Spectroscopic Studies of Hydrogen Dopants in ZnO Crystals

by

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I, Laurent Olivier Lee Cheong Lem, declare that this thesis titled, ‘Spectroscopic Studies of Hydrogen Dopants in ZnO Crystals’ and the work presented in it are my own. I confirm that:

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Abstract

ZnO is a semiconductor with a direct band gap of 3.37 eV and an exciton binding energy of 60 meV at room temperature. These properties make it an attractive material for optoelectronic devices across a wide range of applications. Significant obstacles preventing the wide scale usage of ZnO include the lack of reliable p-type doping and high uncertainty surrounding the nature of its defects. Moreover, as-grown ZnO is intrinsically n-type and it is thought that hydrogen is the cause for the high n-type character.

The aim of this thesis is therefore to elucidate the role of hydrogen with respect to the optical and electrical properties of ZnO as well as its interaction with native defects and impurities.

During this work, hydrogen was introduced in ZnO single crystals through an RF plasma source. Hydrogen incorporation was confirmed by XPS measurements which showed an increase in hydrogenated oxygen states. Hydrogen also modified the near-surface region of the crystals only and not the bulk.

Hydrogen doped ZnO showed significant increases in the carrier concentration as well as in the near band edge (NBE) luminescence. This is attributed to hydrogen introducing new shallow donors. The green luminescence, whose origin is attributed to V_{Zn}, was quenched after hydrogen incorporation, indicating formation of neutral V_{Zn}-H$_2$ complexes. The yellow luminescence in the as-received crystal is identical to that in Li doped ZnO and was assigned to recombinations involving Li$_{Zn}$.

Hydrogen doped ZnO also exhibits a negative thermal quenching (NTQ) of the NBE luminescence where the intensity of the luminescence increases with increasing temperature. Q-DLTS measurements detected new electronic states being created following hydrogen incorporation. A model involving the H-related state
at 11 meV releasing electrons to form free excitons is proposed to explain the NTQ behaviour.

XANES studies of H-doped ZnO showed that hydrogen interacted with oxygen states only but not zinc. This suggests that most of the hydrogen dopants introduced by plasma sit at the oxygen anti-bonding site.

The recombination kinetics of the various luminescence was investigated. While the kinetics of the NBE luminescence followed the expected behaviour for excitonic type recombination, the green and yellow luminescences showed high temperature dependencies and is explained in terms of different recombination mechanisms.

Finally, it was found that hydrogen is stable under normal SEM excitation conditions.
Acknowledgements

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<tr>
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<th>Description</th>
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<tbody>
<tr>
<td>$A^0X$</td>
<td>Neutral acceptor bound exciton</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ASF</td>
<td>Atomic sensitivity factor</td>
</tr>
<tr>
<td>BX</td>
<td>Bound exciton</td>
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<tr>
<td>C-DLTS</td>
<td>Capacitance-based deep level transient spectroscopy</td>
</tr>
<tr>
<td>CB</td>
<td>Conduction band</td>
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<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
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<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
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<tr>
<td>CL</td>
<td>Cathodoluminescence</td>
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<td>$D^{+}X$</td>
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<td>DAP</td>
<td>Donor-acceptor pair</td>
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<tr>
<td>DRCL</td>
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<tr>
<td>EPR</td>
<td>Electron paramagnetic resonance</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
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<td>FX</td>
<td>Free exciton</td>
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<td>IMFP</td>
<td>Inelastic mean free path</td>
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<tr>
<td>LED</td>
<td>Light emitting diode</td>
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<tr>
<td>LO</td>
<td>Longitudinal optical</td>
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<td>LVM</td>
<td>Local vibration mode</td>
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<td>NBE</td>
<td>Near band edge</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>---------</td>
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<td>Q-DLTS</td>
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<tr>
<td>sccm</td>
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<tr>
<td>SEM</td>
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