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Shallow Donor Generation in ZnO by Remote Hydrogen Plasma

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We investigate the effects of a remote hydrogen-plasma treatment on Hall parameters as well as on the bound exciton (BEx) photoluminescence (PL) for a variety of ZnO single crystals: bulk air-annealed, Li-doped, and epitaxially grown on sapphire. We present transport and spectroscopic evidence in favor of the hypothesis that hydrogen behaves as a shallow donor rather than a compensating center in ZnO. Specifically, we show that H-plasma-induced increases in I_4 luminescence (photon energy: ~3.363 eV at 4 K) correlate with increases in free-carrier concentrations from Hall-effect measurements.

Key words: ZnO, shallow donor, hydrogen plasma

INTRODUCTION

Zinc oxide is a promising material for new important optoelectronic and spintronic applications. High-quality single crystals with reproducible characteristics emerge as good candidates for room-temperature excitonic lasers as well as ultraviolet emitters and detectors. The area of ZnO-based nanostructures is rapidly expanding. Zinc oxide doped with magnetic impurities demonstrates characteristics of a room-temperature dilute magnetic semiconductor. However, despite all the progress achieved in understanding the fundamental properties of ZnO, many questions on the nature of its conductivity remain open. For instance, high-quality p-type ZnO with reliable and reproducible properties remains a contested goal.

The fact that as-grown ZnO is always an n-type material regardless of the growth techniques poses a critical question of the nature of the dominant donors. The most reliable information about the energy levels of these donors was obtained from recent electrical and optical experiments. Hall measurements reported by Look et al.[1] revealed two shallow donors with energies of ~30 meV and ~60 meV. Similarly, analysis of low-temperature photoluminescence (LT PL) spectra[2,3] indicated two shallow defects with binding energies of ~45–47 meV and ~53–56 meV.

First-principles calculations based on density functional theory (DFT)[4] showed that shallow donors in ZnO caused by native defects (such as Zn interstitials) have relatively high formation energy. By the same token, DFT theory[5] demonstrated that the interstitial non-amphoteric hydrogen donor (H^+) is the only stable charge state of H in ZnO. By and large, hydrogen in ZnO is a common and likely impurity: hydrogen is present practically in any environment; it is involved in material growth, and it is shown to act as a fast-diffusing species in a ZnO matrix.[6,7] Previous spectroscopic studies[2,3,8–15] and electrical measurements[6,14–19] suggest that hydrogen is a shallow donor impurity in ZnO. However, in many of the quoted papers, additional ambiguities

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are introduced because of the polycrystalline nature of samples, the direct plasma exposure or ion implantation involved, as well as lack of correlation between the spectroscopic and electrical properties of the specimens processed with hydrogen. In our studies, we obtain a consistent correlation between spectroscopic and electrical properties of high-quality ZnO single crystals doped with hydrogen employing remote plasma processing. The main advantage of using a remote plasma is a separate control and measurement of temperature and pressure. For direct plasma processing, specimen temperature is determined by the plasma interior, which makes it difficult to differentiate between thermally and chemically driven changes. Previously, we described the effects of remote hydrogen plasma on the optoelectronic properties of high-quality ZnO single crystals.[20–22] In this paper, we provide additional results supporting our findings that remote hydrogen-plasma processing produces changes in both the electrical and optical properties of ZnO that are consistent with the introduction of new shallow donors.

EXPERIMENTAL DETAILS

The first type of ZnO sample included single crystals grown by a chemical vapor transport (CVT) at Eagle-Picher Technologies (Phoenix, AZ). These samples were cleaved from a nominally undoped wafer, then cut and polished normal to the c axis.[1] The second type of specimen was single-crystal thin films (thickness: 0.53 μm) of ZnO grown on sapphire by molecular beam epitaxy (MBE).[23]

The LT PL experiments were conducted independently with two different setups. In the first case, the PL was excited with a HeCd laser, and measurements were made at 2 K with the sample immersed in liquid helium. The spectra were analyzed with a high-resolution 4-m spectrometer equipped with a model R943-02 photomultiplier tube (Hamamatsu Photonics K.K., Iwata-gun, Shizuoka Pref., Japan) for detection. In the second case, a HeCd laser was used. The sample was mounted inside an evacuated cryostat having a temperature range between 9 K and 300 K. A variable frequency chopper was employed to provide the reference signal. The PL signal was probed by an Oriel-257 grating monochromator (Stratford, CT)) having a spectral resolution of ~0.1 nm and detected by a S-20 photodetector. Hall-effect measurements were carried out in a Lake Shore Model 7507 Hall-effect System (Westerville, OH), operating over the temperature range T = 20–320 K. Secondary ion mass spectrometry (SIMS) experiments were performed on a PHI TRIFT III TOF-SIMS instrument (Chanhassen, MN).

Initially, Eagle-Picher CVT samples were annealed for 30 min in air at various temperatures.[24] Subsequently, they were processed in a ultrahigh vacuum chamber with a remote hydrogen plasma. In our experimental setup,[25] a high-grade hydrogen gas was supplied into a vacuum chamber from a Parker-Balston (Cleveland, OH) hydrogen generator through a needle leak valve and a quartz tube inductively coupled with an Advanced Energy RFX-600 radio-frequency (RF) generator (Fort Collins, CO). The plasma flame inside the quartz tube was controlled by the flow rate and pressure of the gas and the power supplied by the RF generator. The hydrogen flow rate, the gate valve on the turbo pump, and the turbo pump speed determined the amount of plasma leaking into the chamber. We employed a remote H plasma with the following parameters: 13 mtorr of pressure, flow rate of 3 sccm, employing RF power of 40 W, and samples at room temperature. The samples were placed ~20 cm downstream from the plasma-generating coil, with the polar Zn surface facing the plasma. The LT PL and T-dependent Hall measurements were taken before and after each stage of processing.

RESULTS AND DISCUSSION

Figure 1 shows LT PL spectra of the bound exciton (BEx) regions for the as-received, air-annealed at 500°C, 600°C, and 700°C, respectively, and subsequently hydrogenated CVT samples. Transformations of the emission line conventionally labeled as I_4 (photon energy: ~3.363 eV at 4 K) yield the most

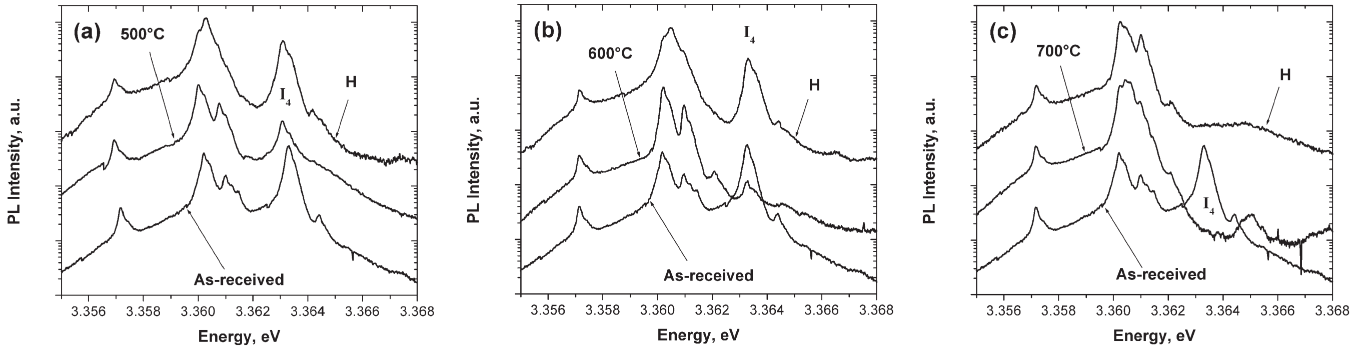

Fig. 1. The LT PL results for the air-annealed CVT samples in the near-band-edge region, T = 4 K. The BEx peaks shown are commonly observed for the as-received CVT material. (a) After anneal in air for 30 min at 500°C, the relative intensity of the I_4 line (~3.363 eV) is reduced. One hour of remote 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 very weak. Two hours 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. Three hours of hydrogenation restore a small shoulder at 3.364 eV.

important information. Several authors have argued in favor of attributing the I_4 to a neutral donor BEx.[1,24,26–29] It seems very likely that the I_4-related donors are among the shallow donors responsible for the predominantly n-type conductivity in otherwise undoped material. Moreover, there have been several recent attributions of this line directly to the H-related donor.[3,30] As seen in Fig. 1a, after air anneal for 30 min at 500°C, the relative intensity of the I_4 line is reduced. We suggest that hydrogen starts diffusing out of the ZnO at this temperature, thus reducing the concentration of excitons bound to hydrogen impurities. One hour of remote H-plasma treatment partially restores the intensity of I_4, indicative of an increased number of H centers for excitonic recombination.

Figure 1b demonstrates similar effects for the ZnO sample that was air annealed for 30 min at 600°C. The I_4 line almost disappeared after annealing, consistent with more hydrogen out-diffusion from the host matrix. After 2 h of hydrogenation, the pronounced I_4 peak reappears. A modest increase in I_4 as a shoulder is evident for the specimen annealed at 700°C (Fig. 1c) following H-plasma treatment.

Temperature-dependent Hall measurements were performed on the air-annealed samples before and after hydrogenation in order to extract carrier concentrations and activation energies. Figure 2 illustrates those measurements for the 500°C air-annealed sample. It is clear that there is no significant change following hydrogenation. Similar results were produced by the samples annealed at different temperatures. At the same time, fitting of the T-dependent data showed that the positions of the two shallow donor levels did not change after hydrogenation and were close to those reported by Look et al.[1] This absence of bulk effects in the Hall results is not surprising because the penetration depth of hydrogen into ZnO is small compared with the thickness involved in the Hall measurement. In the SIMS studies by Ohashi et al.[31] on direct H-plasma-treated ZnO CVT samples, the hydrogen insertion depth was measured to be only ~30 nm, quite small compared to the thickness of the wafer (~0.5 mm). Thus, in order to detect any variations caused by hydrogen, the volume of hydrogenated ZnO must be significant compared with the Hall channel. One approach to achieve this is to reduce the initial carrier concentration of the entire crystal by rendering the bulk single-crystal sample semi-insulating. An alternative approach is to reduce the layer thickness of the semiconductive ZnO so that it is comparable to the insertion depth of hydrogen.

We employed Li doping of the CVT material to produce semi-insulating ZnO samples. The Li diffusion was carried out by positioning 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. After Li processing, no Hall parameters were observable due to the semi-insulating nature of the material. This sample was treated in a remote H plasma for 1 h. Hydrogenation restored measurable conductivity and the Hall coefficient. Figure 3 displays (a) sheet carrier concentration, n_σ, and (b) mobility, μ, as a function of temperature. An ultra-shallow SIMS depth profile was taken on the Li-doped/hydrogenated ZnO specimen. As shown in Fig. 4, the H insertion depth in the case of a remote plasma is ~10 nm, which is somewhat smaller than that for the samples treated with direct plasma.[31] This can be easily explained by the fact that the direct plasma effectively heats up the surface, thus promoting hydrogen diffusion to a greater depth.

Bearing in mind the measured Hall sheet-carrier concentration of 10^{14} cm^{-2} for the Li-doped sample (Fig. 3a) and the measured H insertion depth (~10 nm) (Fig. 4), one finds that the suggested donor concentration at room temperature is at least an order of magnitude higher than the known volume density of 10^{17} cm^{-3} before Li diffusion. The rather weak temperature dependence of n_σ in Fig. 3a is

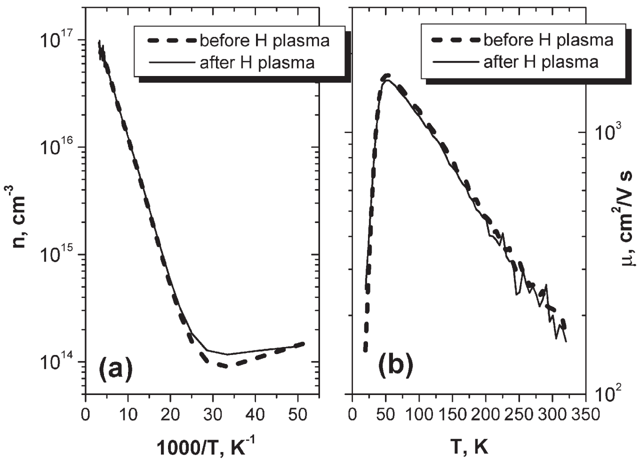

Fig. 2. Hall results for the air annealed at 500°C/hydrogenated CVT sample. (a) Average bulk carrier concentration and (b) mobility seem to be insensitive to the remote H-plasma treatment.

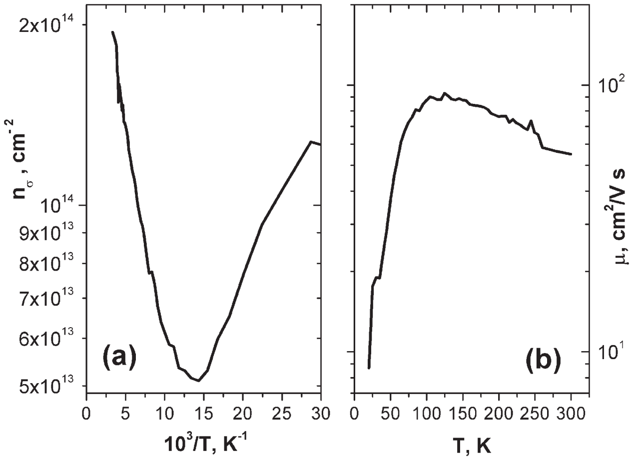

Fig. 3. (a) Sheet-carrier concentration and (b) mobility for the Li-doped CVT sample after hydrogenation. Hall parameters were unobservable before H-plasma treatment because Li treatment makes ZnO semi-insulating.

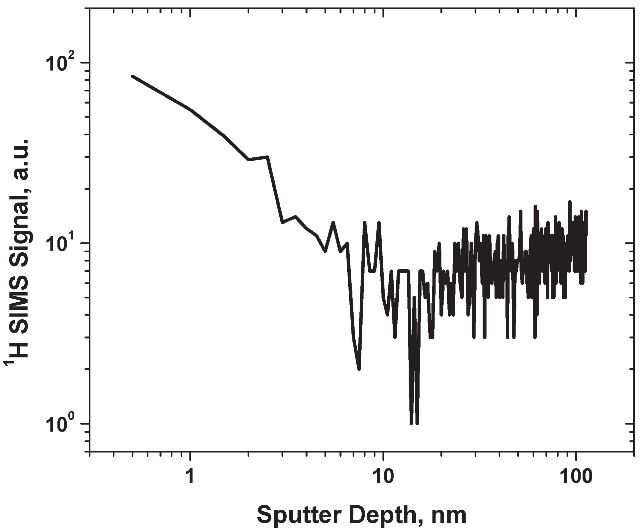

Fig. 4. The H^1 SIMS depth profile of the Li-doped CVT sample after H-plasma treatment. The insertion depth of hydrogen is ~10 nm.

consistent with this higher volume concentration compared with the bulk sample in Fig. 2a. The lack of significant change in the Hall curves of Fig. 2a is understandable because the remote plasma is capable of creating additional sheet concentration only slightly greater than 10^{14} cm^{-2}, while even in the annealed samples the sheet-carrier concentration associated with the bulk donors is almost 10^{16} cm^{-2}.

We performed LT PL measurements on the Li-doped/hydrogenated ZnO sample before and after each processing stage. The results are shown in Fig. 5. After Li diffusion, the I_4 line is absent. We argue that this may be the result of either H out-diffusion caused by high processing temperature or the Li passivation of the donors, or both. Subsequent H-plasma treatment restores a conspicuous shoulder at ~3.364 eV, where the I_4 was expected. This shoulder is similar to the one seen in Fig. 1c, where the annealing temperature was close to the Li in-diffusion temperature. In Figs. 3 and 5, the weakness and broadening of the I_4 emission may be explained by the fact that its PL signal is coming only from the topmost layers of the surface (~100 nm) where the quality of the material is inferior to that of the bulk.

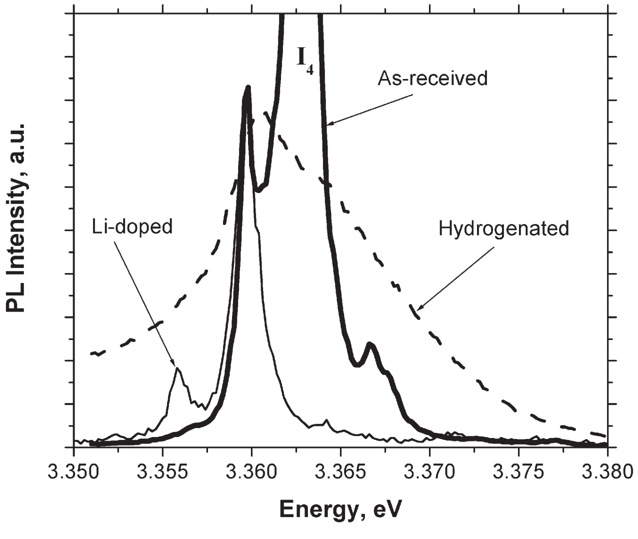

Fig. 5. The LT PL results for the Li-doped CVT sample in the near-band-edge region, T = 10 K and incident power = 0.2 W/cm^2. After Li diffusion treatment, the I_4 line is suppressed. Subsequent H-plasma treatment broadens the BEx emission and restores a shoulder at ~3.364 eV.

The results for the Li-doped/hydrogenated sample are 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, our 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.

The second approach in altering the Hall experiment geometry was to use a thin ZnO film on an insulating substrate. This scheme was realized with a 530-nm-thick, high-quality, ZnO single-crystal MBE-grown on sapphire. Hall measurements were performed before and after hydrogenation (Fig. 6). One can see that hydrogen plasma increases free-electron concentration by at least an order of magnitude in the entire range of temperatures. This effect may be even more extensive if one accounts for the shallow, e.g., ~10 nm, hydrogen insertion depth. In the LT PL spectra, the original line width of the BEx features was too great to discern changes occurring with hydrogenation. In this case, the concentration of shallow donors introduced by H-plasma treatment is much higher than the bulk concentration of the as-received epitaxial film. For this sample, however, as opposed to the Li-doped sample discussed earlier, we are able to observe a direct electronic change caused by the introduction of hydrogen donors.

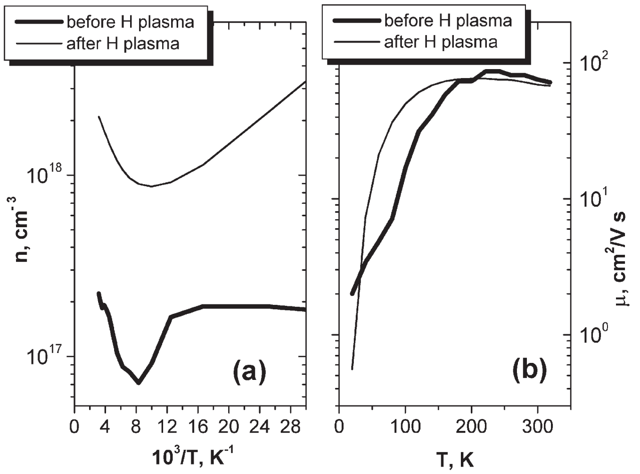

Fig. 6. Hall results for the epitaxial film on sapphire: (a) average bulk carrier concentration and (b) mobility. Remote H-plasma treatment increases free-electron concentration by at least an order of magnitude in the entire range of temperatures.

SUMMARY

We have demonstrated that the remote H-plasma treatment is an effective tool to control the transport and optoelectronic properties of ZnO. The strong dependence of the Hall electrical transport parameters and I_4 BEx luminescence on the introduction and removal of hydrogen provides a clear confirmation of the theoretical prediction that hydrogen acts as a shallow donor impurity in ZnO.

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