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Research Article

FABRICATION AND CHARACTERIZATION OF Fe_3O_4THIN FILMS WITH IMPROVED MAGNETIC PROPERTIES BY SPIN COATING TECHNIQUE

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ABSTRACT

The Fe_3O_4 thin films were deposited onto glass substrates by spin coating method at various temperatures using $FeCl_2$ $4H_2O$, citric acid monohydrate, ascorbic acid and ethanol absolute were used as starting materials. Structural, morphological and optical properties of Fe_3O_4 thin films have been studied. The structural studies revealed that the as-deposited Fe_3O_4 thin films are nanocrystalline in nature with cubic lattice. The morphological investigations show that the total substrate surface is well covered with crack free and homogenous surfaces.

INTRODUCTION

Magnetic phenomena at the atomic scale were discovered in the early twentieth century, whereas the discovery of the first known magnetic material (Fe_3O_4) revolutionized the field of magnetism. The magnetic properties of a material depend on temperature, the applied magnetic field, and pressure. A change in these variables will result in the existence of two or more forms of magnetism. Ferro- and ferrimagnetic materials like Fe_3O_4 and some of their alloys have particles whose shape is asymmetrical when they are obtained by the grinding of bulk materials, whereas they can possess a spherical shape only when manufactured through plasma atomization or wet chemistry or when in aerosol and gas phases. Depending on the procedure used to form particles, they can be crystalline or amorphous spherical in shape. To a large extent, the synthesis process determines the degree of impurities in a particle, as well as the presence of structural defects, and, hence, the division of these defects inside the particle structure can be used to discover its magnetic properties [1-2].

Ferrites are considered as very important class of oxides with significant magnetic properties. Ferrites have been widely studied and applied over the past several decades. To say that ferrites have magnetic properties means they will attract magnets of opposite polarity and iron-based alloys and repel magnets of similar polarity. Ferrites also possess dielectric properties, which mean that they do not conduct electricity when electromagnetic waves pass through them [3]. In various applications, this gives them an advantage over Ni, Fe, and transition metals that possess magnetic properties ("ferromagnetic") because these metals conduct electricity when electromagnetic waves pass through them. The phenomenon of *ferromagnetic* ferrites is the converse of *ferromagnetic* metals. In ferrimagnetism, there is not just one arrangement but distinct alignments of perpendicular and parallel magnetic moments. It is these alignments that give them their remarkable properties. This property can be attained through various crystal structures [4].

Based on distinct magnetic and electrical properties, different phases of iron oxide are being used in the study of high density magnetic storage devices. The three stoichiometric forms of iron oxide are magnetite (Fe_3O_4), hematite (α-Fe_2O_3), and maghemite (γ - Fe_2O_3)[5]. Magnetite is a half metallic material with wide range of applications in electronic and spintronic devices. Hematite is an antiferromagnetic and maghemite is a ferrimagnetic material.

There are several reported ways to synthesize iron-oxide nanoparticles with diameter sizes ranging from 10 to 100 nm including solvo-thermal, hydrothermal [6], sonochemical, sol

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gel [7-12], microwave and co-precipitation methods. We used sol-gel by spin coating method for the chemical modification of magnetite nanoparticles because of its simplicity and cost effectiveness. It is important to note that several reaction conditions such as temperature, pH, changing the iron salt, rate of addition, and preparation methods alter the type of oxides particles obtained (e.g., size, shape, and mineralogy), which requires special attention during the synthesis procedure. However, very little attention has been devoted to use of wet chemical methods especially sol-gel. We here report the preparation of pure magnetite thin films using sol-gel method [13, 16].

In sol-gel film processing, firstly a gel-precursor solution, or sol, is synthesized, then it is applied to a substrate by using spin-on or dip-coating techniques. A gel layer is formed after this step and then it is heated to obtain ceramic film. Generally this process is carried out in two stages. In drying step, by employing a hot plate, heat treatment was done at a temperature like 100 °C. It is followed by a sintering step, which is the final heat treatment, at temperatures between 300 °C and 500 °C [17].

Experimental Details

The aim of this study was to produce magnetite thin films on glass substrates by sol-gel process and characterize them with several methods. Magnetite thin films are important for applications in many different types of devices and for their possible future applications. Glass substrates are used because they have many benefits over other substrates that were previously used for preparing magnetite thin films. Sol-gel process which has many advantages on thin film formation was chosen for the film deposition process. During the study, magnetite phase was observed at sintering temperatures of 300-350 °C. Increasing sintering temperature leads to phase transformations.

For observing the behavior of different starting materials, four different solutions were prepared during the study. In the first one, which will be called (a) from now on, $FeCl_2\ 4H_2O$, citric acid monohydrate, ascorbic acid and ethanol absolute were used as starting materials. In this solution, $FeCl_2\ 4H_2O$ the raw material and citric acid monohydrate the chelating reagent. Ascorbic acid and ethanol absolute were used as antioxidant agent and solvent, respectively. For obtaining the coating solution 0.1 mol $FeCl_2\ 4H_2O$, 0.1 mol citric acid monohydrate and 0.1 ml antioxidant agent were dissolved in 100 ml ethanol absolute. This mixture was stirred at 60 ºC for 6 hr. Then as a drying chemical control agent, 0.1 ml N, N-dimethylformamide was added to the solution. Finally, solution was stirred for half an hr at 60 ºC.

Second solution, (b), was obtained by mixing the 0.01 mol $Fe(NO_3)_3\ 9H_2O$, 0.03 mol dimethylamineborane (DMAB) and 100 ml distilled water. The solution was obtained by stirring the solution at room temperature until the colour of the solution becomes colourless.

For the third solution, (c) , 0.005 mol $Fe(NO_3)_3\ 9H_2O$, 0.02 mol citric acid monohydrate and 0.05 mol of ethylene glycol were dissolved in 100 ml of distilled water. The molar ratio of Fe ion: citric acid: ethylene glycol = 1:4:10 in the solution. This solution was stirred and heated until the gas evolution was observed. In the resulting solution, there exists a complex between iron (III) ions and the polyether formed from citric acid and ethylene glycol. Then this complex was dissolved in methanol to obtain a coating solution.

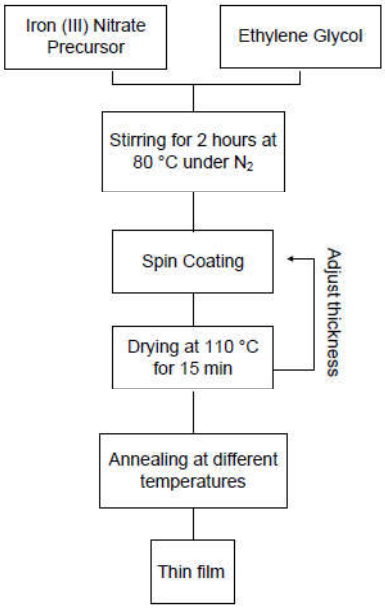
For the fourth solution, (d), 0.3 M iron (III) nitrate hydrate was dissolved in a mixture of 2-methoxyethanol (MET) and acetyl acetone in a molar ratio of 20:2. Mixture was mixed at room temperature for 2 hr prior to obtaining coating solution.

It is seen conclusively that changes in sol concentration has a tremendous effect on phase purity and stability of magnetite thin films along with excellent ferrimagnetic properties. The film samples are coated and labelled as (a), (b),(c) & (d). XRD, FTIR and DFT calculations are studied and their results are analysed.

Spin Coating

The spin coating process was performed by using a spin coater (SPEKTROSPIN – SPIN COATER). After solution preparation, spin coating was performed onto cleaned glass substrates. With the help of a double sided tape, cleaned small substrates with different sizes were stuck onto the head of spin coater. Excess amount of solution was poured onto the substrates by using Pasteur pipettes.

By changing the spinning rate of the spin coater, thickness of the films can be adjusted. In this study, films were coated at 1500, 4000 and 5000 rpm for 60 seconds. For obtaining crack free and homogenous films, very thin films were prepared. In order to obtain thicker films, individual coating steps were repeated. After each coating step, drying was performed and when desired thickness achieved, sintering was performed as the final step. When the thickness of the films increases and reaches to a critical value, cracks on the film surfaces were observed due to the shrinkage during sintering.



The flow chart for the processing of thin films.

Heat Treatment of Thin Films

Heat treatment of thin films begins with the drying step. Drying temperature was decided according to the boiling temperature of the solvent. Since the boiling temperature of the ethylene glycol is 197 ºC, drying temperature is chosen as 110 ºC which is less than 197 ºC and also enough for the removal of water. The most important part of this process is the shrinkage due to removal of water. In order to reduce the shrinkage, the drying furnace is pre-heated to 110 ºC before drying. Specimens were fired at this temperature for 15 minutes. Between each layer, drying step was performed until the desired thickness is obtained. The flow chart shows the followed route starting from the solution preparation step to heat treatment processes.

Sintering is the final heat treatment procedure. The purpose of sintering is changing the as-dried amorphous thin films into crystalline thin films. Sintering procedure was performed in a tube furnace under atmosphere with a 3 ºC/min heating rate. Slow heating rate is important to avoid the crack formation during heating.

For observing the effect of temperature on film formation, distinct temperatures; 250 ºC, 300 ºC, 350 ºC, 400 ºC, 450 ºC, were used in sintering. Sintering duration was chosen as 2 hr and 3.5 hr.

The thickness of the magnetite thin films and its effects on the film formation were also observed during this study. Thickness of one layered films was controlled by changing the spinning rate. One to twenty layered thin films were studied to observe the effect of thickness on microstructure and properties of thin films.

Characterization of Magnetite Thin Films

XRD analysis

X-ray diffraction was used to investigate the crystalline content of the nanoparticles and hybrid materials. Figure 1 shows the XRD patterns of coated Fe_3O_4 (082 237 JCPDS) thin films with tannic acid and strong Bragg reflection peaks (2θ: 18.3, 30, 35.4, 43.1, 53.4, 57 and 62.5º) assigned to (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) Miller indices. Crystallographically, magnetite takes on a cubic inverse spinel structure due to the fact that the oxide ions form a face-centered cubic, with the iron (II) and iron (III) cations occupying one-eighth of the tetrahedral and half of the octahedral holes, respectively.

In addition, diffractograms for the Fe_3O_4 and Fe_3O_4-illustrate well defined and intense peaks mainly related to the crystallographic plane (311), showing the presence of the crystalline phase of Fe_3O_4 thin films, even after the addition of (hybrid materials). The potentially interacts through the (111) plane of the Fe_3O_4 thin films. We based this on reports that assert that the (111) phase is the most exposed to the environment and favourable for binding to oxygen atoms. We noticed that the (111) phase does not produce a large XRD peak due to low intensity typically observed for that plane.

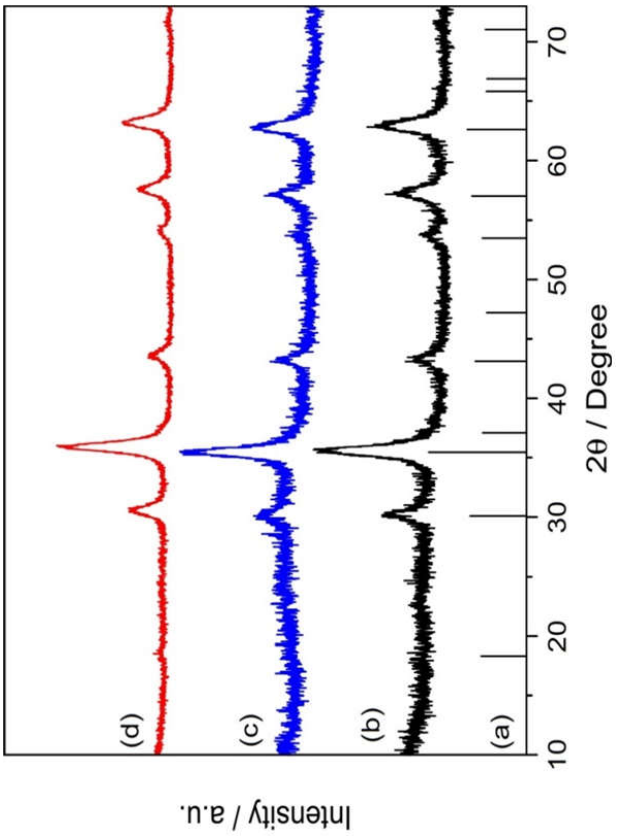


Fig 1 XRD pattern of Fe_3O_4 thin films

FTIR

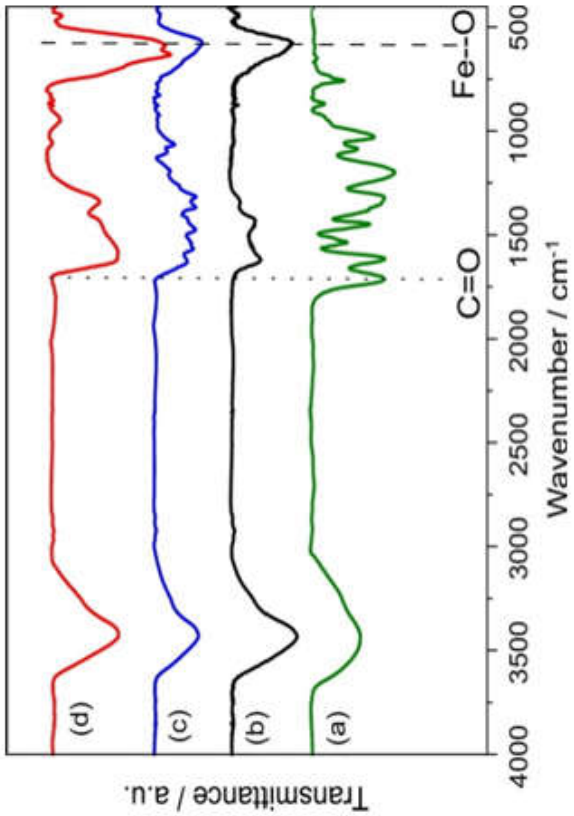


Fig 2 FTIR spectra of Fe_3O_4 thin films

FTIR spectrum in shows that the H-O-H bending vibration at about 1000 - 1600 cm^{-1}, typical of the HO molecule, is less intense. Additionally, the second absorption band, between (900-1000) cm^{-1}, corresponds to bending vibration associated to the O – H bond. The O–H in plane and out of plane bonds appears at (1583.45–1481.23 and 935.41– 838.98) cm^{-1}, respectively. For strong hydrogen bridges its maximum lies at about 900-1000 cm. These first two bonds correspond to the hydroxyl groups attached by the hydrogen bonds in the iron oxide surface, as well as the water molecules chemically adsorbed to the magnetic particle surfaces. In the spectrum showed figure, the sample exhibits two intense peaks, in (582 and 640) cm^{-1} bonds, that are due to the stretching vibration mode associated to the metal oxygen absorption band (Fe – O bonds in the crystalline lattice of Fe_3O_4).They are characteristically pronounced for all spinel structures and for ferrites in particular. This occurs because, in these regions, the contributions from the stretching vibration bonds related to metal in the octahedral and tetrahedral sites of the oxide structure are found. Moreover, the FTIR spectrum shows an absorption bond at 1706 cm^{-1} , which presents the stretching vibration of the carboxyl group (C = O), associated to the oleic acid molecule, adsorbed on to the surface of the crystallites.

SEM

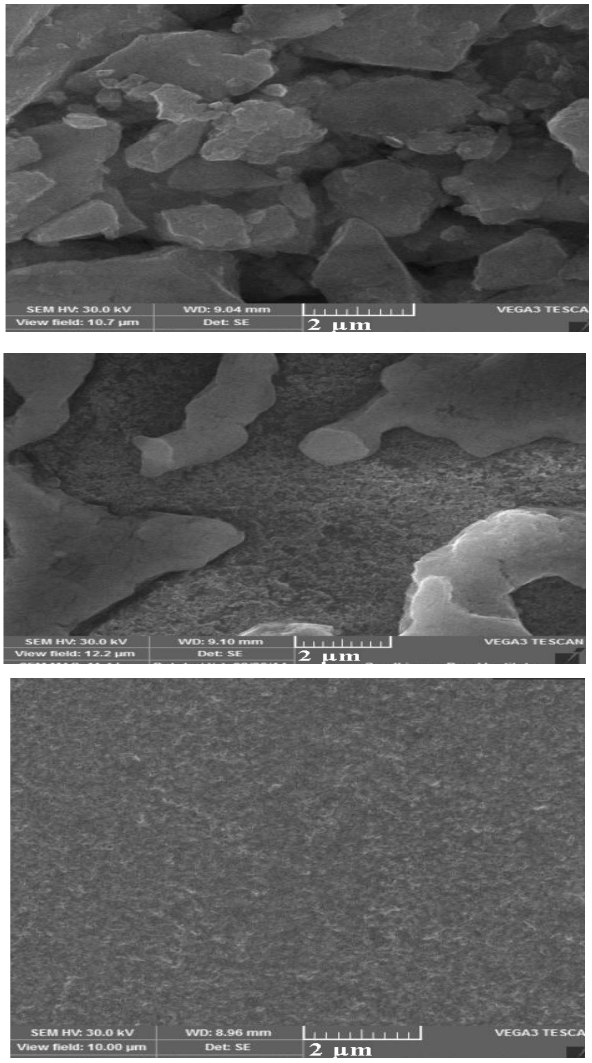


Fig 3 SEMimages of Fe_3O_4 thin films

Surface morphology of thin films was studied by using SEM. Most of the deposited thin films have crack free and homogenous surfaces. Three different deposited films were shown in Figures. Figure shows a film surface coated at 2000 rpm and sintered at 300 ºC for 3.5 h in air and Figure 3 shows a film surface coated at 5000 rpm and sintered at 300 ºC for 2 h in air. As it can be seen in these three figures, crack free and homogenous thin films were deposited by main solution (S1) in the study. In order to compare the film surfaces coated by using different solutions, SEM micrographs of thin films coated by solution S3 was shown in Figure 3 As it can be seen in the figure, surface of the film is smooth and no cracks can be observed. The film shown in Figure.3 was prepared at 5000 rpm and sintered at 300 ºC for 1 h in air.

UV Transmittance

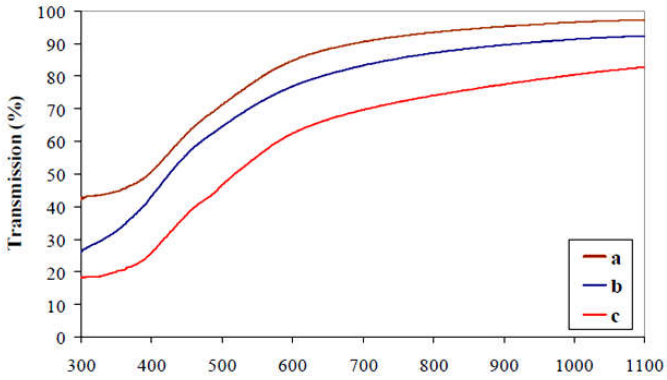


Fig 4 Absorption spectra of Fe_3O_4 thin films

As it can be seen in Figure 4 highly transparent films were obtained at lower sintering temperatures and at lower thicknesses. Highly transparent nature of the magnetite thin films leads itself to be a candidate for magneto-optical applications. It is known that when the magnetite nanocrystals are deposited on a noble metal surface such as gold, the magneto-optical effects significantly increase. This effect can be useful for novel-optical data storage media. High transparency of the films is the result of the high quality (fewer vacancies, holes or cracks) of the film and homogenous dispersion of finely divided particles.

RESULTS AND CONCLUSION

From the results it can be concluded that, magnetite film formation depends on different parameters. These parameters can be listed by means of process sequence in the film formation. Spinning rate affects the thickness of thin films, sintering temperature effects the magnetite phase formation and sintering time affects the grain size of the films.

The coating solution used in this study showed Newtonian behavior. It indicated that thin films produced by using this solution will be homogenous. Magnetite phase obtained in a narrow temperature range. Between 300 °C and 350°C, magnetite phase was observed. Above 350 °C, maghemite and hematite formation was observed. Magnetite thin films are obtained in single layered films.

Increasing number of layers will result in phase transformation because of heat treatment procedure applied between each layer. Therefore phase transformation probability increases in

multi-layered thin films. Thickness of single layered thin films was found between 10-200 nm. The variation in this value depends on the variation in spinning rates and low spinning rates yield higher thickness values.

Magnetite phase was proved by in-plane grazing incidence X-ray diffraction. Diffraction spectrum obtained by conventional methods did not give any result. The reason for this behavior was explained by thickness effects of the films. Diffraction obtained from substrate masked possible diffraction peaks coming from thin film. Grain size of the samples was calculated by Scherrer's equation and found as approximately 15 nm. Thickness of the thin films was also found by using X-ray reflectivity measurements.

From optical measurements, it was seen that transparency of the films increases as thickness and sintering temperature decreases. Between 900-1100 nm wavelengths, prepared thin films gave a maximum transmittance of 95%. As a conclusion, highly transparent films were obtained in this study.

As a final suggestion, giant magneto resistance of the prepared magnetite thin films could not be investigated. To verify the magnetite phase formation, many further characterization techniques could not be used. It is difficult to distinguish magnetite and maghemite phases. Spectroscopic characterization techniques give valuable information about this problem. But they still have some limitations such as thickness effect restrictions of Raman Spectroscopy. Because of 100% spin polarization, magnetite is very important for future spintronic device applications.

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References

1. Grossman H, MyersW, Vreeland V, Bruehl R, Alper M, Bertozzi C, Clarke J (2004) Detectionof bacteria in suspension by using a superconducting quantum interference device. *Proc NatlAcad Sci* 101:129–134
2. Chung S, Hoffmann A, Bader S, Liu C, Kay B, Makowski L, Chen L (2004) Biologicalsensors based on Brownian relaxation of magnetic nanoparticles. *Appl Phys Lett* 85:2971–2973.
3. Akbarzadeh A, Samiei M, Davaran S (2012) Magnetic nanoparticles: preparation, physicalproperties, and applications in biomedicine. *Nanoscale Res Lett* 7:1
4. Rümenapp C, Gleich B, Haase A (2012) Magnetic nanoparticles in magnetic resonance imaging and diagnostics. *Pharm Res* 29:1165-1179
5. M. Aronniemi, J. Lahtinen, and P. Hautojärvi, Characterization of iron oxidethin films. Surface and Interface Analysis, 2004. 36: p. 1004-1006.
6. H. Zhu, D. Yang, and L. Zhu, Hydrothermal growth and characterization ofmagnetite (Fe3O4) thin films. *Surface & Coatings Technology,* 2007. 201: p.5870-5874.
7. Q. Wang, *et al*., Synthesis of Nanocrystalline Magnetite (Fe3O4) Films by Self-Reduction Sol-Gel Route. Materials Science Forum, 2003. 423-425: p.569-572.
8. N. J. Tang, *et al*., Nanostructured magnetite (Fe3O4) thin films prepared by sol–gel method. *Journal of Magnetism and Magnetic Materials*, 2004. 282:p. 92-95.
9. K. Tanaka, *et al*., Preparation of Fe3O4 thin film by the sol-gel method and its magnetic properties. *Journal of Materials Science Letters,* 1989. 8: p. 83-85.
10. H. S. W. Chang, C.-C. Chiou, and Y.-W. Chen, Synthesis, Characterization, and Magnetic Properties of Fe3O4 Thin Films Prepared via Sol-Gel Method. *Journal of Solid State Chemistry*, 1997. 128: p. 87-92.
11. S. N. Malchenko, *et al*., Formation of iron oxide films from stabilized magnetite sols-magnetic liquids. *Thin Solid Films*, 1993. 227: p. 128-132.
12. M. Sedlář and V. Matějec, Preparation of Fe3O4 thin film by the sol-gel method and its magnetic properties. *Journal of Sol-Gel Science and Technology*, 1994. 2: p. 587-589.
13. K. Tanaka, *et al*., Preparation of Fe3O4 thin film by the sol-gel method and its magnetic properties. *Journal of Materials Science Letters,* 1989. 8: p. 83-85.
14. A. Karakuşcu, Characterization of maghemite thin films prepared by sol-gel processing, M.S. Thesis, Supervisor Prof. Dr. Macit Özenbaş, Middle East Technical University, Turkey, 2006.
15. T. Hashimoto, T. Yamada, and T. Yoko, Third-order nonlinear optical properties of sol-gel derived α-Fe2O3, γ-Fe2O3, and Fe3O4 thin films. *Journal of Applied Physics,* 1996. 80(6): p. 3184-3190.
16. T. Hashimoto and T. Yoko, Sol-Gel Preparation and Nonlinear Optical Properties of Transition Metal Oxide Thin Films. Materials Transactions, JIM, 1996. 37(3): p. 435-441.
17. C. Cao, M. Luo, and H. Zhu, PLZT films prepared by sol-gel process. *Journal of Non-Crystalline Solids*, 1999. 254: p. 146-150.

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