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Identification of the local vibrational modes of small nitrogen clusters in dilute GaAsN

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Abstract

Ultra-high-resolution infra-red local vibrational mode (IR LVM) spectroscopy measurements together with density-functional calculations have been used to identify the signatures of close substitutional nitrogen (N_{As}) pairs in $GaAs_{1-x}N_x$ alloys with concentrations of $x<0.025$.

We show that the presence of sub-peaks close to the N_{As} absorption band can be attributed to nitrogen pairs up to fourth neighbor position. Additionally, we suggest that the nitrogen pairs which give rise to the deepest levels below the conduction band edge are the first to be removed upon annealing.

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1. Introduction

Small N aggregates are thought to play a relevant role in the unusual optical and electrical properties of nitrogen-doped III–V compounds [1]. In dilute $GaP_{1-x}N_x$ with less than 1.3% of nitrogen content, they are responsible for deep levels observed in the PL emission spectra [1–5]. Analogously, in GaAs:N, theory predicts that nitrogen pairs with different configurations generate a rich series of localized energy levels, some of them tentatively identified with deep PL centers [1,6]. Yet, direct detection and identification of such N-related defects has been difficult so far, partially due to the structure and quality of the samples examined.

In the present study, we show that even in low concentrations, small nitrogen clusters can also be detected in vibrational spectra, as a series of sub-peaks close to the vibrational band of N_{As} at about $472\,cm^{-1}$ [7]. We employed local vibrational mode (LVM) spectroscopy together with theoretical calculations to explore in detail the origin of these lines.

2. Experimental details

Four $GaAs_{1-x}N_x$ epilayers ($0.0004 \leqslant x \leqslant 0.0075$), 1–4 μm thick, were deposited on semi-insulating GaAs(0 0 1) substrates at 500 °C in a solid-source molecular beam epitaxy (SS-MBE) system (DCA instrument). Active nitrogen species were introduced via a UNI-Bulb rf-plasma nitrogen source. High-resolution X-ray diffraction measurements were used to estimate the substitutional nitrogen content of the layers.

Infra-red (IR) LVM transmission spectra were subsequently recorded using an ultra-high-resolution Fourier-transform infra-red (FTIR) spectrometer (Bruker IFS 120 HR), a liquid-helium-cooled Si bolometer detector, and a globar source. Measurements were made with a spectral

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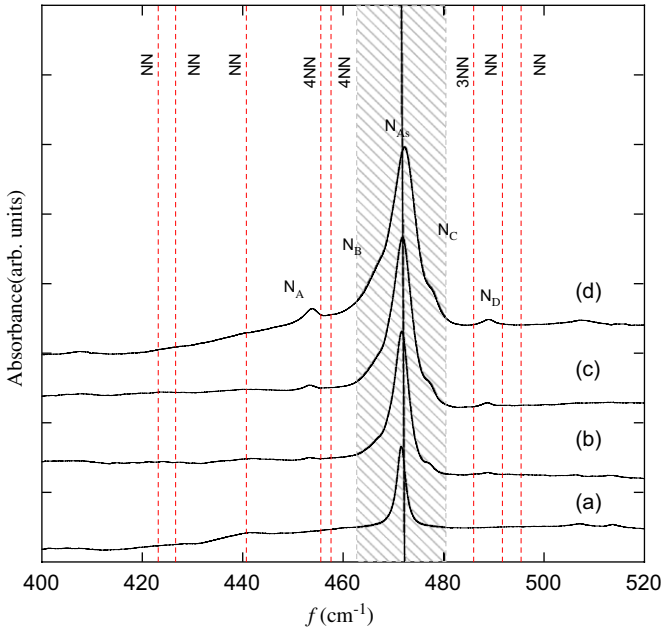

Fig. 1. (Color online) IR LVM transmission spectra for four $GaAs_{1-x}N_x$ epilayers, with (a) $x = 0.0004$, (b) $x = 0.0034$, (c) $x = 0.0052$, and (d) $x = 0.0075$, showing predicted lines ($x = 0.0093$) for isolated N_{As} (full line) and N_{As}–N_{As} pairs (dashed lines). Only the N_{As}–N_{As} vibrational frequencies which fall outside the hatched region are shown (see Table 2).

resolution of $0.25\,cm^{-1}$, with both the samples and detector cooled to $\sim$10 K.

The IR spectra for the MBE-grown $GaAs_{1-x}N_x$ epilayer samples (see Fig. 1) show four absorption features, labeled N_{A-D}, in addition to the expected LVM due to isolated N_{As}. Similar vibronic features in $Al_xGa_{1-x}As$ have been linked to nitrogen dimers [8,9]. The integrated absorption of these subpeaks is approximately two orders of magnitude lower than that of the main mode, and increases super-linearly with nitrogen content; both of these properties suggest that those modes are related to N_{As} clusters.

3. *Ab initio* method

Density functional calculations were performed using the AIMPRO code [10]. The core electrons were treated using the *ab initio* pseudopotentials of Hartwigsen et al. [11]. Non-linear core-correction (NLCC) was included to account for the 3d electrons of Ga [12]. A real-space basis set consisting of Cartesian Gaussian functions was used to expand the Kohn–Sham orbitals. We employed basis of (1, 4, 4) (s, p, d) atom-centered orbitals for Ga and As, optimized for GaAs, and a basis of (4, 4, 4) (s, p, d) orbitals for N, optimized for GaN. The calculated lattice parameter and bulk modulus of GaAs are $a_0 = 5.602$ Å and $B = 74.14$ GPa, comparing well with the experimental values 5.6526 Å and 74.8 GPa [13,14].

The entries of the dynamical matrix were evaluated by displacing the nitrogen atoms and a selected number of their neighbors along the six Cartesian coordinates. The LVM of a single N_{As} atom in GaAs was calculated to be $471.6\,cm^{-1}$ for ^{14}N, coincident with experiment ($472\,cm^{-1}$). The typical error, however, is about $5\,cm^{-1}$.

4. Theoretical model

In the $x \to 0$ limit, the vibrational mode of a substitutional N atom is a T_2 triplet of the T_d point symmetry group, responsible for the prominent IR band at about $472\,cm^{-1}$ (Fig. 1). We first discuss how this mode is perturbed by the presence of remote nitrogen atoms in the GaAsN alloy (Section 4.1). In Section 5 we consider the interaction between close N_{As} atoms.

4.1. Alloying effects

Remote N_{As} atoms in the $GaAs_{1-x}N_x$ alloy modify the properties of the host crystal, such as the lattice parameter and the band structure, and consequently, the interaction of N_{As} with the embodying matrix. In the dilute alloy limit, the frequency shift is approximately proportional to x and can in part be accounted for by considering the deformation of the lattice.

We have modeled the epilayers as a tetragonal system, whose lattice parameters are allowed to relax along the growth direction [0 0 1], but matched to the bulk GaAs substrate in the (0 0 1) planes. The best resolved experimental subpeaks were obtained for $x = 0.0075$, and to model this system as closely as possible, we have chosen a $Ga_{108}As_{107}N$ supercell, which yields $x = \frac{1}{108} \simeq 0.0093$. The lattice parameter along [0 0 1] ($l_{[0\,0\,1]}$) was found by minimizing the energy, using the simplex method [15].

Since the epilayers are nominally lattice-matched to GaAs(0 0 1) substrates, the deformation of the lattice due to biaxial tensile strain lowers the symmetry from T_d to C_{2v}, splitting the T_2 mode of N_{As} into a double degenerate E mode parallel to the growth planes and a B_2 mode along [0 0 1]. The calculated frequencies of these two modes for the concentration of $x = 0.0093$ are 471.51 and $472.11\,cm^{-1}$. However, as the direction of incident light is parallel to the [0 0 1] (normal incidence), only the E components will be detected. For a nitrogen content of $x = 0.0075$, the measured frequency is $472.2\,cm^{-1}$, little larger than the calculated value.

5. Nitrogen clusters

In a random distribution, the concentration of pairs of substitutional nitrogen atoms occupying nearest neighbor (NN), second nearest neighbor (2NN), ..., nth nearest neighbor (nNN) sites of the undistorted (fcc) As sublattice is proportional to the number of such sites. In an undistorted fcc lattice, there are 12, 6, 24 and 12 equivalent sites in the NN, 2NN, 3NN and 4NN shells, respectively (Table 1).

We investigate pairs up to a distance a_0, which corresponds to the 4th neighbor. Only the pairs with n up to four are coupled by chains of two Ga and one As