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# Low temperature growth of nanocrystalline $Fe_2TiO_5$ perovskite thin films by sol–gel process assisted by microwave irradiation

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**Abstract**

Nanocrystalline $Fe_2TiO_5$ thin films have been grown on Si (1 0 0) at room temperature by using simple, cost effective sol–gel process assisted by microwave irradiation for thermal treatment. For comparison purpose the deposited films have been subjected to two kinds of annealing treatments: first set by using conventional annealing and second set by irradiating the deposited films at different microwave powers for 10 min. In both treated films, formation of orthorhombic phase of $Fe_2TiO_5$ structure has been observed. It is evident that there is a dramatic structural modification when the deposited films are exposed to microwave. There was slight stoichiometric change of $Fe_2TiO_5$ thin films treated by conventional annealing and microwave annealing. Microwave exposed films have shown 47% of Fe, 6% of Ti and 47% of O in the films of the $Fe_2TiO_5$, whereas annealed films have shown close to the stoichiometry in $Fe_2TiO_5$ with 30% of Fe, 14% of Ti and 56% of O. Plausible mechanism for the formation of nanocrystalline orthorhombic phase of $Fe_2TiO_5$ perovskite structure at low microwave powers has also been discussed. This new innovative microwave heating could open a door for the advanced nanotechnologies to cut down the process cost in post treatment of the nanomaterials.


*Keywords:* A. Sol–gel process; Microwave irradiation; Annealing; Surface texturing; Perovskite nanostructures; Spin coating; X-ray diffraction; X-ray photoelectron spectroscopy

## 1. Introduction

There have been many investigations of oxide films [1] synthesized from the sol–gel method because of several advantages, such as low processing temperature, homogeneity, possibility of coating on large area substrates, and most important cost effective. Unlike physical vapor deposition (PVD) or chemical vapor deposition (CVD) coating technologies, sol–gel technology does not require any high vacuum equipment. Sol–gel oxide films have many wide applications as functional materials in optical [2], microelectronics [3] and optoelectronic [4] industries, and for the purpose of corrosion [5–10], scratch, abrasion [11] resistance materials as well. Transitional metal oxides and their perovskite structures such as $TiO_2$, $HfO_2$, CdO and $CdTiO_3$, $NiTiO_3$ are widely used in many optical, biomedical [12], and microelectronic applications because of their excellent properties such as chemical resistance, good mechanical strength, transparency, as well as insulating properties. Usually these oxides are prepared by techniques such as chemical vapor deposition and physical vapor deposition. However, it is difficult to prepare large area depositions on irregular surfaces, with high homogeneity by these methods, which could be replaced by sol–gel technology.

There has been growing interest in iron titanium oxide and nickel titanium oxide thin films as a good candidates for new optical fibers [13–15], and as a sensor material for the detection of $NO_2$ [16,17] gas sensing applications. Furthermore, like the other titanium-based systems, $Fe_2TiO_5$ have a lot of potential for applications in non-linear optics, magnetic material. In order to replace other materials, pure and high quality structures are needed.

Microwave irradiation is becoming an increasingly popular method of heating samples in the laboratory to synthesize biological [18], organic [19], polymers [20], and inorganic materials [21]. Coatings with surface laser treatments [22] or microwave exposure [23] leads to enhance structural, morphological, mechanical and tribological properties. Unlike

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conventional annealing process, This could be a great advantage for the inorganic, organic, organic-inorganic hybrid, polymer thin films that are applied on plastic, quartz, glass substrates, where conventional annealing process is a limiting factor. Microwave technique offers a clean, cost effective, energy efficient, quite faster, and convenient method of heating, which results in higher yields and shorter time reactions. This will have strong impact on coatings applied in nanotechnology, microtechnology, and biotechnology industries. Keeping in view the necessity of the coatings that are applied on plastic substrates, microwave irradiation has been chosen as an alternative method for annealing process.

In the present investigation, thin films of $Fe_2TiO_5$ perovskite structure have been deposited on Si (1 0 0) (with 4–5 nm thickness of native $SiO_2$ on surface) substrate at room temperature by sol–gel spin coating process. Two sets of films have been treated as follows: one set by annealing at different temperatures ranging from 400 to 800 °C for 3 h in air, and second set of films have been exposed to (2.45 GHz) at different powers ranging from 100 to 900 W for 10 min in air. The conventional annealed films as well as microwave-irradiated thin films have been subjected to characterization for structural, morphological and compositional properties.

## 2. Experimental procedure

The preparation and deposition of $Fe_2TiO_5$ thin films by sol–gel spin coating process are shown in Fig. 1. Calculated quantity of titanium butoxide (Aldrich, 99.98% purity) has been dissolved in 2-methoxy ethanol (99.98%) solvent along with acetyl-acetone as a complexing and chelating agent. In order to control the grain size, 1.2 g of cetyltrimethyl ammonium bromide (as surfactant to control the growth of $TiO_2$ crystallites) has been dissolved in 20 ml of 2-methoxy ethanol solvent in beaker and the contents were added drop-wise to the titanium butoxide sol under vigorous stirring. The contents were stirred at room temperature for about 6 h. The molar ratio of titanium butoxide, 2-methoxy ethanol and acetyl-acetone were 2:10:0.5. In order to prepare the perovskite nanostructures of $Fe_2TiO_5$, calculated quantity of the corresponding ferric chloride as Fe source has been dissolved in 2-methoxy ethanol solvent. The contents are stirred for 2 h and then added drop-wise to the $TiO_2$ solution. To the above contents calculated quantities of $HNO_3$ (1.2 ml) and of deionizing water (1.5 ml) have been added drop wise as a catalyst to increase the rate of reaction, and for hydrolysis of the sol, respectively. Further the contents are refluxed at 60 °C for 3 h to complete the reaction and obtain homogeneous solution and later cooled to room temperature. The contents were filtered using Whattman filter paper in order to remove any particulates formed during the reaction. The obtained stock solution is used for the deposition of Si substrates by spin coating process.

Si (1 0 0) substrates (with 4–5 nm thickness of $SiO_2$ on surface) have been rinsed with deionized water, and placed in a beaker containing ethanol solvent and were subjected to ultrasonic treatment for 15 min in order to remove any particles on the surface. Then, substrates were rinsed with acetone and blown dry under $N_2$ gas. Cleaned Si (1 0 0) substrates (3 cm × 3 cm) were immediately placed in the spin coating chamber. Using 50 μL pipette, 10 μL of the respective stock solution was placed on the surface of the Si (1 0 0) substrate and spun with 1000 rpm speed for 30 s (cylce-1) to spread the solution on the entire surface of the substrate. This step was followed by 3000 rpm for 30 s (cycle-2) in order to evaporate the solvent and to have homogeneous xerogel film. The steps consisting of cycle-1 and cylcle-2 were repeated 10 times in order to get thickness ∼150 nm thin xerogel film (as deposited). At the end, the obtained xerogel films were subjected to two different treatments, one set has been subjected annealing for 3 h at the rate of 3 °C/min at different substrate temperatures ranging from 400 to 800 °C in air and other set exposed microwave at different powers in air. To evaluate the phase

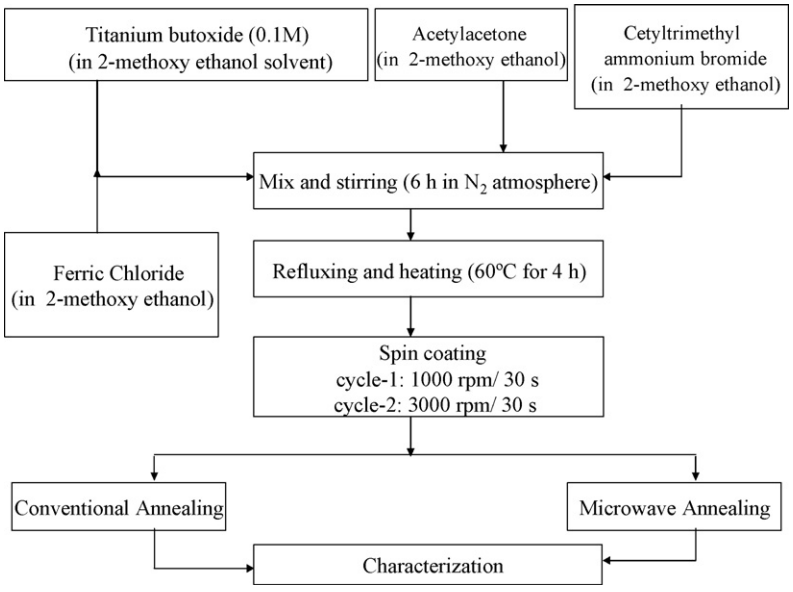


Fig. 1. Flow chart diagram of the preparation of $Fe_2TiO_5$ thin films by sol–gel spin coating process.

formation of the treated films, X-ray diffraction (XRD) technique has been employed. X-ray diffraction (model Bruker D5000) grazing angle mode has been chosen for the present study. The X-ray source was a sealed X-ray 1.5 kW Cu Kα radiation (λ = 1.5406 Å). Morphological studies on the treated films have been carried out by employing high resolution scanning electron microscopy (HRSEM) (model: ZIESS). X-ray photoelectron spectroscopy (XPS) measurements of the $Fe_2TiO_5$ thin films exposed to microwave at 900 W for 10 min as well as annealed at 800 °C for 3 h have been performed using the PHI ESCA system equipped with a Mg X-ray source ($h\nu$ = 1253.6 eV) with a hemispherical analyzer.

## 3. Results

### 3.1. Structural properties

XRD patterns obtained for the $Fe_2TiO_5$ thin films for both annealed and microwave exposed have been shown in Fig. 2a and b, respectively. Conventional annealed films at and above 400 °C exhibit sharp and high intensity peaks, corresponding to orthorhombic phase of $Fe_2TiO_5$. Broad and low intensity peaks with preferential growth of (1 0 1) and (2 3 0) orthorhombic phase of $Fe_2TiO_5$ have been observed for the films exposed to microwave at and above 450 W. As the microwave power increased from 300 W and above there was an increase in the growth of orthorhombic phase of $Fe_2TiO_5$.

In order to observe the perovskite structure thin film growth at 900 W microwave power exposed to different times, xerogel films have been exposed to 900 W microwave power at different timings ranging from 1 to 20 min as shown in Fig. 3a. Quite interestingly, the formation of orthorhombic phase has been observed for the films exposed to microwave at 900 W for 1 min. It is noteworthy to mention here that crystallite size of the films (calculated from the Scherrer's equation ($D = 0.9\lambda/B\cos\theta$; where $D$ = crystallite size (nm), λ = wavelength of the X-ray, $B$ = full width at half maximum for the 100% diffraction plane, and $\theta$ = Bragg's angle)) for the orthorhombic phase exposed to 900 W microwave power has shown slight change: 8 nm for 1 min exposed film to 12 nm for the film exposed to 20 min. In order to observe if the effect of microwave irradiation is limited to surface effect or bulk, experiments have

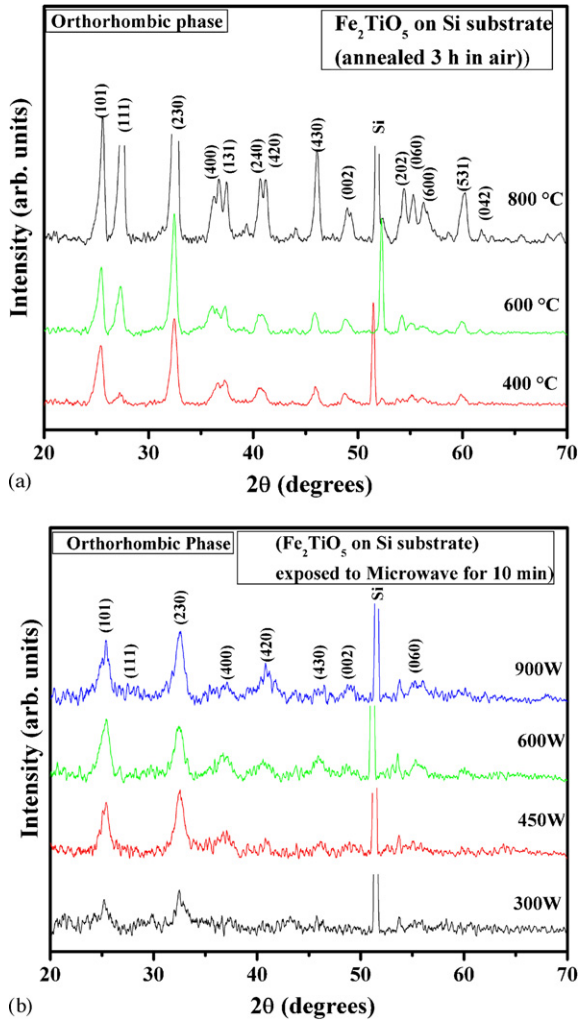


Fig. 2. XRD pattern of $Fe_2TiO_5$ thin films on Si (1 0 0) substrate by sol–gel spin coating process. (a) Annealed at different substrate temperatures in air for 3 h. (b) Exposed to different microwave powers in air for 10 min.

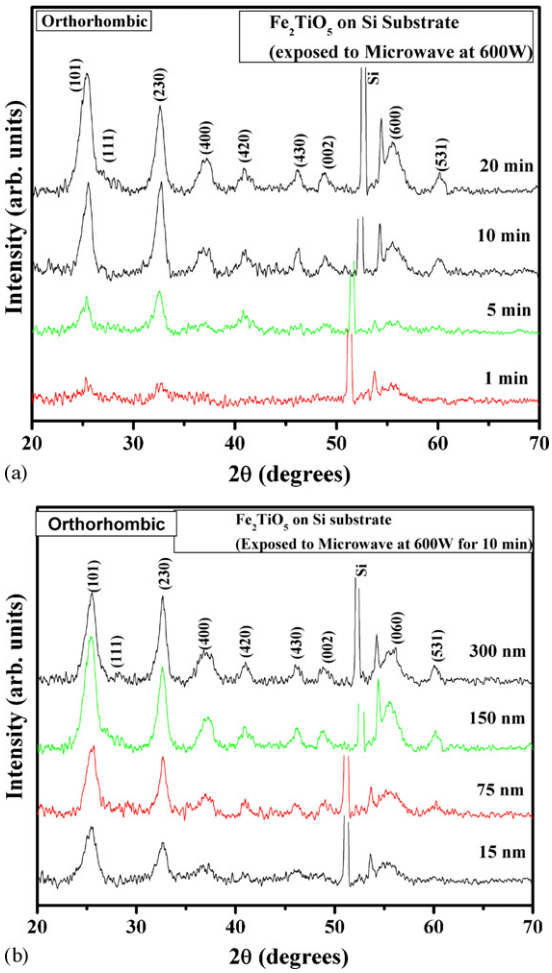


Fig. 3. XRD pattern of $Fe_2TiO_5$ thin films on Si (1 0 0) substrate by sol–gel spin coating process. (a) Exposed to microwave at 900 W for different times. (b) Exposed to microwave at 900 W for 10 min with different thickness of film.

Table 1
Crystallite size ($D$), roughness ($R_a$) of the $Fe_2TiO_5$ thin films

| Microwave annealing | 300 W | 450 W | 600 W | 900 W |
|---|---|---|---|---|
| Crystallite size (nm) (anatase phase) | 6.5 | 7.2 | 9.3 | 10.5 |
| Roughness, $R_a$ (nm) | 2.2 | 2.4 | 2.5 | 2.5 |
| Conventional annealing | 400 °C | | 600 °C | 800 °C |
| Crystallite size (nm) (anatase phase) | 34 | | 39 | 45 |
| Roughness, $R_a$ (nm) | 27 | | 30 | 38 |

(A) Microwave annealing at different powers and (B) conventional annealing at different substrate temperatures.

been carried out with different thicknesses of $Fe_2TiO_5$ from as low as 15–300 nm. XRD patterns of all thin films with different thicknesses (measured by cross sectional SEM) exposed to 900 W microwave power for 10 min have been shown in Fig. 3b. Pretty interestingly, all the films with lowest thickness to highest thickness have shown the growth of orthorhombic phase formation orienting in (1 0 1) and (2 3 0) planes, respectively. All peaks belonging to orthorhombic phase of $Fe_2TiO_5$ are identified with database in Joint Committee of Powder Diffraction System (JCPDS: card #29-0277). Lattice parameters for the annealed as well as microwave exposed films have been calculated and are in agreement with the literature values ($a = b = 0.524$ and $c = 1.483$ nm). Table 1 depicts the crystallite size ($D$) (calculated from the Scherrer's equation), roughness ($R_a$, calculated from AFM roughness profile data) of the $Fe_2TiO_5$ thin films for both microwave exposed films at different powers and conventional annealed films at different substrate temperatures.

### 3.2. Morphological properties

#### 3.2.1. HRSEM

High magnification image of $Fe_2TiO_5$ thin films annealed at 800 °C for 3 h and exposed to 900 W for 10 min have been shown in Fig. 4a and b, respectively. $Fe_2TiO_5$ thin films annealed at and above 400 °C have shown continuous, crack free, dense films The deposited and treated films were uniform, homogeneous, crack free, and highly dense. This could be supported by the fact that the solvent 2-methoxy ethanol (low evaporation rate) used in the present investigation makes the treated films crack free. $Fe_2TiO_5$ annealed films at and above 600 °C have exhibited pebble like structures. The size of the grain also ranges from 25 to 50 nm. It is evident from Fig. 4b that the exposed films were quite smooth, homogeneous and crack free. On the other hand, nanograins as low as 5–12 nm have been formed for the films exposed to microwave at and above 450 W as shown in Fig. 4b. The formed pores in both cases could also be attributed to the low evaporation rate of the solvent. It is noteworthy to mention here that there was two-fold decrease in the grain size of the grown orthorhombic phase of $Fe_2TiO_5$ thin films.

#### 3.2.2. Topography

AFM topographical images of 1 μm × 1 μm area taken on $Fe_2TiO_5$ thin films for 800 °C for 3 h and exposed to 900 W microwave power have been shown in Fig. 5a and b, respectively. It is evident from the image that the annealed film was smooth with low surface roughness (24 nm) and very homogeneous with grain size ranging from 25 to 50 nm. Some of these small grains agglomerated together to form a big grain with size as big as 60 nm. It is evident from Fig. 5b image that the microwave exposed films were also smooth with very low surface roughness (2.2 nm) and very homogeneous with grain size ranging from 10 to 15 nm.

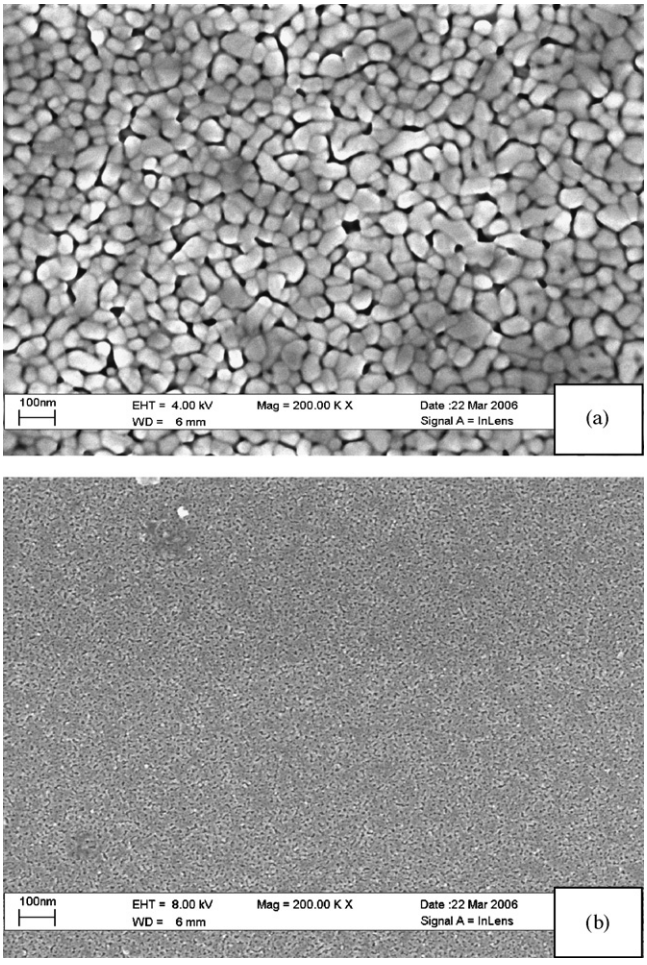


Fig. 4. HRSEM images $Fe_2TiO_5$ thin films on Si (1 0 0) substrate by sol–gel spin coating process. (a) Annealed at 800 °C for 3 h in air. (b) Exposed to microwave at 900 W for 10 min in air.

#### 3.2.3. Compositional properties (XPS)

The XPS analysis of the $Fe_2TiO_5$ thin films has been performed in the binding energy (BE) range of 0–1000 eV, on 0.8 mm × 0.8 mm area as shown in Fig. 6. No contamination species were observed within the sensitivity of the instrument apart from the adsorbed atmospheric carbon. The binding energy (BE) calibration of the spectra has been referred to carbon 1s peak located at BE = 284.6 eV for all the thin films analysed. Peaks corresponding to Ti (3p, 2p, 2s), Fe (3p, 3s, 2p), O 1s and C 1s were observed in the general survey spectra in both annealed as well microwave exposed films of $Fe_2TiO_5$, apart from Auger peaks of Ti LMM, Fe LMM, O KLL.

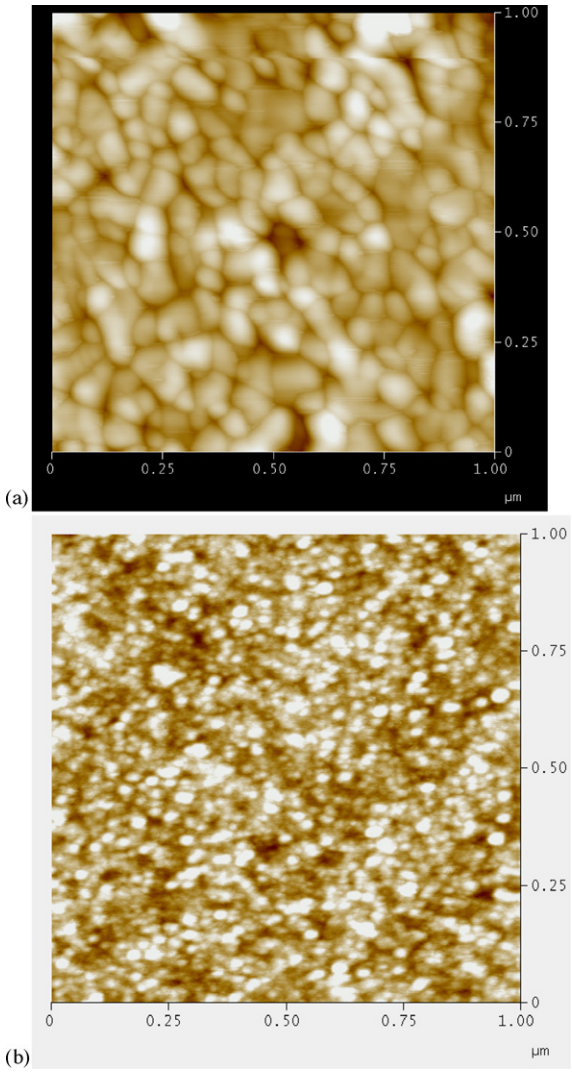


Fig. 5. AFM topographical images $Fe_2TiO_5$ thin films on Si (1 0 0) substrate by sol–gel spin coating process. (a) Annealed at 800 °C for 3 h in air. (b) Exposed to microwave at 900 W for 10 min in air.

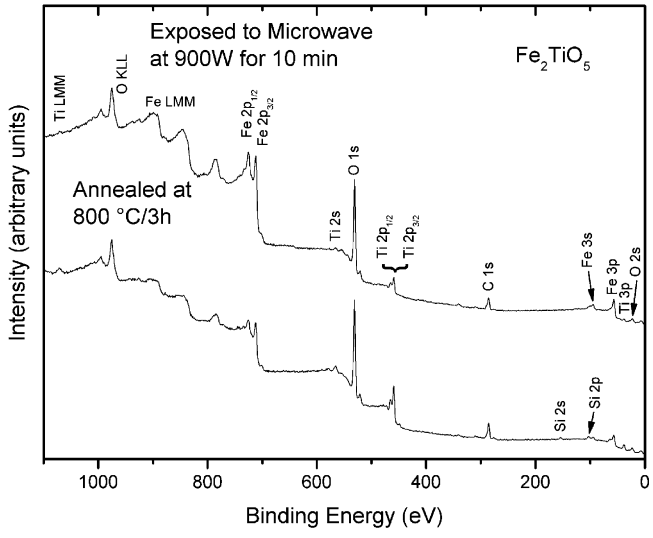


Fig. 6. XPS survey spectra of $Fe_2TiO_5$ thin films on Si substrate by sol–gel spin coating process.

The XPS core levels analysis of the $Fe_2TiO_5$ thin films have been measured for O 1s, C 1s, Ti 2p and Fe 2p as shown in Fig. 7. By using XPS quantitative analysis (individual peak areas and the sensitivity factors), the at.% of concentration of each element on surface has been calculated for both treated films. In C 1s spectra, the peak appeared at 288.3 eV has been attributed to unburnt carbon in the films. There was more of unburnt carbon in microwave exposed films than in annealed films. In case of annealed films a small peak corresponding to Si 2p has been observed. In O 1s spectra the peak appearing at 532.4 eV has been assigned to O in $SiO_2$. This could be due to signal detected from the small pores on the surface of the annealed films. Ti $2p_{3/2}$ has a binding energy 458.8 eV in $TiO_2$. There was slight shift of 0.4 eV in the Ti $2p_{3/2}$ binding energy in the annealed films attributed to oxygen deficiency in the iron titanate. On the other hand, no shift has been observed for the films annealed and microwave exposed films for the Fe $2p_{3/2}$ peak appearing at 710.9 eV. There was also slight stoichiometric change of $Fe_2TiO_5$ thin films treated by microwave annealing process. Microwave exposed films have shown 47 at.% of Fe, 6 at.% of Ti and 47 at.% of O in the thin films of $Fe_2TiO_5$, whereas annealed films have shown 30 at.% of Fe, 14 at.% of Ti and 56 at.% of O in the films of $Fe_2TiO_5$. The theoretical percentage of individual elements in the $Fe_2TiO_5$ are 25 at.% of Fe, 12.5 at.% of Ti and 62.5 at.% of O. In the present case, films treated by conventional annealing process are close to the stoichiometry compared to the microwave exposed process. From the core level spectra of the O 1s, Ti 2p, and Fe 2p peaks of the both annealed and microwave exposed films, by using the tabulated sensitivity factors (2.68 for iron 1.79 for titanium 0.71 for oxygen) [24], we have calculated and found 2:1 for iron and titanium, and 2:5 for iron and oxygen and 1:3 for titanium and oxygen indicating the stoichiometric composition of iron titanate for the both treated films. These results were in good agreement with the XRD analysis, where we have observed the complete formation of base centered orthorhombic crystalline phase of $Fe_2TiO_5$ for the annealed and microwave exposed thin films.

## 4. Discussion

The most prominent characteristic of microwave heating is volumetric heating, which is quite different from conventional heating, where the heat must diffuse in from the surface of the material. Volumetric heating means that materials can absorb microwave energy directly and internally and convert it to heat. It is this characteristic that leads to advantages using microwaves to process materials.

### *4.1. Mechanisms of microwave heating for the formation of nanocrystalline structures*

The interfacial polarization method can be considered as a combination of the conduction and dipolar polarization mechanism. It is important for heating systems that comprise a conducting material dispersed in a non-conducting material. On exposure to an oscillating electromagnetic field of

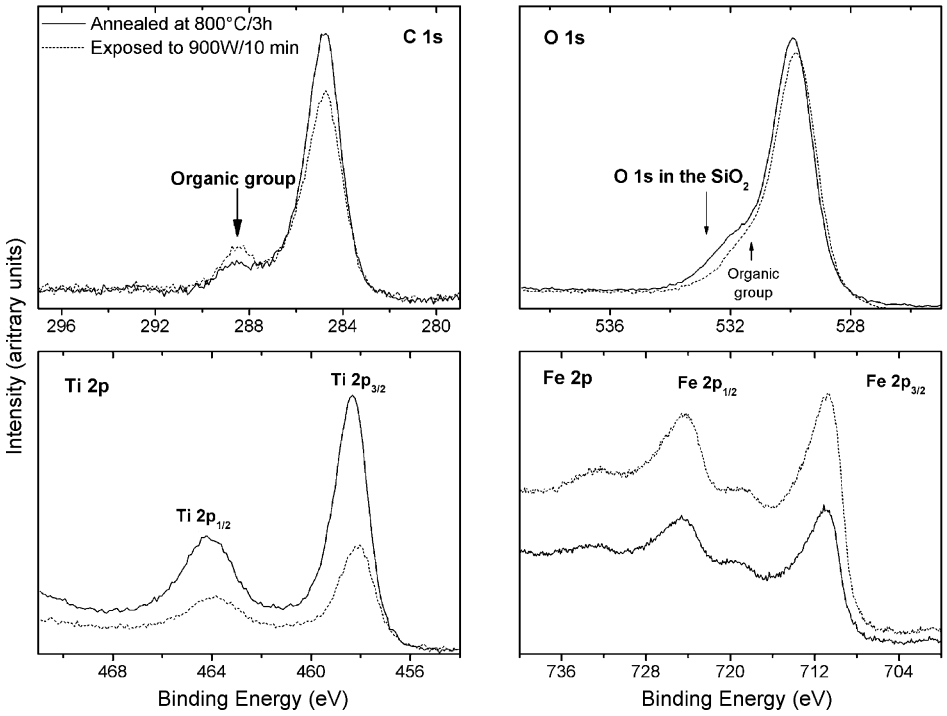


Fig. 7. XPS core level spectra (C 1s, O 1s, Ti 2p and Fe 2p) of $Fe_2TiO_5$ thin films on Si substrate by sol–gel spin coating process.

microwave frequency (2.45 GHz), polar molecules (2-methoxy ethanol and water) try to follow the field and align themselves in phase with the field. However, owing to inter/molecular forces, these molecules experience inertia and are unable to follow the field. This has resulted in the random motion of particles, and this random interaction generates heat, which is sufficient to grow the perovskite nanostructured thin films of $Fe_2TiO_5$.

In the present case, dipolar polarization mechanism is more applicable as this process deals with polar molecules of the solvent (2-methoxy ethanol) as well as water, which have been present in the xero gels of the $TiO_2$, $Fe_2O_3$, $Fe_2TiO_5$ thin films. Quite interestingly, slight cracking of the film has been observed, which could be due to low evaporation of the 2-methoxy ethanol solvent used in the present case. In addition, no break or destruction of the structure of the deposited films has been observed, which could also be due to insufficient energy produced by the microwave photon (0.037 kcal/mol), compared to typical energy required to break a molecular bond (80/120 kcal/mol). Therefore, microwave excitation of molecules does not affect the structure of an inorganic or organic molecule, and the interaction is purely kinetic.

## 5. Conclusions

In conclusion, nanocrystalline perovskite thin films of $Fe_2TiO_5$ have been deposited on Si (1 0 0) substrates at room temperature by sol–gel spin coating process and subjected to two sets of treatments: one set by annealing at different temperatures and other one by exposing to different microwave powers and different exposure timings. The annealed films have shown $Fe_2TiO_5$ orthorhombic phase formation at and above 600 °C substrate temperature, whereas films exposed to microwave have exhibited low intensity orthorhombic phase $Fe_2TiO_5$ at and above 450 W microwave power. HRSEM measurements have exhibited uniform and crack free films with closed and connected grains with sizes of 25–30 nm for the annealed films and lower grain sizes 8–12 nm for the microwave exposed films. There has been also slight stoichiometric change of $Fe_2TiO_5$ thin films treated by conventional annealing and microwave annealing. Microwave exposed films have shown 47 at.% of Fe, 6 at.% of Ti and 47 at.% of O, where as annealed films have shown 30 at.% of Fe, 14 at.% of Ti and 56 at.% of O in the films of $Fe_2TiO_5$ close to the stoichiometry of the $Fe_2TiO_5$. This new innovative heating of thin film materials will open a new door for advanced technologies particularly nano-based technologies in terms of cost. This technique for heating materials will have strong impact on coatings applied in nanotechnology, microtechnology and biotechnology industries.

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