The Arsenic site in oxidized $Al_{0.98}Ga_{0.02}As$

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Introduction

New approaches for growing oxide films on GaAlAs using wet oxidation have been developed in the last several years.[1,2] With a suitable gate oxide, AlGaAs/InGaAs/GaAs-based MOSFET devices could significantly outperform present Si electronics due to the lower effective mass, higher electron mobilities, and higher saturated velocity. In producing these insulating layers, however, the structure of the oxide is not well understood. Of particular interest is the role of residual As which is produced as a result of the oxidation. The As can produce Fermi-level pinning, increase leakage currents, and increase interface recombination. To understand where and in what form the As atoms are, x-ray diffraction and XAFS in addition to other non-x-ray techniques have been employed. The goal of these studies is to correlate the physical structure to electronic properties and sample preparation methods.

Methods and Materials

A ~1 μm $Al_{0.98}Ga_{0.02}As$ film on a GaAs substrate was oxidized using techniques described previously.[3] To study the As specifically in the oxide layer and not in the substrate, the sample was mounted oxide-down to a glass slide using wax. The GaAs substrate was then removed chemically with a phosphoric acid – hydrogen peroxide etch followed by a citric acid –hydrogen peroxide selective etch. The resulting oxide film was then studied with x-ray diffraction using a conventional sealed source system, and As-edge x-ray absorption measurements were performed using the MRCAT ID-10 beamline.

For calibration standards used in the XAFS analysis, As_2O_3 (As^{3+}), As_2O_5 (As^{5+}), and elemental As were obtained from standard chemical supply houses. These standard samples were ground with mortar and pestle and sieved to 400 mesh (< 30 μm) inside an inert-atmosphere glove box. These compounds were all characterized using x-ray diffraction to verify their phase purity.

MRCAT beamline is equipped with an scannable undulator and a double-crystal Si (111) monochromator which allows XAFS measurements over the energy range from 5 KeV to 30 KeV. A harmonic rejection mirror was also used to eliminate the third and higher x-ray harmonics from the monochromator. XAFS data were obtained in transmission mode on standard samples and in fluorescence mode on the oxide sample. We used the ion chambers filled with three different combinations of gases for x-ray detection; 90 % He and 10 % N_2 gases for the detection of incident beam, filled with 100 % N_2 gas for the transmitted beam and 100 % Ar gas for the emitted fluorescence.

Results

The diffraction results indicate that the oxide film is either amorphous or of crystallites smaller than 3-5 nm. The near-edge and extended-range x-ray absorption measurements are used in quite different ways in the analysis: While the extended spectra can be fit to determine quantitative structural parameters, the near edge spectra for this work are largely used to "fingerprint" the As site. By comparing to other known As compounds, in favorable circumstances it is possible to match an unknown sample to a combination of known structures. In this study, we compare to elemental As, GaAs, As_2O_3, and As_2O_5. These spectra are shown in Fig. 1. A comparison of the oxide unknown to merged As_2O_3 and As_2O_5 spectrum is shown in Fig. 2.

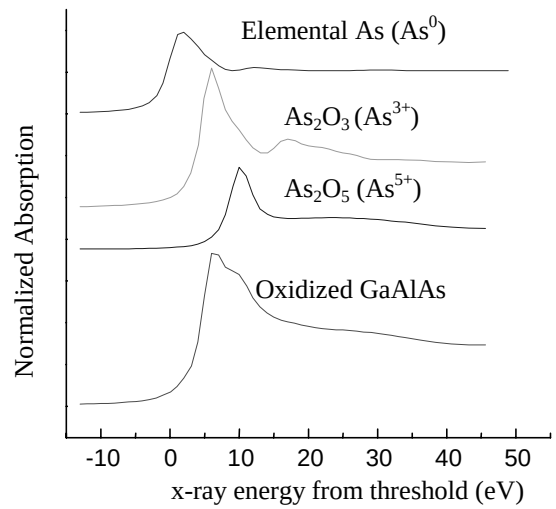

Fig. 1. Near-edge spectra of the oxide film compared with analogous spectra for powders of elemental arsenic, As_2O_3, and As_2O_5. As can be seen, none of these compounds singly agrees well with the oxide data.

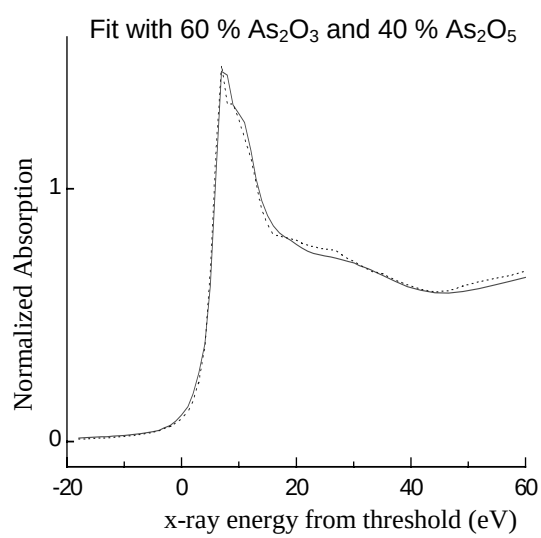

Fig. 2. Near-edge spectra of the oxide film compared with a sum of 60% As_2O_3 and 40% As_2O_5. The small differences between the two spectra are likely due to the disordered environment.

The x-ray absorption near-edge results indicate that the As environment from the oxide agrees most closely with mixed sites: 60±10% of the As atoms in an As_2O_3–like environment, and 40±10% of the atoms in an As_2O_5–like environment.

The XAFS measurements independently agree with the near-edge results. Shown in Fig. 3 are the Fourier transform magnitudes of the oxide sample and several standard compounds. It may be easily seen that the sample is totally inconsistent with either elemental As or As in GaAs. Also, the first-shell sample data appears to be somewhat in between the spectra for the two As oxides. (Because of disorder, higher shell data from the sample is expected to be greatly reduced in amplitude.)

The XAFS results may be quantified by fitting the As-edge data to simulations from the FEFF 6.01 program [4] using FEFFIT [5]. A number of models were considered, ranging from interstitial or substitutional As in Al oxide to elemental As. The only reasonable fits correspond to a combination of 50±10% of the As in an As_2O_3-like site, and 50±10% of the atoms in an As_2O_5-like environment. (Note that the As_2O_5 structure has two inequivalent sites for As.) The fit results are shown in Fig. 4.

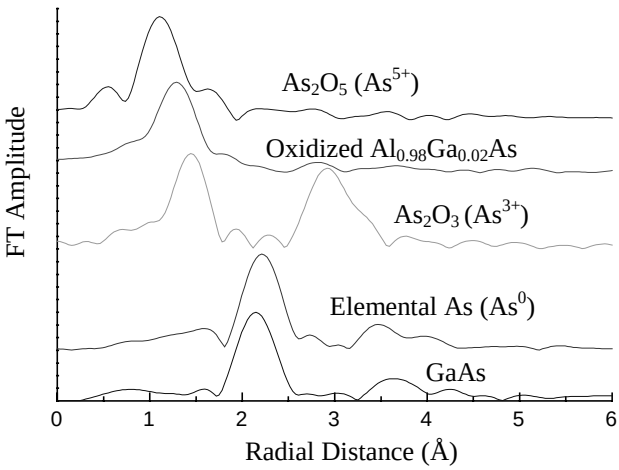

Fig. 3. Magnitudes of the Fourier transforms of the As-edge data for the oxide film sample, As_2O_5, As_2O_3, As, and GaAs.

Discussion and Conclusions

Evidence from the analysis of XAS data from oxidized $Al_{0.98}Ga_{0.02}As$ suggest that the As in this oxide film is largely in the form of As^{3+} and As^{5+} regions that are structurally similar to amorphous As_2O_3 and As_2O_5. If substitutional or interstitial As sites in Al oxides and Al hydroxides exist, they must represent less than approximately 5% of the As sites to be consistent with our results. Similarly, less than approximately 5% of the As exists in elemental As or GaAs in the oxide film. In the GaAs device community, it is believed that understanding the role of As both at the oxide/semiconductor interface and within the oxide is important to the further progress towards workable MOSFET devices. We have focused in this study on the nature of As distributed within the oxide. The results here are not inconsistent with Raman spectroscopy data showing the formation of elemental As (As^0) at the oxide/semiconductor interface [3], as this interfacial region may possibly have been removed along with the substrate during etching.

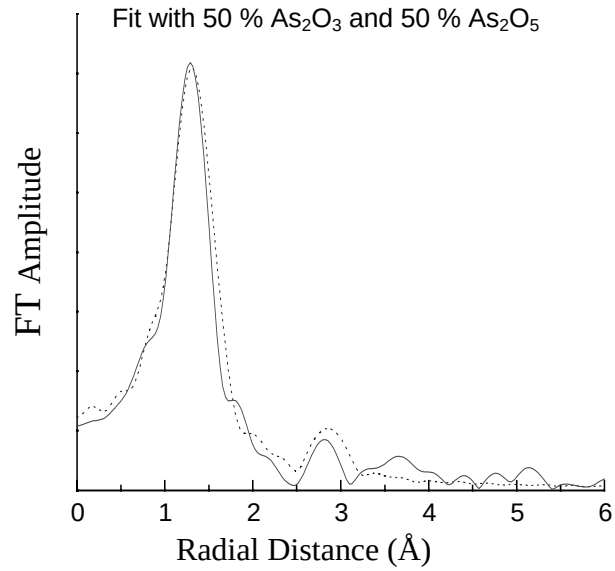

Fig. 4. Magnitude of the Fourier transform of the As-edge oxide data along with the simulation of 50% As_2O_3 and 50% As_2O_5. The Debye-Waller factors for the higher shells in the simulation are increased reflecting the disorder in the sample.

Acknowledgments

This work was supported by AFOSR Grant AF49620-98-1-0120. Portions of this work were performed at the Materials Research Collaborative Access Team at the Advanced Photon Source. The MRCAT is supported by the U. S. Department of Energy under Contract DE-FG02-94-ER45525 and the member institutions. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, under Contract No. W-31-102-Eng-38.

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