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Hydrogen incorporation and diffusivity in plasma-exposed bulk ZnO

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Hydrogen incorporation depths of $>25\ \mu$m were obtained in bulk, single-crystal ZnO during exposure to ^{2}H plasmas for 0.5 h at 300 °C, producing an estimated diffusivity of $\sim 8 \times 10^{-10}$ cm^2/V·s at this temperature. The activation energy for diffusion was 0.17 ± 0.12 eV, indicating an interstitial mechanism. Subsequent annealing at 500–600 °C was sufficient to evolve all of the hydrogen out of the ZnO, at least to the sensitivity of secondary ion mass spectrometry ($<5\times10^{15}$ 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 in the former case. © *2003 American Institute of Physics.*
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Recently, there has been much interest in the properties of hydrogen in ZnO and related oxides.[1–18] Theoretical predictions suggest that interstitial atomic hydrogen will introduce a shallow donor state in ZnO,[1–4] and this assertion is supported by some experimental data for its muonium counterpart,[5,6] by electron paramagnetic resonance data of bulk single crystals[7] and by the fact that hydrogen can lead to electron conduction in other wide-band-gap oxides such as SnO.[19] In addition, the presence of hydrogen in the growth or processing ambient can significantly affect the electrical and optical properties of ZnO,[9–18] but there is little systematic data available on its diffusivity and thermal stability when introduced by different methods.

In this letter, we report on an investigation on the diffusion of hydrogen in ZnO during exposure to ^{2}H 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 N_2 at $\leqslant 600$ °C.

Bulk wurtzite (0001) ZnO crystals from Eagle–Picher (grade I quality) were used in all cases. The samples were nominally undoped with as-received n-type carrier concentrations of $\sim 10^{17}$ cm^{-3} and a room temperature mobility of 190 cm^2/V·s. The samples were exposed to ^{2}H plasmas at temperatures of 100–300 °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 mins cm^{-2}. Secondary ion mass spectrometry (SIMS) measurements were used to obtain the deuterium profiles as a function of plasma exposure or annealing temperature.[20] The electrical properties of some of the samples were examined by electrochemical capacitance–voltage ($C-V$) 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.

Figure 1 shows SIMS profiles of ^{2}H 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.[21] The incorporation depths of ^{2}H are very large compared to those in GaN or GaAs under similar conditions, where depths of 1–2 μm are observed.[22,23] It is clear that hydrogen must diffuse as an interstitial, with little trapping by the lattice elements or by

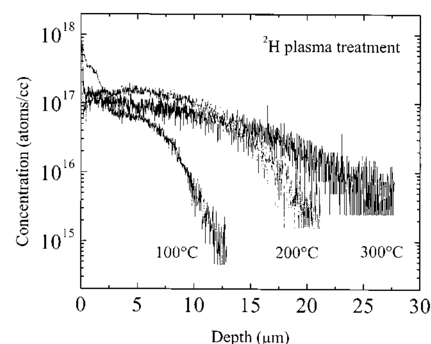

FIG. 1. SIMS profiles of ^{2}H in ZnO exposed to deuterium plasmas for 0.5 h at different temperatures.

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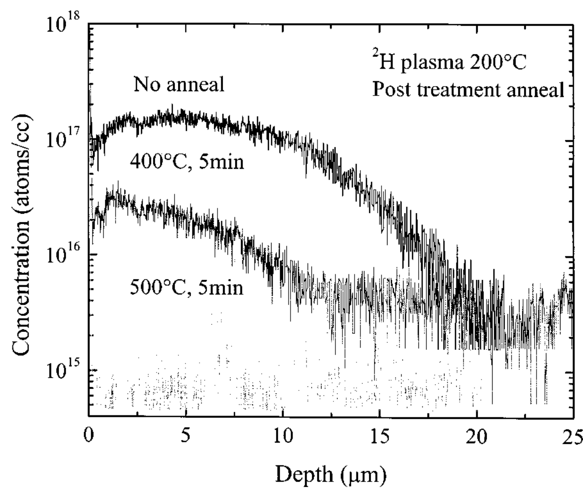

FIG. 2. SIMS profiles of ^{2}H in ZnO exposed to deuterium plasma for 0.5 h at 200 °C and then annealed at 400 or 500 °C for 5 min under flowing N_2.

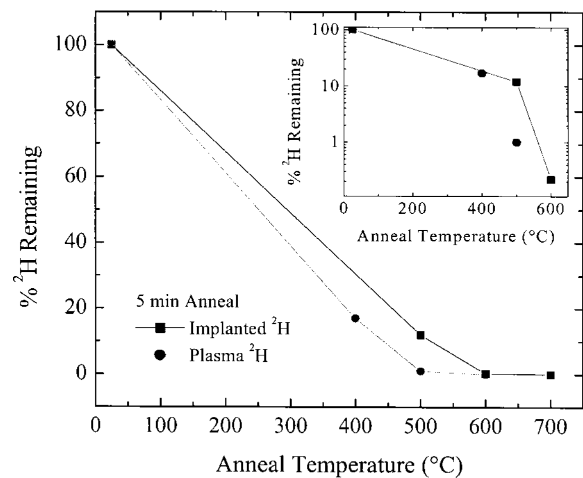

FIG. 3. Percentage of retained ^{2}H incorporated by direct implantation or plasmaexposure, as a function of subsequent annealing temperature. The inset shows the data on a log scale.

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 antibonding 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 ^{2}H concentration has fallen to 5×10^{15} cm^{-3} in Fig. 1, we can estimate the activation energy for diffusion. The extracted activation energy, E_a, is 0.17 ± 12 eV for ^{2}H in ZnO. Note that the absolute diffusivities of ^{1}H would be ~40% larger because of the relationship for diffusivities of isotopes, i.e.,[21]

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

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

Figure 2 shows SIMS profiles of a ZnO sample exposed to a ^{2}H plasma of 0.5 h at 200 °C, then annealed for 5 min under N_2 at different temperatures. There is significant loss of ^{2}H 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 ^{2}H in GaN, where much higher temperatures (≥ 800 °C) are needed to evolve the deuterium out of the sample.[22,23]

To compare these data to the thermal stability of ^{2}H incorporated by direct implantation,[18] Fig. 3 shows the percentage of ^{2}H remaining (measured by SIMS) as a function of annealing temperature for incorporation by either plasma exposure or implantation. The ^{2}H is slightly more thermally stable in the latter case, most likely due to trapping at residual damage in the ZnO carried by the nuclear stopping process. Lavrov *et al.*[24] 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.[24]

Figure 4 shows donor concentration profiles in the ZnO before and after plasma exposure and following subsequent annealing. The ^{2}H plasma treatment causes an increase in donor concentration, consistent with past reports.[10] In that case, the effect was attributed to hydrogen passivation of compensating acceptor impurities present in the as-grown ZnO epitaxial layers.[10] 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. However, if a 600 °C anneal indeed eliminates hydrogen in as-grown material to the same extent as it does in ion implanted and plasma-treated material, then the data in Fig. 4 must be interpreted to mean that the n-type conductivity in the present as-grown ZnO arises from multiple impurity sources[25–27] and not from hydrogen alone. In other words, although hydrogen appears to be a shallow donor, from this study and others, it is not necessarily the *dominant* shallow donor in as-grown ZnO.

PL spectra from a plasma treated sample was measured as a function of measurement temperature. The sample showed 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,[11] but that the degree of

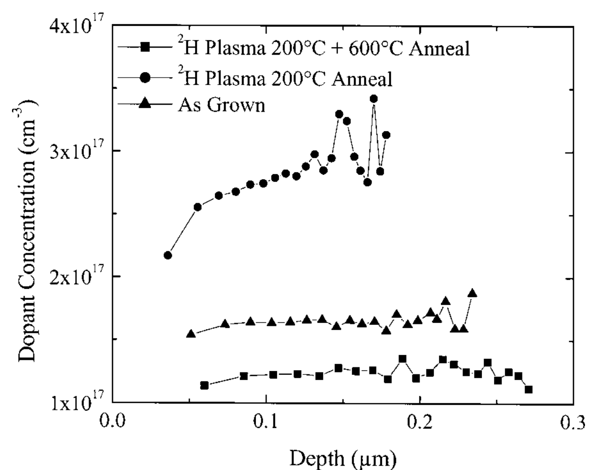

FIG. 4. Donor concentration profiles in ZnO before and after plasma exposure and after subsequent annealing.

improvement depended on the impurity and defect concentration in the original samples.[11,13] 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.

In summary, hydrogen is found to exhibit a very rapid diffusion in ZnO when incorporated by plasma exposure, with an estimated value for D of 8.7×10^{-10} $cm^2/V\,S$ at $300\,^\circ C$. The activation energy for diffusion is indicative of interstitial motion. All of the plasma-incorporated hydrogen is removed from the ZnO by annealing at $\geqslant 500\,^\circ C$. 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 experimentally measured energy as 35 ± 5 meV.[8] The electrical activity and rapid diffusivity of H in 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 $CH_4/H_2/Ar$ plasmas since these could lead to significant changes in near-surface conductivity.

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[1] C. C. van de Walle, Phys. Rev. Lett. **85**, 1012 (2000).
[2] C. C. van de Walle, Phys. Status Solidi B **229**, 221 (2002).
[3] C. Kilic and Z. Zunger, Appl. Phys. Lett. **81**, 73 (2002).
[4] C. C. van de Walle, Physica B **308-310**, 899 (2001).
[5] S. J. F. Cox, E. A. Davis, S. P. Cottrell, P. J. C. King, J. S. Lord, J. M. Gil, H. V. Alberto, R. C. Vilao, DJ. P. Duarte, N. A. de Campos, A. Weidinger, R. L. Lichti, and S. J. C. Irving, Phys. Rev. Lett. **86**, 2601 (2001).
[6] S. J. F. Cox, E. A. Davis, P. J. C. King, J. M. Gil, H. V. Alberto, R. C. Vilao, J. P. Duarte, N. A. de Campos, and R. L. Lichti, J. Phys. C **13**, 9001 (2001).
[7] S. O. Kucheyev, P. N. K. Deenapannay, C. Jagadish, J. S. Williams, M. Yano, K. Koike, S. Sasa, M. Inoue, and K. Ogata, Appl. Phys. Lett. **81**, 3350 (2002).
[8] D. M. Hofmann, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B. K. Meyer, S. B. Schmidt, and P. G. Baranov, Phys. Rev. Lett. **88**, 045504 (2002).
[9] S. J. Baik, J. H. Jang, C. H. Lee, W. Y. Cho, and K. S. Lim, Appl. Phys. Lett. **70**, 3516 (1997).
[10] B. Theys, V. Sallet, F. Jomard, A. Lusson, J.-F. Rommeluere, and Z. Teukam, J. Appl. Phys. **91**, 3922 (2002).
[11] N. Ohashi, T. Ishigaki, N. Okada, T. Sekiguchi, I. Sakaguchi, and H. Haneda, Appl. Phys. Lett. **80**, 2869 (2002).
[12] V. Bogatu, A. Goldenbaum, A. Many, and Y. Goldstein, Phys. Status Solidi B **212**, 89 (1999).
[13] T. Sekiguchi, N. Ohashi, and Y. Terada, Jpn. J. Appl. Phys., Part 2 **36**, L289 (1997).
[14] S. Tüzemen, G. Xiong, J. Wilkinson, B. Mischuck, K. B. Ucer, and R. T. Williams, Physica B **308-310**, 1197 (2001).
[15] C. S. Han, J. Jun, and H. Kim, Appl. Surf. Sci. **175/176**, 567 (2001).
[16] Y. Natsume and H. Sakata, J. Mater. Sci.: Mater. Electron. **12**, 87 (2001).
[17] Y.-S. Kang, H. Y. Kim, and J. Y. Lee, J. Electrochem. Soc. **147**, 4625 (2000).
[18] K. Ip, M. E. Overberg, Y. W. Heo, D. P. Norton, S. J. Pearton, S. O. Kucheyev, C. Jagadish, J. S. Williams, R. G. Wilson, and J. M. Zavada Appl. Phys. Lett. **81**, 3996 (2002).
[19] S. Samson and C. G. Fonstad, J. Appl. Phys. **44**, 4618 (1973).
[20] SIMS performed at Charles Evans and Associates using a Cameca system.
[21] R. J. Borg and C. J. Dienes, *An Introduction to Solid State Diffusion* (Academic, Boston, 1988).
[22] R. G. Wilson, S. J. Pearton, C. R. Abernathy, and J. M. Zavada, J. Vac. Sci. Technol. A **13**, 719 (1995).
[23] S. J. Pearton, J. C. Zolper, R. J. Shul, and F. Ren, J. Appl. Phys. **86**, 1 (1999).
[24] E. V. Lavrov, J. Weber, F. Borrnet, C. G. Van de Walle, and R. Helbig, Phys. Rev. B **66**, 165205 (2002).
[25] D. G. Look, Mater. Sci. Eng., B **80**, 383 (2001).
[26] D. G. Look, J. W. Hemsky, and J. R. Sizelove, Phys. Rev. Lett. **82**, 2552 (1999).
[27] D. C. Look, D. C. Reynolds, J. W. Hemsky, R. L. Jones, and J. R. Sizelove, Appl. Phys. Lett. **75**, 811 (1999).