XAFS Study of metal-doped In$_2$O$_3$

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Abstract. In$_2$O$_3$ has attracted interest recently because of its favorable properties for potential applications as diluted magnetic semiconductors. For these applications the material must be doped to produce the desired magnetic properties, and it is essential to determine the fate of the dopants in order to optimize the materials and understand the magnetic measurements. This paper summarizes some recent XAFS studies of a series of In$_2$O$_3$ films doped with V, Cr, Co, and Fe. XAFS is shown to be a powerful tool to characterize these materials, providing valence information, and detecting both substitutional doping as well as second phase formation. V and Cr are found to take up well ordered substitutional sites with no evidence for second phase formation. For Co the substitutional sites were much more disordered than for V or Cr. Fe doped samples also displayed a range of results with well-ordered substitutional sites in some samples, while others showed extensive second phase formation including magnetite and Fe metal.

1. Introduction

The search for room temperature diluted magnetic semiconductors has spurred investigation of a variety of metal doped oxides. In$_2$O$_3$ is a promising system$^{[1-4]}$ that has seen a lot of previous work in conjunction with applications as transparent conducting films. In that application the primary dopant is Sn, and a number of XAFS studies have been carried out on doped In$_2$O$_3$$^{[5, 6]}$. For magnetic applications the dopants are generally transition metals.

In this paper we present the application of XAFS to a variety of transition metal doped In$_2$O$_3$ films. XAFS has been demonstrated to be a powerful method for characterizing doped metal-oxide films$^{[7]}$. A common problem in such films is the formation of second phases, especially metal phases. For magnetic second phases this can result in a magnetic signal that can confuse the magnetic characterization. These second phases can be difficult to detect since they may be of low concentration, and are often in the form of nanoparticles that are hard to detect by diffraction methods. Both the XANES and EXAFS have been shown to be sensitive to the presence of such nanoparticles. In the XANES the metals show up as a low energy feature in the edge while for the EXAFS the metal-metal bond in the metallic form often shows up as a peak intermediate between the first and second neighbors in metal oxides. For films in which second phase formation is not present the EXAFS can provide valuable information about the substitutional sites, both the position in the lattice and any lattice distortions from the size mismatch of the dopant atoms. The XANES can verify the dopant valence. If it differs from the host In atoms (3+) then charge compensation such as the formation of O vacancies or interstitials must be occurring.
2. Experimental Results

The samples measured include V, Cr, Fe and Co doped In$_2$O$_3$ thin films. The films were grown by PLD and sputtering on Al$_2$O$_3$ substrates with varying O partial pressures. The samples are summarized in Table 1.

Table 1. Summary of the samples measured by XAFS. All were grown on Al$_2$O$_3$ (0001) substrates.

| Sample | Content            | T (°C) | Pressure       | Method     |
|--------|--------------------|--------|----------------|------------|
| Co-1   | In$_2$O$_3$/(5% Co)| 330    | 6x10$^{-4}$Torr| Sputtering |
| Fe-1   | In$_2$O$_3$/(4% Fe)| 600    | 2x10$^{-6}$Torr| PLD        |
| Fe-2   | In$_2$O$_3$/(5% Fe) vac. annealed 450°C | 450 | 2x10$^{-6}$Torr | PLD        |
| Fe-3   | In$_2$O$_3$/(5% Fe)| 450    | 2x10$^{-6}$Torr| PLD        |
| V-1    | In$_2$O$_3$/(5%V)  | 550    | 2x10$^{-6}$Torr| PLD        |
| Cr-1   | In$_2$O$_3$/(3%Cr) | 600    | 2x10$^{-6}$Torr| PLD        |

The samples were measured at beamlines 20-BM-B and 20-ID-B at the Advanced Photon Source. In both cases Si (111) monochromator crystals were used with energy resolution of about 1.4x10$^{-4}$. The samples were mounted on a spinner that rotated at a few Hz to minimize distortion from substrate Bragg peaks. In most cases the samples were mounted with an incident angle of a few degrees and the x-ray polarization was perpendicular to the surface. Fluorescence detection was used with either a 4-element Vortex (20-ID) or a 13-element Ge fluorescence detector (20-BM).

Figure 1 shows the EXAFS data and the Fourier transforms for the Cr, Co and V doped samples. The Cr and V samples showed strong XAFS extending to higher k indicating the metal is residing in reasonably well ordered sites. There is a strong similarity indicating the metals are in similar sites, and there is little indication of metal formation in the near edge spectra (not shown). All of this suggests that the Cr and V are entering substitutional sites, and this will be confirmed in the next section. The Co data shows some similarities to the other two, but the XAFS is strongly damped.

Figure 2a shows the XANES spectra for a set of Fe doped samples. These show a whole range of behavior. For sample Fe-1 the near edge looks very similar to magnetite, and this is confirmed by the EXAFS shown in Fig. 2b. In this sample virtually all of the Fe is in the form of magnetite. Sample Fe-
3 shows a complex structure with an Fe valence of approximately 2+. This sample could not be fit with any simple combination of Fe metal, FeO, magnetite, and hematite. Sample Fe-2 had the expected valence similar to Fe 3+, and the EXAFS looks similar to the substitutional spectra in Fig 1.

3. Analysis and Discussion

In$_2$O$_3$ has the bixbyite structure[8] that has two In sites with near neighbors as shown in Table 2. Site 1 is three times more numerous than site 2. The main difference is in the first shell. For the more numerous site 1 there is a much larger spread of bonds. This opens the possibility that detailed analysis can distinguish site preference for the dopants. However, in all cases the dopant ionic size is much smaller than the host In atoms, and we expect substantial contraction of the lattice about the dopants. This rearrangement can make it difficult to distinguish between sites.

Since the Cr data had the strongest EXAFS and appears to be substitutional, it was chosen for detailed multi-shell fitting to look for the possibility of distinguishing site preference. Examples of fits for the two sites are shown in Fig. 3. These kept the coordination numbers fixed and varied the $r$ and $\sigma^2$ for the four shells. It used a common $\Delta r$ for the site 1 first neighbors. Both fits are reasonable and the resulting parameters similar. For site 1 the long first shell O distance was a problem. To get a good fit it had to be removed from the fit and the coordination numbers of the two shorter distances increased to 3 each. This indicates that the first shell coordination around the Cr is more symmetric than site 1, and could indicate a preference for site 2. However, in both fits there is a strong contraction to an average near neighbor distance of 2.03 Å. In the course of this contraction the site 1 neighbors could become more symmetrically arranged.

As another example of fitting, Fig. 3c shows a fit to the Fe data from sample 5. This assumes both sites are randomly occupied and used common parameters for the corresponding shells in the two sites. Again it was necessary to move the long first shell O in site 1 to values similar to the other two distances. This fit confirms that in this sample the majority of the Fe is substitutional.

| Site 2 |
|---|
| Fe-2 6 @ 2.08 |
| Fe-1 6 @ 2.08 |
| Magnetite 6 @ 2.08 |

Table 2. Near neighbors for the two In sites in In$_2$O$_3$.

| Site 1 | Site 2 |
|---|---|
| 1$^{st}$ neighbor O | 2 @ 2.04 |
| | 2 @ 2.14 |
| | 2 @ 2.41 |
| 2$^{nd}$ neighbor In | 6 @ 3.34$^a$ |
| | 6 @ 3.34 |
| 3$^{rd}$ neighbor In | 6 @ 3.84$^a$ |
| | 6 @ 3.84 |
| 4$^{th}$ neighbor O | 6 @ 3.98$^a$ |
| | 6 @ 3.89 |

$^a$Average of very similar distances.
4. Summary
This paper has shown the potential for XAFS to characterize doped In₂O₃ films with some examples using V, Cr, Fe and Co as dopants. The near edge is sensitive to valence and second phase formation as was shown for some of the Fe doped samples. For the other samples the dopants are found to occupy substitutional sites. These dopants are much smaller than the host In atoms and there is significant contraction of the O near neighbors about the dopant. This complicates the potential for determining any site preference the dopants may have.

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