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Remote hydrogen plasma doping of single crystal ZnO

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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 $I_d$ for a variety of ZnO single crystals—bulk air annealed, Li doped, and epitaxially grown on sapphire. Hydrogen increases $I_d$ intensity in conducting samples annealed at 500 and 600 °C and partially restores emission in the $I_d$ 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. © 2004 American Institute of Physics.

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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 suggests hydrogen is a shallow donor impurity rather than a compensating center, a prediction supported by a number of spectroscopic studies. Some electrical measurements are 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. 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 $I_d$ (photon energy $\sim 3.63$ eV at 4 K) appeared to grow after exposure to the H plasma. Several authors have argued in favor of attributing the $I_d$ to a neutral donor bound exciton (BEx). It seems very likely that the $I_d$-related donors are the shallow donors responsible for the predominant $n$-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) 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 and showed that,
subsequent to annealing, the BE\textit{x} region in the LT PL transformed, with the emission intensity shifting towards lower-energy BE\textit{x} peaks. In particular, the $I_4$ intensity decreased significantly as annealing temperature increased. The present study reproduced these BE\textit{x} 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.\textsuperscript{26} Figure 1 shows spectra of the BE\textit{x} regions for the three samples before and after. In two of the three samples after hydrogenation, $I_4$ 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 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.

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 BE\textit{x} 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 $n_s$ can be plotted, since the electrical thickness is not known. However, the rather weak temperature dependence of $n_s$ suggests that the donor concentration is well above $10^{17} \text{cm}^{-3}$, the value found before Li diffusion. This observation is consistent with a new donor being added by the
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. 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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![Figure 4](https://example.com/figure4.png)

**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.

References: