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Theoretical Studies Of Hydrogen Passivated Substitutional Magnesium Acceptor In Wurzite GaN

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Abstract

Infrared measurements on wurzite GaN codoped with Mg and H reveal strong absorption at 3125 cm^{-1}. Theorectical work provides strong evidence for the H being antibonding to N. We have performed an *ab-initio* study of Mg-H complexes in wurzite GaN, using the Local Density Approximation on a large H-terminated cluster $MgHGa_{25}N_{26}H_{42}$. We have investigated the physical properties of three neutral configurations along the c direction. In all configurations Mg sits in a gallium substitutional site. H is then located in the Mg-N bond centre (BC), in the antibonding site on nitrogen side (AB_N) or in the antibonding position on magnesium side (AB_{Mg}). We found the lowest total energy configuration is hydrogen in the antibonding on the nitrogen site. The stretch mode in this configuration is calculated at 3277 cm^{-1} which agrees with experiment and previous LDA calculations and we predict an unreported infra red active wag mode at 1311 cm^{-1}. The experimental isotopic shift with D is well reproduced. The BC and AB_{Mg} configurations are 0.5 and 3.7 eV higher, producing local modes at 3645 and 2144 cm^{-1}, respectively. No wag modes appear for the BC and AB_{Mg} configurations.

1. Introduction

Hydrogen is often present in semiconductors and may passivate the acceptor or donor electronic level [1]+ [2]+ [3], decreasing the carrier concentration. Hydrogen passivation has been observed in silicon, germanium, III-V and II-VI materials. In wurzite GaN, hydrogen passivates magnesium [4] and calcium [5] acceptors.

Early infra red absorption experiments [6] on Mg doped wurzite GaN, with H incorporated unintentinally, showed two lines at 2168 and 2219 cm^{-1}, which were attributed to a Mg-H centre. However *ab-initio* calculations obtained much higher local vibrational modes (LVM), between 2930 [7] and 3360 cm^{-1} [8] for the lowest formation energy configuration, H antibonding to nitrogen. This disagreement prompted further infrared experiments. New IR experiment [9], sensitive to vibrations on c plane, which detected a new local vibrational mode at 3125 cm^{-1}. For deuterated samples a LVM at 2321 cm^{-1} emerged. The ratio of the last two frequencies to be near $\sqrt{2}$ shows that hydrogen is involved in the complex. This new experimental data is in good concordance with predicted theoretical quantities, validating the antibonding to nitrogen model.

Ab-initio calculations by Neugebauer and Van de Walle [8] and by Bosin, Fiorentini and Vanderbildt [7] have shown that Mg-H LVMs are similar for cubic and for wurzite GaN in the c direction and in the c plane. In this paper we present a study of the Mg-H complex in c direction in wurzite GaN. We compare the total energy and the LVMs of three possible neutral configurations with C_{3v} symmetry. All configurations consider Mg at a gallium

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substitutional site and H sitting in the Mg-N bond centre (BC), in the antibonding site on nitrogen side (AB_N) and in the antibonding position on magnesium side (AB_{Mg}). Calculations of hydrogen passivation of others acceptors (Be, Ca, Zn and Cd) in wurzite GaN are in progress and will be presented in a separate publication.

2. Method

We use an *ab initio* local density functional method on a large H-terminated cluster [10]. Norm conserving pseudopotentials [11] were used. The electronic wavefunction and the charge density were expanded in s- and p-type gaussians atomic orbitals, centred on nuclei and at the centre of all non H-terminated bonds.

The total self-consistent energy is found and the atomic forces calculated analitically. A conjugated gradient algorithm is used to minimize the total energy. In our calculations we use a $MgHGa_{25}N_{26}H_{42}$ atomic cluster, centred on the middle of a Ga-N bond, and all atoms were allowed to relax. We verified the convergence of the results presented here with respect to basis set.

Second derivatives of the energy in respect to the atomic positions are obtained numerically and inserted into the dynamical matrix to calculate the LVMs. In pratice, the numerically calculated second derivatives were determined for the atoms involved in the defect and their first nearest neighbours. Outside the defect region, the second derivatives are calculated using a Keating Potential [12]. We consider non-Coulombic bond stretching and bond bending interactions. The parametrization was chosen to fit the highest frequency at the Γ point and the bulk modulus for cubic GaN.

3. Results

We have determined the relaxed atomic geometry, total energy and LVMs for three neutral configurations, BC, AB_N and AB_{Mg}, along the c direction.

We found AB_N to be the lowest total energy configuration, while BC and AB_{Mg} configurations are 0.5 and 3.7 eV higher, respectively.

For the AB_N configuration nitrogen moved 0.12 Å towards the Mg site, while magnesium moved 0.03 Å away from N, resulting in a Mg-N bond length of 1.89 Å, close to the Ga-N ideal bond length. The N-H bond length is 1.02 Å. In the BC configuration nitrogen and magnesium moved apart 0.03 and 0.35 Å, respectively. The N-H bond length is 0.99 Å. The Mg-N distance is 0.4 Å greater than the perfect bond length, which increases the strain energy.

The local modes are listed in Table 1. The lowest total energy configuration, AB_N, produces 3327 and 2387 cm^{-1} stretch modes for hydrogen and for deuterium respectively, in good agreement with experiment and previous calculations. Replacing ^{14}N by ^{15}N low the 3327 cm^{-1} stretch mode by 6 cm^{-1}. We also predict an unreported wag mode at 1311 cm^{-1}. The BC and the AB_{Mg} configurations produce stretch local modes at 3645 and 2144 cm^{-1}, for hydrogen, and 1552 and 2650 cm^{-1} for deuterium, respectively. These LVMs do not agree with experiment. No wag local modes were found for these two configurations. To verify the local modes dependence on the Keating Potential parametrization, the Keating force contants were varied by 30%. No significant changes on local modes were found.

4. Conclusions

We find that the lowest total energy configuration for the Mg-H complex along the c direction in wurzite GaN hydrogen sits at anti-bonding site at the nitrogen nearest neighbour of Mg_{Ga}. This configuration produces a stretch local mode in good agreement with experiment and previous calculations by Neugebauer and Van de Walle and by Bosin, Fiorentini and Vanderbilt. The experimental isotopic shift for deuterium is well reproduced and is predited to be 6 cm^{-1} lower for ^{15}N-H We also found an unreported infra red active wag local mode for the AB_N configuration at 1311 cm^{-1}. The BC and AB_{Mg} configurations do not show any wag local modes.

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Table 1

Calculated and Experimental LVMs of Mg-H (Mg-D) complex in wurzite GaN (cm^{-1}).

Configurations	**Present**		**Ref. [8]**	**Ref. [7]**	
	(c direction)		(cubic GaN)	(c direction)	(c plane)
	Stretch	Wag	Stretch	Stretch	Stretch
AB_{Mg}	2144				
	(1552)				
BC	3645			3611	3917
	(2650)				
AB_N	3277	1311	3360	3069	2930
	(2387)	(1023)			
Expt. (c plane)	3125				
	(2321)				

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