XAFS Study of Epitaxial $Co_xTi_{1-x}O_{2-x}$ Anatase

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PNC-CAT

Introduction

Co doped TiO_2 anatase is a promising candidate for a room-temperature ferromagnetic semiconductor. Such materials are critically important in the development of spintronics as spin injectors for semiconductor heterostructures that can operate without cryogenic cooling. Co doped anatase is found to be ferromagnetic well above room temperature when doped n-type with oxygen vacancies. Critical to elucidating the mechanism of magnetism in this material is a determination of the local structure surrounding the magnetic impurity. XAFS measurements have been used to investigate the local Co environment and Co valence. Some questions to be answered:

1) Can nanoparticles of Co metal explain the ferromagnetism?

2) What is the Co valence?

3) What is the Co environment: is the Co substituting for Ti in the lattice?

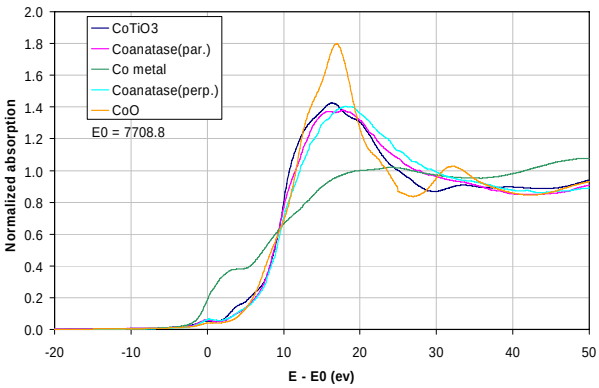
4) What about oxygen vacancies that are required for charge neutrality (each Co substitution for Ti should result in an O vacancy)?

Samples and measurements

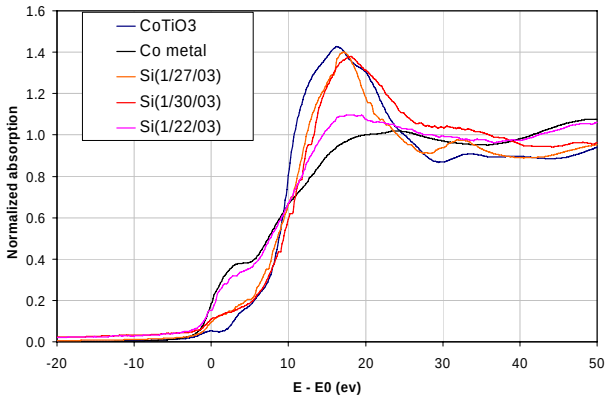
The samples were grown by oxygen plasma assisted molecular beam epitaxy (OPAMBE). Co concentrations were about 5%. Typically the films are about 20 nm thick. Substrates used include $LaAlO_3$(001) and $SrTiO_3$ grown on Si(001). The measurements were made at the PNC-CAT bending magnet and undulator beamlines at the Advanced Photon Source. To improve the Co signal, the samples were oriented at about 1-2° relative the incident beam. Since the samples are oriented, polarization dependent measurements were made with the x-ray polarization parallel and perpendicular to the sample surface.

Near edge results

$LaAlO_3$(001) Substrate: Note the absence of Co metal – all of the Co is Co(2+) similar to $CoTiO_3$

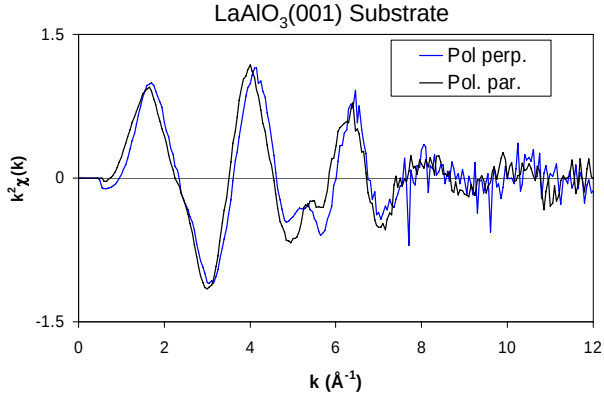


STO/Si(001) Substrate: All three samples have significant contributions from metallic Co

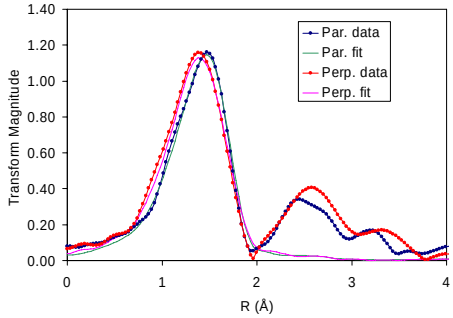


EXAFS results

$LaAlO_3$(001) Substrate



Fit to first shell



Standard procedures were used to fit the spectra to FEFF7 models. The models were calibrated by fitting to CoO and $CoTiO_3$. The fits for the first shell are compared to the Fourier transformed data for the two polarizations. Note the shift in the peak position with polarization.

Comparison of fit results to anatase

Bond	O coordination*	Bond length	Debye-Waller factor
Coanatase in ab plane	5.54 (0.3)	2.04 (0.01)	0.0096 (0.001)
Coanatase along c axis	5.48 (0.3)	2.01 (0.01)	0.0110 (0.001)
Anatase in ab plane	6	1.937	-
Anatase along c-axis	6	1.966	-

*Scaled to unoriented values

The fit results indicate that the Co substitutes for Ti in the lattice. The reduced O coordination suggests there may be some correlation of the oxygen vacancies with the Co atoms.

Acknowledgements

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