Journal of Alloys and Compounds 687 (2016) 42–46

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Impact of the substrate orientation on the N incorporation in GaAsN: Theoretical and experimental investigations

Jian Li [a], Xiuxun Han [a, b, *], Chen Dong [a, c], Changzeng Fan [d], Yoshio Ohshita [e], Masafumi Yamaguchi [e]

[a] Laboratory of Clean Energy Chemistry and Materials, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China
[b] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China
[c] University of Chinese Academy of Sciences, Bejing 100080, PR China
[d] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, PR China
[e] Toyota Technological Institute, 2-12-1 Hisakata, Tempaku, Nagoya 468-8511, Japan

ARTICLE INFO

Article history:
Received 19 May 2016
Accepted 11 June 2016
Available online 14 June 2016

Keywords:
GaAsN
First principle calculation
N incorporation
Growth orientation
Chemical potentials

ABSTRACT

The growth orientation dependence of N incorporation on traditional (100) and high-index GaAs (311)A/B planes has been investigated by the first principle calculation and experimental measurement. Due to the electronegativity and atomic radius differences between As and N atoms, the Ga–N bond is much shorter than the corresponding Ga–As bond as N occupies As atom site. The optimization to energetically preferred construction leads to the inward moving of N atom, while the displacement extent of three surface models exhibits considerable differences. More importantly, the theoretical result reveals a lower formation energy of N doping for N@(311)B GaAs surface and a larger one for N@(311)A GaAs surface as compared with the traditional (100) GaAs plane. The first principle investigations thus suggest the enhanced N incorporation in (311)B GaAsN, which is in good accordance with the secondary ion mass spectrometry (SIMS) measurement results of GaAsN layers by chemical beam epitaxy (CBE).

1. Introduction

The incorporation of small amounts of N to GaAs, principally by the substitution on the group-V sites, leads to a dramatic decrease in the band gap without substantially changing the lattice parameter [1,2], which renders dilute GaAs$_{1-x}$N$_x$ attractive as prototypical strongly disordered random alloys [3–6] and for potential applications in either high-efficiency tandem solar cells [7] or laser devices with technologically important wavelength [8]. However, the solubility of nitrogen into bulk GaAs is extremely low [9,10]. Marked deteriorations in both optical and transport properties have been found to accompany the N incorporation in GaAs, including inhomogeneous linewidth broadening of the photoluminescence (PL) spectra [11,12], dramatic reduction of carrier mobility and lifetime [13–16], and increase in carrier effective mass, *etc* [17]. These phenomena are thought to be evidences of strong disorder and/or high density of N-related defects, which might be partly attributed to the large divergence in both atom size and electronegativity between N and As. To obtain device-level GaAsN material, challenges for enhancing the effective N incorporation and further reducing the defect generation must be addressed. Great research efforts such as thermal annealing have been performed to improve GaAsN alloy quality, but mostly restricted the growth to the traditional orientation (100) [18,19]. A few published studies of GaAsN on high-index substrates verified that the growth surface engineering might be effective to alter the N incorporation behavior in a controllable manner [20–23]. In our previous work, we compared the N incorporation in GaAsN epilayers growth on (211)A/B, (311)A/B, (511)A/B and traditional (100) substrates using a chemical beam expitaxy system, and demonstrated that the N composition was enhanced for the epitaxial growth following (n11)B orientation, but reduced in the (n11)A direction [24,25]. In addition, the doping behavior of Si in GaAsN growing on (100), (311)A/B and (211)B GaAs substrates has also been investigated [19]. It is revealed that (n11)B was the potential substrate orientations to reduce the N–Si passivation and promote Si doping efficiency in GaAsN over a wider N composition range. To

---

[*] Corresponding author. Laboratory of Clean Energy Chemistry and Materials, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China.

E-mail address: xxhan@licp.cas.cn (X. Han).

http://dx.doi.org/10.1016/j.jallcom.2016.06.114
0925-8388/© 2016 Published by Elsevier B.V.

explain the exciting results in above experiments, a simple atomic bonding model of an ideal (311) GaAs surface was utilized to illustrate the energetically active three-dangling-bond (TDB) sites, which facilitates the qualitative construction of a clear N-enhanced incorporation picture, but is insufficient to provide a quantitative interpretation by fully considering the likely-happened surface reconstruction.

To better understand the doping behavior of N on different GaAs surfaces, we calculated the formation energy for N occupying As site in the outermost layer by using first-principles calculations based on density functional theory (DFT). The orientation dependence of N incorporation was discussed based on the calculated results. Moreover, the validity of the theoretical results is verified by experiments. The present work should be helpful to quantitatively clarify experimental findings and provide valuable information on improving the growth of high-quality GaAsN materials with specific applications.

2. Experimental methods and computational details

2.1. Experimental section

Based on the chemical beam epitaxy (CBE) system, the growth of GaAsN alloys were performed simultaneously side by side on (3 1 1) A/B and (1 0 0) GaAs substrates. The constitution structure of the ideal (*n* 1 1) substrate surface can be considered to be composed of (1 0 0) and (1 1 1) components, and the corresponding (1 0 0) and (1 1 1) component ratio is 1:1 for (3 1 1) substrates, as illustrated in Fig. 1. In our CBE system, triethylgallium (TEGa) and trisdimethylaminoarsenic (TDMAAs) were utilized as Ga and As sources with fixed flow rates of 0.1 and 1.0 sccm to grow the GaAs layer. During the GaAsN layer growth, monomethylhydrazine (MMHy) was introduced as N source. The growth temperature is 460 °C. For convenient secondary ion mass spectrometry (SIMS) measurement, a multilayer structure was designed to examine the actual N atomic concentration in GaAsN under different N source supplies. The growth of the multilayer on three different GaAs substrates starts with a GaAs layer, which is followed by three circles of GaAs:N/GaAs growth with 4, 6, and 9 sccm N precursor flow rate applied for the N containing layers.

2.2. Theoretical models

The study of the surface doping requires a slab model, which contains a periodic boundary condition and a vacuum area. Given the complexity of the surface reconstruction, what we primarily concern are the formation energy and local relaxation. Taking the cubic GaAs phase as the basic structural unit, we obtain three kinds of surface models. For (100), (311) A and (311) B GaAs surfaces, the sizes of large super cells used this work are ($11.329 \times 11.329 \times 31.993$ Å^3), ($13.875 \times 16.021 \times 25.674$ Å^3) and ($13.875 \times 16.021 \times 25.674$ Å^3), respectively, as illustrated in Fig. 1. To ensure that the calculated results are reasonable, we calculated the surface energies of several slabs with different thicknesses. The surface energies are satisfactorily converged to <0.001 eV/Å^2 with respect to a twelve layer slab thickness, which is thus adopted in the present calculation. During the structure optimization, the bottom seven layers are fixed while the top five layers are allowed to relax. A vacuum spacing of 15 Å is used to separate the adjacent slabs in all models.

To construct a stable surface, pseudohydrogen atoms H^Z is used to passivate the dangling bonds of GaAs surface, which have a fractional nuclear charge Z and a corresponding fractional electron charge. In the cubic GaAs, a Ga atom surrounded by four As atoms has three valence electrons, thus each Ga atom contributes three fourths (3/4) to each bond. Because H needs two electrons to complete one *s* shell, we choose the $Z = 2-3/4 = 1.25$ pseudohydrogen to passivate the Ga dangling bonds. Similarly, 0.75 pseudohydrogen is applied to passivate the As dangling bonds.

2.3. Methods of calculation

All the first-principles calculations were performed with the VASP (Vienna ab initio simulation package) code [26] based on the density-functional theory [27]. The electron ion-core interactions were described by the projector augmented-wave (PAW) potentials, where the valence electrons are treated within the scalar-relativistic treatment approximation [28]. The following states, $4s^2p^1$,$4s^2p^3$ and $2s^2p^3$, were considered in the valence for the Ga, As and N elements, respectively. The generalized gradient approximation (GGA) in the parameterization of Perdew-Burke-Ernzerhof

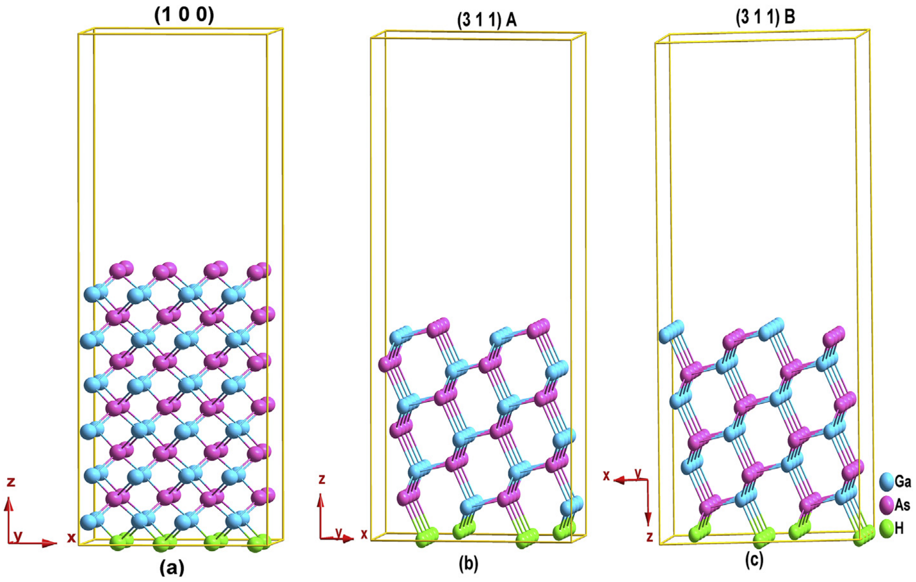

Fig. 1. Crystal structure of GaAs (1 0 0), (3 1 1)A and (3 1 1)B surface, respectively.