

Microstructure of Iron in Thin Film Magnets Prepared by Spin Coating and Sol gel Techniques

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Abstract

Magnetic thin films such as iron and nickel oxides have a variety of technological applications. Iron and Nickel oxide thin films have been synthesized by the Solgel technique and spin coating method. In addition magnetic properties, Iron oxide thin films also exhibit semi conductor properties with possible electron excitation by irradiations of visible light of wavelength below 560 nm. However, low efficiency prevented incorporating iron oxide thin films in devices despite high abundance of iron. Deposition of several layers over a single layer may increase the photo currents. Iron nickel mix oxide thin films have been fabricated over fused quartz substrate. In this study we employed Extended X-ray Absorption Fine Structure (EXAFS), X-ray absorption Near Edge Structure (XANES), and the Mossbauer spectroscopy to characterize iron and nickel oxide thin films produced by spin coating and sol-gel techniques. The effect of number of layers and annealing temperatures were explored.

Keywords

X-ray absorption, Mossbauer, Sol-gel, spin coating, iron thin films

Introduction.

Iron oxide thin films have a variety of technological applications. Magnetic thin films are vastly utilized in magnetic memory and microwave devices [1,2]. Many different methods, such as pulse laser deposition and RF sputtering, were employed to produce magnetic thin films previously [3,4]. Colored iron oxide thin films have been synthesized by the Sol-gel technique. Iron oxide films are used as a catalyst in industry. Iron oxide thin films also exhibit semi conductor properties with possible electron excitation by irradiations of visible light of wavelength below 560 nm⁵. However, low efficiency prevented incorporating iron oxide thin films in devices despite high abundance of iron^{6,7}. Deposition of several layers over a single layer may increase the photo currents. Iron oxide thin films have been fabricated over fused quartz substrate using simple metal organic deposition from Fe-(III) acetylacetonate as the organic precursor. Nevertheless, spin coating has been identified as a low cost method compared to other expensive techniques which require high tech sophisticated equipments and vacuum. This low cost spin coating method has some disadvantages such as the existence of ion contaminants (NO₃⁻, SO₄²⁻, Cl₃⁻). In this study we employed X-ray absorption Near Edge Structure (XANES) and the Pre edge feature that appears in XANES before the main edge to

characterize iron oxide thin films produced by spin coating the number of layers on glass substrate.

Experimental: Thin films with various compositions of iron (III) nitrate and ethylene glycol were deposited on glass substrates in order to find the best composition. Best composition was found to be 14 g of iron (III) nitrate dissolved in 55g of ethylene glycol. All the films described in this report were synthesized using the solution with this special composition. Iron (III) nitrate was dissolved in ethylene glycol in a continuous flow of N₂ gas. Then, the solution under continuous stirring was heated to 80°C for 2 hours in a flow of N₂ gas. Finally this solution was applied to amorphous glass substrates. The rotational speed of the spin coater was gradually increased up to 1000 rev/min with in 1-2 min. Coating time for all samples was 1-2 min. Some samples were prepared by making several layers of film. Samples S₁, S₂, and S₃ corresponded to samples containing 1 layer, 2 layers, and 3 layers respectively. All samples were subsequently annealed at 600 °C in air for 1.5 or 3 hours to crystallize the phase.

Xerogels were prepared by mixing solutions of methanol, 0.15M ammonium hydroxide, Ferric Nitrate and Tetramethylorthosilicate (TMOS). Base catalysis was used in this process to minimize cracking of films during drying. After the gelation, the gel was allowed dry slowly in air for several days. The xerogels were then heated to 600°C in air 1.5 to 3 hours.

Data collection: All x-ray absorption data were collected at beam line F3 at Cornell High Energy Synchrotron Source(CHESS). This beam line uses a monochromator with Si(111) crystal to select X-rays of required energy from the white x-ray beam. Intensities of incident and transmitted x-rays were measured using ionization chambers filled with N₂ gas. Mossbauer experiments were performed in transmission mode at room temperature using Co⁵⁷ source in Rh matrix. The spectrometer was calibrated using 25 µm thick α-Fe standard foil.

Description of the experiment:

X-ray absorption spectroscopy is a technique that is often used to determine the physical and chemical properties of an atom. It is element specific and can be used to probe the local environment of an amorphous or crystalline sample. During the experiment, absorption coefficient of X-ray was measured as a function of energy through the range of 200 eV below the absorption edge to 1000 eV above the edge. In general, the region of the absorption spectrum from 50 eV below the edge to 50 eV above the edge is known as X ray absorption near edge structure. The region beyond 50 eV above the edge is known as Extended X-ray Absorption Fine Structure (EXAFS). Below the absorption edge, no absorption of X rays occur. But as the energy of x-rays approach the edge energy, 7112 eV for iron K edge, a sharp increase in absorption occurs

Iron in all samples was characterized using X ray Absorption Near Edge structure (XANES) and Extended X-ray Absorption Fine Edge Structure (EXAFS). A monochromatic X-ray beam from beamline F3 of Cornell High Energy Synchrotron Source (CHESS) was directed at the sample. The photon energy of the X-rays was gradually increased such that it traversed through the absorption edge of the iron (7112 eV). Below the absorption edge, the photons cannot excite the electrons of the relevant atomic level and thus absorption is low. However, when the photon

energy is sufficient to excite the electrons, a large increase in absorption occurs. This is known as the absorption edge. Above the edge, extra energy of the X rays transfer to ejected photo electrons in the form of kinetic energy. These photo electrons can be backscattered by neighboring atoms. The outgoing photo electrons and back scattered photo electrons can interfere constructively or destructively, depending on the phase shift, producing oscillations in the absorption coefficient. These oscillations are known as EXAFS. The analysis of these oscillations yields the information about the central atom, such as near neighbor bond length, type of near neighbor atoms, and number of near neighbor atoms. The main edge position is sensitive to the electron density around the central atom and therefore changes with the oxidation state of the central atom.

In the Mossbauer spectroscopy, a iron nucleus of the source emits a gamma ray by transition from the excited state to the ground state. This gamma ray can be used to excite another nucleus of the same kind. This excitation is possible if energy of the gamma rays is identical to energy gap between ground state and excited state of absorbing atom. In general, the energy gap in the absorbing nucleus is different from the source nucleus due to hyperfine interactions such as Isomer shift, Quadrupole splitting, and nuclear Zeeman effect. To compensate this variation of the energy gap source nucleus is mounted on a motor that vibrates over a range of velocities and measure the transmission intensity as a function of the velocity. At zero velocity the energy of emitted gamma rays is identical to the energy difference between ground state and excited state. But at velocities other than zero the energy of emitted gamma rays changes by factor of v/c due to Doppler shift where v is the speed of the source and c is the speed of light. The change of energy gap in the absorber due to hyperfine interactions can be compensated by Doppler shift. Therefore by knowing absorption velocities one can extract information about absorbing nucleus.

Data analysis results and discussion:

In order to study the chemical state of iron in thin films prepared under conditions, samples were prepared with different number of layers during spin coating and annealed to 600⁰ C for 1.5 or 3 hours. These samples were used in X-ray absorption and Mossbauer experiments. As shown in the figure 2, the main edge energy position of sample S₁ is same as Fe₂O₃. This indicates that the iron in this sample has same charge state as iron oxide. However, the main edge positions of samples S₂ and S₃ are about 2 eV lower than the iron oxide. This indicates the charge state of iron in these samples is lower than Fe³⁺ or mixture of Fe³⁺ lower oxidation states. Also general shape of the XANES of samples S₂ and S₃ is different from iron oxide or S₁. But XANES spectra of iron film prepared by sol-gel method are very similar in shape and main edge energy position to that of iron oxide. The identical main edge and pre-edge energy positions indicate the similarity of charge state in two samples. The difference in the intensity of the pre-edge may provides information about asymmetry and bonding of iron. But to conclude more careful analysis is required. To investigate possible changes in the oxidation state with annealing time, samples prepared by both methods were heated to 1.5 hours and another set of identical samples were heated to 3 hours. However, regardless of annealing time there is no significant change appears in any of the spectrum. This indicates that phases were crystallized completely after 1.5 hours.

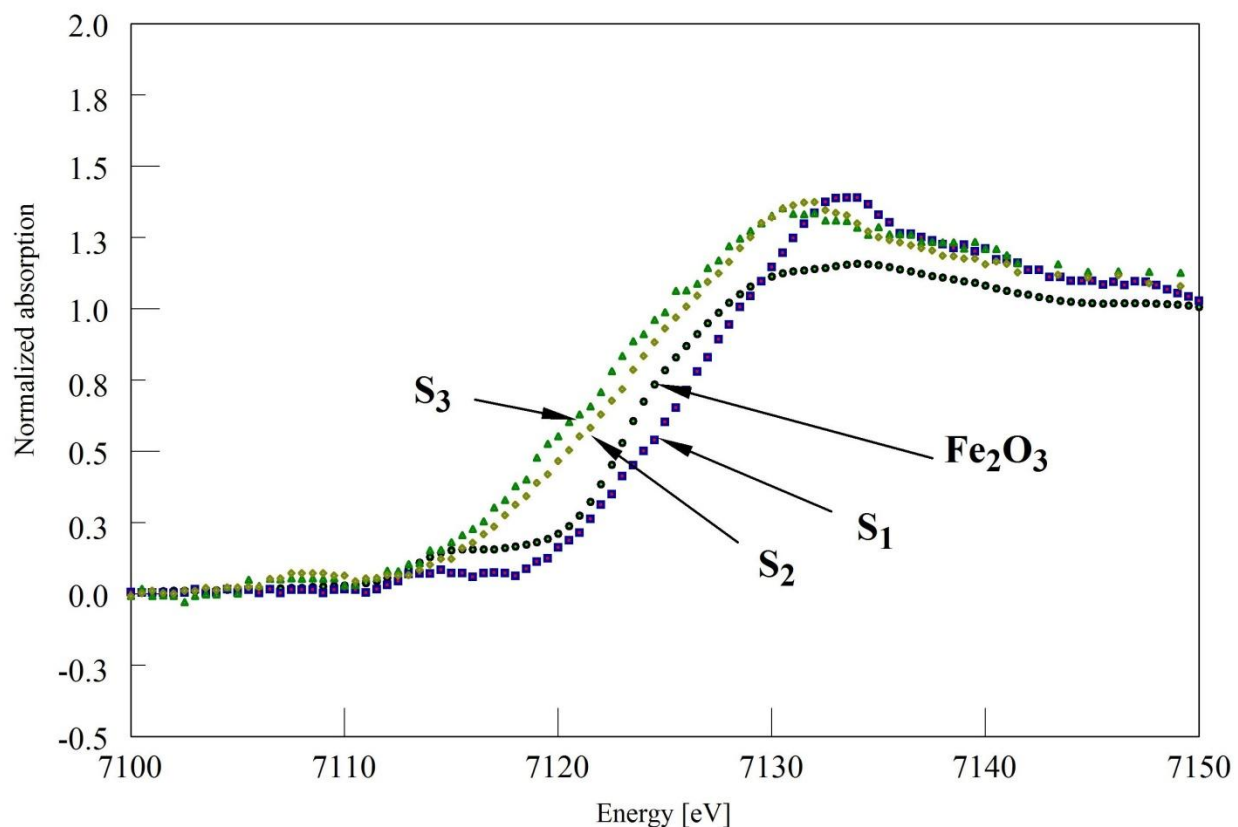


Figure 1: X-ray absorption near edge spectra of Fe_2O_3 and thin films prepared by spin coating. S_1 -1 layer, S_2 -2 layers, S_3 -3 layers.

Figure 1 shows the normalized X-ray absorption near edge spectra of Fe_2O_3 and samples S_1 , S_2 , & S_3 with 1, 2 and 3 layers respectively. As shown in the figure 1, the main edge energy position of sample S_1 is same as Fe_2O_3 . This indicates that the iron in this sample has same charge state as iron oxide. However, the main edge positions of samples S_2 and S_3 are about 2 eV lower than the iron oxide. This indicates the charge state of iron in these samples is lower than Fe^{3+} or mixture of Fe^{3+} lower oxidation states. Also general shape of the XANES of samples S_2 and S_3 is different from iron oxide or S_1 . But as shown in the figure 2b, XANES spectra of iron oxide and iron film prepared by sol-gel method are very similar in shape and main edge energy position except intensity of pre-edge feature appears before the main edge. The identical main edge and pre-edge energy positions indicate the similarity of charge state in two samples. The difference in the intensity of the pre-edge may provides information about asymmetry and bonding of iron. But to conclude more careful analysis is required. To investigate possible changes in the oxidation state with annealing time, samples prepared by both methods were heated to 1.5 hours and another set of identical samples were heated to 3 hours. However,

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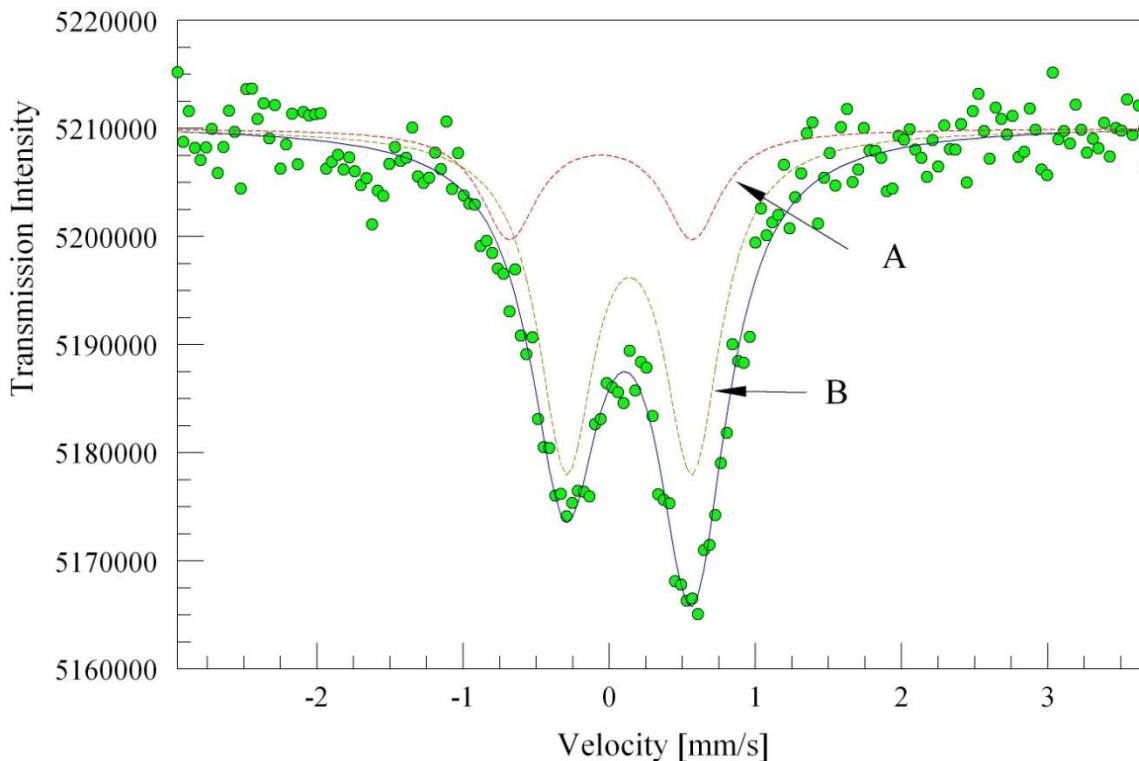


Figure 3a: Mossbauer spectrum of a sample prepared by spin coating.

Figure 3a and 3b show typical Mossbauer spectra of iron film prepared by spin coating and sol-gel method respectively. The Mossbauer spectrum of samples prepared by spin coating can be fitted with two Lorentzian doublets. This indicates presence of two different forms of iron. The isomer shift, 0.53 m/s relative to iron foil spectrum, and quadrupole splitting, 0.8 mm/s, of line B agree with octahedrally co-ordinated Fe^{3+} . However, line A shows very little isomer shift, 0.04 mm/s relative to iron foil spectrum, and quadrupole splitting of 1.3 mm/s. The isomer shift of line A is compatible with Fe^0 but presence of quadrupole splitting indicates non-symetric electron density at the site of iron nuclei. But the intensity of line A is significantly low compared to line B. Therefore amount of Fe^0 is much lower compared to the iron in Fe^{3+} form. In contrast, as shown in figure 3b, the Mossbauer spectrum of iron film prepared by sol-gel method consists of only one quadrupole doublet corresponding to only one form of iron. The isomer shift and quadrupole splitting values are compatible with octahedrally coordinated Fe^{3+} .

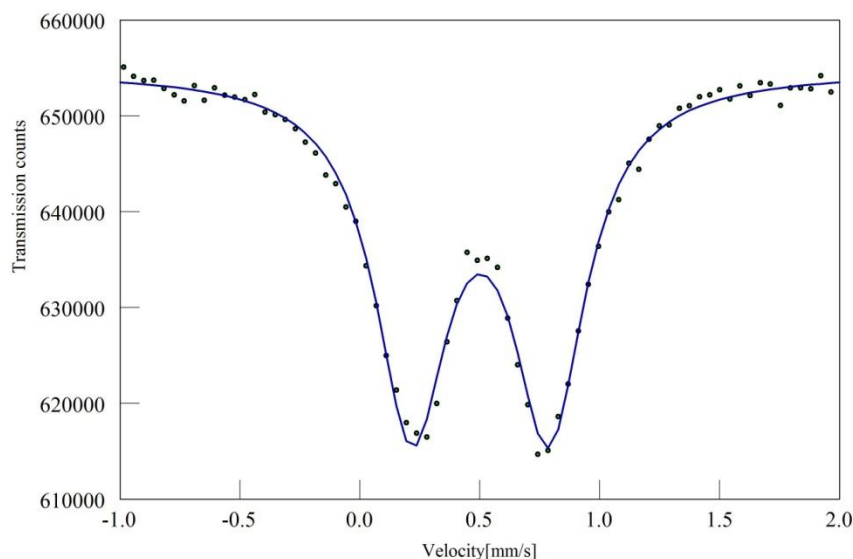


Figure 3b: Mossbauer spectrum of a sample prepared by sol-gel method.

Conclusion:

The structural properties of iron particles in thin films prepared by spin coating and sol-gel method were investigated using X-ray absorption spectroscopy and Mossbauer spectroscopy. Both X-ray absorption and Mossbauer results agree with presence of only Fe^{3+} in samples prepared by sol-gel method. In addition to octahedrally coordinated Fe^{3+} , small amount of non oxidized iron may present in the samples prepared by spin coating method.

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