Enhancement of the UV Emission in Metal Nanoparticle-Coated ZnO

by

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A thesis submitted in partial fulfilment for the degree of Doctor of Philosophy in the School of Mathematical and Physical Sciences Faculty of Science

2018
Declaration of Original Authorship

I, Saskia Fiedler, declare that this thesis titled, “Enhancement of the UV Emission in Metal Nanoparticle-Coated ZnO”, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mathematical and Physical Sciences, Faculty of Science at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis. This document has not been submitted for qualifications at any other academic institution.

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Date: 04/10/2018
Abstract

Large emission enhancement factors resulting from orders of magnitude increases in ultra-violet (UV) luminescence in ZnO have been reported, due to the presence of a surface coating of either Au or Al nanoparticles. Two significantly different models have been proposed to explain the observed increase in the UV light output. One involving the decay of metal nanoparticles localised surface plasmons (LSP) into hot carriers and their radiative recombination following injection into the ZnO conduction and valence bands. The other describes the creation of an additional fast relaxation pathway via a dipole-dipole coupling mechanism between excitons in ZnO and the metal nanoparticle LSPs, resulting in an improved ZnO UV spontaneous emission rate. This work specifically addresses this significant discrepancy in the existing literature, that reports metal nanoparticle-induced light emission in ZnO.

The UV emission enhancement mechanism between a-plane ZnO single crystals and ZnO nanorods coated with Al and Au nanoparticles were systemically investigated in this thesis, using cathodoluminescence (CL) and photoluminescence (PL) spectroscopy in conjunction with ellipsometry, optical absorption and synchrotron valence band spectroscopy measurements. Significantly novel concurrent CL-PL techniques were also employed in this study. The presence of both metal surface films was found to enhance the ZnO UV emission. Moreover, changes to the surface band bending induced by the metal coating was confirmed and their effect on visible deep level (DL) defect related ZnO emission and surface electronic properties was considered.

For 5 nm-Au nanoparticle-coated ZnO nanorods, an up to 3.8-fold enhanced UV emission with no change in the intensity of the visible defect luminescence due to deep level recombination: quenching of the DL is hallmark characteristic of the hot carrier model. The underlying UV enhancement effect was found to be excitation depth-dependent with the largest enhancement being observed with light generation at the surface, closest to the ZnO-Au interface. Concurrent CL-PL showed that UV emission of the Au nanoparticle-coated ZnO samples under simultaneous electron beam and laser irradiation is identical to the electron beam excitation alone, confirming that while LSPs are created in the Au nanoparticles, hot electrons are not injected into the conduction band of the ZnO. Furthermore, time-resolved PL measurements at 10 K revealed that the presence of the Au nanoparticle surface coating on ZnO nanorods produced a 40 ps reduced lifetime compared with the uncoated side of the sample. The corresponding Purcell enhancement
factor of only 1.4 is much lower than the observed UV enhancement of up to 3.8, indicating that the LSP-exciton coupling is not the cause of the UV enhancement. The findings collectively confirm that neither of the two reported models can be responsible for the observed UV enhancement in these samples. Consequently an alternate mechanism is proposed which is consistent with all of the experimental results. This model suggests that the interband transitions in Au in the UV spectral range, from the 5d band to the partly filled 6sp conduction band, can be excited by the exciton emissions in ZnO via a resonance energy transfer mechanism. The creation of this additional, faster relaxation channel increases the exciton spontaneous emission rate, enhancing the observed UV emission of Au nanoparticle-coated ZnO.

In the case of the Al-coating, $a$-plane ZnO single crystals and ZnO nanorods were coated with a 2 nm thin Al film, resulting in an up to 12-fold enhancement of the UV PL emission. The increase was attributed to a strong Al LSP-exciton coupling mechanism. Additionally, below 80 K, the in-diffusion of the Al into the ZnO was found to contribute to measured increase in the total UV emission by increasing the Al $I_6$ bound exciton luminescence. The maximum UV enhancement was found at 80 K, where the bound excitons (BX) in ZnO are mostly thermally dissociated and the luminescence spectra are dominated by the free exciton (FX) emission. The LO-phonon replicas of the FX were also highly-enhanced by the Al-coating, indicating that the LSPs in the Al nanoparticles couple more favourably to the FX in the ZnO than to the BX. It was also found that the LSP-coupling to one of the three A, B and C FXs in ZnO is dependent on the ZnO crystal orientation and thereby the polarisation of the FX in ZnO with respect to the incident laser light. Furthermore, the strength of the LSP-exciton coupling was found to be dependent on the carrier density of ZnO with samples having higher carrier densities exhibiting a greater UV enhancement.

In conclusion, ZnO planar and nanorod samples coated with both Au and Al nanoparticles thin films in this work resulted in a large UV enhancement, arising from two different processes. The UV enhancement of the Au nanoparticle-coated ZnO samples was attributed to interband transitions in the Au nanoparticles, while the origin of the UV enhancement of the Al-coated ZnO samples was assigned to LSP-exciton coupling to preferably the FX in ZnO. The results of this thesis provide insight into why different explanations for the observed metal nanoparticle-induced emission enhancement in ZnO exist in the literature and why comprehensive characterisation of the structural and physical properties of both the ZnO and the metal nanoparticle ZnO composite is essential to establish the exact identity of the primary enhancement mechanism.
To my family — Mama, Papa and Nils.
Acknowledgements

I would like to sincerely thank my supervisor Prof. Matthew R. Phillips for his excellent guidance, support and motivation throughout the 3.5 years at UTS. I am truly grateful that he shared his knowledge and so many stories, particularly on traveling, with me in our weekly meetings! Thanks for helping me to get through the difficult and stressful times — you were always my point of reference.

I would also like to express my thanks to my co-supervisor Assoc. Prof. Cuong Ton-That for his comments and suggestions, particularly on the XPS data.

Special thanks to Dr. Olivier Lee Cheong Lem, who has been a constant source of motivation and great support — I could not have done it without you!

Furthermore, I would like to thank my great colleagues at UTS, especially Dr. Sejeong Kim for her help with the plasmonic simulations, and Dr. Carlo Bradac — you are a true source of inspiration.

Many thanks for the exceptional assistance and support at the UTS Microstructural Analysis Unit, particularly Katie McBean — thanks for proofreading my thesis in a very stressful time, as well as being a great boxing partner. Additionally, I wish to thank Geoff McCredie and Dr. Angus Gentle for their help with all technical issues I encountered during my time at UTS and their excellent support with ellipsometry, UV-Vis spectroscopy and the deposition of metals.

Furthermore, I would like to thank Marie Wintrebert-Fouquet from BluGlass for taking her time to help me with the Hall effect measurements.

I would like to extend my thanks to the great technical support at the Australian Synchrotron and Christian Clarke for collecting last minute XPS data for my thesis.

Special thanks to Markus Schleuning for spending so much time on collecting the time-resolved PL spectra in Berlin, as well as Prof. Axel Hofmann and his group for technical assistance at the Technische Universität Berlin, Germany.

To Prof. Igor Aharonovich for many stimulating discussions and fantastic scuba diving at Gordon’s Bay.

In addition, I wish to thank the Australian Research Council for the financial support during my time at UTS (DP150103317).

Finally, I would like to thank all my friends for being the best I could wish for. In particular, my friends back home for always being supportive, although being on the other
side of the globe, Constanze Matthai, Isabelle Hoffmann, Jacqueline Heu, Nadine Roche, Uta-Pari Kohlhoff and Valentina Ellinghaus.

Thanks for proofreading, Nina Schwarz and being a wonderful friend and dive buddy. Special thanks to Yvonne Bartling, who has become one of my best friends in Sydney in no time; thanks for not only sharing the horse love with me but also Jersey and Lulu.

Steve van den Berg, I am very grateful for your love and great support, especially during the very stressful times. Thanks for being the amazing person you are!

Last but not least, I would like to thank my family, my dad Michael Jansen, my mum Renate Fiedler and my brother Nils Fiedler, for always supporting me and my goals in life, although being 16 000 km away from home. I wish to thank my dad for being supportive in many ways; and I am very grateful for endless conversations on the phone with my mum, her kindness and love. Thanks to my loving brother for always being there for me and for traveling the world together.
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List of Abbreviations

ABX   Neutral Acceptor Bound eXciton
AFM   Atomic Force Microscopy
ALD   Atomic Layer Deposition
ASF   Atomic Sensitivity Factor
BSE   Back Scattered Electrons
BX    Bound eXciton
CCD   Charge-Coupled Device
CL    CathodoLuminescence
DBX   Donor Bound eXciton
DAP   Donor-Acceptor Pair
DL    Deep Level
EL    ElectroLuminescence
EQE   External Quantum Efficiency
FDTD  Finite-Difference Time-Domain
FWHM  Full Width at Half Maximum
FX    Free eXciton
GL    Green Luminescence at 2.3 eV
GL₁   Green Luminescence at 2.45 eV
HMT   HexaMethyleneTetramine
IQE   Internal Quantum Efficiency
LED   Light Emitting Diode
LEE   Light Extraction Efficiency
LO    Longitudinal Optical
LSP   Localised Surface Plasmon
LSPR  Localised Surface Plasmon Resonance
MFP   Mean Free Path
MQW   Multiple Quantum Well
NBE   Near Band Edge
ND    Neutral Density
OL    Orange Luminescence
PL    PhotoLuminescence
RL    Red Luminescence
sccm  standard cubic centimetres per minute
SE    Secondary Electrons
SER   Spontaneous Emission Rate
SEM   Scanning Electron Microscopy
SPP   Surface Plasmon Polariton
SX    Surface eXciton
TES   Two-Electron Satellite
TE Transverse Electric
TEM Transmission Electron Microscopy
TM Transverse Magnetic
TR-PL Time-Resolved PhotoLuminescence
UV Ultra-Violet
UV-Vis Ultra-Violet Visible
XPS X-Ray Photoelectron Spectroscopy