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An ab initio-based approach to phase diagram calculations for GaN(0 0 0 1) surfaces

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Abstract

Surface phase diagrams of GaN(0 0 0 1)-(2 × 2) and pseudo-(1 × 1) surfaces are systematically investigated by using our ab initio-based approach. The phase diagrams are obtained as functions of temperature T and Ga beam equivalent pressure p_{Ga} by comparing chemical potentials of Ga atom in the vapor phase with that on the surface. The calculated results imply that the (2 × 2) surface is stable in the temperature range of 700–1000 K at 10^{-8} Torr and 900–1400 K at 10^{-2} Torr. This is consistent with experimental stable temperature range for the (2 × 2). On the other hand, the pseudo-(1 × 1) phase is stable in the temperature range less than 700 K at 10^{-8} Torr and less than 1000 K at 10^{-2} Torr. Furthermore, the stable region of the pseudo-(1 × 1) phase almost coincides with that of the (2 × 2) with excess Ga adatom. This suggests that Ga adsorption or desorption during GaN MBE growth can easily change the pseudo-(1 × 1) to the (2 × 2) with Ga adatom and vice versa.

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1. Introduction

GaN thin films are usually fabricated by metal organic vapor phase epitaxy (MOVPE) and molecular beam epitaxy (MBE), where temperature and pressure of species are crucial growth parameters. Atomic structure of the reconstructions during and after MBE growth on the GaN(0 0 0 1) surface under Ga-rich conditions have been subjects of a number of experimental investigations. The (2 × 2) and pseudo-(1 × 1) surfaces have been observed on the GaN(0 0 0 1) under Ga-rich conditions by scanning tunneling microscopy (STM) [1,2]. Furthermore, Xie et al. proposed MBE growth model on the basis of their STM observations, where the GaN growth proceeds via 'ghost' island with the (2 × 2) structure to normal island formation with the pseudo-(1 × 1) structure under excess Ga fluxes [3]. In order to clarify surface structures and elementary growth processes on the GaN(0 0 0 1), there have been some theoretical studies based on ab initio calculations such as surface structures, migration potential and stable adsorption sites. Northrup et al. proposed the structure of the pseudo-(1 × 1) as the most stable state under Ga-rich limit to clarify the relative stability among various surface structures [4]. Ishii investigated stable adsorption behavior on the (2 × 2) under N- and Ga-rich conditions [5]. Although these ab initio studies successfully elucidate some aspects in the surface-related problems of GaN, their results are limited at 0 K without incorporating the growth parameters such as temperature and beam equivalent pressure (BEP). In order to make up the deficiency in the previously reported ab initio calculations, we have newly developed ab initio-based approach to include temperature and BEP and successfully applied to the surface reconstructions for and elemental growth processes on the GaAs(0 0 1) and GaN(0 0 1) surfaces [6,7]. In this study, we extend our ab initio-based approach to investigate Ga adsorption behavior on the GaN(0 0 0 1)-(2 × 2) and pseudo-(1 × 1) surfaces and predict phase diagrams as functions of temperature and Ga BEP. The growth model proposed by Xie et al. is also discussed on the basis of the surface phase diagrams obtained in this study.

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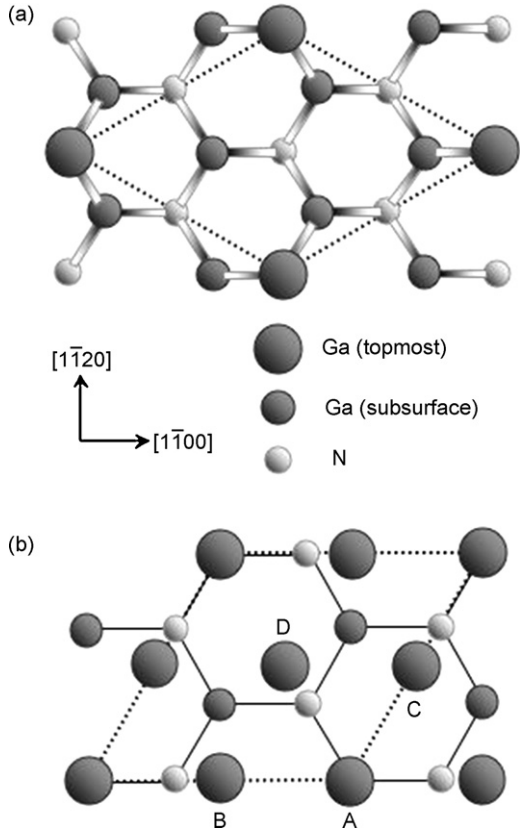

Fig. 1. Schematic of top view for (a) GaN(0 0 0 1)-(2 × 2) and (b) pseudo-(1 × 1) surfaces considered in this study. Dotted line denotes (2 × 2) surface unit cell. Lattice sites for Ga atoms in the topmost layer on the pseudo-(1 × 1) are denoted by A–D. Thin solid lines in (b) represent interatomic bonds between N in the fourth layer and Ga in the third layer.

2. Computational methods

Fig. 1 shows the schematic of the (2 × 2) with Ga adatoms and pseudo-(1 × 1) considered in this study. The pseudo-(1 × 1) structure shown in this figure corresponds to registry B proposed by Northrup et al. [4], which consists of two monolayers of excess Ga on the GaN(0 0 0 1). On these surfaces, the adsorption–desorption behavior of Ga can be described by comparing the free energy of ideal gas per one particle (chemical potential) μ with the adsorption energy E_{ad}. The chemical potential μ_{Ga} of the ideal gas such as Ga atom is given by the following equation [8,9]:

$$\mu_{Ga} = -k_B T \ln\left[\frac{k_B T}{p_{Ga}} g\zeta_{trans}\right] \quad (1)$$

Here k_B is Boltzmann's constant, T the gas temperature, g the degree of degeneracy of electron energy level, p the beam equivalent pressure of the particle, and ζ_{trans} is the partition function for the translational motion.

The adsorption energy E_{ad} is obtained by total energy for the solid phase and chemical potential in the vapor phase. In the total energy calculations for the (2 × 2) and pseudo-(1 × 1) surfaces with various atomic arrangements, we used the first-principles pseudopotential method based on the local-density functional formalism [10] within the generalized gradient approximation [11], combined with Troullier–Martins pseudopotential for Ga [12] and Vanderbilt pseudopotential for N [13]. The wave functions are expanded by the plane-wave basis set corresponding to sufficient kinetic energy cut-off 28 Ry. The conventional repeated slab geometry is employed to simulate the surface. The unit super cell consists of eight atomic layers of GaN, an atomic layer of fictitious H atoms and a vacuum region equivalent to about 15 atomic layers in thickness. Using these chemical potentials μ and adsorption energies E_{ad}, the adsorption–desorption behavior of Ga on the (2 × 2) and pseudo-(1 × 1) surfaces is clarified as functions of temperature and Ga pressure. Relative stability between various surface structures is determined by comparing μ with E_{ad}. That is, net

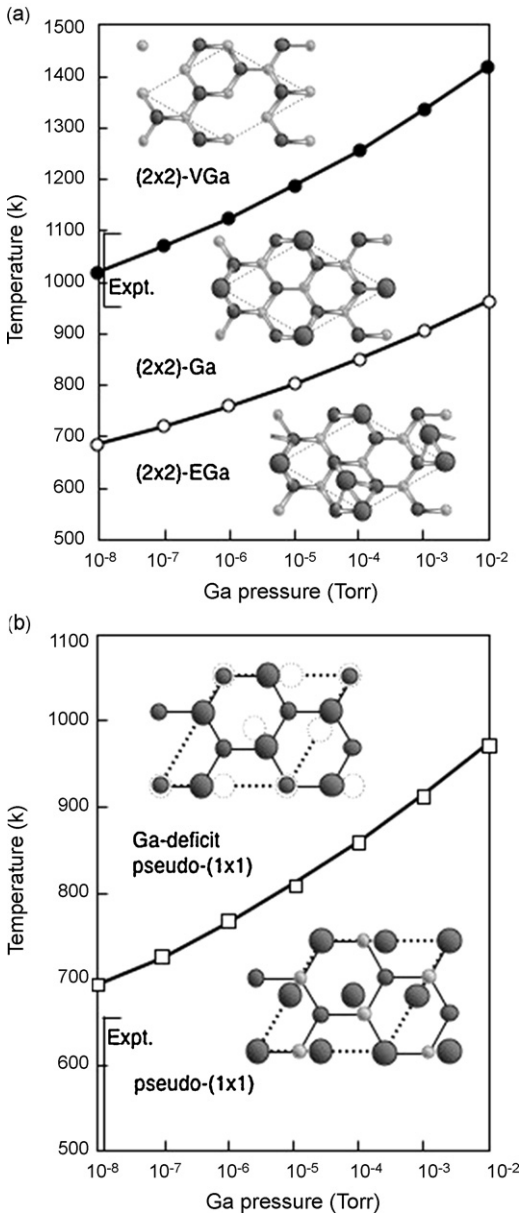

Fig. 2. Calculated phase diagram of (a) GaN(0 0 0 1)-(2 × 2) and (b) pseudo-(1 × 1) surfaces as functions of temperature and Ga BEP. Experimental results (Expt.) shown by vertical line are attached to temperature axis. Dotted line in (b) denotes the initial lattice sites for topmost Ga on the pseudo-(1 × 1).