Supporting Information

Distribution pattern and allocation of defects in hydrogenated ZnO thin film

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Table S1. DLE/NBE emissions intensity ratios of ZnO thin film before and after thermal treatment in hydrogen

<table>
<thead>
<tr>
<th>Sample</th>
<th>DLE/NBE intensity ratio</th>
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<tbody>
<tr>
<td>ZnO</td>
<td>0.41</td>
</tr>
<tr>
<td>ZnO-H/350 °C</td>
<td>1.06</td>
</tr>
<tr>
<td>ZnO-H/400 °C</td>
<td>1.15</td>
</tr>
<tr>
<td>ZnO-H/450 °C</td>
<td>1.28</td>
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Fig. S1 Cross-section SEM image of as-deposited ZnO thin film.
Fig. S2. XRD patterns of ZnO thin films. (a) as-deposited, and hydrogenated at (b) 350 °C, (c) 400 °C, and (d) 450 °C.
SIMS depth analysis and measurement of surface electrical current by PF-TUNA (Figs. S3 and S4)

The depth profiles of ZnO before and after thermal treatment were assessed by the SIMS analysis. For clear interpretation and better understanding of the data, the oxygen signal was deliberately excluded from the depth profiles since “SIMS analysis of oxygen in oxides” can lead to “systematic errors in the quantitative data interpretation” due to “secondary ion interaction and signal saturation”. As can be seen (Fig. S3), the as-deposited ZnO already contains a sufficient amount of so-called “hidden” hydrogen which is always present in as-prepared ZnO in the form of neutral interstitial hydrogen. Notably, the accumulation of hydrogen on the surface is higher than that in the bulk. After annealing, the concentration of hydrogen in ZnO decreases by one order of magnitude. This phenomenon can be referred to the heating and cooling ZnO film in vacuum (more details can be found in Experimental) which results in almost complete desorption of so-called “hidden” and a certain part of adsorbed hydrogen, respectively. Furthermore, the SIMS depth profiles also demonstrate that the amount of surface and bulk hydrogen after treatment becomes relatively comparable which can be explained by the out diffusion of hydrogen due to the high temperature treatment.
The SIMS analysis also confirms continuous slight etching of ZnO by hydrogenation at different temperatures. As can be seen from Fig. S3, the thicknesses of the film before and after hydrogenation at 350 °C, 400 °C, and 450 °C are ~93, ~90 nm, ~83 nm, and ~78 nm, respectively. It represents decrease of band-edge recombinations in the bulk,\textsuperscript{4} which contributes to reduced NBE emission in the PL spectra.

To better understand the influence of hydrogenation on the change of carrier concentration in ZnO, the surface electrical currents were measured. As can be seen from Fig. S4, the as-deposited ZnO shows a maximum current amplitude at about 180 pA. On the other hand, after thermal treatment in hydrogen at 350 °C, 400 °C, and 450 °C, the maximum current amplitudes reach 1.4 nA, 1.3 nA, and 2.0 nA, respectively. Thus, the surface electrical conductivity is increased by several times after thermal treatment which verifies the dominant presence of oxygen vacancies and substitutional hydrogen in ZnO and their role as shallow donors.\textsuperscript{5,6}
Fig. S3 SIMS depth profiles of ZnO thin films. (a) as-deposited, and hydrogenated at (b) 350 °C, (c) 400 °C, and (d) 450 °C.
Fig. S4 Two-dimensional maps of peak currents measured by PF-TUNA on ZnO films. (a) As-deposited, and hydrogenated at (b) 350 °C, (c) 400 °C, and (d) 450 °C.
References


