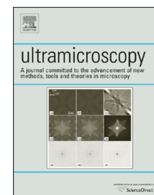
Ultramicroscopy 176 (2017) 93–98

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic



The atomic structure of polar and non-polar InGaN quantum wells and the green gap problem

C.J. Humphreys [a,*], J.T. Griffiths [a], F. Tang [a], F. Oehler [b], S.D. Findlay [c], C. Zheng [d], J. Etheridge [e], T.L. Martin [f], P.A.J. Bagot [f], M.P. Moody [f], D. Sutherland [g], P. Dawson [g], S. Schulz [h], S. Zhang [a], W.Y. Fu [a], T. Zhu [a], M.J. Kappers [a], R.A. Oliver [a]

[a] Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge CB3 0FS, UK
[b] CNRS/C2N, Paris Sud University, Route de Nozay, 91460 Marcoussis, France
[c] School of Physics and Astronomy, Monash University, Victoria 3800, Australia
[d] Monash Centre for Electron Microscopy, Monash University, Victoria 3800, Australia
[e] Department of Materials Science and Engineering, Monash University, Victoria 3800, Australia
[f] Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK
[g] School of Physics and Astronomy, Photon Science Institute, University of Manchester, Manchester M13 9PL, UK
[h] Tyndall National Institute, Lee Maltings Complex, Dyke Parade, Cork, Ireland

ARTICLE INFO

Article history:
Received 18 August 2016
Received in revised form
10 January 2017
Accepted 22 January 2017
Available online 3 February 2017

Keywords:
Gallium nitride
Atomic structure
Quantum wells
Quantitative STEM
Aberration-corrected electron microscopy

ABSTRACT

We have used high resolution transmission electron microscopy (HRTEM), aberration-corrected quantitative scanning transmission electron microscopy (Q-STEM), atom probe tomography (APT) and X-ray diffraction (XRD) to study the atomic structure of (0001) polar and (11-20) non-polar InGaN quantum wells (QWs). This paper provides an overview of the results. Polar (0001) InGaN in QWs is a random alloy, with In replacing Ga randomly. The InGaN QWs have atomic height interface steps, resulting in QW width fluctuations. The electrons are localised at the top QW interface by the built-in electric field and the well-width fluctuations, with a localisation energy of typically 20meV. The holes are localised near the bottom QW interface, by indium fluctuations in the random alloy, with a localisation energy of typically 60meV. On the other hand, the non-polar (11-20) InGaN QWs contain nanometre-scale indium-rich clusters which we suggest localise the carriers and produce longer wavelength (lower energy) emission than from random alloy non-polar InGaN QWs of the same average composition. The reason for the indium-rich clusters in non-polar (11-20) InGaN QWs is not yet clear, but may be connected to the lower QW growth temperature for the (11-20) InGaN QWs compared to the (0001) polar InGaN QWs.

© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Bob Sinclair and Nestor Zaluzec have pioneered the use of electron microscopy and analysis to characterise the structure of materials at the nanoscale. High resolution electron microscopy has been central to the research of Sinclair, particularly aberration-corrected transmission electron microscopy. He has utilised high resolution electron microscopy to analyse a wide range of materials and devices, from seminal work on silicide thin-films on silicon [1] to quantum dots in living mice [2].

Zaluzec has developed state-of-the-art instrumentation for electron and X-ray spectroscopy, and analytical electron microscopy. He has recently investigated how aberration-corrected transmission electron microscopes can be re-engineered to improve the sensitivity of spectroscopy in analytical modes. He has studied a wide range of materials, from ground-breaking research on high-T_c superconductors [3] to InGaN quantum wells in light emitting diodes [4].

The present paper reports some of our research on the unusual atomic structure of InGaN quantum wells, which relates to the work of Zaluzec [4] and for which aberration-corrected electron microscopy has been essential.

* Corresponding author.
E-mail addresses: colin.humphreys@msm.cam.ac.uk (C.J. Humphreys), jg641@cam.ac.uk (J.T. Griffiths), ft274@cam.ac.uk (F. Tang), fabrice.oehler@lpn.cnrs.fr (F. Oehler), scott.findlay@monash.edu (S.D. Findlay), changlin.zheng@monash.edu (C. Zheng), joanne.etheridge@mcem.monash.edu (J. Etheridge), tomas.martin@materials.ox.ac.uk (T.L. Martin), paul.bagot@materials.ox.ac.uk (P.A.J. Bagot), michael.moody@materials.ox.ac.uk (M.P. Moody), danny.sutherland@manchester.ac.uk (D. Sutherland), philip.dawson@manchester.ac.uk (P. Dawson), stefan.schulz@tyndall.ie (S. Schulz), siyuan.zhang@mpie.de (S. Zhang), wyfu@hku.hk (W.Y. Fu), mjk30@cam.ac.uk (M.J. Kappers), rao28@cam.ac.uk (R.A. Oliver).

http://dx.doi.org/10.1016/j.ultramic.2017.01.019
0304-3991/© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

2. The surprising success of InGaN quantum wells

The use of InGaN light emitting diodes (LEDs) in solid state lighting and high brightness displays is rapidly increasing [5], and it seems likely that InGaN LEDs will become the dominant form of lighting throughout the world, saving over 10% of electricity globally and 10% of carbon emissions from power stations. At the heart of these LEDs are polar InGaN/GaN quantum wells (QWs) which emit visible light with high internal quantum efficiency (IQE). For example, such blue light emitting LEDs can exhibit IQE values as high as 90% at room temperature [6]. This high efficiency is surprising because the lattice mismatch of GaN on sapphire (the usual substrate in commercial GaN LEDs) is 16%, which leads to a high density of misfit dislocations at the GaN/sapphire interface and to threading dislocations passing through the InGaN QWs with a density of at least $10^8 cm^{-2}$. In other light-emitting semiconductors, such as GaAs, the dislocation density needs to be less than $10^3 cm^{-2}$ to prevent significant loss of light due to the non-radiative recombination of carriers at the dislocations. It is known from cathodoluminescence (CL) studies that dislocations in InGaN are non-radiative recombination centres. Hence a key question is why the efficiency of blue emitting InGaN/GaN LEDs is so high when the dislocation density is so large.

3. The green gap problem in LEDs

White LEDs used for lighting typically use a blue-emitting InGaN/GaN LED covered with a yellow emitting phosphor, the combination of blue and yellow light producing a cool white light. If a warmer white light is desired, a red emitting phosphor is used as well. However, the obvious way to produce white light is to mix red, green and blue LEDs. This would produce even more efficient white light than using a blue LED with phosphors because the Stokes shift energy loss of converting a high energy blue photon to a lower energy yellow or red photon would be avoided, as would efficiency losses in the phosphors themselves. However, we cannot do this efficiently at present due to the “green gap” problem. The experimentally determined external quantum efficiency (EQE) of 400nm (violet) LEDs is very high, over 80%, and for 650nm (red), it is also very high, over 70%, but for green and yellow emission the EQE drops to about 20% [7]. This “Green Gap” has important technological consequences. If one wishes to make white light by mixing red, green and blue LEDs, one red, one blue and three green LEDs are typically required, making such a white light source expensive.

The green gap in nitride LEDs may in part be attributed to internal electric fields due to the large spontaneous and piezoelectric polarisations that produce high fields of $\sim 10^6 Vcm^{-1}$ across the QWs. The active region in nitride LEDs is one or more InGaN QWs sandwiched between the wider bandgap GaN barriers to confine the carriers. The epitaxial InGaN QWs are strained because InGaN has a larger lattice parameter than GaN. Commercial InGaN/GaN QW LEDs are grown in the polar [0001] direction. The strain in an InGaN QW increases as the indium content increases, hence the piezoelectric field across an InGaN QW increases as the indium content increases. This field separates the electrons and holes to opposite sides of the QW, the separation increasing as the indium content increases. Hence the electron-hole wave-function overlap decreases as the indium content increases. This may result in the efficiency of InGaN/GaN green LEDs being less than that of blue LEDs because the decreased electron and hole overlap in green QWs results in increased radiative lifetimes, which in the presence of non-radiative recombination paths can lead to reduced values of the IQE and EQE. The electric field across an InGaN QW can be suppressed by growing the InGaN/GaN QW structure along a non-polar direction. This would be expected to produce green LEDs with high efficiency, hence we have recently explored this and obtained some surprising results.

4. The atomic structure of polar

It was realised as long ago as 1997 that since blue InGaN QWs emitted brilliant light despite having a very high density of dislocations, and since cathodoluminescence showed that dislocations were non-radiative recombination centres in InGaN, there must be some microstructural feature of the InGaN QWs that was localising the carriers and preventing them from moving to the dislocations. There was at the time broad agreement in the GaN scientific community that indium-rich clusters in the InGaN QWs were responsible for localising the carriers [8-16]. Since the bandgap of InN is smaller than that of GaN, indium-rich clusters in an InGaN QW will have a smaller bandgap and hence localise the carriers. The widespread belief in this localisation mechanism was based upon three pieces of scientific evidence. First, high resolution transmission electron microscopy (HRTEM) revealed localised regions of strain contrast about 2nm across which were interpreted as being highly indium rich. This was supported by data from electron energy loss spectroscopy (EELS) [8-16]. Second, photoluminescence (PL) measurements of the temperature dependence of the peak photon energy emitted from an InGaN QW revealed an S-shaped dependence characteristic of carrier localisation [17]. Thirdly, thermodynamic calculations revealed that InGaN was an unstable alloy which would decompose into indium rich and indium poor regions [18]. These three independent pieces of evidence appeared to provide strong scientific support for there being gross indium-rich clusters in InGaN QWs, and this was universally accepted by the scientific community.

In 2003, it was shown that InGaN QWs were extremely sensitive to radiation damage in TEM and that HRTEM images acquired immediately after first irradiating a region of an InGaN QW showed no detectable indium-rich regions [19-21]. The papers further revealed that continued exposure to the electron beam led to the formation of locally strained regions that appeared similar to those previously attributed to indium rich clusters. So it was concluded that the indium-rich clusters observed by many others were due to electron beam damage. This was subsequently supported by multiple research groups by a variety of methods [22-27].

However, InGaN can decompose if there are macrosteps on the growth surface, since indium is incorporated differently at treads and risers of these macrosteps, which leads to compositional growth striations [28]. A recent example of this is atomic-level ordering in InGaN quantum dots in GaN nanowires. This was attributed to a non-flat growth front at vicinal surface facets [29]. In other recent work, indium fluctuations were observed in InGaN/GaN core-shell nanorods, and these were correlated with atomic steps at the GaN/InGaN core-shell interface giving rise to a change in the growth mode from 2D (planar) to 3D (faceted) [30]. Apart from these examples of faceted growth, there is now almost universal acceptance that in (0001) InGaN quantum wells grown by 2D layer-by-layer growth, as in planar LEDs, there are no gross indium-rich clusters.

Galtrey et al [31] used atom probe tomography (APT) not only to confirm that there were no indium-rich clusters in (0001) InGaN QWs but also to demonstrate that InGaN was a random alloy. APT was also used to show that an electron beam in TEM can create In-rich clusters in InGaN [32]. These results appeared to conflict with the thermodynamic calculations that showed that InGaN should decompose into indium rich and indium poor regions at the growth temperature used [18]. However, these

Download English Version:

https://daneshyari.com/en/article/5466886

Download Persian Version:

https://daneshyari.com/article/5466886

Daneshyari.com