

Microwave irradiation as an alternative source for conventional annealing: a study of pure TiO₂, NiTiO₃, CdTiO₃ thin films by a sol–gel process for electronic applications

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 6965

(<http://iopscience.iop.org/0953-8984/18/30/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 12:26

Please note that [terms and conditions apply](#).

Microwave irradiation as an alternative source for conventional annealing: a study of pure TiO₂, NiTiO₃, CdTiO₃ thin films by a sol–gel process for electronic applications

A R Phani¹ and S Santucci

INFN and Department of Physics, University of L'Aquila, via Vetoio, 67010 Coppito- L'Aquila, Italy

E-mail: Phani_ayala@yahoo.com

Received 7 March 2006

Published 14 July 2006

Online at stacks.iop.org/JPhysCM/18/6965

Abstract

The lower temperature and shorter timescale for microwave irradiation may be ascribed to the activating and facilitating effect of microwaves on solid-phase diffusion. Using the microwave-heating process, it is possible to achieve enhanced mechanical properties such as greater hardness, improved scratch resistance, and structure texturing. In the present investigation, thin films of pure TiO₂ and their respective perovskite-structured thin films, namely NiTiO₃ and CdTiO₃, have been prepared by simple and cost-effective sol–gel processing on Si(100) substrates and subjected to irradiation with different microwave powers for 10 min. X-ray diffraction (XRD), scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS) techniques have been employed to characterize the structural, morphological and elemental composition of the films. It is evident that there is a dramatic change in the structural and morphological properties of the films irradiated in microwaves compared to conventional annealing at high temperature. A plausible mechanism for the formation of the anatase phase of TiO₂ and perovskite structures with a rhombohedral phase formation at low microwave powers has also been discussed. This new innovative microwave heating could open a door for advanced technologies to cut process costs in the post-treatment of materials.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

There have been many investigations of oxide films [1] synthesized by the sol–gel method because of several advantages, such as low processing temperature, homogeneity, the

¹ Author to whom any correspondence should be addressed.

possibility of coating on large-area substrates and, most important, cost effectiveness. Unlike physical vapour deposition (PVD) or chemical vapour 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 the optical [2], microelectronics [3] and optoelectronics [4] industries, and for the purpose of corrosion [5–10], scratch and abrasion [11] resistant materials as well. Transitional metal oxides such as TiO_2 and HfO_2 are widely used in many optical, biomedical [12] and microelectronic applications because of their excellent properties, such as chemical resistance, good mechanical strength, and transparency, as well as insulating properties. Usually, these oxides are prepared using techniques such as chemical vapour deposition and physical vapour deposition. However, it is difficult to prepare large-area deposition on irregular surfaces with high homogeneity by these methods, which could be replaced by sol-gel technology.

In recent years, there has been growing interest in cadmium titanium oxide and nickel titanium oxide thin films as good candidates for new optical fibres [13–15], and as sensor materials for the detection of NO_2 [16, 17] gas sensing applications. In order to replace other materials, pure and high-quality structures are needed. Keeping the applications in mind, two kinds of treatment process have been adopted in the present investigation: conventional annealing and, alternatively, microwave exposure.

Microwave irradiation is becoming an increasingly popular method for heating samples in the laboratory for synthesizing biological [18], organic [19], polymer [20] and inorganic materials [21]. Coatings with surface laser treatments [22] or microwave exposure [23] lead to enhanced structural, morphological, mechanical and tribological properties. Unlike the conventional annealing process, the microwave technique offers a clean, cost-effective, energy-efficient, faster, and convenient method of heating, which results in higher yields and shorter-time reactions. This will have a strong impact on coatings applied in the nanotechnology, microtechnology, and biotechnology industries. This could be a great advantage for the hard, protective, corrosion-, abrasion- and wear-resistant, thermal barrier, optical, optoelectronic, microelectronic and polymer thin films that are applied on plastic, quartz and glass substrates, where the conventional annealing process is a limiting factor. Keeping in view the necessity of the coatings that are applied on plastic substrates, microwave irradiation has been chosen as an alternative method for the annealing process.

In the present investigation, thin films of TiO_2 have been deposited on a Si(100) substrate (with a thickness of 4–5 nm of SiO_2 on the surface) at room temperature using the sol-gel spin-coating process. Two sets of films have been treated as follows: one set by annealing at different temperatures ranging from 200 to 1000 °C for 3 h in air, and a second set of films has been exposed to 2.45 GHz microwave radiation at different powers ranging from 100 to 900 W for 10 min. The conventionally annealed films, as well as the microwave-irradiated thin films, have been subjected to characterization for structural, morphological and compositional properties.

2. Experimental procedure

The preparation and deposition of TiO_2 thin films by the sol-gel spin-coating process is shown in figure 1. A calculated quantity of titanium butoxide (from Aldrich, of 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 cetyl trimethyl ammonium bromide (as a surfactant to control the growth of TiO_2 crystallites) has been dissolved in 20 ml of 2-methoxy ethanol solvent in a beaker and the contents were added drop-wise to the titanium butoxide sol under vigorous stirring. The contents were stirred at

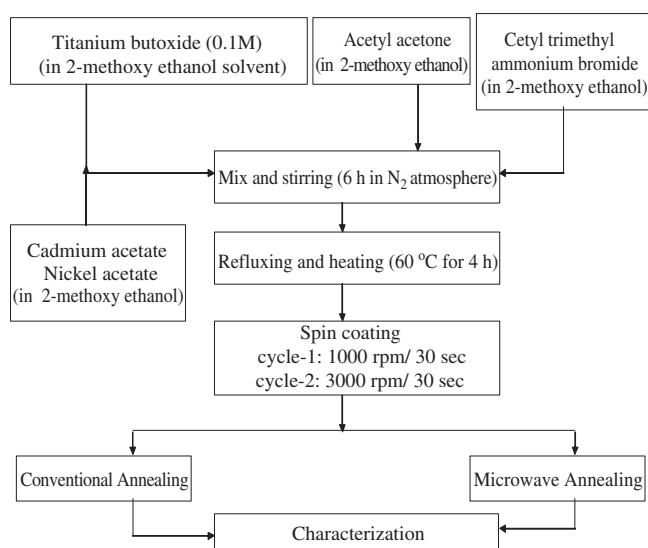


Figure 1. Schematic diagram of the sol-gel TiO_2 , CdTiO_3 and NiTiO_3 thin films prepared by the spin-coating process.

room temperature for about 6 h. The molar ratio of titanium butoxide, 2-methoxy ethanol and acetyl-acetone were 2:10:0.5. To the above contents, calculated quantities of HNO_3 (1.2 ml) and 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 later cooled to room temperature. The contents were filtered using Wattman filter paper in order to remove any particulates formed during the reaction. The stock solution that was obtained is used for the deposition of Si substrates by the spin-coating process. In order to prepare the perovskite nanostructures, such as CdTiO_3 and NiTiO_3 , calculated quantities of the corresponding acetates (in this case cadmium acetate and nickel acetate) have been added to the stock solution and then subjected to hydrolysis for the formation of ABO_3 structures.

Si substrates (with a thickness of 4–5 nm of SiO_2 on the surface) have been rinsed with deionized water and placed in a trough containing ethanol solvent and subjected to ultrasonic treatment for 15 min in order to remove any particles on the surface. Later substrates were rinsed with acetone and blow dried under N_2 gas. Cleaned Si(100) substrates (of $3 \times 3 \text{ cm}^2$) were immediately placed in the spin-coating chamber. Using a $50 \mu\text{l}$ pipette, 10–15 μl of the respective stock solution was placed on the surface of the Si(100) substrate and spun at a speed of 1000 rpm for 30 s (cycle-1) to spread the solution over 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 an homogeneous xerogel film. The steps consisting of cycle-1 and cycle-2 were repeated ten times in order to get a thickness of ~ 150 nm of thin xerogel film (as-deposited). At the end, the obtained xerogel films were subjected to two different treatments: one set was subjected to annealing for 3 h at different temperatures ranging from 200 to 1000°C in air, and the other set was exposed to microwaves at different powers in air. The as-deposited TiO_2 , CdTiO_3 and NiTiO_3 films were placed on an alumina plate inside the microwave oven and were placed 6 cm away from the centre of the glass plate. After placing the samples, the microwave door was closed and microwave power was set for the desired power and exposed time. Later, after exposure, the samples were left inside until they reached room

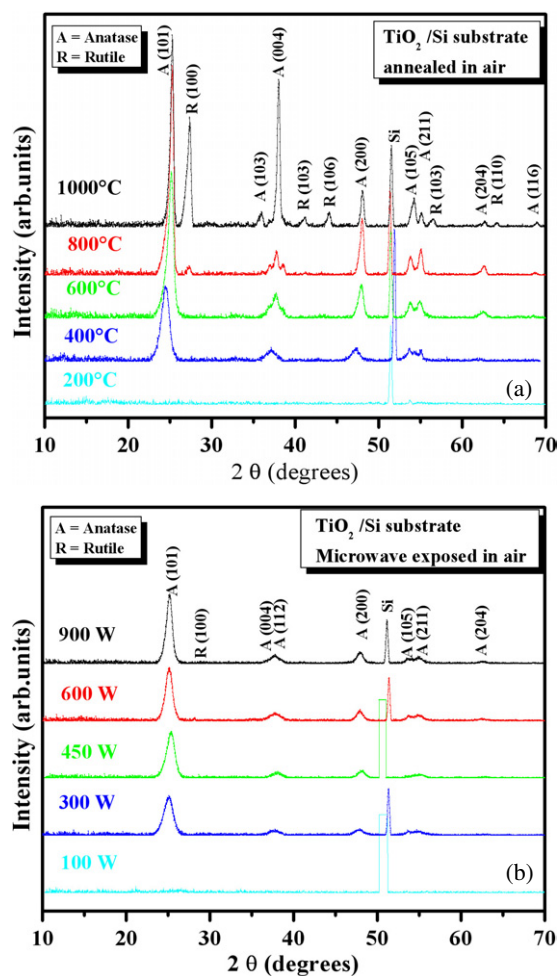


Figure 2. XRD pattern of TiO_2 thin films on Si(100) substrate by the sol-gel spin-coating process: (a) annealed at different substrate temperatures in air; (b) exposed to different microwave powers in air. Films annealed at and above 400°C have shown TiO_2 anatase phase with a (101) preferential orientation. On the other hand, films exposed at and above 300 W have also shown the formation of TiO_2 anatase phase in the (101) plane.

temperature. The conventionally annealed films, as well as the microwave-irradiated films, have been subjected to characterization for structural, morphological and compositional properties.

3. Results

3.1. Structural properties

To evaluate the phase formation of the treated films, the x-ray diffraction (XRD) technique was employed. For x-ray diffraction (using the Bruker model D5000), the grazing-angle mode was chosen for the present study. The x-ray source was a sealed x-ray of 1.5 kW Cu radiation ($\lambda = 1.5406 \text{ \AA}$). XRD patterns obtained for TiO_2 thin films both annealed at different substrate temperatures and microwave exposed at different powers are shown in figures 2(a) and (b),

Table 1. Crystallite size (D) of the TiO_2 , CdTiO_3 and NiTiO_3 thin films for (A) microwave annealing at different powers and (B) conventional annealing at different substrate temperatures.

	TiO ₂ : anatase phase	450 W	600 W	900 W
A	Microwave annealing			
	Crystallite size (nm)	7.5	8.2	10.2
B	Conventional annealing	400 °C	600 °C	800 °C
	Crystallite size (nm)	22	24	28
	(anatase phase)			
	CdTiO ₃ : rhombohedral	450 W	600 W	900 W
A	Microwave annealing			
	Crystallite size (nm)	7.5	8.2	10.2
B	Conventional annealing	400 °C	600 °C	800 °C
	Crystallite size (nm)	22	24	28
	NiTiO ₃ : rhombohedral	450 W	600 W	900 W
A	Microwave annealing			
	Crystallite size (nm)	7.5	8.2	10.2
B	Conventional annealing	400 °C	600 °C	800 °C
	Crystallite size (nm)	22	24	28

respectively. Films annealed at 200 °C were amorphous and sharp. High-intensity peaks with preferential growth of the (101) anatase phase of TiO_2 have been observed for the films annealed at and above 400 °C substrate temperatures. On the other hand, small growth of the rutile phase of TiO_2 has been observed for 1000 °C annealed films at $2\theta = 27.4^\circ$, belonging to the (100) plane. On the other hand, films exposed to a microwave power of 100 W exhibited an amorphous nature, and films exposed to microwave powers of 300 W and above have revealed the presence of the anatase phase of TiO_2 . As the microwave power increased from 300 to 900 W, there was an increase in the growth of the anatase phase of TiO_2 . All peaks belonging to the anatase phase of TiO_2 were well matched with the database in JCPDS (card #21-1732).

In order to observe film growth at different times, xerogel films have been exposed to 600 W at different timings ranging from 10 min to 10 s. The x-ray diffraction patterns of TiO_2 thin films deposited on Si substrates and exposed to a microwave power of 600 W for different exposure times ranging from 10 min to 10 s have also shown growth of the TiO_2 anatase phase. Quite interestingly, the formation of the anatase phase has been observed for the films exposed to microwaves at 600 W for 30 s onwards. Details of the growth of the TiO_2 anatase phase at different microwave parameters have been reported elsewhere [24]. It is worth mentioning here that the crystallite size of the films (calculated from the Scherrer equation for the anatase phase) exposed to microwaves has increased from 8 nm for 300 W exposed film to 12 nm for 900 W exposed film. On the other hand, films treated with conventional annealing have also exhibited an increase in crystallite size, from 20 nm for 400 °C film to 30 nm for the film annealed at 800 °C. Table 1 depicts the crystallite size of the TiO_2 , CdTiO_3 and NiTiO_3 thin films exposed to different microwave powers and annealed at different substrate temperatures.

XRD patterns obtained for the CdTiO_3 and NiTiO_3 thin films both annealed and exposed to microwaves are shown in figures 3(a) and 4(a) and 3(b) and 4(b), respectively. In both cases, films annealed at 500 °C were amorphous, with a broad peak with 2θ ranging from 28° to 36°. Sharp, high-intensity peaks with the preferential growth of (104) and (110) rhombohedral phases of CdTiO_3 and NiTiO_3 have been observed for the films annealed at and above 600 °C. On the other hand, films exposed to microwave powers of 300 W and below have shown an amorphous nature of the rhombohedral phase of CdTiO_3 and NiTiO_3 ; as the microwave power increased from 300 W, there was an increase in the growth of the rhombohedral phase

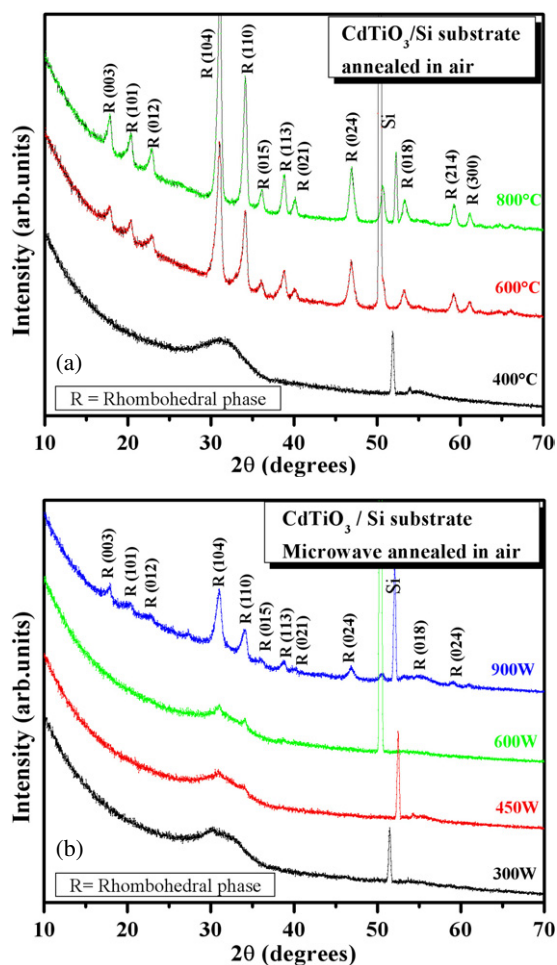


Figure 3. XRD pattern of CdTiO₃ thin films on Si(100) substrate by sol–gel spin coating process. (a) Annealed at different substrate temperatures in air. (b) Exposed to different microwave powers in air. Films annealed at and above 500 °C have shown CdTiO₃ rhombohedral phase with (104) and (110) preferential orientation. On the other hand, films exposed at and above 450 W have also shown formation of CdTiO₃ rhombohedral phase with (104) and (110) preferential orientation.

of CdTiO₃ and NiTiO₃. All peaks belonging to the rhombohedral phase of CdTiO₃ and NiTiO₃ were well matched with the database in the Joint Committee of Powder Diffraction System (JCPDS: card #29-0277 for CdTiO₃ and card #03-0395 for NiTiO₃, respectively). Lattice parameters for the annealed films as well as the microwave-exposed films have been calculated and agree well with the literature values.

3.2. Morphological properties

3.2.1. HRSEM. Morphological studies of the treated films have been carried out by employing high-resolution scanning electron microscopy (model: Zeiss). Large-area high-magnification images of TiO₂ films exposed to a microwave power of 900 W and annealed at 800 °C are

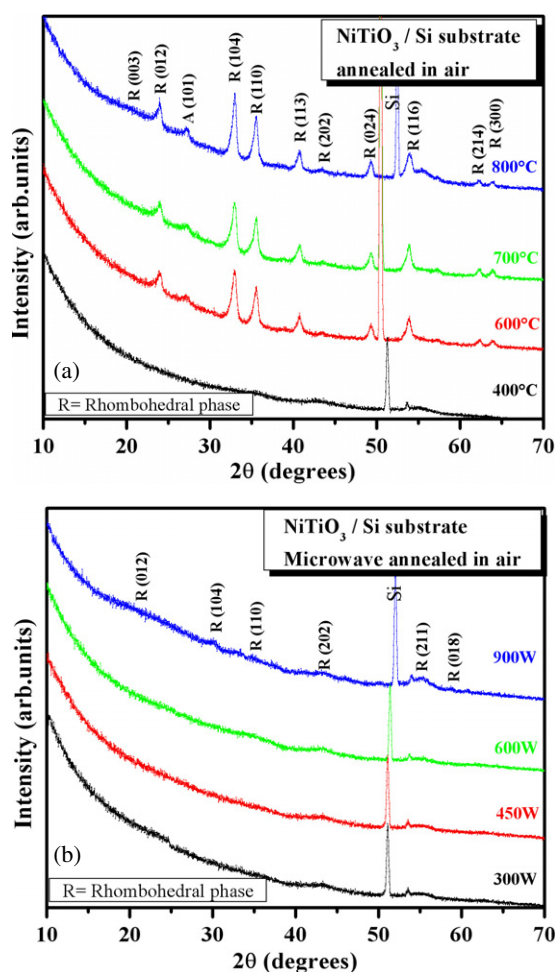


Figure 4. XRD pattern of NiTiO_3 thin films on Si(100) substrate by sol-gel spin-coating process. (a) Annealed at different substrate temperatures in air. (b) Exposed to different microwave powers in air. Films annealed at and above 500°C have shown NiTiO_3 rhombohedral phase with (104) and (110) preferential orientation. On the other hand, films exposed at and above 450 W have also shown formation of NiTiO_3 rhombohedral phase with (104) and (110) preferential orientation.

shown in figures 5(a) and (b), respectively. 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 (with a low evaporation rate) used in the present investigation caused the treated films to be crack-free. The high-magnification images revealed that the microwave-treated films were mostly nanostructured, with grain sizes ranging from 8 to 12 nm compared to conventional annealing, where the grain size for the annealed films ranged from 25 to 35 nm with increasing annealing temperature. It is worth mentioning here that no rupturing of the film on the surface has been observed due to the abrupt heating of the film by microwave radiation. This could be supported by the slow evaporation of 2-methoxy ethanol solvent preventing cracks and rupturing.

High-resolution scanning electron microscopy images of perovskite nanostructured CdTiO_3 thin films, annealed and microwave exposed, are shown in figures 6(a) and (b),

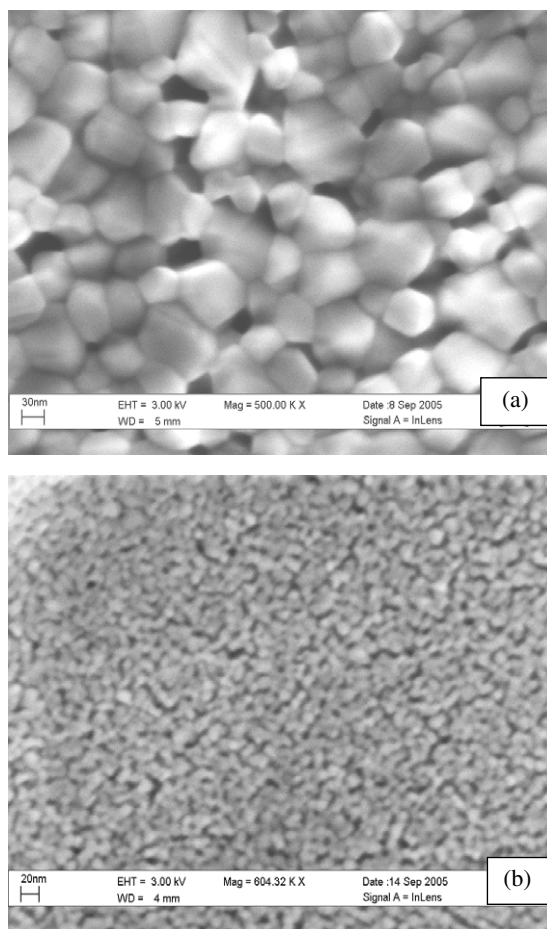


Figure 5. HRSEM images of TiO₂ thin films on a Si(100) substrate by the sol-gel spin-coating process: (a) annealed at different substrate temperatures in air; (b) exposed to different microwave powers in air. SEM measurements exhibited grain sizes of 25–30 nm for the annealed films and much lower grain sizes of 8–12 nm for the microwave-exposed films. Both treated films were homogeneous, uniform and crack-free.

respectively. CdTiO₃ films annealed at and above 600 °C exhibited lotus-leaf-like structures. These structures have been formed by connection of the dense grains that were formed. The size of the grains also ranges from 20 to 50 nm. During the formation of these structures, there was a lot of gaps left between the grains, causing pores. The size of the pores that were formed ranges from 8 to 12 nm. On the other hand, nanograins as low as 5–12 nm have been formed for the films exposed to microwaves at and above 450 W, as shown in figure 6(b). The pores formed in both cases could also be attributed to the slow evaporation of the solvent.

High-resolution scanning electron microscopy images of perovskite nanostructured NiTiO₃ thin films, annealed and microwave exposed, are shown in figures 7(a) and (b), respectively. NiTiO₃ films annealed at and above 600 °C exhibit closely packed structures. These structures have been formed by the agglomeration of small grains with a size ranging from 20 to 30 nm. On the other hand, nanograins as low as 5–12 nm have been formed for films exposed to microwaves at and above 450 W, as shown in figure 7(b).

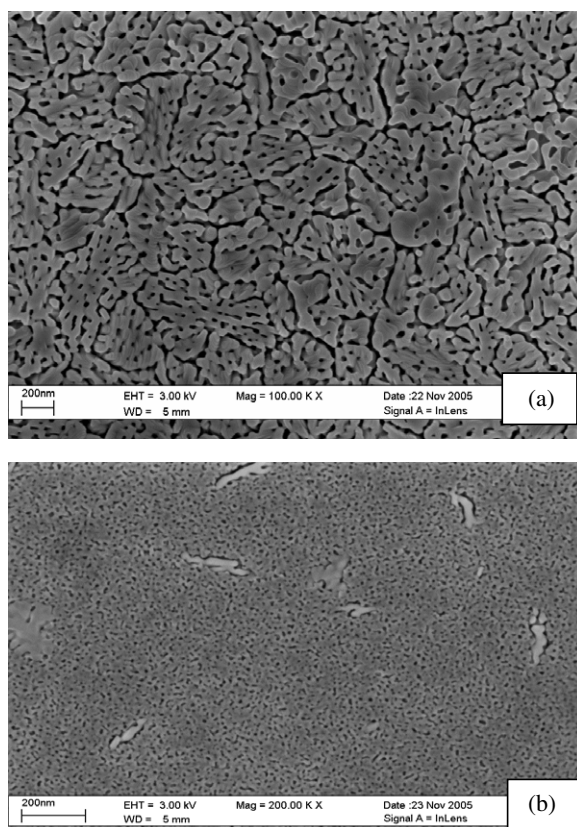


Figure 6. HRSEM images of CdTiO₃ thin films on a Si(100) substrate by the sol-gel spin-coating process: (a) annealed at different substrate temperatures in air; (b) exposed to different microwave powers in air. SEM measurements have exhibited lotus-leaf-like structures with densely formed grains for the annealed films and much lower grain sizes of 8–12 nm for the microwave-exposed films. Both treated films were homogeneous, uniform and crack-free, with the formation of small pores between the grains.

3.3. Compositional properties (XPS)

X-ray photoelectron spectroscopy (XPS) measurements of the TiO₂, CdTiO₃ and NiTiO₃ thin films exposed to microwaves 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 analyser. The XPS analysis of the TiO₂, CdTiO₃ and NiTiO₃ thin films has been surveyed in the 0–1000 eV range of binding energies (BE), on a 0.8 mm × 0.8 mm area, as shown in figures 8(a)–(c), respectively. No contamination species were observed within the sensitivity of the instrument, apart from the adsorbed atmospheric carbon. The binding energy calibration of the spectra has been referred to the carbon 1s peak located at BE = 284.8 eV for all the thin films analysed. Peaks corresponding to C 1s, Ti 2p, Ti 2s and O 1s were observed in the general survey spectra in both annealed as well as microwave-exposed films of TiO₂. There was a slight stoichiometric change for both the treated films. Microwave-exposed films have shown 35% of Ti and 65% of O in the films close to the stoichiometry of the TiO₂ [25]. This unchangeable behaviour in the composition of the microwave-exposure films makes the process favourable for new innovative annealing

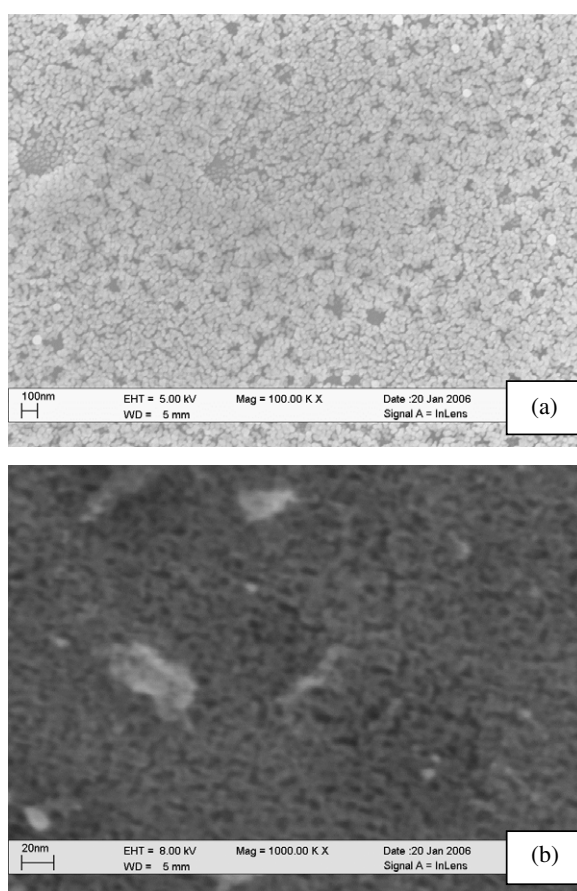


Figure 7. HRSEM images of NiTiO_3 thin films on a $\text{Si}(100)$ substrate by the sol-gel spin-coating process: (a) annealed at different substrate temperatures in air; (b) exposed to different microwave powers in air. SEM measurements have exhibited densely packed grains with sizes of 20–30 nm for the annealed films and much lower grain sizes of 8–12 nm for the microwave-exposed films.

processes for ceramic, inorganic and polymer films with nanostructures having grain sizes in the nanometre range. On the other hand, conventionally annealed films (800 °C) have shown 25% Ti and 75% of O in the films.

There was also a slight stoichiometric change in the case of CdTiO_3 and NiTiO_3 thin films treated by conventional annealing and microwave annealing. Microwave-exposed films have shown 19% of Cd, 19% of Ti and 62% of O in the films close to stoichiometry of the CdTiO_3 , and conventionally annealed films (800 °C) have shown 18% of Ni, 18.5% of Ti and 63.5% of O in the CdTiO_3 thin films. Microwave-exposed films have shown 19% of Ni, 19% of Ti and 62% of O in the films close to stoichiometry of the NiTiO_3 , and conventionally annealed films (800 °C) have shown 18% of Ni, 18.5% of Ti and 63.5% of O in the NiTiO_3 thin films.

4. Discussion

Originally, microwaves were principally used for communication. Now, microwave irradiation is becoming an increasingly popular method of heating samples in the laboratory to synthesize

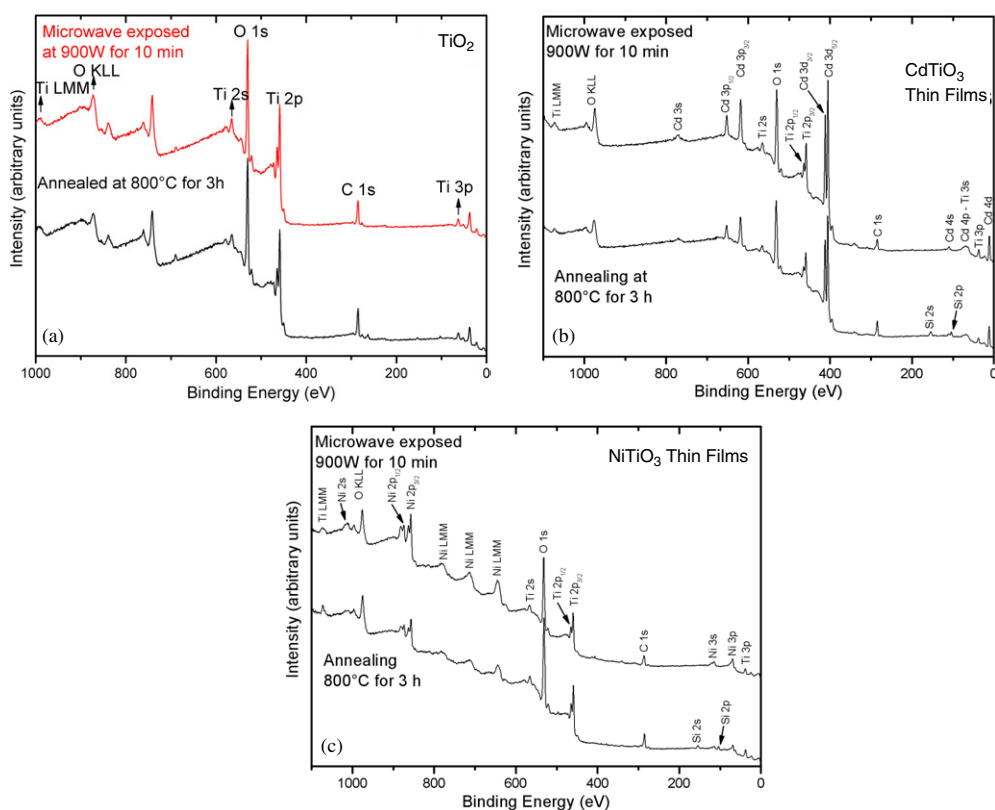


Figure 8. XPS of TiO_2 , CdTiO_3 , and NiTiO_3 thin films on a Si substrate by the sol-gel spin-coating process. (a) Survey spectra of microwave-exposed and conventional annealing of TiO_2 . (b) Survey spectra of microwave-exposed and conventional annealing of CdTiO_3 . (c) Survey spectra of microwave-exposed and conventional annealing of NiTiO_3 . X-ray photoelectron survey spectra indicates a closer stoichiometric ratio (65% O and 35% Ti) for microwave-exposed films compared to a lower stoichiometric ratio (75% O and 25% Ti) for annealed films. Near stoichiometry of CdTiO_3 and NiTiO_3 thin films has been observed for the films exposed to microwaves compared to conventional annealing.

biological, organic, inorganic, and polymer nanostructured materials, in particular in the synthesis of nanoparticles. Coatings with surface laser treatments or microwave exposure lead to enhanced structural, morphological, mechanical and tribological properties. To compete with the existing, established conventional heating method, the properties resulting from the use of microwaves must be unique or enhanced relative to conventional processing, or significant cost, energy or space saving must be utilized. 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.

In this present investigation, the thermal phenomena occurring with microwave heating are of interest. For conventional heating by convection and radiation, all the heat must diffuse in from the surface of the material, and the inside of the material can be heated by conduction only. Since conduction is a diffusion process, heat cannot be intensified, or the maximum temperature is always on the surface. To avoid overheating the surface, normally the temperature of the

heating source cannot exceed the desired final temperature T_f , thus the overall heating rate is restricted by the heating sources. Although the response of the surface temperature to the outside heating source could be very quick, the temperature response of the material other than on the surface is limited by the coefficient of thermal diffusivity, A , which is defined as follows:

$$A = \kappa / \rho_d C_p$$

where ρ_d , C_p and κ are density, specific heat and thermal conductivity of the material, respectively. However, when time approaches infinity, the materials can attain the final temperature T_f uniformly. This is one advantage of the conventional heating process.

For microwave heating, due to the appearance of internal heating, the heating rate can be made large by adjusting the microwave power source, so rapid heating is one of the advantages of microwave heating. Another characteristic of microwave heating is the inverse temperature distribution. The maximum temperature is always inside the material rather than on the surface if microwave power is the only heating source. In most cases, this is a disadvantage, since uniform heating is desired during processing. Uniform heating is important, sometimes critical, when processing materials. In ceramics sintering, non-uniform temperature distributions can lead to undesired properties or failed results. Non-uniform heating in microwave processing results from several sources. First, non-uniformity stems from the uneven distribution of the electric field. Secondly, non-uniformity is a result of the interactions between electromagnetic waves and materials. The third origin of non-uniformity is due to heat loss on the boundary.

There is another type of thermal phenomenon occurring with microwave heating that is of interest. The properties of the materials often change during the process. Of these properties, the change in dielectric loss factor is most important for some materials. The change in the material properties can also induce thermal runaway, which is the topic of this discussion. The relation between the power density absorbed by a material and the electric field has been given by [26]

$$P_{\text{dis}} = \omega \epsilon'_{\text{eff}} |\mathbf{E}|^2 = Q_{\text{abs}}$$

From an electromagnetic point of view, P_{dis} is the power density dissipated in the materials. Q_{abs} is the heat generation term, ω is the angular frequency, $|\mathbf{E}|$ is the root mean square (rms) magnitude of the electric field in the material, and ϵ'_{eff} is the imaginary part of the complex permittivity of the material. It is this equation that connects the electromagnetic waves with the heat transfer phenomenon.

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

The fundamental mechanism of microwave heating involves the agitation of polar molecules or ions that oscillate under the effect of an oscillating electric or magnetic field; particles try to orient themselves or try to be in phase with the field. However, the motion of these particles is restricted by resisting forces (interparticle interaction and electric resistance), which restrict the motion of the particles and generate random motion, producing heat. In the present case, the dipolar polarization mechanism is more applicable, as this process deals with polar molecules of the solvent (2-methoxy ethanol) as well as water, which are present in the xerogels of the TiO_2 , CdTiO_3 and NiTiO_3 thin films. Quite interestingly, slight rupturing of the film or cracking of the film has been observed, which could be due to slow 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 ($0.037 \text{ kcal mol}^{-1}$), compared to the typical energy required to break a molecular bond ($80/120 \text{ kcal mol}^{-1}$). 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, TiO₂ and TiO₂ based perovskite thin films of CdTiO₃ and NiTiO₃ have been deposited on Si(100) substrates at room temperature by the sol-gel spin-coating process and subjected to two sets of treatments: one set by annealing at different temperatures and the other set by exposure to different microwave powers and different exposure timings. The annealed films have shown the TiO₂ anatase phase at and above 400 °C substrate temperature, whereas films exposed to microwaves have exhibited low-intensity anatase phase TiO₂ at microwave powers of 300 W and above. HRSEM measurements have exhibited uniform and crack-free films with grain sizes of 25–30 nm for the annealed films and much lower grain sizes 8–12 nm for the microwave-exposed films. The microwave-irradiated films were homogeneous and uniform with near-stoichiometric composition, containing 35% of Ti and 65% of O in the exposed films. Near-stoichiometric perovskite nanostructures of CdTiO₃ and NiTiO₃ have been synthesized. This new innovative heating of thin-film materials will open a new door for advanced technologies, particularly nano-based technologies in terms of cost. On the other hand, this technique has a lot of advantageous such as: (a) an increased rate of reaction; (b) an efficient source of heating; (c) higher yields (in the case of organic synthesis); (d) uniform heating; (e) selective heating; (f) environmentally friendly processing; and (g) greater reproducibility of the reactions. This technique for heating materials will have a strong impact on coatings applied in the nanotechnology, microtechnology, and biotechnology industries. This could be a great advantage for the hard, protective, corrosion, abrasion and wear resistant, thermal barriers and optical, optoelectronic, microelectronic, polymer thin films that are applied on plastic, quartz and glass substrates, where the conventional annealing process is a limiting factor.

References

- [1] Briker C J and Scherer G W 1990 *Sol-Gel Science* (Orlando, FL: Academic)
- [2] Mane R S and Lokhande C K 2002 *Mater. Chem. Phys.* **78** 15–7
- [3] Yu H Y, Li M F, Cho B J, Yeo C C, Joo M S, Kwong D L, Pan J S, Ang C H, Zheng J Z and Ranganadhan S 2002 *Appl. Phys. Lett.* **56** 1332
- [4] Basak D, Amin G, Mallik B, Paul G K and Sen S K 2003 *J. Cryst. Growth* **256** 73–7
- [5] Phani A R, Heafke H, Gammel F and Hack T 2005 *Mater. Corros.* **56** 284
- [6] Conde A, Duran A and De Damborenea J J 2003 *Prog. Organic Coatings* **1273** 1–9
- [7] Voevodin N N, Grebasch N T, Soto W S, Kasten L S, Grant J T, Arnold F E and Donley M S 2001 *Prog. Organic Coatings* **41** 287–93
- [8] Ferizzi L, Rodriguez F J, Rossi S, Deflorian F and Di Maggio R 2001 *Electrochem. Acta* **46** 3715–24
- [9] Hussmann E K and Schanabel R 1983 *SPIE* **400** 107
- [10] Gray J E and Luan B 2002 *J. Alloys Compounds* **336** 88–113
- [11] Grunniger M F, Watchman J B and Haber R A 1987 *J. Am. Ceram. Soc.* **8** 596
- [12] Trapalis C C, Keivanidis P, Kordas G, Zaharescu M, Crisan M, Szatvanyi A and Gartner M 2003 *Thin Solid Films* **433** 186–90
- [13] Fades B D, Zelinski B J and Uhlmann D R 1993 *Ceramic Films and Coatings* ed J Watchman and J R A Haber (Park Ridge, NJ: Noyes Publications) p 224
- [14] Dislich H 1993 *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Speciality Shapes* ed L C Klein (Park Ridge, NJ: Noyes Publications) p 50
- [15] Pettit R B, Ashley C S, Readand S T and Brinker C J 1993 *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics and Speciality Shapes* ed L C Klein (Park Ridge, NJ: Noyes Publications) p 80
- [16] Bein T, Brown K, Fye G C and Brinker C J 1989 *J. Am. Ceram. Soc.* **111** 7640
- [17] Yan Y and Bein T 1994 *Interfacial Design and Chemical Sensing* ed T E Mallouk and D J Harrison (Washington, DC: American Chemical Society) p 16
- [18] Wan B and Lai H 2000 *Bioelectromagnetics* **21** 52
- [19] Lindtrom P, Tierney J, Wathey B and Westman J 2001 *Tetrahedron* **57** 9225

-
- [20] Akyel C and Belgin E 1989 *Energy* **14** 839
 - [21] Lee W C, Lui K S and Lin I N 1999 *Japan. J. Appl. Phys.* **38** 5500
 - [22] Wang K L, Zhang Q B and Zhu Y M 2001 *Appl. Surf. Sci.* **174** 191
 - [23] Shigeng S 1997 *Phys. Status Solidi a* **164** 779
 - [24] Phani A R, Grossi V, Passacantando M and Santucci S 2006 *Thin Solid Films* (Communicated)
 - [25] Castain J (ed) 2004 *Hand Book of X-Ray Photoelectron Spectroscopy* (Eden Praire, MN: Perkin-Elmer Corp) USA
 - [26] Metaxas A C and Meredith R J 1988 *Industrial Microwave Heating* (London: Peter Peregrinus, Ltd)