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Theoretical studies of Nitride Surface and Growth Properties

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Introduction

This grant was awarded to study the growth and related surface properties of GaN. The project funded a postdoctoral research assistant and a project studentship for a period of three years each.

Although the work to a great degree followed the original plan, the initial results concerning strain caused us to reduce our efforts in this area. In carrying out the molecular dynamics simulations we considered that the possibility of obtaining reliable melting points with relatively small unit cells to be a significant result and therefore pursued this aspect more vigorously. In order to give us more confidence in these results we felt obliged to perform additional calculations on some better documented materials systems - Si and Ge - in order to better support our conclusions for the nitrides. Also, being aware of the possibility that our structural results could be affected to some degree by the nature of our basic first principles calculations, specifically the adequacy of the exchange-correlation potential employed, we also performed some studies involving the so-called screened exchange formalism. The results of this work could have wider significance in the general context of all first principles calculations on semiconductor materials.

Basic calculational formalism

The principal calculations of total energy and structures were performed within the framework of density-functional theory (DFT) using the generalised gradient approximation of Perdew and Wang as implemented within the CASTEP code. These employed norm-conserving, non-local atomic pseudopotentials including Ga 3d states as part of the valence electrons in order to give reliable results. Cut-off energies of 900 eV were enforced, leading to convergence of total energy differences to better than 1 meV/atom. In modelling surfaces we utilised a supercell containing six GaN bilayers and a 10 angstrom vacuum region between layers. The lower-lying four of these bilayers were fixed at the respective unstrained or strained bulk optimized configurations (we had previously established that this was a sufficient bulk-like thickness to ensure reliability of our calculations). All other atoms in the above layers, together with any adatoms, were allowed to fully relax to their lowest energy configuration commensurate with the symmetry of the surface. The dangling bonds on the lower surface were saturated with fractionally charged H atoms in order to "neutralize" this surface.

Strained 1x1 GaN surfaces

Following initial unstrained calculations involving the bare surfaces we carried out a number of total energy calculations for the wurtzite structure GaN(0001) (Ga-terminated) and $\bar{0001}$ (N-terminated) surfaces with a 1x1 surface unit cell overlaid by Ga and N atoms in the atop position (directly above atoms in the top layer), T4 position (directly above atoms in the subsurface layer) and H3 position (directly above the "hole" in the layers below). These calculations were performed for unstrained and \pm biaxially strained layers and involved the full range of accessible chemical potentials for the system. Our results for the unstrained surface were in agreement with both experiment and previously published theoretical studies. We were thus able to approach the strained calculations with some confidence. In all cases the most stable configurations were found to be those with Ga adsorbates, while the N-covered surfaces were found to be unstable in all situations, irrespective of strain conditions. In the case of the GaN (0001) surface, we obtained some evidence of a reordering of the formation energy of the T4 and H3

configurations (the Ga T4 configuration normally has the lowest energy) under compressive biaxial strain conditions, but the difference in energy was only marginal. It was found that in the case of the GaN (0001) surface, the formation energy of the Ga atop configuration is lower than that of H3, with T4 having the highest energy and with the inherent differences between the formation energies being more marked than for the GaN (0001) surface. As a consequence of this starting point, and with a much larger formation energy difference between the different configurations, there was no re-ordering compared to that seen in the unstrained situation as a function of strain. We thus established that despite clear changes in the formation energy with strain this does not in itself substantially affect the relative formation energies of the different configurations and hence there appeared to be little reason to expect changes in observed growth or surface reconstructions as a consequence of the imposition of moderate strain.

Studies of 2x2 surfaces incorporating varying numbers of N atoms

Our main purpose in studying these surfaces was to obtain a clear picture of the energetics concerning the incorporation of N atoms on the growing GaN (0001) surface, both in the case of the standard 2x2 surface model and the laterally contracted Ga bilayer model. This latter structure, which was proposed by Northrup et al (*Phys. Rev. B* **61** 9932(2000)), features 4 atoms in a $\sqrt{3} \times \sqrt{3}$ surface unit cell above only 3 atoms in the underlying layer.

In the standard 2x2 surface we found, in common with other calculations that the N-H3 adatom is the most stable configuration under nitrogen-rich conditions and that under Ga-rich conditions the Ga adatom or adlayer is preferred. However, when considering the laterally contracted bilayer structure our results demonstrated that although the Ga layers are still the most energetically favourable, the displacement of 1 Ga atom by N leads to a more energetically stable situation than that of the N-H3 adatom under Ga-rich conditions. In practice, we found that a number of results for the contracted bilayer model are significantly different from those of the standard model. In the contracted bilayer model we observed a virtually linear relationship between the Ga-rich formation energy and the number of N atoms in the adlayer, whereas in the standard model this is not the case as the 2N-2Ga top layer, containing a strongly bonded N-dimer, "bucks the trend". The key results for the formation energies in the case of both the standard and laterally contracted bilayer models are shown in figs 1 and 2.

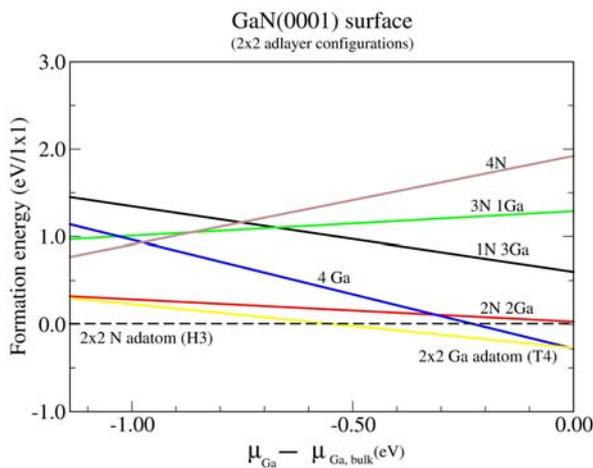


Fig 1 Formation energies for standard adlayer

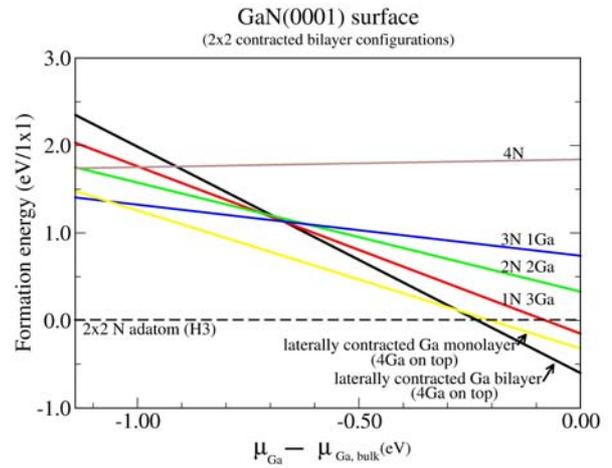


Fig 2 Formation energies for contracted bilayer

Studies of 2x2 surfaces incorporating varying numbers of Al, In and As atoms

As an aid to the study of alloy growth we carried out a series of calculations involving the incorporation of a varying number of Al, In and As atoms together with N onto the GaN (0001) surface, and phase diagrams, showing the various surface phases as a function of chemical potential, were constructed for each species. Formation energy diagrams and structural parameter data for all these configurations have been published. In all situations where at least 3 N atoms were present on the surface significant surface reconstruction involving the formation of an N trimer with 3 N atoms displaced from the atop positions were observed. For most surfaces, independent of the number of N atoms it was found that the surfaces were unstable relative to the bare Ga-terminated surface. However, in the case of one particular configuration, consisting of 3 N atoms and 1 In atom, we found that this was clearly more stable than the clean surface (0001) adlayer under nitrogen rich conditions, as can be seen in fig 3

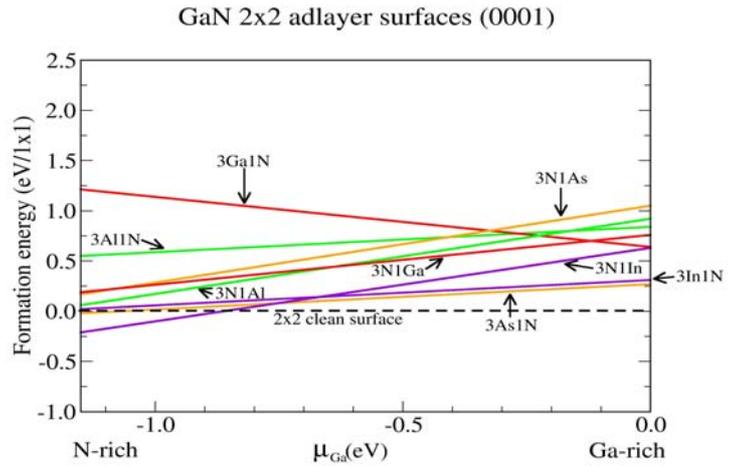


Fig 3 Formation energy of Ga 2x2 surface for 1 and 3 N substitutions

Molecular dynamics calculations

The latter part of the project concerned the use of molecular dynamics simulations within the density functional theory framework to study thermal expansion properties and melting points. Calculations of this type are generally very highly computationally intensive, involving hundreds of atoms. In practice, in carrying out preliminary calculations on silicon and germanium, for which more experimental information, and some previous theoretical studies by others was available for comparison, we obtained some rather surprising results: we were able to obtain results in good agreement with experiment with a rather limited size unit cell, which was much smaller than traditionally employed.

An isothermal-isobaric ensemble was employed in the simulations. This utilised a relatively small number of particles per unit cell to obtain the thermal expansion coefficients over a range of temperatures. The number of atoms used varied from a minimum of only 8 up to a maximum of 54 atoms. A number of calculations were performed over a range of temperatures from near zero Kelvin to above the expected melting points. We normally used 5000 time steps in the thermalization process. The average values of the lattice constant and potential energy were obtained from a full structural relaxation at each step of the simulation and this information was used to extract the temperature-dependent thermal expansion coefficients. Figure 4 shows a smoothed analytic fit to our calculated results for the lattice constant of Si as a function of temperature, together with the experimental results of Yim and Paff (from *J. Appl. Phys.* Vol. 45, 1456(1974)). Despite employing only an 8-atom unit cell in these calculations it is notable that the trend in the theoretical results matches very closely with that of experiment. The initial offset in lattice constant is due to the usual slight difference encountered when comparing calculated lattice constants with experiment. We also saw clear evidence of the position of the melting point in the form of a discontinuity in the potential energy versus T plots, as can be seen in fig 5, from which we deduced a value of 1674 ± 26 K. This should be compared to the experimental value of the melting point of 1686 K. Similarly good results were obtained for the melting point of Ge (1200 ± 20 K in our calculations cf 1208 K from experiment), for which calculations involving larger unit cells were seen only to confirm the initial results with smaller unit cells. Given that it is only relatively recently that Alfe and Gillan (*Phys. Rev. B* 68, 202512 (2003)) succeeded for the first time in obtaining a reliable theoretical estimate for the Si melting point using a much larger unit cell, it is for this reason that we consider our results employing a much smaller unit cell to be so significant. These preliminary results, to justify our approach with regard to our nitride material calculations, have been submitted for publication and the additional results for the nitrides are in preparation.

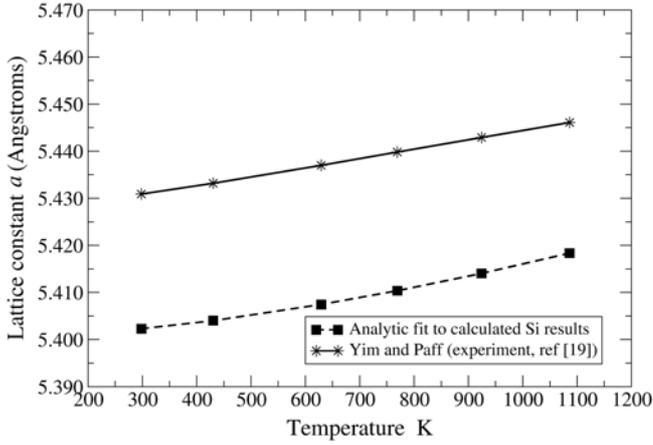


Fig. 4 Calculated and experimental lattice constant of Si versus temperature, T

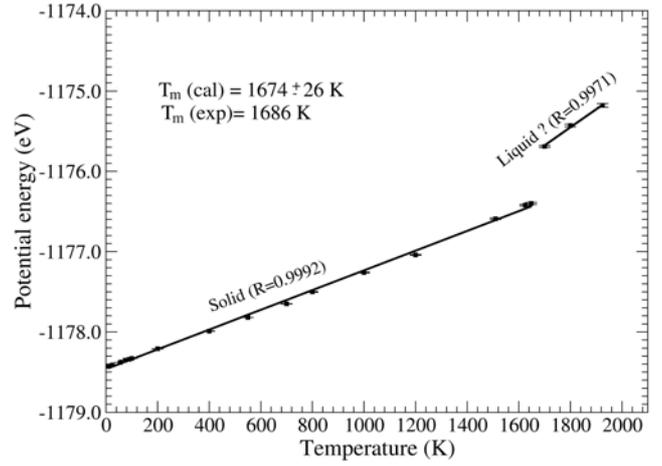


Fig 5 Discontinuity in potential energy versus T indicating value of melting point

Extending the Density Functional Calculations: Screened Exact-Exchange

The standard Kohn-Sham density functional theory is a well established method for calculating the properties of condensed matter systems from first principles. It is, in principle, an exact theory of the electronic ground state, although in practice approximations must be made in the treatment of exchange and correlation effects. Computationally cheap exchange-correlation functionals such as the LDA and GGA provided us with a good description of the structural properties of GaN. However, other properties, which might have an influence on the results obtained, such as the electronic band gap, are not so well described. The reason for this may be in part due to the fact that DFT is only an exact theory of the ground state, and so should not necessarily be expected to predict excited state properties, but is mainly due to the approximations made in the LDA and GGA.

The screened exchange (sX) method involves a generalisation of the Kohn-Sham formalism so that the exchange-correlation potential includes a non-local component in the form of an integral operator. This is essentially the Hartree-Fock method with the exchange interaction screened at long range. In order to investigate the properties of GaN (and related materials) further, we have implemented the screened exchange method to calculate the electronic band structure and compared this with the results of the standard LDA and GGA schemes. The aim of this was to investigate if there were any other structural effects which could have been affected by the choice of scheme employed.

The standard Kohn-Sham scheme involves the mapping of the true many-electron wavefunction onto a fictitious non-interacting system with the same density profile. The local Kohn-Sham potential for the non-interacting system includes a component associated with exchange and correlation effects. In the screened exchange scheme a non-local component is included in the exchange-correlation potential. It is given by

$$V_{sX}(r, r') = - \sum_i \frac{\psi_i(r') e^{-k_{TF}|r-r'|} \psi(r)}{|r' - r|}$$

where the $\psi_i(r)$ are the single-particle Kohn-Sham orbitals. The exponential constant, k_{TF} , is the Thomas-Fermi screening length and is calculated from the average electron density of the system (note that without the screening term, this simply reduces to the Hartree-Fock exchange potential)

We have implemented the screened exchange method within the CASTEP density functional code. The computational cost of a screened exchange calculation scales as the number of basis functions cubed, and is significantly more expensive than the LDA or GGA. For band structure calculations, it is possible to use the LDA to perform the self-consistent electronic minimisation before using screened exchange for

the band structure itself. This does not significantly alter the results and saves a great deal of computational time. Furthermore, a single evaluation of the screened exchange eigenvalues on a set of bands calculated with the LDA yields energies that differ by no more than a few percent from the self-consistent screened exchange results.

Our initial results are extremely encouraging. For GaN and related materials we have been able to calculate, from first principles, the electronic band gap to within a few percent of the experimental value. Comparing this to the standard LDA or GGA calculations, which often underestimate the band gap by around 50% (and even up to 100% in the case of elemental Ge), the sX results are excellent.

One very important application of our DFT calculations is to calculate the geometry of the material by finding the structure that minimises the total energy. To do this efficiently, we need to be able to calculate the derivatives of the energy with respect to both the atomic coordinates and the lattice vectors. The derivatives with respect to the coordinates, i.e. the forces on the atoms, can be calculated efficiently using the Hellman-Feynman theorem, and this has no contributions from exchange and correlation. However, derivatives with respect to the lattice vectors, which relate to the stress tensor do have contributions from exchange and correlation, and this must be taken into account if a new exchange-correlation functional is to be used. While it is always possible to calculate the stress numerically by using finite differences, this will generally require several evaluations of the total energy, which could prove computationally restrictive. We have derived and implemented a formula to compute directly the contribution to the stress tensor from exchange and correlation effects when using the screened exchange method in Kohn-Sham density functional theory. The formula is also applicable when using related functionals such as Hartree-Fock (HF) or exact exchange (EXX). This has paved the way for full geometric relaxation of the structure when using such functionals, without the need for expensive numerical differentiation. The formula is derived in reciprocal space, appropriate for plane-wave based calculations, and has been implemented within the efficient, and fully parallel, DFT code, CASTEP.

The equilibrium lattice parameters obtained from screened exchange are somewhat lower than both the LDA results and experimental results. This may be a property of the functional itself; after all it has not been extensively tested as to its accuracy when calculating geometries. It may also be due to the fact that we are using LDA pseudopotentials which may not be appropriate for screened exchange calculations. However the question of how best to define pseudopotentials appropriate for screened exchange, and the determination of the extent to which this may affect structural calculations, remains open.

Dissemination and exploitation

The results of the project have been published (or are expected to be published), as listed below. They have also been presented at a number of UK and international conferences. In particular, we have regularly attended and presented the results of our work at the UK Nitrides Consortium meetings (one of these took place at Durham in 2004 with our assistance as local organisers) as well as at the Warwick and Belfast CMMP meetings and at Daresbury. Presentation of the results to an international audience was made at the 2004 ICPS meeting in Flagstaff and at other meetings in San Francisco and New Jersey in the USA.

Publications

Ab initio studies of strained wurtzite GaN surfaces, V. Timon, S. Brand, S. J. Clark and R. A. Abram, Journal of Physics: Condensed Matter Vol 16 531-542 (2004).

Theoretical adlayer surface morphology of wurtzite 2x2 reconstructions of the GaN (0001) surface, V. Timon, S. Brand, S. J. Clark and R. A. Abram, Journal of Physics: Condensed Matter Vol 17 17-26 (2005) (This was chosen by the IOP Editors as an IOP "Select" article based on one or more of the following criteria: Substantial advances or significant breakthroughs/high degree of novelty/significant impact on future research.)

First-principles calculations of 2x2 reconstructions of GaN surfaces involving N, Al, Ga, In and As atoms, S. Brand, S. J. Clark, M. C. Gibson and R. A. Abram, Phys. Rev. B. Vol 72 035327 (2005).

First principles calculations of 2x2 reconstructions of GaN surfaces, V. Timon, M. Gibson, S. Clark, S. Brand and R. Abram, ICPS-27, Flagstaff, Arizona, 26-30 July 2004, Physics of Semiconductors, Pts A and B: 373-4, 2005.

Screened exchange calculations of semiconductor bandstructures, M. Gibson, S. Clark, S. Brand and R. Abram, ICPS-27, Flagstaff, Arizona, 26-30 July 2004, Physics of Semiconductors, Pts A and B: 1125-6, 2005.

Molecular dynamics calculations of the thermal expansion properties and melting points of Si and Ge, V. Timon, S. Brand, S. J. Clark and R. A. Abram, submitted to Journal of Physics: Condensed Matter.

Contributions to the Stress Tensor from the Screened Exchange Density Functional, M. C. Gibson and S.J.Clark, Submitted to Physical Review.

Presentations/posters

Calculation of stress tensors with non-local density functionals, M. C. Gibson, S. J. Clark, S. Brand and R. A. Abram, UKNC meeting, Nottingham, 14 June 2005 (poster)

Screened Exchange Calculations and their application to semiconductors, M. C. Gibson, S. J. Clark, S. Brand and R. A. Abram, MRS Spring Meeting, San Francisco 2005 (poster)

Non-local treatment of exchange in density functional theory, M. C. Gibson, S. Brand and R. A. Abram and S. J. Clark, Electronic Structure (ES04) Conference, New Jersey 2004 (poster)

Molecular dynamic calculations of GaN wurtzite and zinc-blende thermodynamic properties, V. T. Salinero, S. Brand, S. J. Clark and R. A. Abram, UKNC meeting, Manchester, 13-14 January 2005 (talk)

Molecular dynamic calculations of GaN thermodynamic properties, V. T. Salinero, S. Brand, S. J. Clark and R. A. Abram, CCP9 Workshop, Daresbury Lab., 29-30 November 2004 (poster)

Resolving discrepancies concerning the enthalpy of formation of gallium nitride, M. C. Gibson, S. J. Clark, S. Brand and R. A. Abram, CCP9 Workshop 2004, Daresbury Lab., 29-30 November 2004 (poster)

Theoretical adlayer surface morphology in wurtzite 2x2 reconstruction GaN (0001) surface, V. T. Salinero, S. Brand, S. J. Clark and R. A. Abram, CMMP, Warwick, 4-7 April 2004 (poster)

First principles calculations of gallium nitride surfaces, M. C. Gibson, S. J. Clark, S. Brand, CMMP, Warwick, 4-7 April 2004 (poster)

First principles calculations of adlayers on GaN surfaces, V. Timon, S. Brand, S. J. Clark and R. A. Abram, UKNC meeting, Durham, 6-7 January 2004 (talk).

A first-principles study of cubic-phase GaN surfaces, M. C. Gibson, S. Brand and S. J. Clark, CMMP, Belfast, 6-9 April 2003 (poster).

Ab initio studies of strained wurtzite GaN surfaces, CMMP, Belfast, 6-9 April 2003 (poster)