

Investigation into the crystal structure of gallium-selenide nanowires

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1 Introduction

Gallium-selenide films grown by heteroepitaxy on silicon substrates exhibit two primary growth structures: layered GaSe and defected zinc-blende Ga_2Se_3 . The latter is seen when growing on the (100) surface of silicon, and an emergent structure of nanowires is observed.

My project for the ten week summer program at the University of Washington physics department was to investigate the nanowire structure, attempting to determine the atomic configuration by examining the total energy of the different theorized structures. I worked under Prof. Marjorie Olmstead on this project, and the gallium-selenide results were from experiments by Taisuke Ohta. I also had help from Prof. Fumio Ohuchi, Prof. John Rehr, Dr. Fernando Vila., and Micah Prange.

It was decided that I should use a software package called VASP (the Vienna Ab-initio Simulation Package) to examine the gallium-selenide system. This software had to be purchased first, which took several weeks, so in the meantime I worked with a program called FEFF, examining the local density of states of the silicon substrate. At the time of writing, this project is still in progress.

2 Gallium-Selenide Nanowires

As mentioned in the introduction, epitaxially grown gallium-selenide assumes two primary structures, layered and defected zinc-blende (Fig. 1). The former occurs on silicon (111), and the latter on silicon (100). Depositing gallium-selenide directly on silicon results in the formation of amorphous silicon-selenide, upon which a crystalline film will not grow. Hence, a monatomic layer of arsenic is deposited first to passivate the surface. The arsenic atoms each bond to two silicon atoms and one other arsenic, forming symmetric As:As dimers [2].

The Ga_2Se_3 is imaged using a scanning tunneling microscope [1], revealing the nanowire structure (Fig. 2). Based on these images and other experimental data, a structure for the nanowires has been

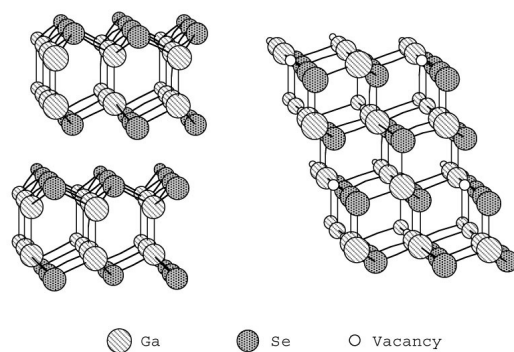


Figure 1: The two structures of gallium-selenide: layered GaSe (left) and defected zinc-blende Ga₂Se₃ (right).

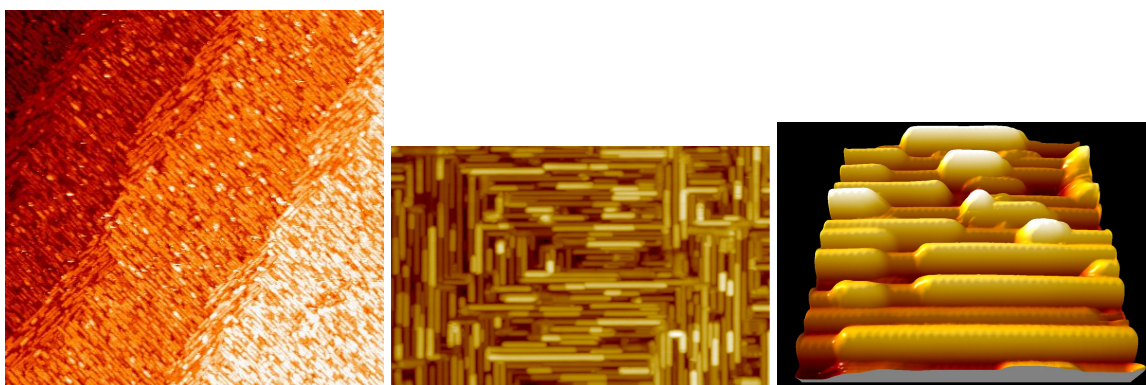


Figure 2: STM images of Ga₂Se₃ films exhibiting nanowire structure, at various magnification. Left: 400x400 nm, showing terracing on silicon substrate. Center: 100x64 nm. Right: 20x20 nm, 3D rendered.

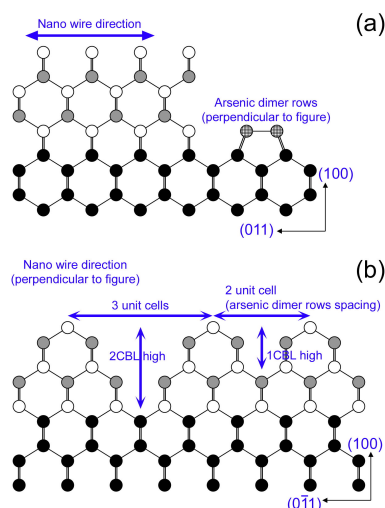


Figure 3: Proposed structure of Ga₂Se₃ nanowire. (a) Side view of length of wire. (b) Cross-sectional end view.

proposed. As seen in Fig. 3 the wires are believed to follow the lines of the As dimer pairs. Experiments indicate that the arsenic migrates off the silicon surface [ref Taisuke], and it is not known where it ends up. This is one of the things I hoped to determine in the course of this project. It is also uncertain where the vacancies required by the 2:3 stoichiometry are located.

These nanowires have the potential to yield some very interesting device properties. Because the gallium-selenide lattice constant is closely matched to that of silicon, it is well suited to integration with existing semiconductor technologies. Also, Ga_xSe_y is a semiconductor with a narrow bandgap, so it could find applications in opto-electronic devices. The electronic and optical properties of the nanowires have not yet been measured, as manipulating wires only a couple nanometers in width would not be an easy task. One of the hopes in modeling and studying them theoretically is that one might determine whether it is worth the great effort to perform such experiments.

3 FEFF

3.1 The Code

So far this paper has been presenting work done by other people, but will now focus on my own work for the summer. In the interim of obtaining VASP, I worked with a code written by Prof. John Rehr's group at the University of Washington. FEFF is an *ab-initio* code designed for simulating x-ray absorption and reflection experiments, and is also capable of calculating local density of states for a given cluster of atoms. Briefly, the density of states (DOS) for electrons in a solid is the the number of states per unit energy per unit volume. This dictates the electronic structure of the crystal, and can reveal a lot about bonding mechanisms and electronic properties. Such calculations would be useful and interesting, but working with FEFF was primarily suggested as an exercise for me to familiarize myself with this sort

of software, and to get me thinking critically about the relevant concepts of solid state physics.

The FEFF input file consists of a list of Cartesian coordinates for the cluster of atoms and a series of "cards" (a reference to antiquated computer punch cards) determining which calculations are done and specifying variable values. Each species of atom is given a unique *ipot* tag of value 1, 2, 3, and so on. A single atom has *ipot*=0, and is modeled as excited, having an electron-hole pair.

The code is structured as a series of six modules, each successive module using the output of those previous. The first module calculates the potential using a self-consistency loop. The second module then calculates the angular momentum projected density of states, and outputs the results as a table giving the number of electrons at each energy step for the s, p, d, and f orbitals. (The spacing of the energy steps is set by the card GRID.) This is done for the excited atom with *ipot*=0, and for one atom each having *ipot*=1, 2, etc, as mentioned above. For my purposes I had the program stop after module two in order to reduce run time.

Module two starts by calculating the potential due to the cluster surrounding a given atom. The electron wavefunctions are obtained using this potential, and then the single electron potential for that atom is determined. This is compared to the starting potential, and the steps are repeated. This self-consistency loop runs for a given number of times, or until the change is within some specified tolerance. [3]

3.2 Calculations with FEFF

For my calculations, I created model clusters using Cerius, a fancy software package designed for simulating molecular dynamics. With that program I was able to start with a single unit-cell of silicon and build up a solid crystal by repeating the unit cell and changing atom species as desired. Cerius has several options for output file type, and *.bgf works best as it outputs a list of cartesian coordinates in angstroms, easily compatible with the FEFF format. A simple awk script made the conversion.

Learning how to use FEFF is mainly comprised of learning the function of the various cards. Two of these merit mention in this paper. The SCF and FMS cards are of key importance for the types of calculation I was doing. The number following each card specifies the cluster radius used for that module, calculating potentials and DOS respectively. To adjust the number of atoms in a cluster, one simply alters these values, runs the code, and checks the cluster size used. The rule of thumb is that a cluster of around 55 atoms is good for the SCF loop. For the FMS (full multiple scattering) calculations, the only guide line is that you can expect to need a larger cluster than used in SCF. Generally one runs the code with increasing radius until convergence is seen in the density of states output (or whatever you are interested in).

This turned out to be a crucial issue for my project. Fig.4 shows density of states output for bulk silicon, with increasingly large clusters. It is seen that convergence has not been reached, even with cluster sizes larger than 200 atoms. Attempting to further increase the radius resulted in a calculation that never terminated.

The run time of FEFF goes like n^3 where n is the number of atoms. Hence, while a cluster of 20 atoms may run on a G4 processor in ten minutes, a cluster of 200 takes roughly 1,000 times longer, which is more than six days. I started out running FEFF on a 1.25 GHz G4 processor, but soon this was impractical. I moved on to a machine with dual G5 processors, and then to a cluster with six nodes,

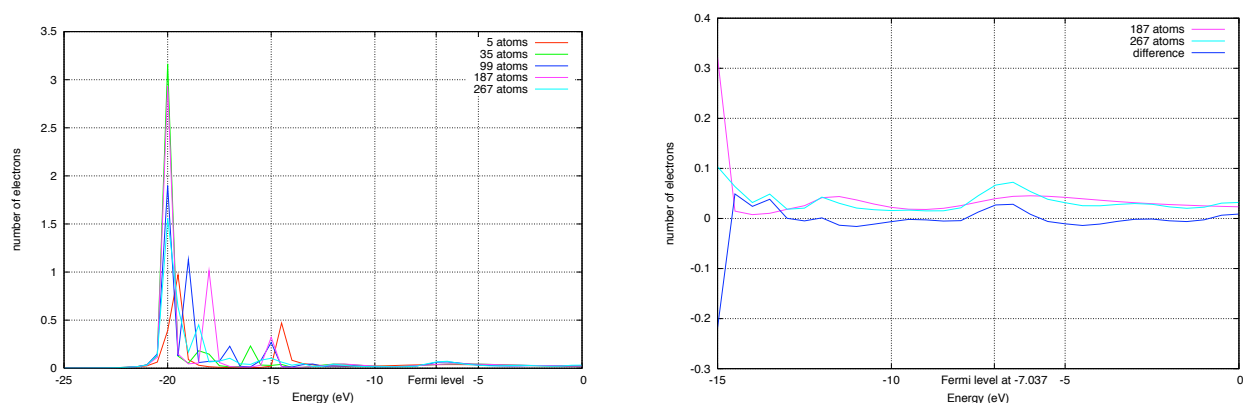


Figure 4: S-orbital density of states for bulk silicon, calculated with various cluster sizes (left). A detail from the same data, with the two largest cluster calculations shown, and the difference between them, illustrating non-convergence (right).

each having two 1.8 GHz Athlon processors. Using the cluster, calculations on a 200 atom cluster still required a day or so, but the bigger problem turned out to be memory limitations. This problem may be resolved by running on only four of the six available nodes, which will still take a long time, but will reduce memory demands. Also, I recently learned that it is possible to turn off calculations for d and f orbitals, which will dramatically reduce run time and will be entirely acceptable for silicon where the action takes place in the s and p orbitals.

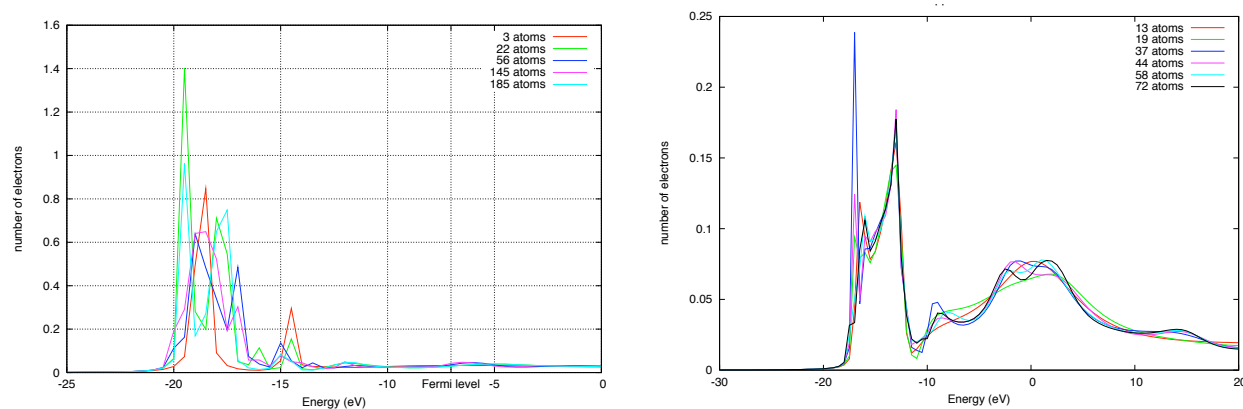


Figure 5: S-orbital density of states for arsenic terminated silicon, calculated with various cluster sizes (left). S-orbital density of states for copper, illustrating convergence (right).

Despite the lack of success with bulk silicon, I tried running a model of arsenic terminated silicon. The results are seen in Fig. 5, and again have not converged. Also shown are DOS calculations for copper which illustrate a successful run. I ran copper in order to check my work because it is known to be well suited to FEFF. Sure enough, these gave good results with cluster sizes smaller than 100 atoms.

So why does FEFF not work for the materials I am interested in? The problem is that FEFF models electron waves in the solid. If the model cluster is smaller in diameter than the electron mean free path for that material, then the computation is "seeing" the edges of the cluster so that certain electron wavefunctions that would be free to occur in practice will not be allowed in the calculation. The mean free path in copper is much shorter than that of silicon, so it works well with a reasonable small cluster. For silicon, with a mean free path on the order of 20 angstroms a cluster of 500 atoms will probably be necessary.

This issue of mean free electron path and cluster size was the main problem I ran into, but there were other difficulties involved. As mentioned earlier, FEFF performs its calculations on one atom for each unique *ipot* tag. If the atom happens to be at an edge or a corner of the cluster it can be expected to have a misleading density of states due to dangling bonds at the surface. It turns out that the ordering of atoms in the coordinates list is crucial, as FEFF just grabs the first atom on the list (for *ipot*=1, 2, etc.) for its calculations. It wasn't until after running the calculations shown in Fig. 5 that I realized these were results for an atom at the corner of the cluster, and thus couldn't be expected to settle down into convergence. The results in Fig. 4 are better because they were redone after this realization. Hence, one task for the future is to redo the arsenic terminated model using an atom at the center of the terminated surface by simply reordering the input file. Another improvement will be to hydrogen terminate the cluster on the silicon surfaces, which will tie up free bonds without distorting the lattice overly much.

Another step to take is to model the arsenic dimerization. When the dimer pairs form, the crystal lattice is deformed locally to accommodate the strain. Based on the experimental measurements by Uhrberg *et al*[2] I adjusted the top few crystal layer to simulate this effect. This may effect a noticeable change in the density of states, though the other difficulties will have to first be overcome.

4 VASP

In the last few weeks of my summer project I was able to start working with the Vienna Ab-initio Simulation Package. VASP works differently from FEFF in that it treats a crystal in reciprocal space rather than real space. Thus, the input consists of coordinates for a single unit cell, which is then represented in reciprocal space as having periodicity in k . While I don't understand the calculation details, tutorial runs of the code have taught me the following.

VASP takes as input the above mentioned unit cell coordinates along with Z numbers and a list of pseudopotentials for the atoms. The code uses a self-consistency loop to determine the energy of the configuration. It can relax a set of atoms to a given lattice constant, or relax both lattice constant and the atom positions to find the minimum energy. These are the types of calculations I will be using it for, though it is capable of much more. Like FEFF, the code is controlled by cards with variable values (though they don't use the 'card' terminology) and there are a plethora of output files for every run.

5 Conclusions and Future Steps

Though I don't have original results to show for my summer's work, I did determine that FEFF was ill-suited to making density of state calculations for silicon based materials. I gained an understanding

of the relevant background relating to gallium-selenide films, on which I will continue to work. Now that I have had some exposure to the two codes, FEFF and VASP, I should be in good shape to continue this project and start to investigate the nanowire structure as initially desired.

I will start with a model of a thick silicon substrate with an arsenic layer and a piece of nanowire, in its proposed form, on top. The model should be about 20 atoms thick, two unit cells wide, and half a cell long in order to be the smallest repeatable part of a long nanowire. It will be interesting to see if the arsenic moves up into the gallium-selenide layer and where vacancies settle. Then I can play around with the initial structure to see different equilibria are found. I'll also try adding a few atoms to the silicon surface at a time, starting with just an As:As dimer pair on the surface and then introducing gallium and selenium.

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