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Radiation Physics and Chemistry 75 (2006) 1635–1637

Radiation Physics and Chemistry

www.elsevier.com/locate/radphyschem

Nitrogen defect levels in InN: XANES study

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Accepted 27 July 2005

Abstract

The local and electronic structure of nitrogen-related defects in thin film of InN (0 0 0 1) has been studied using synchrotron-based X-ray absorption near edge structure (XANES) spectroscopy. Several defect levels within the band gap and the conduction band of InN were clearly resolved in XANES spectra around the nitrogen K-edge. Theoretical analysis of XANES data includes advanced "ab initio" simulations: self-consistent full multiple scattering calculations using muffin-tin approximation, non-muffin-tin finite difference approach to study the influence of non-muffin-tin effects on XANES shape as well as advanced local density approximation scheme for optimization of initial geometry around nitrogen defects. Theoretical analysis of XANES data allows to attribute the level observed at 1.7 eV above the conduction band mimimum to antisite nitrogen and a sharp resonance at 3.2 eV above the conduction band minimum to molecular nitrogen.
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PACS: 61.10.Ht

Keywords: Defects; InN; XANES

1. Introduction

The interest in InN has increased significantly (Bhuiyan et al., 2003) during the last few years as rapid advances in thin film deposition techniques have led to much better quality samples, leading to the more consistent information on properties of InN. In order to fully realize the potential of InN, a fundamental understanding of point defects and surface and interface properties is required (Van de Walle and Neugebauer, 2004), as these may control some vital characteristics of nitride semiconductors, ranging from the type of conductivity to the dopant diffusion. InN is the least studied of the group III-nitrides and there are almost no reports on experimental observation of defects in InN. To our knowledge, the present work provides the first direct experimental identification and characterization of point defects in InN and formation of molecular nitrogen below the surface of ion-bombarded InN. Point defects, such as interstitials and antisites, are also known to form quite efficiently in the nitride semiconductors under ion-bombardment (Jiménez et al., 1997). Both nitrogen interstitials, vacancies

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0969-806X/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.radphyschem.2005.07.021

and antisites can be created simultaneously within the collision cascade by displacement of nitrogen atoms from their original crystalline sites. X-ray absorption Near Edge structure (XANES) spectroscopy (and close to it EELS method) is a powerful method to study the electronic structure of unoccupied electronic states for InN (Mkhoyan et al., 2003; Lee et al., 2004). Recently it was shown that NEXAFS can be used for the analysis of fine details of local structure around specific atomic site (Smolentsev et al., 2005; Chan et al., 2005).

Here we report direct observation of nitrogen interstitials and antisites as well as molecular nitrogen in ion-bombarded InN, using synchrotron-based XANES spectroscopy.

2. Methods

The InN(0 0 0 1) samples used in this study were 750 nm thick and grown with unintentional n-type doping (carrier concentration of $10^{19}\,cm^{-3}$) by plasma assisted molecular beam epitaxy on a sapphire substrate with a GaN(0 0 0 1) buffer layer (Kinsey et al., 2004). All measurements were performed in a UHV chamber attached to beam line 24A1 of the National Synchrotron Radiation Research Center, Taiwan, equipped with microchannel plates detector for XANES measurements and a low-energy ion gun for sample bombardment with nitrogen or argon ions. XANES spectra were recorded in the surface-sensitive partial electron yield (PEY) (with the cutoff kinetic energy of 100 eV).

For theoretical simulations of the N K-edge XANES spectra we have used two approaches: (1) full multiple scattering (MS) theory within muffin-tin (MT) approximation for the potential using FEFF8.4 package (Rehr and Ankudinov, 2005) with self-consistent potentials and Hedin–Lundqvist exchange; (2) non-muffin-tin FDMNES code (Joly, 2001), which allows the XANES to be calculated by solving the Schrödinger equation using the finite difference method (FDM). There are no principal restrictions on the shape of potential in FDMNES approach, and we found that this non-muffin-tin method must be applied in the case of simulation of the spectra produced by molecule-like N_2 defect having rather short N–N interatomic distance. In this case the non-muffin-tin effects are extremely important for description of the molecule potential in the local region near N_2 group having strongly covalent bonding, because for covalent bond the potential inside touching muffin-tin spheres around two N atoms cannot be considered any more as having spherical symmetry.

3. Results and discussion

In Fig. 1 we present experimental and theoretical spectra for both InN without defects ("as grown") and InN with defects after irradiation by 2 keV N_2^+ ion beam. The spectrum from the as-grown sample exhibits some characteristic peaks originating from the transitions of N 1s core electrons to unoccupied states having p-symmetry relative to nitrogen atoms. As one can see all maxima of "as grown" sample are reproduced well enough by theoretical simulation using MS theory for large cluster (about 200–300 atoms).

After nitrogen bombardment of the InN film, the spectra become broader. This observation is consistent with the expected increasing of bombardment-induced structural disorder within the surface region. In addition, two relatively intense new peaks appear in the spectrum of ion-bombarded InN films: one at about 399 eV and another at about 400.6 eV. To analyze the nature of these new peaks we performed theoretical simulations of possible N defects in irradiated InN film.

First we considered possible substitution (antisite) defect (N atom in the position of In atom in the crystal

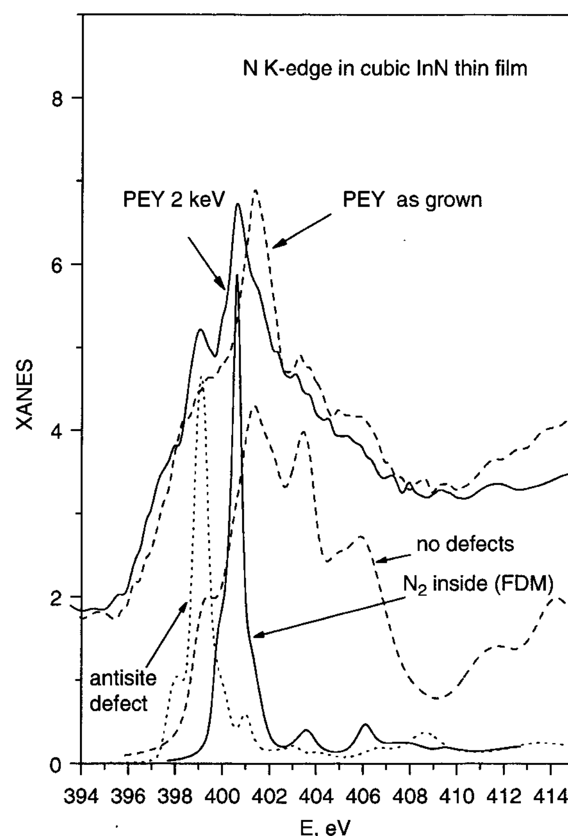

Fig. 1. Top: experimental N K-edge XANES spectra of InN: as grown (dashed line) and after irradiation by 2 keV N_2^+ ion beam (solid line). Bottom: theoretical XANES signal from N atoms of perfect InN crystal (dashed line), molecule-like N_2 defects inside InN (solid line), and antisite defect, i.e. N atom in the position of In atom (dotted line).

lattice of InN film). We have used large InN cluster (the same as for "as grown" spectrum simulation), but substituted In atom in absorbing atom position by N atom. The spectrum of this antisite defect is presented by dotted line in the bottom part of Fig. 1. Its energy position agrees well with new peak appearing at low energy side of the spectrum for irradiated InN. Thus it is possible to attribute the peak at 399 eV to such kind of N antisite defect.

Now let us consider the main peak of the N K-edge XANES after irradiation by 2 keV N_2^+ ion beam (about 400.6 eV). Recently it was shown that nitrogen can exist in the crystal lattice of some materials like silicon oxides in the form of interstitial molecule N_2 (Chung et al., 2005). We have simulated XANES spectrum of two N atoms in the InN lattice—one of them from normal nitrogen position and another one in the interstitial volume at the distance close to interatomic distance in N_2 molecule. The result in presented by solid line in the bottom part of Fig. 1. As one can see the sharp shape and energy position of this peak agree well with the main peak of irradiated InN (labeled as "PEY 2 keV"). Thus this new peak (at 400.6 eV) can be attributed to the signal from molecule-like N_2 defects inside the InN matrix. Such kinds of defect have been observed recently also in GaN:O films (Ruck et al, 2004).

4. Conclusions

In conclusion, our XANES measurements around the N K-edge of InN have provided the first direct experimental evidence of several defects and their energy levels created by ion-bombardment within the energy gap and the conduction band of InN. Theoretical analysis made it possible to atribute new peaks at XANES of irradiated InN film to antisite N defect (399 eV) and N_2 molelule-like defects inside InN matrix (400.6 eV).

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