Methods in Characterizing the SrTiO$_3$/GaAs Interface

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Characterizing the interface that occurs between a thin-film deposition of SrTiO$_3$ on a GaAs substrate is of significant interest in order to determine the electrical capabilities that may be possible with this type of system. Imaging the interface by using transmission electron microscopy as well as determining important chemical and electrical information by using Electron Energy Loss Spectroscopy (EELS) are critical in determining if the system is actually appropriate for the desired applications. In addition to these experimental calculations, however, it may be useful to determine theoretical calculations in order to confirm and interpret the results. In particular, these may be determined for EELS by using a simulation program called FEFF9, which employs use of full multiple scattering calculations in order to produce these theoretical results.

Introduction

There have been many studies performed on the interface between SrTiO$_3$ and GaAs. The interface is primarily being examined in the interest of using it in transistors, where the GaAs substrate would act as the semi-insulating base material and the SrTiO$_3$ would act as the barrier oxide layer between the GaAs and the gate material. These materials were specifically chosen due to the fact that they both exhibit desirable electronic characteristics. GaAs is known to be a direct band gap semiconducting material that forms with a cubic, zinc blende structure, and has a lattice parameter of 5.653Å. SrTiO$_3$ possesses the ability to be a good substrate for other oxides, which is critical in order for the transistor gate material to be deposited. SrTiO$_3$ has a simple cubic perovskite structure with a lattice parameter of 3.905Å. Due to the mismatch in lattice constants, SrTiO3 must be used on the (100) plane and deposited on the (110) plane of GaAs.

The deposition of SrTiO$_3$ on GaAs has typically been performed using molecular beam epitaxy, and the thin GaAs substrate has an initial 0.5 monolayer of Ti prelayer deposited on it. This is done because it has been experimentally determined that this prelayer allows the SrTiO$_3$ to grow in a more crystalline, ordered structure with fewer oxygen vacancies. The presence of oxygen vacancies at the interface in the structure is extremely undesirable because it degrades the quality of the system and reduces overall conductivity. The system without the Ti prelayer also exhibits Fermi level pinning between the GaAs and SrTiO$_3$, which reduces the flow of charge through the GaAs.

Typical methods for investigating what interactions are taking place within the interface of a material include Transmission Electron Microscopy (TEM), Z-contrast imaging, and Electron Energy Loss Spectroscopy (EELS). The TEM images are used in order to analyze the atomic structure and visually determine the bonding that forms in the system, while the EELS spectra that are produced provide elemental and bonding information. These methods may be used in complement to one another; however it may be somewhat difficult to visually observe characteristics such as oxygen vacancies or interfacial titanium atoms by using the TEM images. Therefore, it is useful to find an additional method of confirming the EELS results that have been produced. The method to be used in this project is a simulation program called FEFF9, which produces full multiple scattering simulations of the EELS spectra for a given crystal structure or system. This program is a real space program, which means that it is significantly faster than calculations such as density function theory that use Fourier based methods, which require very large systems of atoms.

Method

The simulation program, FEFF9, produces the required theoretical results by performing cluster calculations within a finite framework of atoms that make up the desired network and that are provided by their real space coordinates to the program. These approximations are determined using ab initio multiple scattering calculations, as well as the muffin tin approach to the electronic potentials. Initially, a single atom within the cluster is selected to be the recipient of the electron beam and thus experience the electron loss that causes the scattering. The multiple scattering calculations then simulate a wave scattering out from this central atom, which approximates the actions of the inelastically scattered electrons used in EELS, and this wave provides information necessary to produce the desired spectrum. The muffin tin potentials used in the calculations mean that FEFF9 approximates averaged spherical electrical potentials around the atoms, with constant potentials assumed interstitially. This is used alternatively to den-
sity function theory, which separately calculates all the potentials around an atom. This is a somewhat more accurate method, but it takes significantly longer than the muffin tin potentials to calculate, and does not produce significantly better results. There are many variables within FEFF9 that should be set in order to obtain the best and most accurate simulation of the desired network. Most importantly, the Full Multiple Scattering (FMS) and Self Consistent Field (SCF) must be specified. FMS is an equation in the program that uses a size limit within the network of atoms in order to limit the number of atoms included in the calculation and then perform a matrix inversion according to a geometric series on this set. The SCF determines the self consistent potentials to be calculated, and aids in converging the calculations, especially near edge calculations. It is generally appropriate to include one fewer shell in the SCF than in the FMS to make the best approximation. In addition, variables to describe beam angle and energy, as well as convergence and divergence semi-angles of the detector must be provided. Specifications for which edge the electron should be ejected from as well as whether or not there is a core hole must also be made.

The initial calculations performed using FEFF9 were done on bulk SrTiO$_3$. Scattering calculations for the oxygen K edge as well as the titanium L$_2$ and L$_3$ edges were made. Separate calculations were performed to introduce peak broadening to these calculations, and to calculate with and without core holes. This was done in order to observe what effects this will produce and which spectrum most closely matches the experimental data previously obtained. Once these calculations were obtained, the network of atoms for the SrTiO$_3$/GaAs interface was constructed and FEFF calculations for the oxygen K edge and titanium L edges for atoms along the interface were made. The same calculations then were performed with missing oxygen atoms in order to determine the effect of vacancies on the scattering pattern.

**Data and Analysis**

**Oxygen K edge (bulk SrTiO$_3$)**

The first spectrum collected for the theoretical oxygen K edge comparison was performed under the following conditions: incoming beam energy of 200keV, FMS of 6.17435, SCF of 5.8575, beam direction in the [100], collection semi-angle of 17.5mrad, and convergence semi-angle of 15mrad. There was a core hole present, with no peak broadening. The second spectrum was taken under the same conditions; however in this case peak broadening was present.

Figure 1 depicts the multiple scattering calculations for the EELS spectra versus the experimental spectrum. The experimental spectrum depicted does not depict an entirely clear agreement with the calculated spectra, however this may be attributed to the difficulties potentially associated with obtaining high quality experimental oxygen data for this type of material.

**Titanium L edge (bulk SrTiO$_3$)**

The first spectra collected for the theoretical titanium L$_2$ and L$_3$ edge comparisons were performed under the following conditions: incoming beam energy of 200keV, FMS of 7.03984, SCF of 6.76366, beam direction in the [100], collection semi-angle of 17.5mrad, and convergence semi-angle of 15mrad. There was a core hole present, with no peak broadening. The second set of spectra was taken under the same conditions; however in this case peak broadening was present.

Figure 2 depicts the multiple scattering calculations for the EELS spectra versus the experimental spectrum. The peak locations appear to be in approximate agreement with one another, which again confirms that the settings and hypotheses used in the FEFF9 program are correct.

**Oxygen K edge (SrTiO$_3$/GaAs interface)**

The real space coordinates for the SrTiO$_3$ and GaAs interface were used in the FEFF9 input file, and an oxygen atom at the center of the interface was chosen as the target from which to eject the electron. The same parameters used for the bulk SrTiO$_3$ calculations were...
applied in these calculations.

Figure 3 displays the differences between the bulk and interface calculations made using FEFF9. There are no vacancies present in these calculations, and as is expected, the spectra look very similar. After these simulations were produced, vacancies began to be introduced into the system by removing the real space coordinates for oxygen atoms near the targeted central atom. The vacancies were introduced initially in the unit cell directly surrounding the targeted atom, and then moved further outward from this unit cell in order to determine what effect this produced in the simulation.

As shown in Figure 4, one vacancy appeared to produce little change in the spectra beyond the immediately surrounding 2 Å distance. At this distance, the first peak on the graph appears shifted from the graph of the calculation with no vacancies such that it is closer in intensity to the second peaks in the graph.

Figure 5 shows that two vacancies appeared to produce little change in the spectra beyond the immediately surrounding 2 Å distance, very similar to the effect of one vacancy. These vacancies were introduced at varying locations around the central atom in a number of FEFF9 runs, and all produced approximately identical calculations. At this distance, the first peak on the graph appears shifted from the graph of the calculation with no vacancies such that it is closer in intensity to the second peaks in the graph.

Figure 6 shows that three introduced vacancies surrounding the atom does not appear to affect the intensity of the peaks, although it does appear to somewhat flatten and broaden the peaks. These vacancies were introduced in a similar manner as with two vacancies, introduced at varying locations around the central atom in a number of FEFF9 runs, with all producing approximately identical calculations.

Four vacancies introduced surrounding the atom, as displayed in Figure 7, both broadens and shifts the third peak on the graph of the calculation outward.

Titanium L edge (SrTiO$_3$/GaAs interface)

The real space coordinates for the SrTiO$_3$ and GaAs interface were used in the FEFF9 input file, and a tita-
Discussion

The calculated results obtained using the methods described confirm the results experimentally obtained from the given samples. Performing the calculations on the bulk material provides a good basis for understanding the underlying atomic interactions before attempting to calculate the interactions at the interface. Once good results for the bulk material were produced that show that it is possible to model the SrTiO$_3$ system accurately, the interface results were able to be obtained and compared to see how they differ from these bulk results. The calculations for the interface with vacancies could then be compared to see what effect these vacancies cause. The calculations for one and two vacancies closest to the central atom in the oxygen K edge calculations cause an upward shift of the first peak, which could be attributed to the orbitals around the atom being occupied differently than with no vacancies. The calculations for three vacancies primarily show a peak broadening and reduction in intensity, which can be expected due to the decrease in crystallinity of the system caused by introducing the vacancies. A decrease in crystallinity means that the electrons surrounding the atoms will not scatter as coherently as in a crystalline system, which makes the peaks produced in analyzing these systems with EELS or FEFF9 less intense. A similar broadening occurred in the titanium L edge calculations with introduced vacancies. Four vacancies surrounding the atom in the oxygen K edge produce a broadening and shift, and again the shift can be attributed to different orbital occupancies surrounding the atom.

Conclusion

The full multiple scattering calculations produced by the program FEFF9 are good methods for confirming experimental EELS results as well as providing a basis of support for hypotheses that may be made about the material in question. The presence of oxygen vacancies, which cannot readily be seen using microscopy methods, may be shown to exist by way of calculations made in this manner. This method also is faster than other calculations, such as density function theory, so it is easier to apply and use as a comparison method. Overall, this program is a very useful tool for data analysis.

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