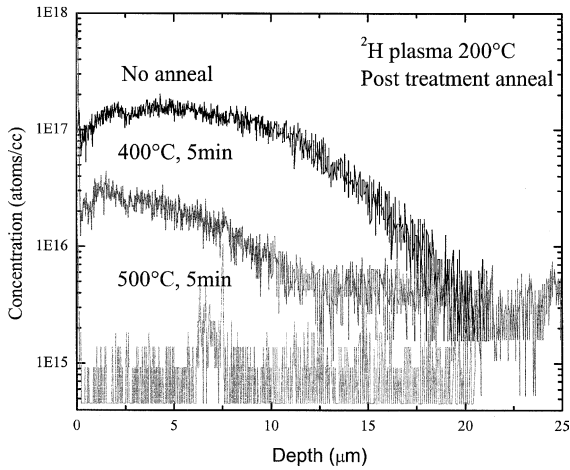


Fig. 3. SIMS profiles of ^2H in ZnO exposed to deuterium plasma for 0.5 h at 200 °C and then annealed at 400 or 500 °C for 5 min.

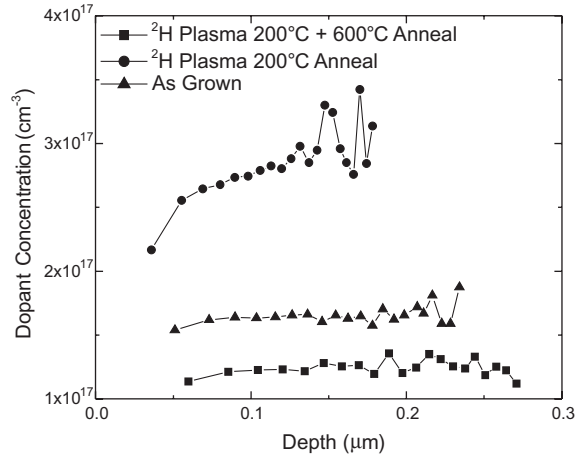


Fig. 5. Donor concentration profiles in ZnO before and after plasma exposure and after subsequent annealing.

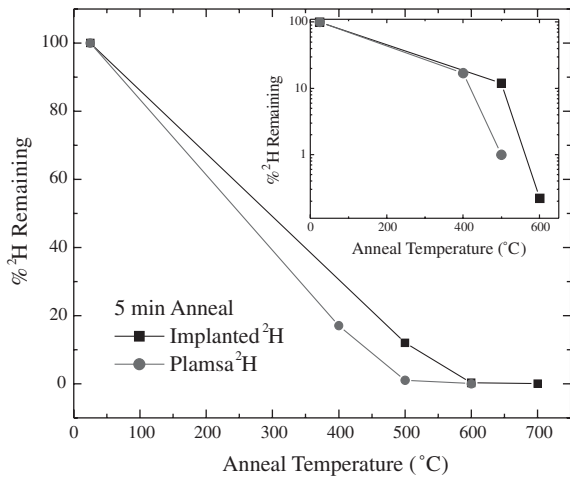


Fig. 4. Percentage of retained ^2H incorporated by direct implantation or plasma exposure, as a function of subsequent annealing temperature. The inset shows the data on a log scale.

carried by the nuclear stopping process. Lavrov et al. [23] have identified two hydrogen-related defects in ZnO, by using local vibrational mode spectroscopy. The H-I center consists of a hydrogen atom at the bond centered site, while the H-II center contains two inequivalent hydrogen atoms bound primarily to two oxygen atoms [23].

Fig. 5 shows donor concentration profiles in the ZnO before and after plasma exposure and following subsequent annealing. The ^2H plasma treatment causes an increase in donor concentration, consistent with past reports [9]. In that case, the effect was attributed to hydrogen passivation of compensating acceptor impu-

rities present in the as-grown ZnO epitaxial layers [9]. An alternative explanation is that the hydrogen induces a donor state and thereby increases the free electron concentration [1]. Subsequent annealing reduces the carrier density to slightly below the initial value in the as-received ZnO, which may indicate that it contained hydrogen as a result of the growth process. We emphasize that the n-type conductivity probably arises from multiple impurity sources [24–26] and we cannot unambiguously assign all of the changes to hydrogen.

Fig. 6 shows the PL spectrum from a plasma treated sample as a function of measurement temperature. The sample shows strong band-edge luminescence and a small deep-level band (~2.6 eV). Past reports have shown that the efficiency of band-edge emission was increased by plasma hydrogenation of various types of ZnO [10], but that the degree of improvement depended

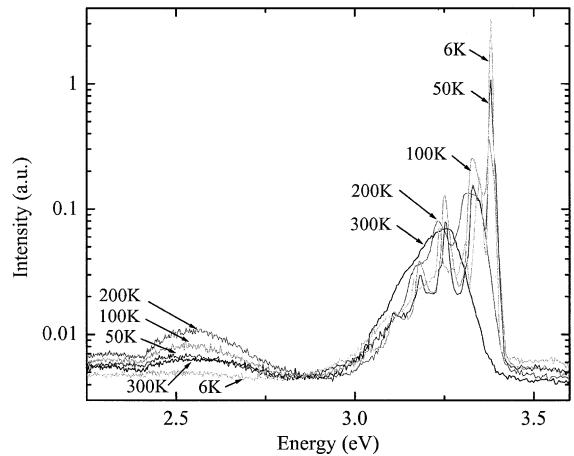


Fig. 6. PL spectra from ^2H plasma exposed ZnO.

on the impurity and defect concentration in the original samples [10,12] We did not observe any significant difference in the intensity or shape of the PL spectra as a result of plasma hydrogenation of our samples.

More detail on the measurement temperature dependence of the band-edge and deep-level emissions from the plasma deuterated ZnO are shown in Fig. 7. As expected and as reported previously [12], the band-edge intensity increases significantly as the temperature is lowered and the deep-level emission is quenched. The overall intensity of the plasma treated ZnO remains much higher than the material hydrogenated by direct implantation of protons or deuterons. Fig. 8 shows 300 K PL spectra from ZnO after ^2H implantation at a dose of $10+15+ \text{cm}^{-3}$, followed by annealing at different temperatures [17]. The implantation step severely degrades the band-edge intensity, and even annealing at 700 °C where all of the ^2H has been evolved from the

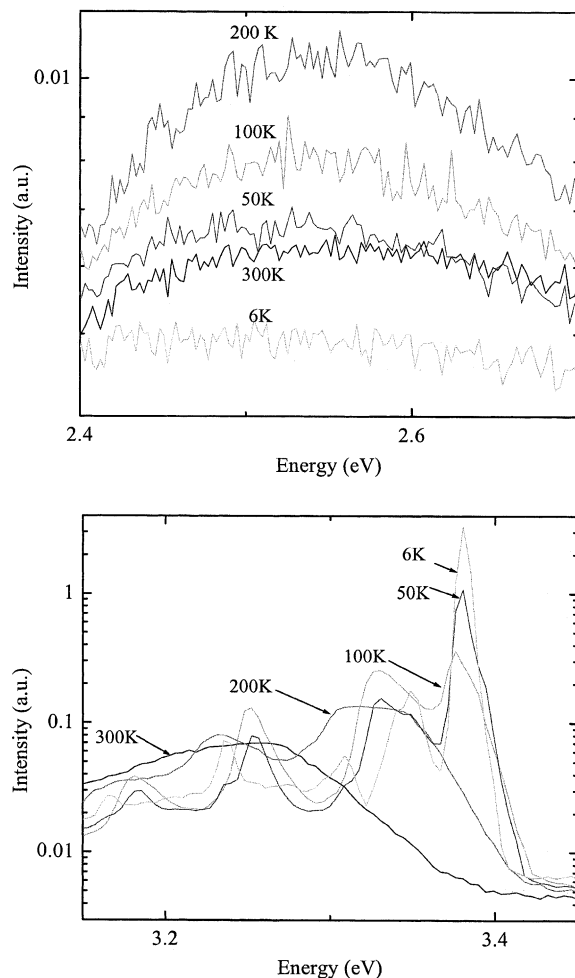


Fig. 7. Detailed band-edge and deep-level emission PL spectra from ^2H plasma exposed ZnO.

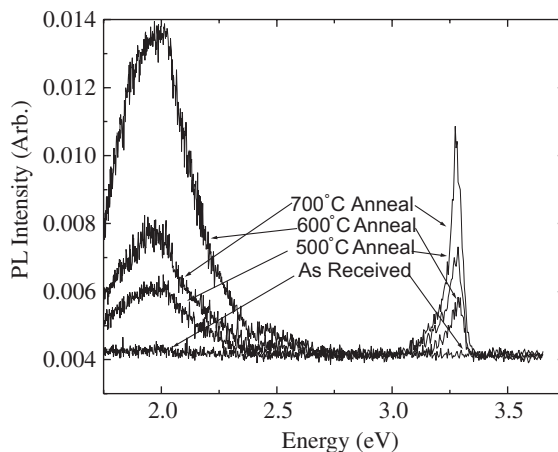


Fig. 8. 300 K PL spectra from ^2H implanted ZnO, as a function of subsequent annealing temperature.

ZnO leave the intensity about two orders of magnitude lower than in the implanted material [17].

4. Summary and conclusions

Hydrogen is found to exhibit a very rapid diffusion in ZnO when incorporated by plasma exposure, with D of $8.7 \times 10^{-10} \text{ cm}^2/\text{Vs}$ at 300°C. The activation energy for diffusion is indicative of interstitial motion. All of the plasma-incorporated hydrogen is removed from the ZnO by annealing at ≥ 500 °C. When the hydrogen is incorporated by direct implantation, the thermal stability is somewhat higher, due to trapping at residual damage. The free electron concentration increases after plasma hydrogenation, consistent with the small ionization energy predicted for H in ZnO [1] and the experimentally measured energy of 60 ± 10 meV for muonium in ZnO [5]. The electrical activity and rapid diffusivity of H or ZnO must be taken into account when designing device fabrication processes such as deposition of dielectrics using SiH_4 as a precursor or dry etching involving use of $\text{CH}_4/\text{H}_2/\text{Ar}$ plasmas since these could lead to significant changes in near-surface conductivity.

Acknowledgements

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