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Effects of carbothermal annealing on structure defects and electrical and magnetic properties in Fe-doped In_2O_3

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Fe-doped In_2O_3 powders were treated by the carbothermal annealing method, and phase transition from a paramagnetic insulator to a ferromagnetic metallic state was observed. No trace of any other impurity phase was detected in the carbothermally annealed samples with Fe content up to 16%. Rietveld refinements of X-ray diffraction and X-ray photoelectron spectra revealed that a large amount of interstitial indiums and oxygen vacancies were introduced with carbothermal annealing. These defects play an important role in inducing the ferromagnetism and metallic conductivity.

Keywords: Sol–gel; Exchange interaction; Interstitials; Vacancies

Diluted magnetic semiconductors (DMSs), which are formed by introducing magnetic ions into a semiconductor, have been intensively studied due to their potential applications in spintronics [1,2]. For developing applicable spintronic devices the ferromagnetic Curie temperature (T_c) of DMSs should be above room temperature. Dietl et al. [3] predicted that 5% Mn-doped ZnO should exhibit room-temperature ferromagnetism (RTFM) mediated by additional holes. This theoretical work stimulated a large number of experimental investigations searching for RTFM in oxide-based diluted magnetic semiconductors (O-DMSs). Numerous oxide semiconductors, including In_2O_3, TiO_2, ZnO, SnO_2 and CeO_2 doped with various transition metal ions, have been shown to exhibit RTFM [4–16]. However, the origin of RTFM in these materials is still unclear. According to the Zener model, ferromagnetism is mediated by holes in the valence band, and the concentration of such holes should be above 10^{20} cm^{-3} in order to get a T_c higher than RT [3]. Coey et al. [17] proposed an impurity band exchange model to explain RTFM in O-DMSs. In this model magnetic interaction is mediated by impurity band donors and the ferromagnetic transition occurs when the number of bound magnetic polarons reaches the percolation threshold. For enhancing T_c, effective hybridization at the Fermi level between the donor states and the 3d states of the magnetic dopant is required. Recently, the mechanism of carrier-mediated FM has also been proposed to explain the FM in Co-doped TiO_2 [18], Co-doped ZnO [19] and Cr-doped In_2O_3 [20].

Although the mechanism of the magnetic interaction in O-DMSs is still unclear, it has been recognized that defects are requisite for inducing FM in O-DMSs. Defects usually acting as donors in oxide semiconductors can be generated by various methods, such as preparation in low O_2 partial pressure [7,21], high vacuum annealing [22], hydrogenated annealing [23,24] and Zn vapor annealing [9]. In this study Fe-doped In_2O_3 powders were fabricated using a sol–gel method, and carbothermal annealing was performed to study the effects on the structure, electrical and magnetic properties.

Polycrystalline $(In_{1-x}Fe_x)_2O_3$ powders were synthesized using a sol–gel method. Given amounts of $In(NO)_3$ and $Fe(NO)_3$ were weighed and dissolved in distilled water. Ammonia solution was slowly dropped into indium nitrate solution until the pH value of the solution was about 8.5. The hydrated formed precipitate was washed with distilled water and then mixed with aqueous citric acid and $Fe(NO)_3$ solution. Finally, a little nitric acid was added to the mixture to obtain a translucent, homogeneous and stable sol. The sol was evaporated in a water bath at 80 °C for 2 h, then dried at 110 °C until a xerogel was formed. The obtained xerogels were sintered at 700 °C for 2 h in air to obtain $(In_{1-x}Fe_x)_2O_3$ powders.

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In performing the carbothermal treatment the as-sintered powders samples were mixed with a given amount of active carbon (molar ratio of $(In_{1-x}Fe_x)_2O_3$:C is 4:1) and annealed at 850 °C for 4 h under an Ar atmosphere. For resistivity measurement, the bulk samples were obtained by pressing the powders into a rectangular-shaped pellet.

X-ray diffraction (XRD) data for phase identification and Rietveld refinement were collected using a Panalytical X'Pert diffractometer equipped with an X'Celerator detector. XRD patterns were refined using the GSAS program [25]. A vibrating sample magnetometer was used to measure magnetization vs. applied magnetic field. X-ray photoelectron spectroscopy (XPS) was recorded on a VG ESCALAB210 spectrometer with Mg Kα as the X-ray source operating at a constant pass energy of 30 eV.

The crystal structure of In_2O_3 is known as the bixbyite structure, which can be obtained by the ordered removal of a quarter of the anions from the fluorite structure. The In^{3+} cations occupy two distinct octahedral sites: the 8b sites, with six equidistant oxide neighbors; and the 24d sites, which have three inequivalent metal–oxygen distances. The oxygen ions occupy 48e sites and are coordinated with four In ions. There are also three distinct interstitial sites: 16f sites, coordinated with four In ions; 24c sites; and 8a sites, coordinated with six oxygen ions.

Different synthesis method or annealing treatment may influence the solubility of Fe ions in In_2O_3 lattice. In our experiment, the solubility for the sample sintered under air is as high as 25%. Above $x = 0.25$ some $InFeO_3$ was detected. For the carbothermally annealed sample the solubility decreases to 16%. Above $x = 0.16$ a small amount of the impurity phase FeO was detected. Figure 1 shows the refinement plots of typical as-sintered and carbothermally annealed samples $(In_{0.9}Fe_{0.1})_2O_3$ for. It is shown that both the as-sintered and the carbothermally anneal samples were well crystallized, and no other impurity phases were detected. The results of the refinement parameters are shown in Table 1. From these results, it can be seen that the substituted Fe ions are not randomly distributed (10% Fe in each site), but preferentially occupy the disorder 24d sites (24d site: 11.4% Fe; 8b site: 5.9% Fe) in the as-sintered sample and preferentially occupy the symmetry 8d sites (24d site: 8.3% Fe; 8b site: 15.1% Fe) in the carbothermally annealed sample. In performing the refinement of carbothermally annealed $(In_{0.9}Fe_{0.1})_2O_3$ sample, indium atoms were added in interstitial 24c and 8a sites. The refinement showed a significant improvement, with evidence that the reliability factors R_{WP} (a small value means good fitting) dropped from 4.1% for the sample without interstitial indium (In_i) to 3.1% for the sample with interstitial indium, suggesting that indiums existed in the interstitial sites. The occupancies of indiums in the interstitial 24c and 8a sites were 17.9% and 5.9%, respectively. The oxygen ion occupancies were also selected for refinement. The refined value was 90.6% for the carbothermally annealed sample and 98.1% for the as-sintered sample, indicating that a large number of oxygen vacancies (V_o) are present in the carbothermally annealed sample.

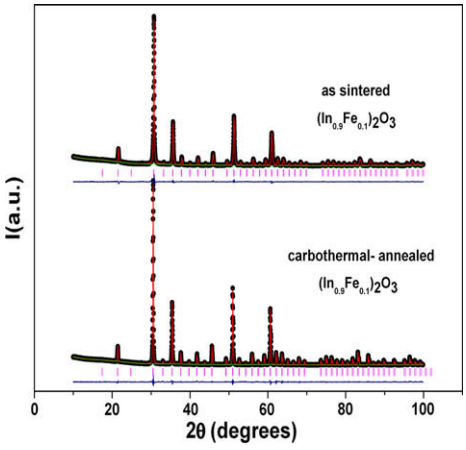

Figure 1. Rietveld refinement of the XRD patterns for as-sintered and carbothermally annealed $(In_{0.9}Fe_{0.1})_2O_3$ samples.

Table 1. Refinement parameters obtained from Rietveld analysis of XRD patterns for as-sintered and carbothermally annealed $(In_{0.9}Fe_{0.1})_2O_3$ samples.

Parameter	$(In_{0.9}Fe_{0.1})_2O_3$	
	Carbothermally annealed	As-sintered
Cation 8b		
U_{iso} (Å^2 × 100)	1.357 (52)	2.184 (54)
Occupancy (In/Fe)	0.849 (8)/0.151 (8)	0.941 (7)/0.059 (7)
Cation 24d		
U_{iso} (Å^2 × 100)	1.665 (18)	1.865 (22)
x	0.466413 (37)	0.467150 (38)
Occupancy (In/Fe)	0.917 (3)/0.083 (3)	0.886 (2)/0.114 (2)
Oxygen 48e		
U_{iso} (Å^2 × 100)	0.36 (14)	0.80 (7)
x	0.39045 (33)	0.39382 (29)
y	0.15622 (29)	0.15869 (26)
z	0.38190 (31)	0.38126 (28)
Occupancy	0.906 (3)	0.981 (7)
Indium 24c/8a		
U_{iso} (Å^2) (24c/8a)	0.800 (39)/0.205 (56)	
Y (24c)	0.8132 (26)	
Occupancy (24c/8a)	0.179 (8)/0.059 (7)	
Reliability factors		
R_P	0.0224	0.0206
R_{WP}	0.0312	0.0275
χ^2	3.587	2.923

The chemical state of Fe and oxygen ions in the $x = 0.1$ sample was investigated by XPS. Figure 2(a) shows the Fe2p core-level photoemission spectra of as-sintered and carbothermally annealed $(In_{0.9}Fe_{0.1})_2O_3$ samples. Binding energies were corrected by setting the C1s signal at the location of 284.6 eV. For the as-sintered sample, the binding energy of $Fe2p_{1/2}$ and $Fe2p_{3/2}$ were located at 724.5 and 711.3 eV, respectively, indicating that Fe is present as a Fe^{3+} species. For the carbothermally annealed sample, however, the observed XPS peaks can be divided into Fe^{2+} peaks ($Fe2p_{3/2}$: 710.1 eV; $Fe2p_{1/2}$: 723.0 eV) and Fe^{3+} peaks ($Fe2p_{3/2}$: 711.3 eV; $Fe2p_{1/2}$: 724.7 eV). The Fe^{2+}/Fe^{3+} ratio is about 1:3, according to the ratio of the areas for the Fe^{2+} and Fe^{3+} peaks. The presence of Fe^{2+} is due to the existence of the oxygen vacancies which sit close to the Fe sites. It is worth mentioning that a characteristic shake-up satellite peak for Fe^{3+} species in the carbothermally annealed sample is