SOL-GEL SYNTHESIS AND CHARACTERIZATION OF Mn DOPED TiO_2 THIN FILMS

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Abstract

Manganese (3%, 6%, 9% and 12%) doped titanium oxide, $MnTiO_2$ thin films were prepared by sol–gel synthesis and deposited onto the silicon substrates using spin coating technique. The morphologies of the Mn doped TiO_2 thin films were analyzed using scanning electron microscope (SEM) and the surface observation showed a rather good density of grains without cracks. The crystalline phase and particle size of the films were examined by X-ray diffraction (XRD) measurement. The calculated crystallite sizes (by Scherrer's relation), lattice constants and cell volumes were increased with increasing Mn doping percentage. Furthermore, capacitance-voltage measurements of all the films were performed with varying frequencies (0.1 kHz to 100 kHz) using a LCR meter and the effects of dopant concentration of manganese on the dielectric behavior in $MnTiO_2$ thin films were investigated.

Keywords: Mn doped TiO_2 thin films, Sol-gel synthesis, Dielectric behavior

Introduction

Titanium dioxide (TiO_2) is an important function material with good chemical stability, low cost, low toxicity, natural abundance and environmentally friendly nature. It is currently being intensively studied for various applications in environment and energy areas, such as, photocatalysts, pollutant cleansers, lithium ion batteries, supercapacitors, gas sensors, solar energy cells, and so forth. The materials' morphology has a great influence on their performance. TiO_2 nanoparticles are of particular interest in as much as they have been widely used in important technological applications. TiO_2 nanoparticles fabricated by anodisation, with highly ordered structures and large specific surface areas, are of enhanced or new properties compared to other morphologies. Modified TiO_2 nanoparticles, with better performances, have a wider range of applications, such as dye sensitized solar cell, catalys, etc.

The dye-sensitized TiO_2 solar cells are inexpensive and have high photon to electron conversion efficiency TiO_2 is probably the most investigated photocatalyst system and has been found to be capable of decomposing a wide variety of organics; it is becoming a promising material for lithium rechargeable batteries. Synthesis of transition metal oxide nanoparticles often involve water as solvent or reactant and thus result in particles with hydroxylated surfaces that influence properties of materials. Oxide nanoparticles lacking such hydroxylated surfaces are expected to have properties that are different from their counterparts, particularly in terms of their subsequent chemical behavior. The advanced materials chemistry goal is to synthesise TiO_2 crystals with required shape, which results in potential materials with shape dependent properties. Crystal surface energy is responsible for crystal growth rate. The surface energy of the crystals can be enhanced or reduced by surfactant adhesion which results in crystal growth.

As MnO_2 is one of the most promising pseudocapacitive materials with high theoretical specific capacitance and it is suitable for a pseudocapacitive electrode in hybrid system with

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other active electrode materials like TiO_2. Metal ions doping is one of the effective approaches to improve the properties of TiO_2 nanoparticles. Whereas, there are few reports on the capacitance properties of Mn-doped TiO_2 nanoparticles. In this research, Mn-doped TiO_2 thin films were prepared by the solid state reaction method and their morphologies and structures were discussed in detail.

Experimental Details

Manganese (3%, 6%, 9% and 12%) doped titanium oxide; Mn-doped TiO_2 thin films were synthesized by solid state reaction method, using high purity (99.9% reagent grade) Mn and TiO_2 powders. These powders were weight on the basis of stoichiometric composition. The resultant, stoichiometric composition of the $Mn_xTi_{1-x}O_2$ (x = 0.03, 0.06, 0.09 and 1.2) powders were ground by agate mortar to obtain the homogeneity and annealed at 500°C for 1 hours. Each mixture was mixed with 2-methoxyethanol ($CH_3OCH_2CH_2OH$) solution and then heated up to 100˚C with indirect heat treatment for 1hr. Finally, homogeneous precursor solutions or coating solutions are obtained. The silicon substrates were cleaned by standard cleaning method. The resulting precursor solutions are deposited on silicon substrates by spin coating technique. After spin coating, deposited thin films are heat treated at 500˚C for 1hr. The surface morphology and the thickness of the films were analyzed by scanning electron microscope (SEM). The phase and crystallinity of the films were characterized by X-ray diffraction (XRD) analysis with Cu-$K_{\propto 1}$ radiation. The capacitance- voltage measurements and the dielectric properties of the films were carried by using LCR meter.

Results and Discussion

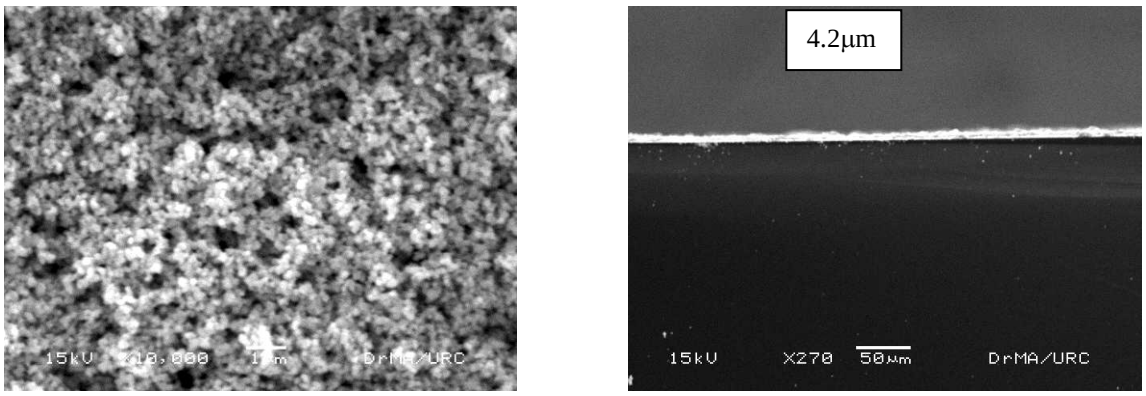
SEM Analysis

The surface morphologies and the cross sectional views of Mn-doped TiO2 thin films were evaluated using SEM as shown in Fig 1 (a-d). These results showed a well-developed grain size and dense microstructure in all samples. The effect of doping on grain size is usually interpreted in terms of dopant solubility and distribution of doping ions between the surface and interior parts of the grain. The values of the average grain sizes and thickness of the thin films were presented in Table 1.

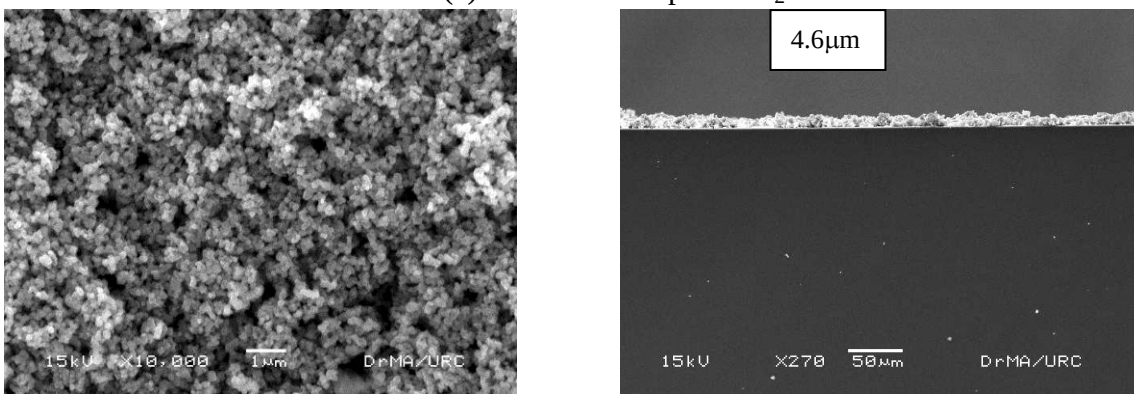
Table 1 The values of the average grain sizes and thickness of manganese (3%, 6%, 9% and 12%) doped titanium oxide thin films

Thin film	Average Grain Size (μm)	Thickness (μm)
3% Mn doped TiO_2	0.26	4.2
6% Mn doped TiO_2	0.27	4.6
9% Mn doped TiO_2	0.22	5.5
12% Mn doped TiO_2	0.25	9.8

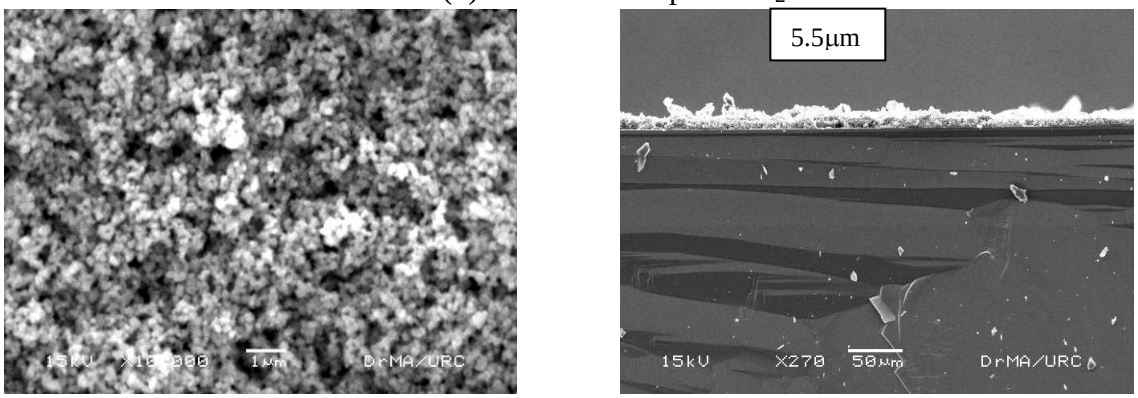
SEM image of Mn-doped TiO_2thin film **Cross sectional image Mn-doped TiO_2 thin film**



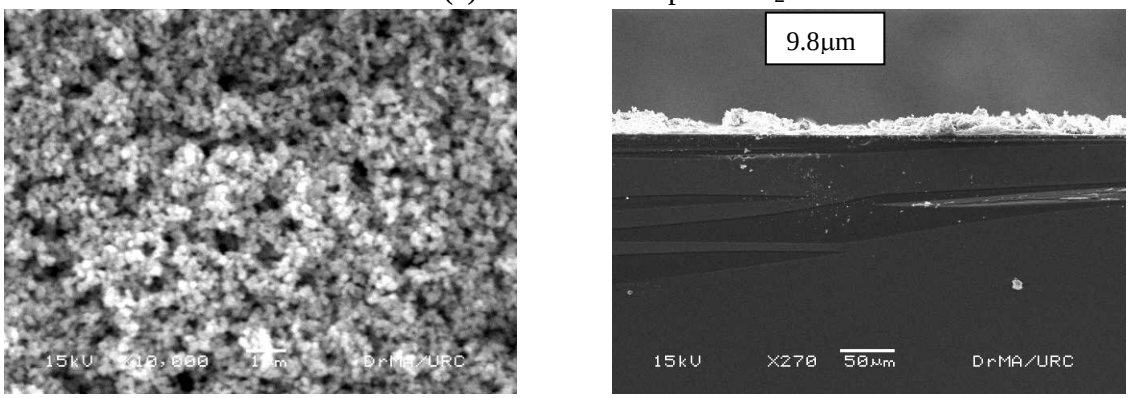
(a)For 3% Mn-doped TiO_2



(b)For 6% Mn-doped TiO_2



(c)For 9% Mn-doped TiO_2



(d)For 12% Mn-doped TiO_2

Figure 1(a) Scanning Electron Microscopy (SEM) of Mn-doped TiO_2 thin films

X-ray Diffraction (XRD) Analysis

The crystal structures of Mn doped TiO_2 thin films were clarified by XRD measurements. Fig.2 (a-d) shows the X-ray diffraction patterns for Mn-doped TiO_2 nanoparticles with different weight percentages (3%, 6%, 9% and 12%). The samples were scanned from (2θ = 24.885 – 24.927) using XRD machine with Cu source which has a wavelength of 0.154056 nm. The patterns of Mn-doped TiO_2 particles demonstrate its crystalline nature. All the peaks were indexed within the tetragonal system with body centred anatase phase, which crystal structure is composed of stacked edge sharing TiO_6 octahedra. The variation in the lattice parameters of Mn-doped TiO_2 thin films with change in dopant concentration may be attributed to the change in ionic radius. The XRD patterns showed that the increased dopant concentration leads to decrease in intensity of diffraction peaks with preferred orientation at (101) planes. The crystallite size was calculated using Scherrer's formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

The intensity, peak positions (2θ), full width half maximum (FWHM), lattice parameters and crystallite sizes (D) of manganese (3%, 6%, 9% and 12%) doped titanium oxide thin films are listed in Table 2 (a-d).

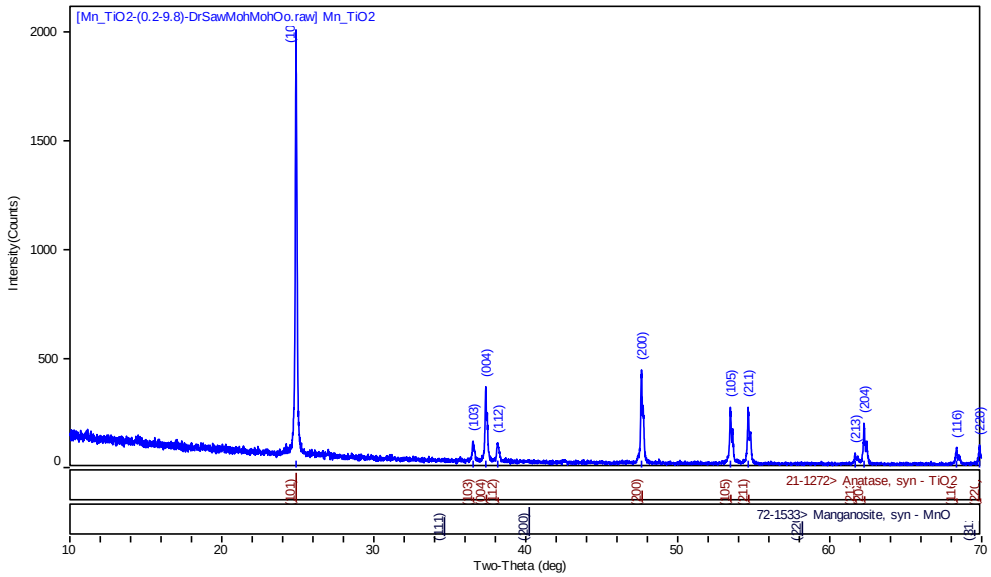


Figure 2(a) X-ray diffraction of 3% Mn-doped TiO_2 thin film

Table 2(a) (hkl) plane, full width half maximum (FWHM) and crystallite sizes (D) of 3% Mn-doped TiO_2 thin film

No	(hkl) plane	FWHM (deg)	Crystallite size D (nm)
1	(101)	0.138	56.214
2	(103)	0.163	46.279
3	(112)	0.209	40.219
Average crystallite size			47.571

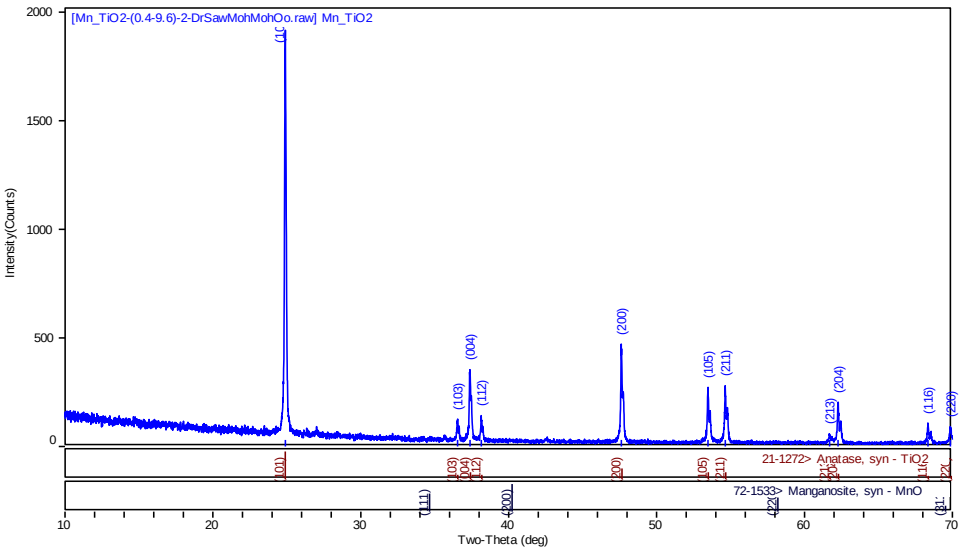


Figure 2 (b) X-ray diffraction of 6% Mn-doped TiO_2 thin film

Table 2(b) (hkl) plane, full width half maximum (FWHM) and crystallite sizes (D) of 6% Mn-doped TiO_2 thin film

No	(hkl) plane	FWHM (deg)	Crystallite size D (nm)
1	(101)	0.136	59.819
2	(103)	0.160	52.287
3	(112)	0.168	50.033
Average crystallite size			52.046

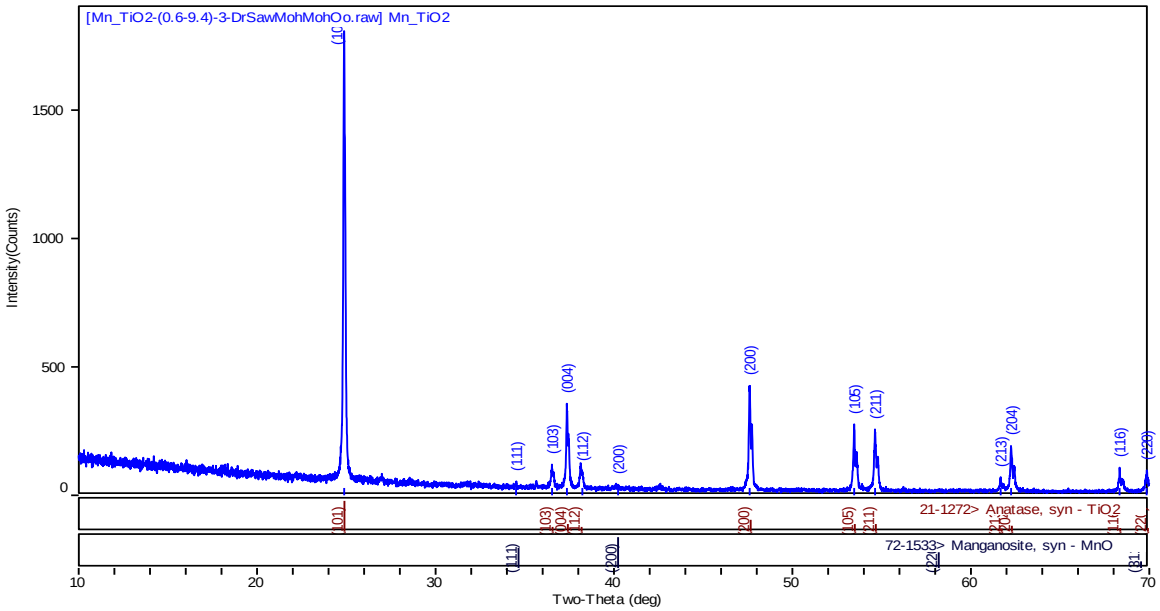


Figure 2 (c) X-ray diffraction of 9% Mn-doped TiO_2 thin film

Table 2 (c) (hkl) plane, full width half maximum (FWHM) and crystallite sizes (D) of 9% Mn-doped TiO_2 thin film

No	(hkl) plane	FWHM (deg)	Crystallite size D (nm)
1	(101)	0.138	58.950
2	(103)	0.134	62.397
3	(112)	0.251	33.496
Average crystallite size			51.614

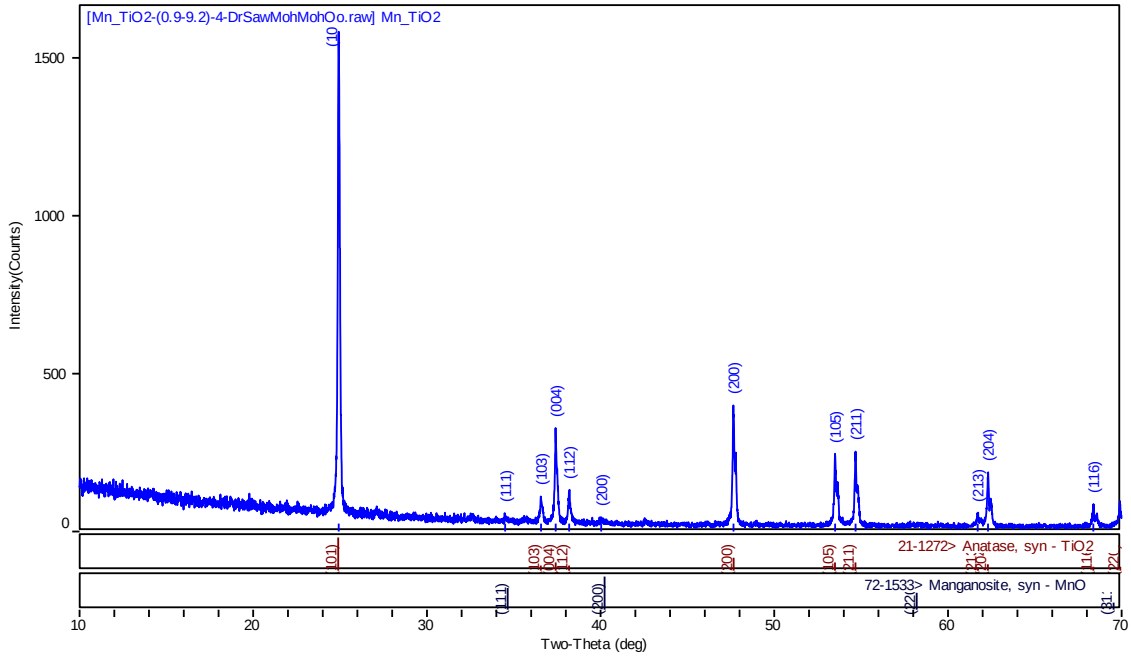


Figure 2 (d) X-ray diffraction of 12% Mn-doped TiO_2 thin film

Table 2 (d) (hkl) plane, full width half maximum (FWHM) and crystallite sizes (D) of 12% Mn-doped TiO_2 thin film

No	(hkl) plane	FWHM (deg)	Crystallite size D (nm)
1	(101)	0.153	53.175
2	(103)	0.183	45.719
3	(112)	0.162	51.892
Average crystallite size			50.262

Table 3 The intensity, peak positions (2θ), full width half maximum (FWHM), lattice parameters and crystallite sizes (D) of manganese (3%, 6%, 9% and 12%) doped titanium oxide thin films (101)

Thin Films	Intensity (cps)	Peak positions (2θ)	FWHM	Lattice parameter	Crystallite size D (nm))
3% Mn-doped TiO_2	1963	24.888	0.138	a =b= 3.8512 c = 9.5057	56.214
6% Mn-doped TiO_2	1868	24.900	0.136	a =b= 3.8488 c = 9.5121	59.819
9% Mn-doped TiO_2	1758	24.885	0.138	a =b= 3.8538 c = 9.4797	58.950
12% Mn-doped TiO_2	1540	24.927	0.153	a=b = 3.8487 c = 9.5064	53.175

Dielectric Properties

The dielectric constants of manganese (3%, 6%, 9% and 12%) doped titanium oxide, $MnTiO_2$ thin films were calculated from capacitance-voltage measurements at the frequency range of 0.1 kHz to 100 kHz. The dielectric constant varies with the applied voltage. The dielectric constant and dielectric loss of the films as function of applied voltage, Mn content and frequency are shown in Fig 3 (a-b). Dielectric constant (ε) can be calculated by the equations below,

$$C_0 = \varepsilon_0 A/t,$$

$$\varepsilon = C/C_0$$

where,

C = capacitance using the material as the dielectric in the capacitor,

C_0 = capacitance using vacuum as the dielectric

ε_0= Permittivity of free space (8.85 x 10-12 F/m)

A = Area of the plate/ sample cross section area

t = Thickness of the sample

The maximum value of dielectric constant was occurred at the 12% manganese doped titanium oxide thin film measured in a frequency range of 0.1 kHz. The dielectric constants of the films decrease with the increasing of dopant concentration are shown in Fig 3 (a-b) and the results are listed in Table 4.

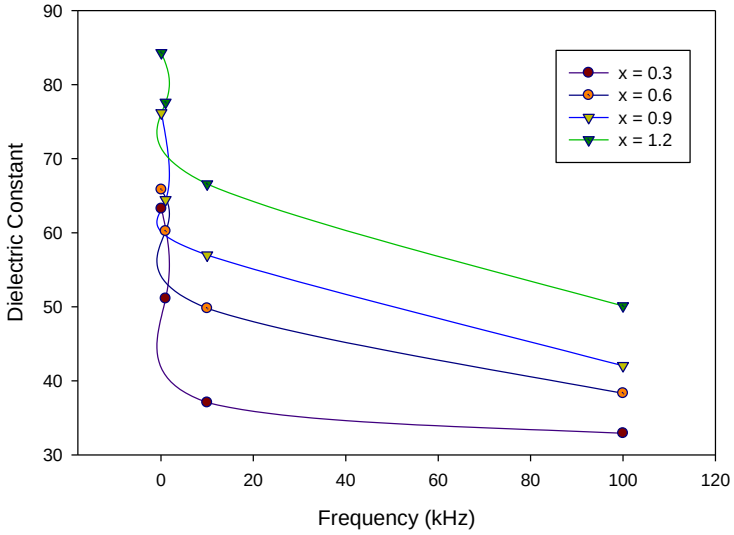


Figure 3 (a) The dependence of dielectric constant of manganese (3%, 6%, 9% and 12%) doped titanium oxide thin films as a function of frequency

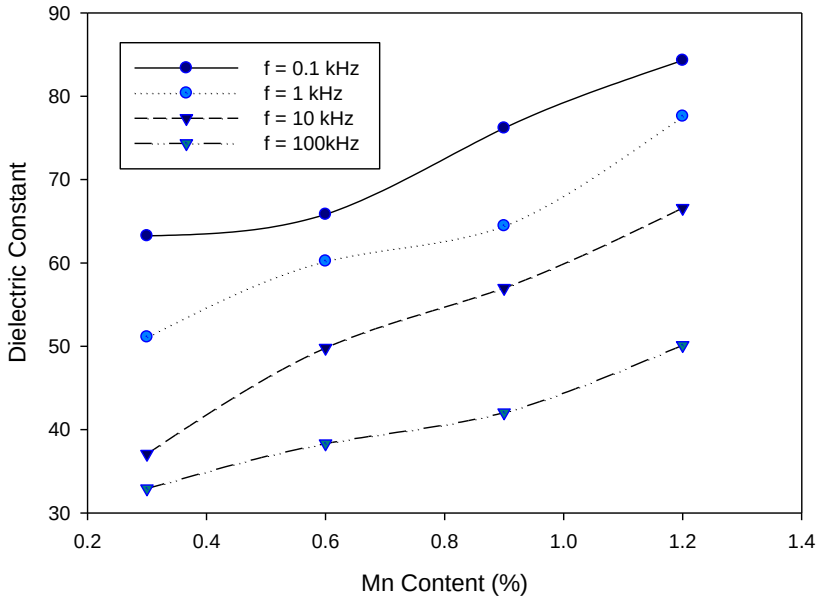


Figure 3 (b) The dependence of dielectric constant of the TiO_2 thin films on the Mn content

Table 4 The values dielectric constant of manganese (3%, 6%, 9% and 12%) doped titanium oxide thin films a function of frequency

	Dielectric Constant			
Thin Films	**f = 0.1 kHz**	**f =1kHz**	**f = 10kHz**	**f = 100kHz**
3% Mn doped TiO_2	63.2498	51.1118	37.0679	32.9160
6% Mn doped TiO_2	65.8172	60.2164	49.7984	38.3176
9% Mn doped TiO_2	76.1762	64.4514	56.9802	42.0378
12% Mn doped TiO_2	84.3017	77.5989	66.5661	50.1149

Conclusions

Manganese (3%, 6%, 9% and 12%) were doped titanium oxide, Mn-doped TiO_2 thin films were prepared by solid state reaction method and deposited onto the silicon substrates using spin coating technique. However, in 9% and 12% (over 6%) of Mn- doped TiO_2, the more Mn content, the less crystallite size. The crystallite size of the thin films calculated from XRD depending on the influence of Mn content. By the characterization of Scanning Electron Microscopy (SEM), grain sizes of the samples are in the range of 0.22 nm and 0.27 nm and it has been confirmed that the crack free and uniform surface of the films. XRD patterns indicated that all the films were well crystallized and tetragonal structure. The average crystallite size is around 57 nm and the largest crystallite size is 6% of Mn-doped TiO_2. The dielectric constants of the films increase with the increasing of dopant concentration of manganese. The maximum value of dielectric constant was occurred at the 12% manganese doped titanium oxide thin film measured in a frequency range of 0.1 kHz. These results showed a dependence of the structural and electrical properties of the TiO_2 films on the Mn concentration. According to the experimental result, TiO_2 films on the Mn Concentration with good dielectric properties can be used for measuring device in electronic applications.

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