First Principle Study on the Domain Matching Epitaxy Growth of Semiconductor Hetero-Interface

Vu Ngoc Tuoc*

Department of Theoretical Physics, Institute of Engineering Physics (IEP), Hanoi University of Technology (HUT), 01 Dai Co Viet Str., Hanoi 10000, Vietnam

In conventional lattice-matching epitaxy with lattice misfit of less than 7–8%, the thin films grow pseudomorphically (i.e. film take lattice constant of the substrate up to some “critical thickness” of one to several monolayers). Above this misfit, it was surmised that the film will grow textured or largely polycrystalline. The recent discovery of Domain Matching Epitaxy Growth method had proposed the new growth technology using Pulsed laser deposition (PLD), by which the epitaxial growth of hetero-thin films with very large lattice mismatch is possible by matching of domains where an integer multiples of major lattice planes match across the interface. Misfit dislocation generated along the interface (i.e. critical thickness is less than one-monolayer). Based on all of these exciting technology applications, there is an urgent need to study the material properties, structure correlations and defect microstructure for this thin film growth mode. In this work, we performed an ab-initio study of the structural properties of that pseudomorphic-like growth of semiconductor hetero-interface using the well-known density functional-based tight-binding (DFTB) simulation tool. We examine the simulation study of domain matching growth of GaN(0001)/Si(111) - a Hex-on-Cub problem.

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1. Introduction

Although the growth of large GaN single crystals is presently a research area of great effort, device applications of GaN are still based on heteroepitaxial GaN substrates grown on sapphire or SiC. A step of great technological and commercial potential is a further integration of laser structures into data processing devices by the implementation technology by Pulsed Laser Deposition (PLD), by which the epitaxial growth of hetero-thin films with very large lattice mismatch is possible by matching of domains where an integer multiples of major lattice planes match across the interface. Thus the Domain Matching Epitaxy (DME) growth technology is an unified model for thin film epitaxy where single crystal films with large lattice misfits are grown by domain matching. It involves matching of lattice planes between the film and the substrate having similar crystal symmetry. Although a single lattice mismatch of those systems is very large, however it is possible by nearly-perfectly matching of domains where integral multiples of major lattice planes match across the interface.

There are many interesting material systems in nature which meet a slightly-off perfect integer domain matching (DM) ratio e.g. for interface strain in Cu-on-Si(100) following (1) \( \varepsilon = \frac{a_t}{a_s} - 1 > 7 - 8\% \Rightarrow \varepsilon = \frac{(m/n)}{a_t/a_s} - 1 \ll 1\% \)

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2. Simulation Structure

The heteroepitaxial growth of (0001) GaN thin films directly on (111) Si by laser-molecular beam epitaxy without the formation of a SiNx interlayer at the GaN/Si interface is reported in J. Narayan et al.2 Author find that SiNx can be formed subsequently as a result of nitrogen diffusion to the
lattice constant of a stacking layers of GaN(0001) on Si(111), with in-plane interface by creating a supercell configuration containing the top-left inset in Fig. 1). We modeled this received high resolution transmission electron microsc (TEM) (see inset). The atomic structure of the interfaces was studied by selected area by electron diffraction (see the bottom right of GaN on Si(111) was determined using X-ray diffraction GaN/Si(111) interface. In Fig. 1 the orientation relationship that there is 6-to-5 domain misfit, follows eq. (1), is very small (ε~0.3%). Then the structure optimization was performed by using the slab-supercells of total 441-atoms, which contains 6 by 6 GaN unit cell with 5 atoms layers and 5 by 5 unit Si(111) with 6 atomic layer, include 111 hydrogen surface-terminated atoms. Edge slab layers are terminated with hydrogen and a thick vacuum layer. We limited only the system of N-terminated interface since Nitrogen is much more electronegative than Galium therefore Nitrogen will naturally bond to Silicon, more easily than Galium. Noticed that Pauling negativity numbers of Ga, Si and N are 1.6, 1.8 and 3.0 correspondingly. Therefore the strongest GaN/Si interfacial bond should involve N-atom face bonding to Si-atom face. Whereas the modern ab-initio method can treated a system up to around a hundred atoms supercell so that the choice of calculation method in this study had fallen on a semi ab-initio Density-Functional-Based Tight-Binding (DFTB) method.

3. Density-Functional-Based Tight-Binding (DFTB) Simulator

The spin-polarized, charge self-consistent, DFTB approach is based on a second-order expansion of the spin-dependent Kohn-Sham total energy functional with respect to a given reference charge and magnetization density. The method has been extensively discussed elsewhere and briefly outlined here as:

1. Expand the orbitals as a linear combination of Slater type orbitals (LCSTO):

\[
\psi_n(r) = \sum_{\text{atomic site } i} \sum_{\text{orbital } \nu} C_{in\nu} \phi_{n\nu}(r - R_i)
\]  

The basis functions \( \phi_{jn}(r - R_i) \) centered on the atomic nucleus \( i \), with position \( R_i \), are themselves a linear combination of single Slater orbitals \( \phi_{jn}(r) = (\sum_{\lambda=1}^N \sum_{m=0} a_{\lambda j} \alpha(r) e^{-\alpha(r)/m}) Y_{l,\lambda}^m \). The angular and magnetic quantum number are indicated with \( l \) and \( m \). \( Y_{l,\lambda}^m \) is the corresponding real spherical harmonic.

2. Tight-binding expansion of the wave functions (calculation of the matrix elements in the two-centers approximation):

\[
\sum_{\text{atomic site } i} \sum_{\text{orbital } \nu} |H_{iv,ji} - ES_{iv,ji}|C_{iv,ji} = 0
\]

with

\[
H_{iv,ji} = \langle \phi_{iv} | \hat{H} | \phi_{ji} \rangle \text{ and } S_{iv,ji} = \langle \phi_{iv} | \phi_{ji} \rangle
\]  


### Table 1 Detailed stoichiometric analysis for the MD relaxed stable configuration.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Layer thickness (Å)</th>
<th>Change compare with bulk value</th>
<th>Eff. Charge (+e)</th>
<th>Net Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si1st</td>
<td>2.355 [2.364]</td>
<td>–0.38%</td>
<td>3.99 [4.0]</td>
<td>+0.00</td>
</tr>
<tr>
<td>Si2nd</td>
<td>0.786 [0.788]</td>
<td>–0.25%</td>
<td>3.999</td>
<td>+0.00</td>
</tr>
<tr>
<td>Si3rd</td>
<td>2.373</td>
<td>+0.38%</td>
<td>3.990</td>
<td>+0.01</td>
</tr>
<tr>
<td>Si4th</td>
<td>0.834</td>
<td>+5.8%</td>
<td>4.005</td>
<td>–0.005</td>
</tr>
<tr>
<td>Si5th</td>
<td>2.285</td>
<td>–3.3%</td>
<td>4.134</td>
<td>–0.134</td>
</tr>
<tr>
<td>Si6th</td>
<td>interface distance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt;Si-N&gt; = 1.82 Å</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>natural Si-N bond:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.94 Å</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[β-Si3N4 = 1.74 Å]</td>
<td></td>
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</tr>
</tbody>
</table>

(\( ^\circ \)) the value in a [] bracket is the bulk material value.

Fig. 1 the DME growth of (0001) GaN thin films directly on Si(111) (after J. Narayan).
$E_{\text{int}} = \sum_{i} n_{i} (\langle \psi_{i} | H_{0} | \psi_{i} \rangle + \frac{1}{2} \sum_{\mu, \nu} \gamma_{\mu \nu} \Delta q_{\mu} \Delta q_{\nu} + E^{\text{rep}})$ (5)

where $\Delta q_{\mu}$ - charge fluctuation decomposed into atomic contribution (Mulliken charge), $\gamma_{\mu \nu}$ - some integral coefficient, $E^{\text{rep}}$ - repulsive term (see Ref. 4–7)).

With all matrix elements and orbitals are derived from Density Functional calculation, the advantage of DFTB method relies on the use of small basic set of atomic orbitals (in order to reduce the matrix dimension for diagonalization speed-up) and the restriction to two center nonorthogonal Hamiltonian (allowing extensive use of look-up table). What it distinguishes from semi-empirical method is the explicit calculation of the basic wave function which allow deeper physics insight and better control of the approximation used. The method solved Kohn-Sham equation self-consistently using Mulliken charge projection. This approach have proved to give transferable and accurate interaction potential as well as numerical efficiency allowing Molecular Dynamic (MD) simulation of supercell containing several hundreds to a thousand atoms. Thus this is particular suitable to study the electronics proper and dynamics of large mesoscopics system and organic molecule such as CNT’s, DNA stands or absorbate on surface, semiconductor hetero-structure etc. see review in Ref. 7). The advantage of DFTB parameterization is that only few, possibly well chosen systems are needed to creat the parameters, i.e. in DFTB fit systems can also be purely ideal systems, if they are chemically acceptable and can be described carefully with an ab-initio approach. Next this well tested parameter, e.g. in an attention for solid state systems and for defect physics as in current case, can be used for much larger system due to its transferability. In our calculation the parameter and its transferability have been successfully applied in several DFTB works.8–10)

4. Results and Conclusion

It has been shown that the Ga-3d electrons despite of their localization do not behave as proper core electrons and even may undergo a hybridization with the N-2s orbitals in the LDA representation. So far from argument that the lattice parameters and the electronic structure of Ga-compounds calculated treating the 3d-electrons as valence are closer to the experimental values, we use the DFTB created parameter set9,10 with the 3d electrons explicitly included in the valence, i.e. include ten d-electron to total 13 valence electrons for Ga atom in calculation. For all our calculation we treated Si(3s, 3p), N(2s, 2p), Ga (3d,4s,4p) as the valence electrons so that our slab supercell has a total number of 2187 valence electrons.

By varying the interface distance between GaN(0001) and Si(111) and lead the supercell to relaxed in the growth direction (i.e. perpendicular to the interface direction) we can obtain a interface stoichiometry. For various configurations obtained the energetically most stable has shown in Fig. 2. It is well known that while the film thickness is less than a “critical value”, measured by one to several monolayers, the lattice mismatch, in conventional means, will cause a strain at the interface which is relaxed by the relaxation mechanism of creating surface roughness, i.e. irregularities which form surface relief. Alternatively if the thickness of a strained layer exceeds that “critical value” the interface prefer to release its strain by dislocation introduction. Therefore the first outcome from the study on the DME growth mode is (i) there is the misfit dislocation generated along the interface resulting from that the critical thickness is less than one-monolayer, i.e. equivalent zero monolayer. This means that there is no conventional lattice-matching surface roughness or the dominant strain relaxation mechanism is the defect introduction - a line dislocation at the interface, in this case. Subsequently the interface and the subsequent layer from the interface are relatively flat despite the lattice misfit is very high. These can be clearly observed from the real interface image in Fig. 1 and simulation configuration in Fig. 2. (ii) There is also no more dislocation beneath the plane interface, i.e. no buffer region. This means that out of the interface plane there will be nearly perfect crystal symmetry, i.e. no buffer region with no interstitial sites, excepts some variation in the layer distance in growth direction, see more in Table 1. Thus the misfit induced reordering in creating interface terrace dislocation and relaxed in growth direction is possible very useful quality of DME technology making it very attractive for ultra thin growth mode where the interface flatness and avoiding amorphous sub-interface buffer layer are important.

Figure 2(a) shows most stable MD relaxed configuration within a lateral view from growth direction, which confirm the good flatness of the atomic layer and the cage correspond to the “terrace” line dislocation, Fig. 2(b) shows the top view with the arrows marked the along the corresponding experimental dislocation line (see also in Fig. 1 where the dislocation marked by “T sign”). In Fig. 2 the Si atoms marked by bronze, Nitrogen by blue, Ga by red and H by

![Figure 2](image-url)
white accordingly. Figure 3 shows the graph of total energy per slab atom as a function of the interface distance.

Obtaining the stable interface configuration by MD relaxation, the work of separation, $W_{\text{sep}}$, is calculated. Follows R. Yang and S. Tanaka\textsuperscript{11,12} this is defined as the reversible work needed to separate the interface into two free surfaces in a thought experiment whereby plastic and diffusional processes are suppressed, i.e. two fixed separate surfaces with the same positions as in the interface. Next, each separate surface is relaxed into a free surface in order to obtain the work of adhesion, $W_{\text{ad}}$, which is defined here as the work needed to separate an interface into two relaxed free surfaces. These two works $W_{\text{sep}}$ and $W_{\text{ad}}$ are fundamental quantities which characterizes the strength of the interface. All surface calculations are performed with the same supercell used for the interface calculations. As a result we have received $W_{\text{sep}} = 0.818$ [J/m$^2$] and $W_{\text{adh}} = 0.742$ [J/m$^2$]. Here it should be noticed that the $W_{\text{adh}}$ is lower than $W_{\text{sep}}$ owing to surface reconstruction.

Since DFTB method can provide detailed chemical bonding states between constituent atoms, the origin of the interface strength and the effect of the interfacial atomic pair configuration is discussed. The overlap population between orbitals $i$ and $j$ at the $n_{th}$ band is defined in the Mulliken scheme as follows:

$$q_{i,j}^{n} = A_{i}^{n} A_{j}^{n} S_{i,j}$$

where $A_{i}^{n}$ is the eigenvector component of the $i^{th}$ orbital in the $n^{th}$ orbital in the $n^{th}$ band, and $S_{i,j}$ is the overlap integral. Together with the effective charge $Q_{a}$ of an atom $a$:

$$Q_{a} = \sum_{n_{occ}} \sum_{i \in a} \sum_{j} q_{i,j}^{n}$$

Subtraction of $Q_{a}$ from the number of valence electron provides the net charge, $Q_{a}^\ast$. A detailed configuration analysis is shown on Table 1, in which the position of each layer is determined by taking an average of positions of all atoms in a layer planes.

As described above, the analysis shows the interface distance between Si(111) and N-terminated face of GaN(0001) is 1.82 Å, which is less than the natural Si-N bond length (1.94 Å) but larger than the most stable $\beta$-Si$_3$N$_4$ bond value (1.74 Å). Further the layer distance between the interface atomic layers (Si$_{6th}$ and N$_{1st}$) and the subsequent atomic layers (Si$_{5th}$ and Ga$_{1st}$), is changed, decreased by about 3.3% and 1.8% relative to those in bulk respectively i.e. the subsurface layer move out towards the surface layer, thereby reducing their inter-layer separation. Along with upward movement towards vacuum of the second nearest layer atoms (Si$_{4th}$ and N$_{2nd}$) by ~5%. Next the net charge analysis show the Si atoms at the interface Si$_{6th}$ exhibits positive net charge (+0.768e) and that of Si$_{5th}$ and N$_{1st}$ are negative (~0.134e and ~0.65e accordingly). This indicates that an amount of charge transfer takes place from Si interface layer toward N interface layer making the interface charged and a smaller amount to Si bulk by the presence of the heterointerface.

In Fig. 4 we employed the Density of States (DOS) for bulk GaN and whole slab as well as the site-projected and $l$-projected Partial Density of states (PDOS) for separate slab
layer and selected interface site (see Fig. 5). From these DOS and PDOS results obtained, we may draw the following conclusions:

1. Bulk Si and GaN exhibits covalent bonding. Its covalent nature can be seen by the Fermi level in their DOS, Figs. 4(a)–4(b). However the slab DOS, Fig. 4(c), shows that the polarity of the charged interface induced a weak metallic component of bonding that can also be seen in the DOS by the present of some finite density of state at the Fermi level. This new charged interface induced state appear in the energy range between 1.5–2 eV around the Fermi level.

2. Further the layer PDOS analysis in Fig. 5(a) reveals that, an interface-induced state that cross the Fermi level come from the N-interface layer DOS (of atoms Nitrogen 226–261) due to the excess of electron charge, whereas the Si-interface layer (atoms 201–225) not play any role due to the lack of electron charge.

3. Recently studying GaN grown on (0001) surfaces on 6H–SiC which has two different surface terminations with nominally the same lattice mismatch, Sakaki and Matsuoka proposed a model concept about central factor for determining the interface quality that is not the smallness of the lattice misfit, resulting in the mechanical strain as widely assumed, but electrical polarity of the interface. Further Yuan and Dow John using arguments based on both electronic structure calculations and ionic radii, had pointed out the effect of the positive charge at the Si-terminated interface to facilitate lattice matching of SiC/GaN interface by changing the radii of interfacial N anions deposited on the substrate. Thereby explain the observation that the Si-terminated interface produces smoother GaN film surfaces serving the superior substrate for GaN to the C-terminated surface. A similar material and symmetry also occurs here in our problem with GaN/Si. In fact the polarity of the interface by charge transfer from Si to N and positive charge at the Si-terminated interface have played here very important role that lead to stronger attraction of GaN’s N-face to substrate and hence to smoother and more perfect flat interface. These interface charges approximately +0.77e and –0.65e on the interface atoms Si and N faces respectively (see Table 1). Since the N-terminated interface are much stronger bonded to Si, due to the electronegativity of atoms involved, rather than Ga-terminated one and due to bond character here a transfer of electron charge from Si to N have occurs. Additionally some other charge was taken to Si-second layer and this was shorten by comparing with natural Si-N bond length toward the value of the most stable ceramic silicon nitride \( \text{Si}_2\text{N}_4 \).

4. the site PDOS and l-DOS for the selected interface atoms (N\(_{250}\) and Si\(_{217}\), which are in the front row of the interface plane see Fig. 2(a)) are shown in Fig. 6.
It was convinced that the charge transfer and interface-induced state involve the p-orbital from N-face atom. In summary, we have studied the structural and electronic properties of the DME growth GaN(0001)/Si(111) interface by the DFTB calculations, which match the 6 to 5 stacking of DME ratio and allows reducing SiN$_x$ phase formation to less than one monolayer ($x\sim 4/3$). The polarity of the interface by charge transfer from Si to N has very important role lead to stronger attraction of N-face than to Ga-face. The interface charged and relatively large, induces the shortening the Si-N interface bond and one layer away from interface. Moreover the DOS at Fermi level is relative high expose a new interface-induced state arising from p-orbital of N atoms interface.

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