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We demonstrate that remote plasma hydrogenation can increase electron concentrations in ZnO single crystals by more than an order of magnitude. We investigated the effects of this treatment on Hall concentration and mobility as well as on the bound exciton emission peak I_4 for a variety of ZnO single crystals–bulk air annealed, Li doped, and epitaxially grown on sapphire. Hydrogen increases I_4 intensity in conducting samples annealed at 500 and 600 °C and partially restores emission in the I_4 range for Li-diffused ZnO. Hydrogenation increases carrier concentration significantly for the semi-insulating Li doped and epitaxial thin film samples. These results indicate a strong link between the incorporation of hydrogen, increased donor-bound exciton PL emission, and increased *n*-type conductivity.
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ZnO has attracted considerable attention from the semiconductor community in recent years as a promising material for important new applications, yet many fundamental questions on the nature of its conductivity remain open. Thus, high-quality *p*-type ZnO with reproducible properties remains a contested goal. Similarly, theory[1–3] suggests hydrogen is a shallow donor impurity rather than a compensating center, a prediction supported by a number of spectroscopic studies.[4–14] Some electrical measurements[12–18] are also consistent with H donor character, although the polycrystalline samples, direct plasma exposure, or the ion implantation involved may introduce additional complications. This letter presents strong transport and spectroscopic evidence in favor of the hydrogen shallow donor hypothesis.

In our studies, we employ a remote hydrogen plasma treatment of the surface of ZnO. The main advantage of this approach, as opposed to the direct plasma treatment techniques, is a separate control and measurement of the temperature and pressure at the free surface of the specimen. Therefore, chemically driven changes occur without major thermal variations.

Recently, we described the effects of remote hydrogen plasma on the optoelectronic properties of high-quality single-crystalline ZnO.[19,20] We observed, among other effects, that H plasma induces a relative intensity increase in the luminescent features often associated with shallow donors. Thus, in the low temperature (LT) photoluminescence (PL) spectra, the intensity of the peak commonly designated as I_4 (photon energy ~3.363 eV at 4 K) appeared to grow after exposure to the H plasma. Several authors have argued in favor of attributing the I_4 to a neutral donor bound exciton (BEx).[4,21–25] It seems very likely that the I_4-related donors are the shallow donors responsible for the predominantly *n*-type conductivity in otherwise undoped material. The nature of these shallow donors is the primary focus of this letter.

Here, we demonstrate that H-plasma processing introduces changes in both the electrical and optical properties of ZnO that are consistent with the introduction of new shallow donors. Specifically, we show that H-plasma-induced increases in BEx luminescence in ZnO correlate with increases in free carrier concentrations from the Hall effect measurements.

The first set of samples included three single crystal ZnO specimens grown by a chemical vapor transport (CVT)[21] at Eagle-Picher Technologies. They were cut and polished normal to the crystallographic *c* axis and later annealed in air for 30 min at 500, 600, and 700 °C. Results from a similar set of annealed samples appeared previously[23,25] and showed that,

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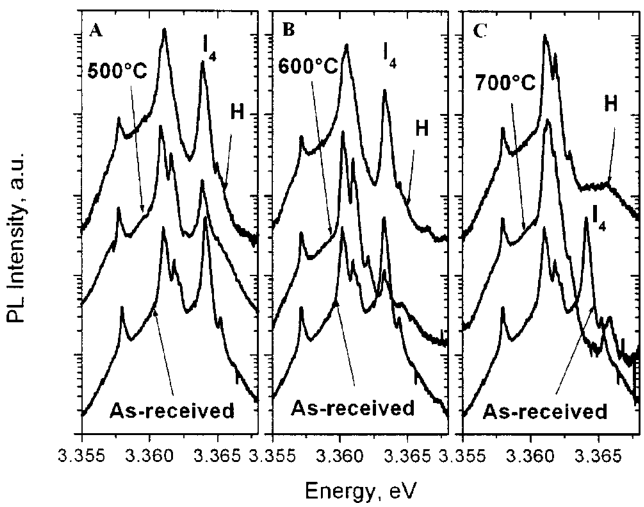

FIG. 1. PL results for the air-annealed CVT samples in the near band edge region, $T=10$ K, incident power=0.2 W/cm^2. The BEx peaks shown for the as-received CVT material are commonly observed. (A) After anneal in air for 30 min at 500 °C, the relative intensity of the I_4 line ($E=3.363$ eV) is reduced. 1 h of remote H-plasma treatment partially restores the intensity of I_4. (B) After anneal in air for 30 min at 600 °C, the I_4 line is not discernible. 2 h of hydrogenation bring back the I_4. (C) After anneal in air for 30 min at 700 °C, the I_4 line is not discernible, 3 h of hydrogenation restore a small shoulder around 3.363 eV.

subsequent to annealing, the BEx region in the LT PL transformed, with the emission intensity shifting towards lower-energy BEx peaks. In particular, the I_4 intensity decreased significantly as annealing temperature increased. The present study reproduced these BEx results.

The three annealed specimens were exposed at room temperature to the remote hydrogen plasma produced by an inductive coupling with a rf generator. The remote plasma was created from hydrogen gas with a pressure of 13 mTorr, flow rate 3 sccm, employing rf power of 40 W and the samples at room temperature. A more detailed explanation of the experimental setup appears elsewhere.[26] Figure 1 shows spectra of the BEx regions for the three samples before and after. In two of the three samples after hydrogenation (A) and (B), the I_4 emission line remarkably regains most of the intensity lost due to thermal treatments. Only a modest increase in I_4 as a shoulder is evident for the specimen annealed at 700 °C (C) following H plasma.

Temperature-dependent Hall measurements were performed on the three air-annealed bulk samples before and after hydrogenation. For experimental details, see Ref. 21. No conspicuous change was recorded for either concentration or mobility of the free charge carriers. An exception was the 700 °C specimen—it showed low-temperature anomalies that a subsequent H-plasma treatment removed. Given the small—tens of nanometers—penetration depth of the H-plasma ions in the ZnO [estimated from our secondary-ion mass spectroscopy (SIMS) data, see also Ref. 27] compared to the thickness of the bulk wafer, the absence of bulk effects is not surprising. In order to detect such Hall variations, one requires either a reduced initial bulk carrier concentration or a reduced thickness of the conductive layer comparable to the diffusion depth of hydrogen species. We report here the results of both approaches using, respectively, bulk CVT-grown ZnO rendered semi-insulating via Li diffusion and using an epitaxial thin film of ZnO on sapphire.

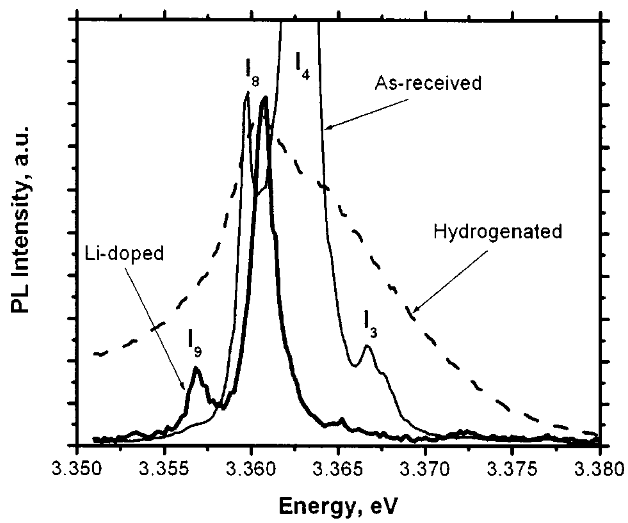

FIG. 2. PL results for the Li-doped CVT sample in the near band edge region, $T=10$ K, incident power=0.2 W/cm^2. After Li-diffusion treatment, the I_4 line is suppressed. Subsequent H-plasma treatment broadens the bound-exciton emission and restores a shoulder at ~3.364 eV.

Figure 2 presents LT PL results for the CVT Eagle-Picher sample that was Li-diffused and then hydrogenated. The Li diffusion was carried out by placing the sample on top of a 2-cm-high open quartz tube, placing LiOH powder in the bottom of the tube, and then heating the whole assembly in a furnace at 800 °C. The as-received ZnO exhibits strong excitonic features, including a pronounced I_4 peak. Li doping removes this I_4 line. Subsequent hydrogenation increases and broadens the BEx features, creating a conspicuous shoulder where the I_4 is expected. Prior to hydrogenation, no Hall measurements were possible, as expected for the semi-insulating Li-doped ZnO crystal. Hydrogenation restores measureable conductivity and Hall coefficient, as shown in Fig. 3. Here, only sheet carrier concentration n_σ can be plotted, since the electrical thickness is not known. However, the rather weak temperature dependence of n_σ suggests that the donor concentration is well above 10^{17} cm^{-3}, the value found before Li diffusion. This observation is consistent with a new donor being added by the

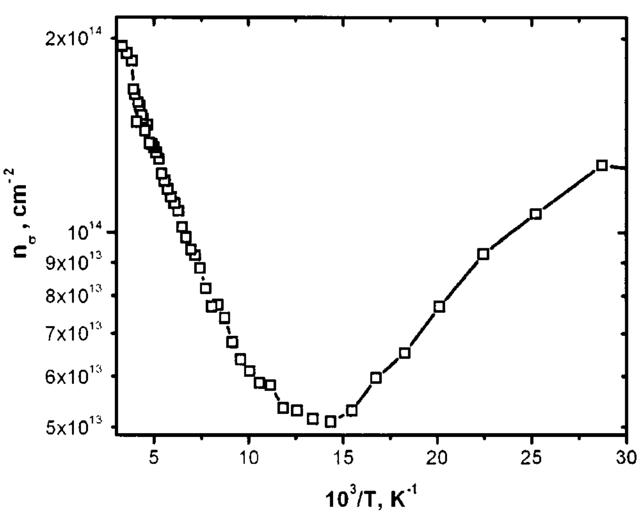

FIG. 3. Sheet carrier concentration for the Li-doped CVT sample after hydrogenation. Hall parameters were unobservable before H-plasma treatment since Li diffusion makes ZnO semi-insulating.

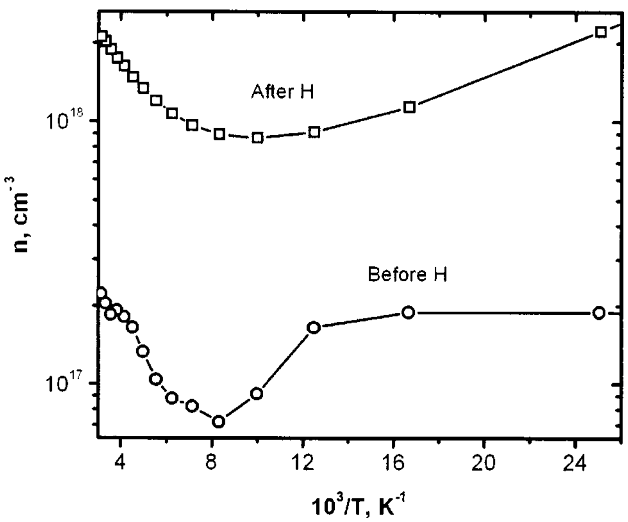

FIG. 4. Hall results for the epitaxial film on sapphire. Remote hydrogen plasma treatment increases free electron concentration by at least an order of magnitude in the entire range of temperatures.

hydrogenation, rather than an alternative explanation in which the Li would simply deplete near the surface and ''re-expose'' the existing donors. Indeed, SIMS measurements of the average surface Li concentration show no such depletion. Furthermore, the mobility is lower than that before Li diffusion, which is consistent with a larger donor concentration as well as the additional acceptors introduced by the Li.

Finally, we hydrogenated a thin film of ZnO grown on sapphire by molecular beam epitaxy.[28] Figure 4 compares its free temperature-dependent Hall carrier concentration plots before and after remote H-plasma treatment. Here, the significant rise in free electron concentration indicates an order of magnitude increase in the number of donors created by hydrogenation. Electron mobility (not shown) also increases after hydrogenation in most of the temperature range. Unfortunately, the excitonic PL emission (not shown) is several meV wide and does not reveal very sharp features such as I_4 either before or after H-plasma treatment. Hydrogen, however, induced observable changes in other parts of the PL spectrum, such as a passivation of the ''green'' band, a higher intensity of the violet/near UV emission, and a suppression of a free exciton recombination, consistent with our previous reports.[19,20]

In summary, we have shown that the remote hydrogen plasma treatment of ZnO is an effective tool to control its transport and optoelectronic properties. The strong dependence of the Hall parameters and the I_4 BEx luminescence on the presence of hydrogen, described above, indicates a convincing connection between the shallow donor and a hydrogen-related impurity.

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[1] C. G. Van de Walle, Phys. Rev. Lett. **85**, 1012 (2000).
[2] C. G. Van de Walle, Physica B **308–310**, 899 (2001).
[3] C. G. Van de Walle, Phys. Status Solidi B **229**, 221 (2002).
[4] K. Thonke, Th. Gruber, N. Teofilov, R. Schonfelder, A. Waag, and R. Sauer, Physica B **308–310**, 945 (2001).
[5] S. F. J. Cox, E. A. Davis, S. P. Cottrell, P. J. C. King, J. S. Lord, J. M. Gil, H. V. Alberto, R. C. Vilao, J. Piroto Duarte, N. Ayres de Campos, A. Weidinger, R. L. Lichti, and S. J. C. Irvine, Phys. Rev. Lett. **86**, 2601 (2001).
[6] S. F. J. Cox, E. A. Davis, P. J. C. King, J. M. Gil, H. V. Alberto, R. C. Vilão, J. Piroto Duarte, N. Ayres de Campos, and R. L. Lichti, J. Phys.: Condens. Matter **13**, 9001 (2001).
[7] D. M. Hofmann, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B. K. Meyer, S. B. Orlinskii, J. Schmidt, and P. G. Baranov, Phys. Rev. Lett. **88**, 045504 (2002).
[8] K. Shimomura, K. Nishiyama, and R. Kadono, Phys. Rev. Lett. **89**, 255505 (2002).
[9] A. Y. Polyakov, N. B. Smirnov, A. V. Govorkov, K. Ip, M. E. Overberg, Y. W. Heo, D. P. Norton, S. J Pearton, B. Luo, F. Ren, and J. M. Zavada, J. Appl. Phys. **94**, 400 (2003).
[10] A. Y. Polyakov, N. B. Smirnov, A. V. Govorkov, E. A. Korzhukova, V. I. Vdovin, K. Ip, M. E. Overberg, Y. W. Heo, D. P. Norton, S. J Pearton, J. M. Zavada, and V. A. Dravin, J. Appl. Phys. **94**, 2895 (2003).
[11] E. V. Lavrov, J. Weber, F. Börrnert, C. G. Van de Walle, and R. Helbig, Phys. Rev. B **66**, 165205 (2002).
[12] Y. Natsume and H. Sakata, J. Mater. Sci.: Mater. Electron. **12**, 87 (2001).
[13] Y. Natsume and H. Sakata, Mater. Chem. Phys. **78**, 170 (2002).
[14] C. H. Seager and S. M. Myers, J. Appl. Phys. **94**, 2888 (2003).
[15] S. Kohiki, M. Nishitani, T. Wada, and T. Hirao, Appl. Phys. Lett. **64**, 2876 (1994).
[16] S. J. Baik, J. H. Jang, C. H. Lee, W. Y. Cho, and K. S. Lim, Appl. Phys. Lett. **70**, 3516 (1997).
[17] B. Theys, V. Sallet, F. Jomard, A. Lusson, J.-F. Rommeluere, and Z. Teukam, J. Appl. Phys. **91**, 3922 (2002).
[18] Z. Zhou, K. Kato, T. Komaki, M. Yoshino, H. Yukawa, M. Morinaga, and K. Morita, J. Eur. Ceram. Soc. **24**, 139 (2004).
[19] Y. M. Strzhemechny, J. Nemergut, J. Bae, D. C. Look, and L. J. Brillson, Mater. Res. Soc. Symp. Proc. **744**, M3.9.1 (2003).
[20] Y. M. Strzhemechny, J. Nemergut, P. A. Smith, J. Bae, D. C. Look, and L. J. Brillson, J. Appl. Phys. **94**, 4256 (2003).
[21] D. C. Look, D. C. Reynolds, J. R. Sizelove, R. L. Jones, C. W. Litton, G. Cantwell, and W. C. Harsch, Solid State Commun. **105**, 399 (1998).
[22] D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, T. C. Collins, W. C. Harsch, and G. Cantwell, Phys. Rev. B **57**, 12151 (1998).
[23] D. C. Look, Mater. Sci. Eng., B **80**, 383 (2001).
[24] D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, Appl. Phys. Lett. **81**, 1830 (2002).
[25] D. C. Look, R. L. Jones, J. R. Sizelove, N. Y. Garces, N. C. Giles, and L. E. Halliburton, Phys. Status Solidi A **195**, 171 (2003).
[26] Original idea suggested in: G. Lucovsky, D. V. Tsu, S. S. Kim, R. J. Markunas, and G. G. Fountain, Appl. Surf. Sci. **39**, 33 (1989).
[27] N. Ohashi, T. Ishigaki, N. Okada, H. Taguchi, I. Sakaguchi, S. Hishita, T. Sekiguchi, and H. Haneda, J. Appl. Phys. **93**, 6386 (2003).
[28] K. Iwata, P. Fons, A. Yamada, K. Matsubara, and S. Niki, J. Cryst. Growth **209**, 526 (2000).