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OCCURRENCE OF 'ACCIDENTAL' InN QUANTUM DOTS IN INDIUM GALLIUM NITRIDE/GALLIUM NITRIDE HETEROSTRUCTURES

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ABSTRACT

Nakamura and co-workers were first to report the observation of spontaneously formed In-rich clusters in InGaN quantum wells (QW), using transmission electron microscopy (TEM) [1,2]. Some of the present authors have argued that the exceptional optical efficiency of nitride devices is due to the presence of nearly pure InN QD which form accidentally during crystal growth [3]. Pure InN QD with very small radius would emit light in the required spectral region, under the opposing effects of intrinsic electric fields and quantum confinement [4]. We have recently used extended X-ray absorption fine stucture to examine nanostructure [5] of molecular beam epitaxial (MBE) quantum boxes (QB), and photoluminescence excitation spectroscopy to examine their optical properties [6]. As revealed by AFM, QB are densely packed mesoscopic structures, 10-40 nm wide and 2-3 nm high. Our analysis of the QB EXAFS shows that the filling factor is of order 1%: e*ach QB therefore contains a single QD*. The optical evidence suggests that InN dots may be *cubic*. In contrast, TEM shows that QD in thick epilayers are sparsely distributed [7]. We re-examine recent TEM data on QW in the light of these results.

INTRODUCTION

At most temperatures of growth, InGaN is not thermodynamically stable. Like vinegar mixed with oil, InN is expected to form a suspension in GaN. Quantum dots might form as 'droplets' of such a suspension. The observation of a distinctive nanostructure in InGaN was first posited by Chichibu et al. in 1996 [1]. Cross-sectional transmission electron microscopy (TEM) images of InGaN quantum well (QW) showed a number of distinct spots, about 3 nm in diameter, which were attributed to indium rich regions resulting from partial phase separation of InGaN alloy. By using energy dispersive x-ray spectroscopy (EDX), Narukawa et al. [2] later confirmed the existence of structured regions of indium-rich material in InGaN QW. Transmission electron micrographs of strongly luminescent InGaN epilayers also reveal objects, that may be identified as quantum dots: these dots are a few nm wide and well separated [7]. Whether any of the observed microscopic objects can be shown to be *responsible* for InGaN luminescence is still an open question. However, the localisation of excitation in InN-rich regions is believed to provide an explanation for the efficient optical luminescence of InGaN [3,4].

Recently, a few crystal growth teams have developed techniques of nanostructure fabrication, which favour self-organised 'island' growth. As applied to nitrides, self-assembly of InGaN 'quantum boîtes (boxes)', QB, with radii about 50 nm and less than 5 nm thick, and of different mean composition from the surroundings, may be compared with the decomposition that occurs spontaneously during conventional growth of luminescent quantum wells. While the commercial nitride devices are all grown by MOCVD, quantum boxes are generally grown using MBE [8]. Engineered quantum dots are expected to play an increasing role in the development of future optoelectronic (and spintronic) semiconductor devices, perhaps even exceeding the successes enjoyed by quantum wells in the past 20 years. Their attraction is therefore partly commercial. In addition, the materials physics of nanostructures is far from well understood.

SAMPLE DETAILS AND EXPERIMENTAL TECHNIQUES

In this presentation, we compare extended X-ray absorption fine structure (EXAFS) of an InGaN QB sample, 12 monolayers (ML) thick and containing nominally 25% of InN, with that of an $In_{0.25}Ga_{0.75}N$ epilayer and an InN sputtered film, obtained in previous work [9]. **Note that measurement of the ultrathin MBE sample necessitated the summing of 220 individual spectra, each of which required an acquisition time of about 10^3 s.**

EXAFS provides a unique probe of local structure on an atomic length scale. The local environment of a probe atom in a solid influences its X-ray absorption spectrum (XAS) and introduces a series of intensity oscillations above the characteristic edge. The fine structure oscillations are due to interference between outgoing and reflected photoelectron waves. The indium K-edge has an energy of about 28 keV, making it necessary to use a synchrotron source of tunable X-rays to achieve sufficient brightness to carry out the XAS measurement in a reasonably short time (minutes to hours). In samples that are dilute with respect to the probe species, it is preferable to monitor the absorption strength via the X-ray fluorescence (XRF) yield: this is the technique, used here, of FLEXAFS.

The EXAFS results were supported by microspectroscopic measurements, carried out using the SYCLOPS microscope, described previously at this meeting [10] and by conventional photoluminescence excitation (PLE) studies of the same or similar samples [6].

EXPERIMENTAL RESULTS

Figure 1 shows the experimental XAS of the QB sample. In order to carry out structural analysis, XAS, which is a function of photon energy, must be transformed into EXAFS, a function of excess photoelectron momentum, as shown in Figure 2. The fit of the resulting oscillations to a three-shell model, carried out by using EXCURV98 [11], is also shown on the figure. A Fourier Transform of the EXAFS spectrum produces an atomic radial distribution function (RDF), which provides an approximate but convenient visualisation of the atomic shells of neighbours in the vicinity of the probe atom. Figure 3 compares the RDF of the QB sample with that of a 25% alloy and with that of a sputtered InN film [9]. While the In-N1 bond lengths are similar in these different samples, the second shell In-M1 distances are markedly different.

Table 1 summarises the data analysis for three samples of interest, in a simple tetrahedral geometry that does not distinguish the wurtzite and cubic lattices. (A good summary of the geometrical properties of nitride semiconductors can be found in Ref. 12.) The InGaN epilayers all show In and Ga in a common metal shell, at a distance that varies only weakly with the InN content of the films, from 3.26(3) Å in ~17% alloy to 3.29(3) Å in ~39% alloy. These distances compare to Vegard's law estimates of ~3.24 Å and ~3.32 Å, respectively. In-edge EXAFS cannot be used to determine the InN content of InGaN alloys when it falls below about 10-15%.

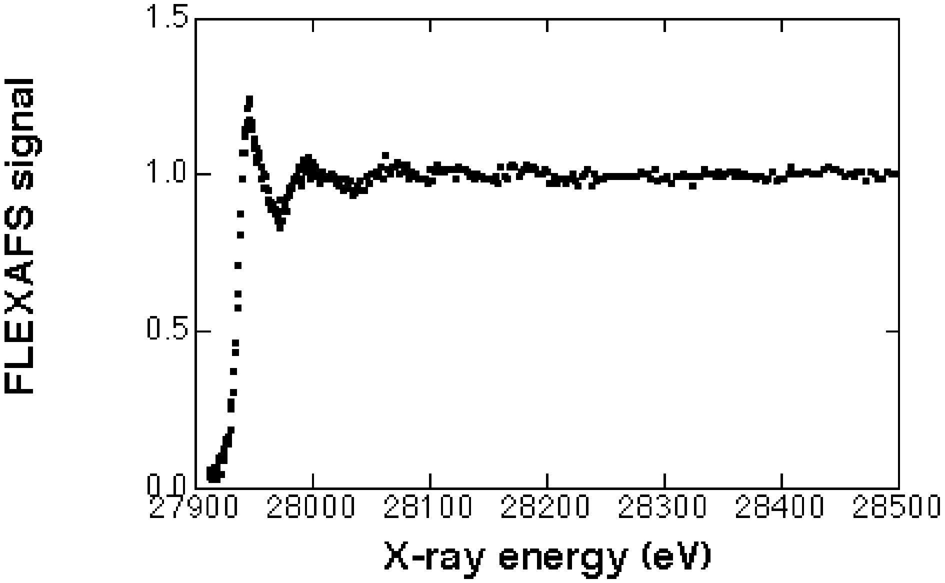

Figure 1. X-ray absorption of an InGaN “quantum boite”, showing EXAFS oscillations above the In K-edge.

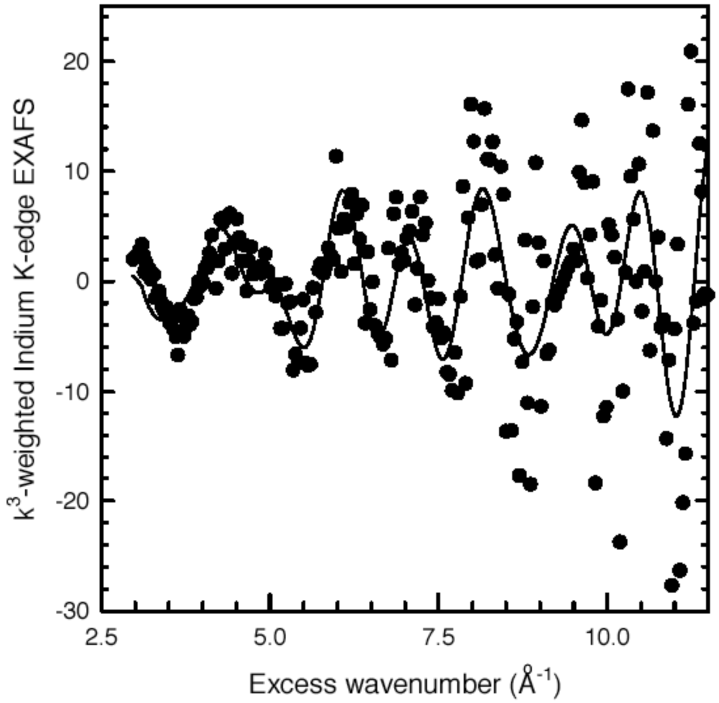

Figure 3. EXAFS oscillations, derived from the XAS of the QB sample, and a three-shell fit to the data (see text and Table 1).

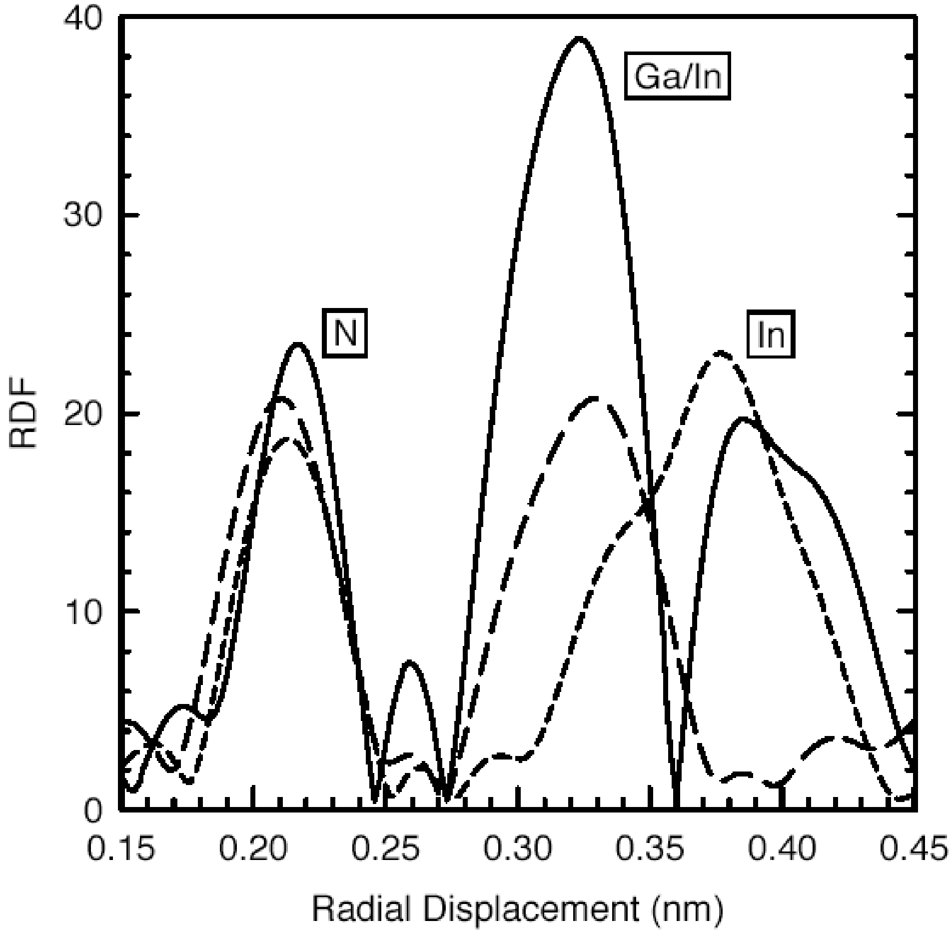

Figure 3. Radial Distribution Functions derived from EXAFS of InGaN QB (——), InGaN epilayer (———) and InN sputtered film (-----).

	In-N1 distance/ Å N	In-M1 distance/ Å N	In-M2 distance/ Å N
InN sputtered film	2.16(2) 4	3.53(3) 12	
25% InGaN epilayer	2.11(2) 4	3.28(3) 3.1 In 8.9 Ga	
25% InGaN QB	2.10(2) 4	3.22(3) 7.4 Ga	3.56(3) 4.6 In

Table 1: Fitting parameters of EXAFS data for 3 comparable samples.

The composition estimates otherwise agree with those determined by using widely accepted techniques, such as Rutherford backscattering spectrometry (RBS).

In strong contrast to the alloy, EXAFS of the QB sample shows at least 3 clear shells of neighbours within a radius of about 4.5 Å from the Indium target. The inner metal shell contains only Ga atoms, while the outer shell contains In, constrained by the requirement that N(Ga1) + N(In1) = 12. The two metal shells are located at ~3.2 Å and ~3.5 Å, respectively.

DISCUSSION AND CONCLUSIONS

We conclude that there are two distinct environments for In atoms in QB material. One is InN-like, while the other resembles the In environment in an indium-poor InGaN alloy, with a mean second shell separation of 3.21 Å. According to Vegard's law, this value of lattice constant would correspond to a relaxed alloy with an indium nitride fraction of 6%. The relative amounts of indium in the two phases is in the ratio [InN]:[InGaN] ~ 4.6: 7.4 = 0.6, which implies that the InN phase occupies only a small fraction of the total volume of the QB material. We can estimate the filling fraction only if we know the composition of both phases. If we assume that there is spinodal decomposition *on a nanometre scale,* the dots will be 94% indium nitride and the filling fraction is 4%. This figure is in remarkably good agreement with that estimated by direct TEM observation in References [1,2]. Moreover, TEM composition measurements also support the picture of nearly pure InN dots embedded in alloy that was first advanced in Reference [3]. Comparing the volumes of boxes and dots, we find that each box contains about one dot on average. PLE measurements [6] further suggest that the limiting energy of these dots corresponds to the band gap of *cubic* GaN.

ACKNOWLEDGEMENTS

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