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**INTERFACIAL REACTION STUDIES USING ONIOM**

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## Introduction

Organometallic vapor phase epitaxy (OMVPE) is widely used in both scientific studies and industrial manufacturing of compound semiconductor devices and circuits. III-V compounds have been at the center of this development for many years. The nitrides, in particular, permit the extension of III-V optoelectronics and photonics to the blue and ultraviolet range of the electromagnetic spectrum[1]. There is growing interest in extending OMVPE to indium nitride (InN), which exhibit large thermal decomposition at their optimum growth temperature. To overcome decomposition of the deposited compound, the reaction must be conducted at high pressures. But high pressure OMVPE must be carried out at high flow velocity to keep the Grashof number ($G_e$) small compared to the square of the Reynolds number ($R_e$), to prevent onset of turbulence and thus non-uniform film growth. The $G_e / R_e^2$ ratio is proportional to $\mathbf{g}\left(\dfrac{\mathbf{P}}{\mathbf{u}}\right)^2$, where $\mathbf{g}$ is the gravity vector, $\mathbf{P}$ the standard pressure, and $\mathbf{u}$ the standard flow rate. On the ground, high pressure OMVPE must be carried out at a sufficiently high $\mathbf{u}$ to maintain a small ratio, which results in an inefficient growth rate. Alternatively, under conditions of reduced gravity, an increase in $\mathbf{P}$ could be coupled with a smaller $\mathbf{u}$ without an onset of turbulence. In order to extend OMVPE processing to elevated pressures, new reactor designs have been recently built to reach pressures as high as 100 atm. Epitaxy simulations that couple fluid dynamic equations with homogeneous and heterogeneous reactions have been helpful in both reactor and process design. At the present time, there is a need for obtaining input parameters for modeling these experiments under different conditions of pressure and gravity.

In this report, we focus on the calculations of the energetics and chemical kinetics of heterogeneous reactions for OMVPE. The work described in this report builds upon our own previous thermochemical[2] and chemical kinetics studies[3]. The first of these articles refers to the prediction of thermochemical properties, and the latter one deals with the prediction of rate constants for gaseous homolytic dissociation reactions.

The calculations of this investigation are at the microscopic level. The systems chosen consisted of a gallium nitride (GaN) substrate, and molecular nitrogen ($N_2$) and ammonia ($NH_3$) as adsorbants. The energetics for the adsorption and the adsorbant dissociation processes were estimated, and reaction rate constants for the dissociation reactions of free and adsorbed molecules were predicted. The energetics for substrate decomposition was also computed.

The GaN substrate mainly exists in three crystal structures: rocksalt, wurtzitic, and zincblende. At ambient conditions, the common structure is wurtzitic. The rocksalt structure can be induced at very high pressures. The zincblende structure can be obtained by epitaxy of GaN thin films on cubic structures such as Si, MgO and GaAs. So far, we have limited our calculations to zincblende crystals. In this structure, both atoms have a face-center cubic sub-lattice (see Figure 1a), offset along the diagonal of the cube by $^1/_4$ of the diagonal. A side view of a 3x3x1 unit-cell slab is shown in Figure 1b, where the terminal atoms at the top (red) are Ga atoms and at the bottom (blue) are N atoms. The

surface consists of parallel ridges and ditches. All non-terminal atoms form tetrahedral bonds. The terminal atoms have only one or two bonds, corresponding to an edge or the surface, respectively.
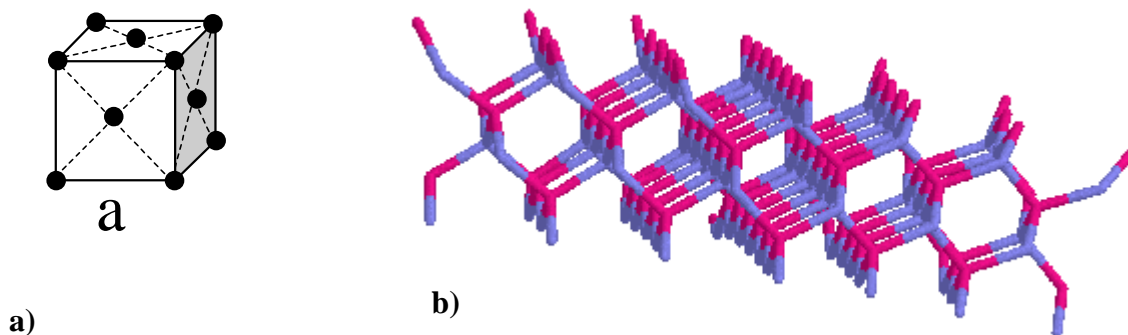


**a)**

**b)**

Figure 1: a) Face-center cubic lattice. b) Zincblende slab seen from its narrow side

## Method

The ONIOM[4] method, implemented in the Gaussian98 program[5], was used to perform the calculations. This approach has been selected since it allows dividing the system into two layers that can be treated at different levels of accuracy. The atoms of the substrate were modeled using molecular mechanics[6] with universal force fields[7], whereas the adsorbed molecules were approximated using quantum mechanics, based on density functional theory methods[8] with B3LYP functionals[9] and 6-311G(d,p) basis sets. Calculations for the substrate were performed in slabs of several unit cells in each direction. The $N_2$ and $NH_3$ adsorbates were attached to a central location at the Ga-lined surface.

## Results

*Selection of the surface size.* In order to select an adequate surface size, the following properties were analyzed as a function of number of atoms: (a) lattice constant; (b) density; (c) Ga-N average bond distance; and (d) energy per Ga-N unit. The average Ga-N bond distance was calculated using only those N atoms that were tetrahedrally bonded to four Ga atoms; the average lattice constant was obtained using only atoms that had a coordination number of 12 with the same type of atoms; the density was based on the calculated lattice constant and the fact that a unit cell contains four Ga-N units. As an example, Figures 2a and 2b display the first two properties as a function of number of surface atoms. A compromise between property and number of atoms led us to select a 5 x 5 x 3 slab, which gave the values shown by the arrows. The experimentally determined lattice constant is 4.52 Å and the zincblende crystal has a density of 6.15 g cm$^{-3}$. The selected slab has a calculated average lattice constant of 4.44 ± 0.05 Å, a density of 6.37 ± 0.07 g cm$^{-3}$; and an average Ga-N bond distance of 1.92 ± 0.02 Å. The energy for N decomposition of the substrate was estimated to be 151 ± 14 kJ mol$^{-1}$.

*Interaction of the surface with the adsorbates.* As an example, Figure 3 shows the 5x5x3 unit-cell GaN substrate with an ammonia molecule (with light colors) adsorbed at

the Ga-lined surface.  Lowest energy was obtained for an $NH_3$ molecule with its N atom sitting above a square of Ga atoms, 3.6 to 3.9 Å away.
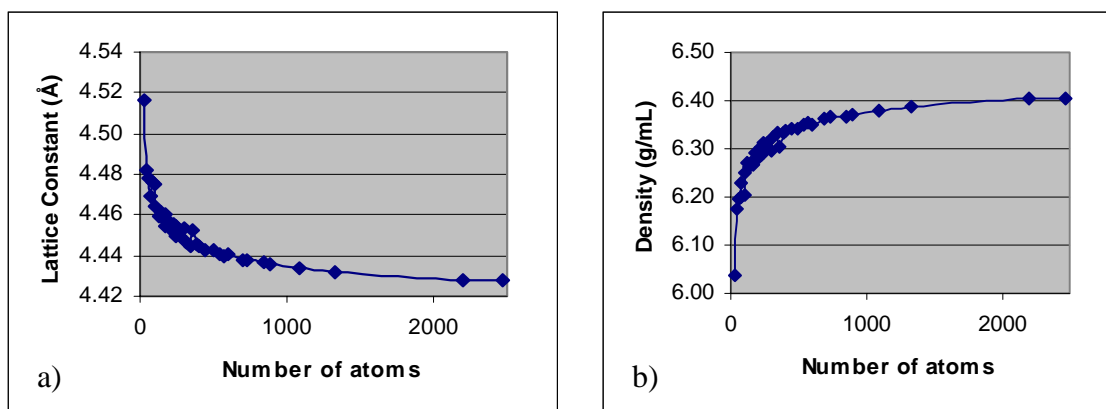


Figure 2: Properties of zincblende slabs as a function of number of atoms: a) average lattice constant; b) density.
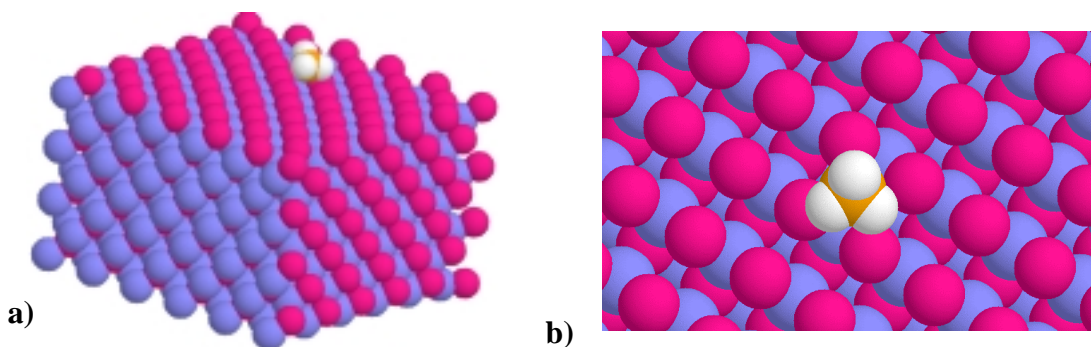


Figure 5:  5x5x3 unit-cell zincblende GaN substrate with an adsorbed $NH_3$ molecule. a) complete substrate; b) enlarged view of adsorbate.

According to the calculations, $NH_3$, $^2NH_2$, $^3NH$, and $^4N$ physisorb to the surface by 14, 12, 10, and 6 kJ $mol^{-1}$, respectively.  Dissociation of a $^2H$ atom from the first three adsorbed species requires 470, 412 and 360 kJ $mol^{-1}$, respectively, similar to the free molecule.  As a rough estimation, the H dissociation rate constants were calculated assuming that vibrational frequencies are inversely proportional to bond distance.  The dissociation rate constants for adsorbed $NH_3$ between 700 and 1300 K were twice as large as for free $NH_3$.

$N_2$ is adsorbed almost parallel to the surface, with one N atom 3.60 Å above a Ga atom and the second N atom above a triangle determined by other three Ga atoms.  Its binding energy is 12 kJ $mol^{-1}$. 942 and 947 kJ $mol^{-1}$ are required to dissociate free $N_2$ and adsorbed $N_2$, respectively.  (The experimental dissociation energy of $N_2$ at standard conditions is 949 kJ $mol^{-1}$.)  The reaction rate constant for the dissociation of $N_2$ increases by a factor of two with adsorption, factor which decreases with increasing temperature.

## Conclusions

Performing calculations at two different level of accuracy for interfacial reactions seems an adequate approach to study interfacial reactions. The calculated energies indicate that: (a) the chemisorption energy of N in the substrate is about 150 kJ mol$^{-1}$; (b) the five species considered (N$_2$, $^3$N, NH$_3$, $^2$NH$_2$, and $^3$NH) physisorb to the GaN substrate (by 12, 6, 14, 12 and 10 kJ mol$^{-1}$, respectively); (c) dissociation of N$_2$ into two $^4$N atoms and of a $^2$H atom from NH$_3$, $^2$NH$_2$ and $^3$NH is endothermic; and (d) the above dissociations are a few kilojoules per mole lower for the free molecules than for the adsorbants. Roughly calculated rate constants indicate that: (a) dissociation of free N$_2$ is twice as fast as adsorbed N$_2$, and (b) dissociation of adsorbed NH$_3$ is twice as fast as free NH$_3$. The latter result would indicate that dissociation of NH$_3$ on a GaN substrate is kinetically driven.

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