Surface relaxation and band structures

Atomic Geometry, Energetics & Electronic Structure of GaAs (110) surface

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Motivation

*God made solids…..
…….but surfaces were the work of the devil.*
W. Pauli

**Why surfaces?**

**Why GaAs(110)?**
Slab approach

Explore:
- surface energy
- atomic geometry
- electronic structure
GaAs (110) surface unit cell

Primitive fcc cell
- 2 atoms per cell

tetragonal cell
- 4 atoms per unit cell
- building (110) surface

\[
\text{cell} = \begin{bmatrix}
\text{aLat} \cdot [1, 0, 0, 0], \\
\text{aLat} \cdot [0, \sqrt{2}/2, 0, 0], \\
\text{aLat} \cdot [0, 0, 1, 1]
\end{bmatrix};
\]

primitive vectors of the tetragonal cell
GaAs (110) surface unit cell

primitive vectors + high symmetry k-points

GaAs110.sx

GaAs_110noH.sx

atomic coordinates

GaAs110.sx

cell = \[
\begin{array}{ccc}
  a\text{Lat} * [ & 1, & 0 \\
  a\text{Lat} * [ & 0, & 1/\sqrt{2} ] \\
  c\text{Lat} * [ & 0, & 0 ]
\end{array}
\];

species {
  include species_1;
  atom { coords = a\text{Lat}/2 * [ 0, 0, 0 ]; };
  atom { coords = a\text{Lat}/2 * [ 1, 1/\sqrt{2}, -1/\sqrt{2} ]; };
  atom { coords = a\text{Lat}/2 * [ 0, 0, -2/\sqrt{2} ]; };
  atom { coords = a\text{Lat}/2 * [ 1, 1/\sqrt{2}, -3/\sqrt{2} ]; };
  atom { coords = a\text{Lat}/2 * [ 0, 0, -4/\sqrt{2} ]; };
  atom { coords = a\text{Lat}/2 * [ 1, 1/\sqrt{2}, -5/\sqrt{2} ]; }
}

species {
  include species_2;
  atom { coords = a\text{Lat}/2 * [ 1/2, 1/\sqrt{2}, 0 ]; };
  atom { coords = a\text{Lat}/2 * [ 3/2, 2/\sqrt{2}, -1/\sqrt{2} ]; };
  atom { coords = a\text{Lat}/2 * [ 1/2, 1/\sqrt{2}, -2/\sqrt{2} ]; };
  atom { coords = a\text{Lat}/2 * [ 3/2, 2/\sqrt{2}, -3/\sqrt{2} ]; };
  atom { coords = a\text{Lat}/2 * [ 1/2, 1/\sqrt{2}, -4/\sqrt{2} ]; };
  atom { coords = a\text{Lat}/2 * [ 3/2, 2/\sqrt{2}, -5/\sqrt{2} ]; }
}

input.sx

\begin{verbatim}
\text{aLat} = 10.47; \\
\text{cLat} = 37.017; // 6L slab + 4L vacuum \\
\text{structure} {
  include "./structures/GaAs110.sx";
  include "./structures/GaAs_110noH.sx";
}
\end{verbatim}
GaAs (110) input file

```plaintext
basis {
  eCut    = 10.;
  kPoint { coords = [1/2 ,1/2 , 0 ];
           weight = 1;
           relative;
  }
  folding = [2, 2, 1 ];
}

Hamiltonian {
  xc       = LDA;
  ekt      = 0.;
  nEmptyStates = 0;
}

main {
  CCG { maxSteps = 1000;
        dEnergy = 1.e-6;
        printSteps = 25;
  }
}

ideally no dispersion of the band structure along z direction

k-point mesh \rightarrow in xy plane

all state CCG scheme doesn't allow empty states
```
GaAs (110) unPassivated – output files

- Energy convergence
- Electrostatic potential
- Charge density

- GaAs is ionic to a certain extent
- Charge-density maximum → towards the anion
passivation with Hydrogen

electron counting rule

Ga : $-\frac{3}{4}e^-$ to a bond $\rightarrow$ passivated by $-\frac{5}{4}e^-$

As : $-\frac{5}{4}e^-$ to a bond $\rightarrow$ passivated by $-\frac{3}{4}e^-$

- no charge transfer
- use of thinner slab
- treatment of slabs with no equivalent sides (i.e. GaN(0001)

ideal GaAs(110) surface

calculate:
- total energy
- electrostatic potential
- charge density
structure relaxation with quasi Newton scheme

main {
  quasiNewton {
    convergence {
      \text{dEnergyStruct} = 1.e-4;
    }
    CCG {
      maxSteps = 1000;
      \text{dEnergy} = 1.e-6;
      printSteps = 25;
    }
    output {
      saveWaves = 1;
    }
  }
}

gas movable;

\begin{align*}
\text{Ga} & \quad \text{As} \\
& \quad \text{H} \quad \text{H}
\end{align*}
After an ionic step → charge density doesn’t correspond to the new atomic geometry

- Born–Oppenheimer surface has to be approximated after each ionic step.
Check the displacement of atoms in each layer.

Compare your calculated structural parameters:

<table>
<thead>
<tr>
<th></th>
<th>aLat [Å]</th>
<th>x [Å]</th>
<th>z [Bohr]</th>
<th>ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT-LDA (E_{xc}=8Ry)</td>
<td>[5.55]</td>
<td>[4.29]</td>
<td>2.17</td>
<td>28.6</td>
</tr>
<tr>
<td>Experiment</td>
<td>10.69</td>
<td>1.30</td>
<td>2.48</td>
<td>31.1</td>
</tr>
</tbody>
</table>

energetics
- Total energy of the bulk GaAs is needed
- The same special k-points and cut off energy with the slab is needed

projected band structure
- projection of the bulk bands onto the first surface BZ

Same lateral unit cell (x-y) as for the surface

```python
aLat = 10.47;

structure {
    include "../structures/bulk.sx"
}

basis {
    eCut = 10.;
    kPoint { coords = [1/2, 1/2, 1/2];
        weight = 1;
        relative;
    }
    folding = [2, 2, 5];
}
```

```python
bulk.sx
```
Surface energies

Energy necessary to cut the crystal at some plane

\[ E_{\text{SURF}} = \left( E_{\text{SLAB}} - E_{\text{BULK}} \right) / 2 \]

the slab has 2 surfaces

\[ E_{\text{hydrogens}} = \left( E_{\text{SLABbothH}} - 3 \cdot E_{\text{BULK}} \right) / 2 \]

energy of the hydrogen saturated surface

<table>
<thead>
<tr>
<th></th>
<th>Formation energy [eV/1 \times 1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT [1]</td>
<td>1.13</td>
</tr>
<tr>
<td>Experiment [3]</td>
<td>1.17 ± 0.2</td>
</tr>
<tr>
<td>Your calculations relaxed</td>
<td></td>
</tr>
<tr>
<td>Your calculations unrelaxed</td>
<td></td>
</tr>
</tbody>
</table>

surface band structure

structure {
    include "../structures/GaAs110.sx"
    include "../04_relSurf/relSlab.sx"
}

basis {
    eCut = 10;
    kPoints {
        from { coords = G; label="G"; }
        to { coords = XPrime; label="XPrime"; nPoints=3; }
        to { coords = M; label="M"; nPoints=4; }
        to { coords = X; label="X"; nPoints=3; }
        to { coords = G; label="G"; nPoints=4; }
    }
}

initialGuess {
    waves { lcao { maxSteps = 1; rhoMixing = 0.05; } }
    rho { file = "../04_relSurf/rho.sxb"; }
}

main {
    DIIS_CCG {
        ... ... ...
        keepRhoFixed;
        ... ... ...
    }
}

GaAs110.sx

global G, X, XPrime, M, aLat1, aLat2;
aLat1 = aLat;
aLat2 = aLat/sqrt(2);

G = [0.0, 0.0, 0.0];
X = [0.0, pi/aLat2, 0.0];
M = [pi/aLat1, pi/aLat2, 0.0];
XPrime = [pi/aLat1, 0.0, 0.0];
projected bulk band structure

- Same set of $k_z$ as for the surface
- Several $k\mathcal{O}=k_z$ in $[-\pi/\alpha_\mathcal{O},\pi/\alpha_\mathcal{O}]$

Mirror symmetry

$k\mathcal{O}:[0,\pi/\alpha_\mathcal{O}]$

global Gx , Gy ...

aLat1 = aLat;

Gx = 0;
Gy = 0;
Xx = 0;
Xy = pi/aLat2;
Mx = pi/aLat1;
My = pi/aLat2;
XPx = pi/aLat1;
XPy = 0;

Z1=0.0*pi/aLat3;
Z2=0.1*pi/aLat3;

.......

structure {
    include "../structures/bulk.sx";
}

input.sx

kPoints {
    from { coords = [Gx ,Gy ,Z1]; label="G";}nPoints=4;
    to { coords = [Mx ,My ,Z1]; label="M"; nPoints=4;}
    to { coords = [Xx ,Xy ,Z1]; label="X"; nPoints=3;}
    to { coords = [Gx ,Gy ,Z2]; label="G"; nPoints=0;}
}

....
band structure alignment

![Graph showing band structure alignment with VBM and V SHIFT annotations.](image-url)
band structure alignment

band structure of the unrelaxed surface

band structure of the relaxed surface
Charge densities of the $C_3$ and $A_5$ states at M point

Ga-derived empty surface state $C_3$  As-derived filled surface state $A_5$

Localized surface states

Optional Exercise
- Explore the nature of other surface states
  (for example the A3 state in the pocket in the valence band)
- Explore the nature of surface states in the ideal GaAs(110) surface
Optional Exercises

- Optimization of surface relaxation
- Explore the origin of other surface states
- Photoelectric threshold (or ionization potential)
  *Minimum energy to knock one electron out from the valence band*
- Study the Ga- and As- terminated GaAs(110) surfaces