Direct experimental observation of the local electronic structure at threading dislocations in metalorganic vapor phase epitaxy grown wurtzite GaN thin films

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The electronic structure of pure edge threading dislocations in metalorganic vapor phase epitaxy grown wurtzite GaN thin films has been studied directly by atomic resolution *Z*-contrast imaging and electron energy loss spectroscopy in a scanning transmission electron microscope. Dislocation cores in *n*-type samples grown in N-rich conditions show no evidence for the high concentration of Ga vacancies predicted by previous theoretical calculations. Nitrogen *K*-edge spectra collected from edge dislocation cores show a sudden and significant increase in the intensity of the first fine-structure peak immediately above the edge onset compared to the bulk spectra. The origin of this increase is discussed. © *2000 American Institute of Physics.* [S0003-6951(00)03404-5]

The benign effect of high density of threading dislocations[1] on GaN high efficiency light emitting diodes has led to considerable interest in determining their fundamental properties. Although early work[1,2] suggested that threading dislocations are not nonradiative recombination centers, the increase in optical properties that is achieved[3] by reducing the threading dislocation density in the epitaxial lateral overgrowth method,[4] provides circumstantial evidence that dislocations do have a deleterious effect. Furthermore, recent more direct evidence indicates that threading dislocations *can* be optically and electrically active. In particular, atomic force microscopy (AFM) combined with cathodoluminescence (CL)[5] and plan-view transmission electron microscopy (TEM) combined with CL[6] clearly show threading dislocations to be related to dark spots in band edge emission CL images. This effect is consistent with theoretical calculations suggesting that dislocations should be charged depending on doping and growth conditions.[7,8] The presence of charged dislocations is further supported by low transverse mobility measurements,[9] near surface electrical properties observed by AFM and scanning capacitance microscopy,[10] and selective photoelectrochemical etching.[11] These observations have been used in calculations of dislocation scattering.[12] However, our detailed experimental results show that the density of acceptor states must be less than is assumed in these calculations.

Our experiments used both a 200 kV JEOI 2010F and a 300 kV VG HB603U field emission microscope, which have point resolutions of $\sim$0.14 nm operating in scanning model.[13,14] This experimental setup allows atomic resolution imaging and spectroscopy to be obtained. The incoherent ''*Z*-contrast'' image[15] of a threading dislocation along the *c* axis is used to determine the core structure and position the electron probe for electron energy loss spectroscopy (EELS).[16] Core loss EELS probes the unoccupied density of states near the conduction band minimum and is exactly analogous to near edge x-ray absorption spectroscopy (XAS), but with a much higher spatial resolution afforded by the microscope. Here, EELS spectra were acquired directly from the dislocation core and compared with bulk spectra taken from no more than 2 nm away. The sample under investigation in this work was grown on a sapphire substrate by low-pressure metalorganic vapor phase epitaxy under a nitrogen rich (high V/III ratio) growth condition and doped with Si at a level of $\sim 2\times 10^{18}\,\mathrm{cm}^{-3}$. The free carrier mobility is about 200 $\mathrm{cm}^2/\mathrm{V\,s}$. The threading dislocation density was determined by TEM to be $\sim 3\times 10^{11}\,\mathrm{cm}^{-2}$, with the majority being pure edge dislocations.

Pure edge dislocations can be distinguished from those with a screw component by differences in the strain contrast in TEM images.[17] Figure 1(a) shows a two beam bright field image of the sample tilted close to the zone axis $[1\bar{1}02]$ and imaged with $\mathbf{g}=(1\bar{1}0\bar{1})$. Both pure edge and mixed type dislocations are visible in this image, but they have markedly different diffraction contrast. The mixed type exhibits strong contrast at both ends, as is indicated by the black arrows in Fig. 1(a), while the pure edge dislocations show no such contrast (as is indicated by a white arrow). This same lack of strain contrast is also observed in the *Z*-contrast image which means that by choosing only the dislocations that exhibit the smallest contrast in the end-on *Z*-contrast images [Fig. 1(b)], we are able to select pure edge dislocations.

The core structure of such a dislocation is shown in Fig. 2(a), and clearly shows the eight-fold ring structure, as previously reported.[13] On the basis of the prior theoretical calculations, this *n*-type sample grown under N-rich growth conditions is expected to show the Ga-vacancy core structure. Since atoms contribute to the image according to their

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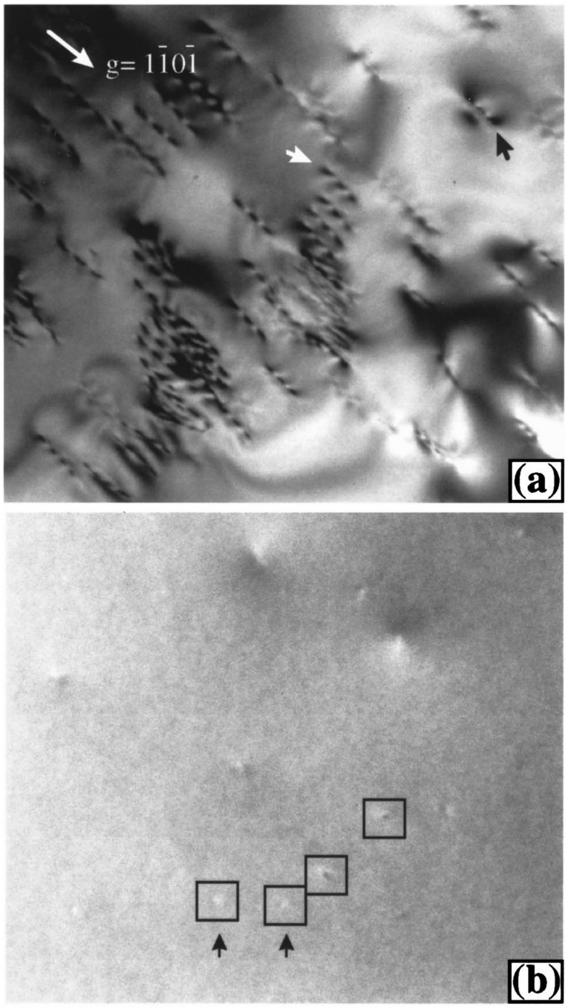

FIG. 1. (a) Two beam bright field image of a plan view sample tilted close to the [1–102] zone axis showing the different diffraction contrast from a pure edge dislocation (indicated by a white arrow) and a mixed type dislocation (indicated by a black arrow). (b) *Z*-contrast image obtained at the exact [0001] zone axis. The end-on dislocations are indicated for clarity.

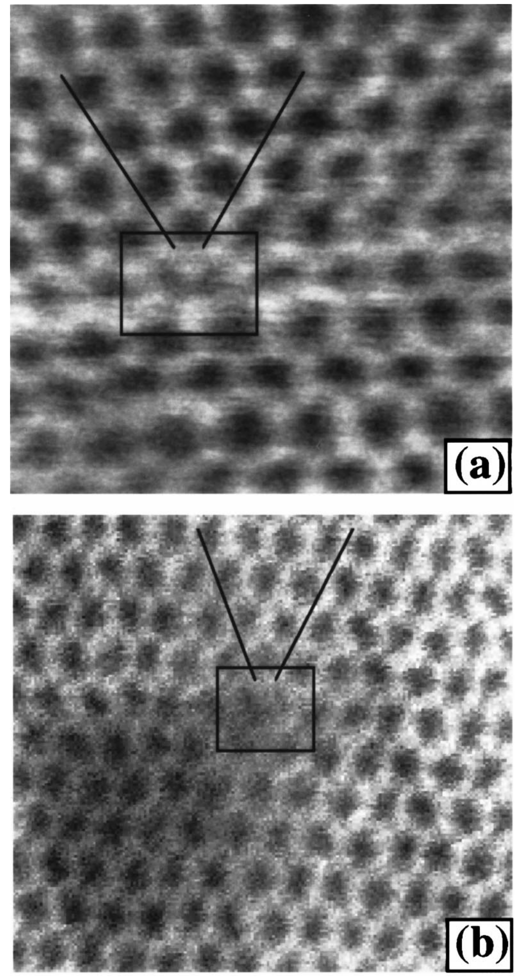

FIG. 2. *Z*-contrast images of pure edge dislocations obtained with (a) the 0.14 nm probe in the VG Microscopes HB603 showing the presence of a core column and (b) the 0.2 nm beam in the JEOL 2010F used for EELS.

mean square atomic number (*Z*), the light N atoms contribute only 5% of the image contrast in a full GaN atomic column. Thus, it is immediately apparent from the image that the Ga vacancy concentration must be much less than 100%. At the typical thicknesses used for *Z*-contrast imaging, the image intensity is roughly proportional to the number of atoms in a column.[15] Therefore, our sensitivity to Ga vacancies is limited just by the statistical varyiations in column intensities close to the dislocation core. Integrated columnar intensities were obtained from a maximum entropy analysis[13] and showed a mean deviation of 15%. From this data we therefore estimate Ga vacancy concentration in the range 0%–15% per *c*-axis repeat, implying a significantly lower line charge than previously assumed for threading dislocations.

In order to investigate the local electronic structure of the dislocations, we chose to use the nitrogen *K*-edge spectrum. This absorption edge gives information on transitions from the 1*s* core level to the unoccupied density of states in the conduction band with 2*p* symmetry. Figure 2(b) shows the dislocation image obtained from the 2010F with the larger beam diameter used for EELS, and Fig. 3(a) shows experimental nitrogen *K*-edge spectra obtained from several pure edge dislocation cores as well as nearby perfect regions of the film for comparison. Each spectrum is the summation of 13 spectra from 8 dislocation cores with an acquisition time of 5 s for each individual spectrum. The energy resolution is 1.2 eV (as measured from the full width at half maximum of the zero loss peak). Other than a power law background subtraction,[18] the spectra are as acquired.

It can be clearly seen that there are dramatic changes in the fine structure of the nitrogen *K*-edge spectra on and off the dislocation core. In particular, in the core spectrum, the first peak 2.2 eV above edge onset (398 eV) rises significantly relative to the second peak. It should be noted that the fine structure changes observed here are significantly different from the effects of beam damage, which can therefore be excluded.[19] In addition, the change in fine structure is only observed if we position the probe exactly on the core (a misplacement of the probe by as little as 0.6 nm means that the spectrum does not show the increase in the first peak). Simulations of the electronic structure using the multiple scattering methodology of the FEFF eight codes[20] are shown in Fig. 3(b). These simulations take account of the collection conditions on the relative weighting of the in-plane and *c*-axis component of the experimental spectrum[21] and show a similar trend to the experimental results.

The increase in absorption just beyond the band gap is most likely due to the broken symmetry in the region of the

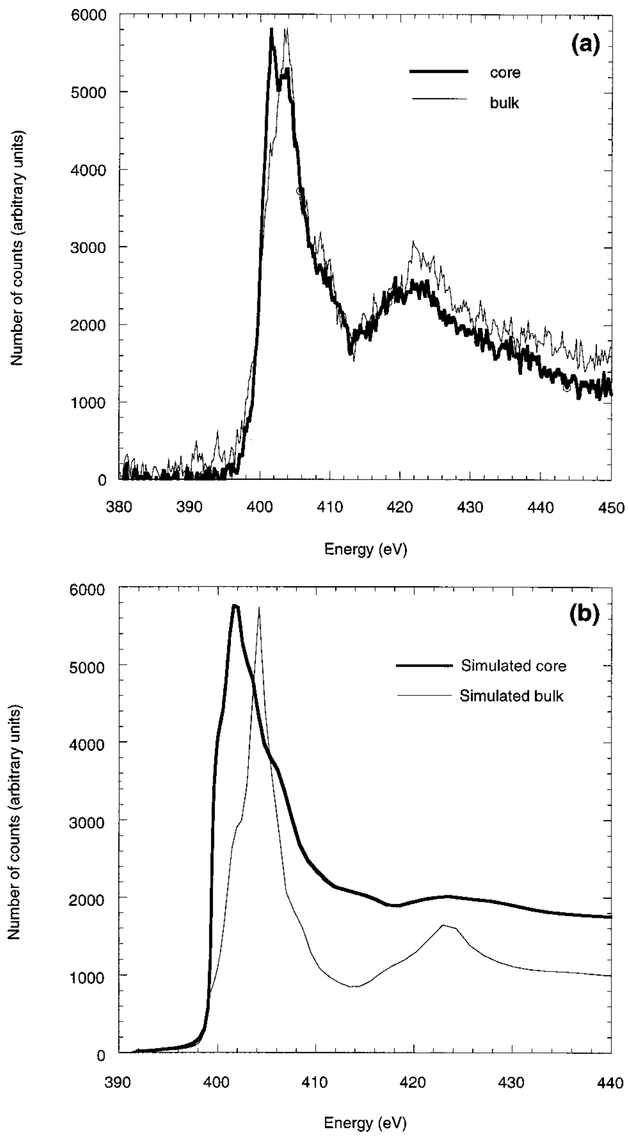

FIG. 3. (a) EELS spectra obtained from the pure edge dislocation (arrowed) and (b) nearby bulk compared to multiple scattering simulations.

core. Studies of the polarization dependence of XAS have shown the first peak of the spectrum to correspond to transitions to final states in the c direction, i.e., to states that originate from the mixing of s and p_z molecular orbitals, while the second peak is related to final states in the $a-b$ plane, i.e., from the mixing of p_x and p_y orbitals.[22] By comparison of Fig. 3(a) with XAS nitrogen K-edge spectra[23] it is clear that the general shape of the acquired EELS data is very similar to the x-ray absorption spectrum obtained when the photoelectric vector, **E**, is perpendicular to the c axis. This is not surprising as the effective collection angle used in this experiment (~40 mrad) is much larger than the characteristic angle, $\theta_E = 1$ mrad, and therefore momentum transfer perpendicular to the beam (i.e., c axis) should swamp the component parallel to the c-axis.[21] This strong increase of states along the c axis, i.e., more $s-p_z$ hybridization, is also seen in the cubic form of GaN, and it therefore most likely just reflects the broken C_{6v} symmetry of the core. It is noteworthy that no absorption is seen in the band gap. This is consistent with any Ga vacancy induced acceptor states being full, as expected if the dislocation line is charged, or may be simply due to a low matrix element between the core states and the defect states. A full understanding of this subtlety requires extensive *ab initio* simulations.

In conclusion, we show that pure edge threading dislocations in n-type GaN grown under N-rich conditions have a Ga vacancy concentration of 0%–15% in the core, significantly less than previously assumed. EELS studies show a significant increase in the first peak above the nitrogen K-edge onset at the dislocation core compared to the perfect region, reflecting the reduced C_{6v} symmetry of the core. No absorption was observed below the band gap, consistent with the dislocation line being negatively charged.

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