Evidence for molecular N_2 bubble formation in a (Ga,Fe)N magnetic semiconductor

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Introduction

Fe-doped GaN semiconductors are of interest for combining the properties of semiconductors and magnetic materials [1,2]. Depending on the growth temperature used, Fe can either be distributed homogenously in the GaN host lattice or it can accumulate in the form of Fe-N nanocrystals. As a result of the small size of the nanocrystals and the sensitivity of Fe-doped GaN to specimen preparation for electron microscopy, the formation and physical properties of Fe-N nanocrystals in GaN are not yet fully understood.

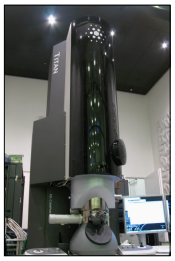
Fe-doped GaN

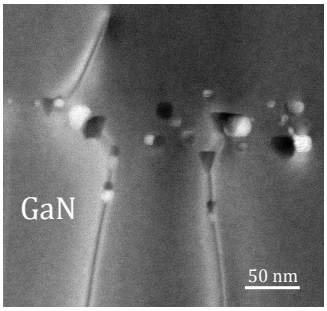
Fe-doped GaN layers were grown by metalorganic chemical vapour deposition on (001) plane sapphire at a substrate temperature of 800-1050℃. The growth conditions, the effect of growth temperature and the results of magnetic measurements are described elsewhere [2].

(S)TEM characterisation

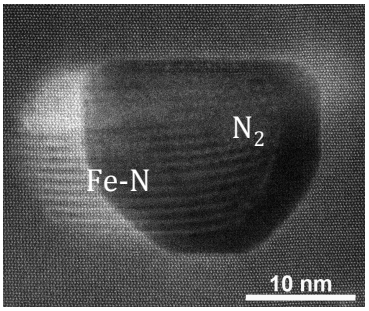
Cross-sectional (Ga,Fe)N samples were prepared using mechanical polishing and Ar ion milling with a Fischione 1010 system. Each cross-sectional specimen was finished by low-energy Ar ion milling at 500 eV in order to minimize sample damage.

TEM studies were carried out using FEI Tecnai G2 and Titan microscopes, with the latter equipped with a monochromator, energy dispersive x-ray spectroscopy, electron energy-loss spectroscopy and probe aberration corrector.
The dedicated EELS experiments were performed on 5th-order aberration corrected Nion UltraSTEM at acceleration voltage of 100 kV.





ADF STEM image of Fe-N precipitates and N_2 bubbles.



ADF STEM image of an Fe-N nanocrystal and an associated N_2 bubble.

Fe-N precipitates in the GaN matrix were observed using several TEM techniques. Precipitates larger than 10 nm were associated with molecular N_2 filled bubbles, while particles without N_2 bubbles typically had sizes of ≈5 nm. The precipitates were identified as hexagonal ε-Fe_3N (P6322, a=0.474 nm c=0.44 nm) and γ-Fe_4N (Pm-3m , a= 0.379 nm)

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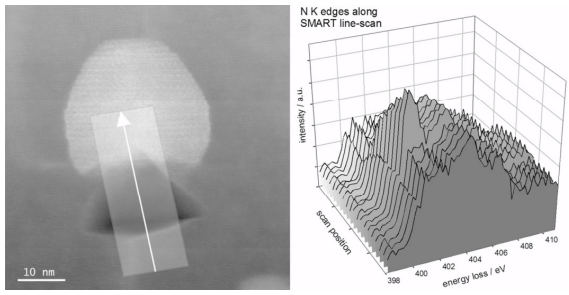
References

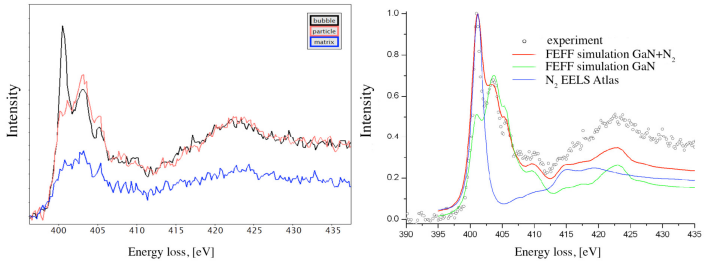
[1] A. Bonanni and T. Dietl, *Chem. Soc. Rev.* **39**, 528 (2010)
[2] A. Navarro-Quezada et al., Phys. Rev. B **81**, 205026 (2010)
[3] K. Sader, et al. *Ultramicroscopy* **110,** 998 (2010)

STEM EELS experiment

A dedicated EELS study in SuperSTEM facility was performed across a single Fe-N nanocrystal associated with a N_2 bubble embedded in the GaN host. A 100 kV acceleration voltage and a distributed-dose acquisition routine [3] was used to either minimize or control electron beam induced damage during the experiment.



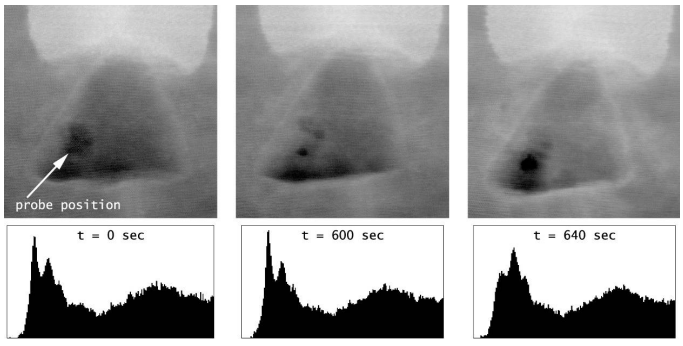
HAADF STEM image and line-scan EELS measurement of an Fe-N nanocrystal associated with a N_2 bubble in GaN. The EELS spectra acquired from the area indicated by the box. A systematic change in the N *K* edge fine structure.



Background-subtracted N *K* edge spectra measured from the Fe-N nanocrystal, N_2 bubble and GaN host lattice. The N K edge shows a typical three-peaked structure between 400 and 407 eV. A Characteristic strong first peak was observed in the EELS spectrum measured from the N_2 bubble. The N spectrum for GaN was calculated using self-consistent real space multiple-scattering calculations using FEFF 9.05, which allows to include the experimental conditions.

The "Puncture" experiment

Direct evidence for the presence of N_2 gas was provided by using the electron beam to puncture the bubble and to release the gas into the microscope. We used a static sub-Angstrom beam with a current of ~350 pA to make a hole, while recording EELS spectra every 40 seconds.



ADF STEM images and EELS of the N edge recorded during the experiment. The intensity of the first characteristic peak of the N K edge was observed to decrease suddenly when the gas was released.

Summary

- electron microscopy techniques have been used to identify and characterise Fe-N nanocrystals associated with N_2 bubbles in GaN.
- N K ELNES measurements and simulations verify the existence of N_2 gas bubbles associated with many larger Fe-N nanoparticles.
- A controlled beam-damge "puncture" experiment further verifies the existence of the N_2 gas bubbles.