Full Length Research Paper

Effect of the thickness on electrical properties of TiO$_2$ thin films, prepared by thermal chemical spray pyrolysis deposition

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Thin films of titanium dioxide TiO$_2$ were prepared using thermal chemical spray pyrolysis technique on glass substrate preheated at (210 ^{o}C) with spray rate 3sec./1min, for different thickness (100, 200, 300, 400 and 500 nm). The investigation of (XRD) indicates that the (TiO$_2$) films are polycrystalline type of (anatase). The effect of thickness on some of the electrical properties such as electrical direct conductivity (D.C.) and Hall coefficients has been studied. It is found that (TiO$_2$) films have two activation energies within thermal range (20-200)^{o}C, the first (E$_{a(1)}$) at low temperatures varies from (0.0259-0.1465)eV, while the second (E$_{a(2)}$) varies from (0.60975- 2.1972) eV, these results observed that the increase in thickness caused increase in D.C. conductivity. Hall coefficients results has shown that the conductivity samples of (TiO$_2$) films was (n-type) for the films at thickness (100-200-300) nm, while it was (p-type) at the thickness (400-500) nm. This inverted (transmutation) in type of carriers charge because of impact defect due to crystal growth in material or because thermal oscillation for atoms around them position in lattice, at high temperatures which may be release atom from its location and leave space behind it, this defect is called vacancies defect.

Keywords: Thin films, Titanium dioxide, chemical spray pyrolysis, electrical properties.

INTRODUCTION

Titanium dioxide (TiO$_2$) has been intensively studied over last decades, because of its wide interesting technological applications, such as optics industry (Sankar and Gopchandran, 2009), dye sensitized solar cells (Kao et al., 2009), dielectric applications (Yang and Wolden, 2006), (TiO$_2$) occurs in three crystalline polymorphs: anatase (tetragonal), rutile (tetragonal), brookite (orthorhombic) (Saila, 2003), Heating the anatase (TiO$_2$) films at a temperature near 900°C convert to rutile phase (Stamate et al., 2008), (TiO$_2$) films can be prepared by different techniques, such as thermal evaporation in vacuum deposition (TEVD) (Brugnian et al., 1984), chemical vapor deposition (CVD) (Sun et al.,

pulse laser deposition (PLD) (Jae-Yeol et al., 2006), chemical spray pyrolysis deposition (CSPD) (Oja et al., 2006), DC magnetron sputtering method (Stamate et al., 2005), sol-gel technique (Mechiakh and Bensaha, 2006) ultrasonic spray pyrolysis method (Bles et al., 2002), magnetron sputtering method (Cheol et al., 2005). Among these methods, in this study TiO$_2$ films are prepared using low cost techniques which is thermal chemical spray pyrolysis method, the features of this method of deposition are large and deposition with uniformity, low fabrication cost, simplicity, fast, vacuumless, low deposition temperature (Chopra, 1969). Spray pyrolysis involves spraying of an aqueous solution containing soluble salts of the constituent atoms of the desired compounds on heated substrates, the liquid droplets vaporize before reaching the substrate or react on it after splashing, the preheating of the substrate is in the range of (200-500)^o C (Chopra, 1969).

The aim of this research project is preparing and stu-

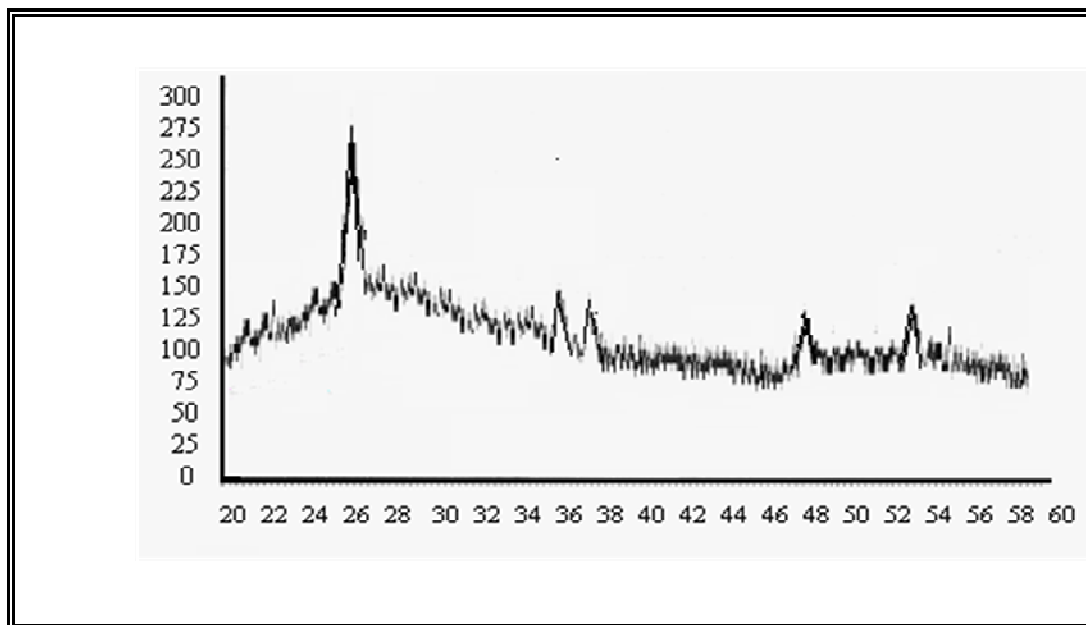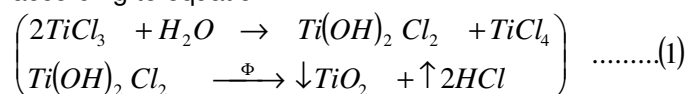*Corresponding Author E-mail: areeje_iraq@yahoo.com;
Tel: 077025147212008)

Figure 1. The (XRD) of TiO_2 thin film

dying (TiO_2) thin films, for different thickness by chemical spray pyrolysis technique, on a glass substrate temperature was (210 ^{o}C), and studying the effect of thickness on the electrical properties of (TiO_2) films, such as activation energy, charge carriers concentration, Hall coefficient and Hall mobility.

Experimental Details

Anatase TiO_2 were prepared by spraying an aqueous solution of titanium chloride $TiCl_3$, which prepared with molarity (0.05M), (0.38565) ml. of ($TiCl_3$) was dissolved with (50 ml) of distilled water (H_2O), then the resulting solution was sprayed on preheated glass substrate at temperature (210° C). TiO_2 thin films were formed according to equation:

$$\left(\begin{array}{l} 2TiCl_3 \;+H_2O \;\;\rightarrow \;\;Ti(OH)_2\,Cl_2 \;\;+TiCl_4 \\ Ti(OH)_2\,Cl_2 \;\;\;\xrightarrow{\;\Phi\;}\; \downarrow TiO_2 \;\;+\uparrow 2HCl \end{array} \right) \;\;........(1)$$

The resulting films were transparent, white yellowish colour, stable free from pinholes and have good adhesive properties. They were prepared with different thickness (100, 200,300,400 and 500)nm. The TiO_2 films were polycrystalline as shown in Figure 1, are a good agreement with the ASTM card.

RESULTS AND DISCUSSION

D.C. conductivity

The variation of conductivity with temperature (T) is main

tool in investigation properties of semiconductors. It is very useful to determine the extrinsic range the activation energies of impurity centers and in the intrinsic range the main energy gap. The d.c. conductivity for (TiO_2) thin films with different thickness has been studied as a function of (10^3/T) within thermal range (20-200)^{o}C as in Figure (2). It may be seen that the conductivity at room temperature (R.T.) increase approximately from ($7.391\times10^{-7}-$ 6.313×10^{-6}) (Ω.cm)$^{-1}$, theoretically this attributed to improve the crystal defect and state density. It was found that there are two stages of conductivity throughout the heating temperature range. In this case the first activation energy (E_{a1}) occurs at low temperature within thermal range (293-363)K, while the second activation energy (E_{a2}) occurs at low temperature within thermal range (373-473)K .

Hall coefficients

The variation of Hall voltage (V_H) as a function of current (I) for (TiO_2) thin films has been studied as shown in Figure (3). It was noticed that Hall coefficients results has shown that the conductivity samples of (TiO_2) films was (n-type) for the films at thickness (100-200-300) nm, while (p-type) at the thickness (400-500) nm., this inverted (transmutation) in type of carriers charge because of impact defect due to crystal growth in material or because thermal oscillation for atoms around them position in lattice, at high temperatures which may be release atom from its location and leave space behind it, this defect is called vacancies defect (Al-Jamal, 2000). Hall coefficient, the mobility and concentrations of charge
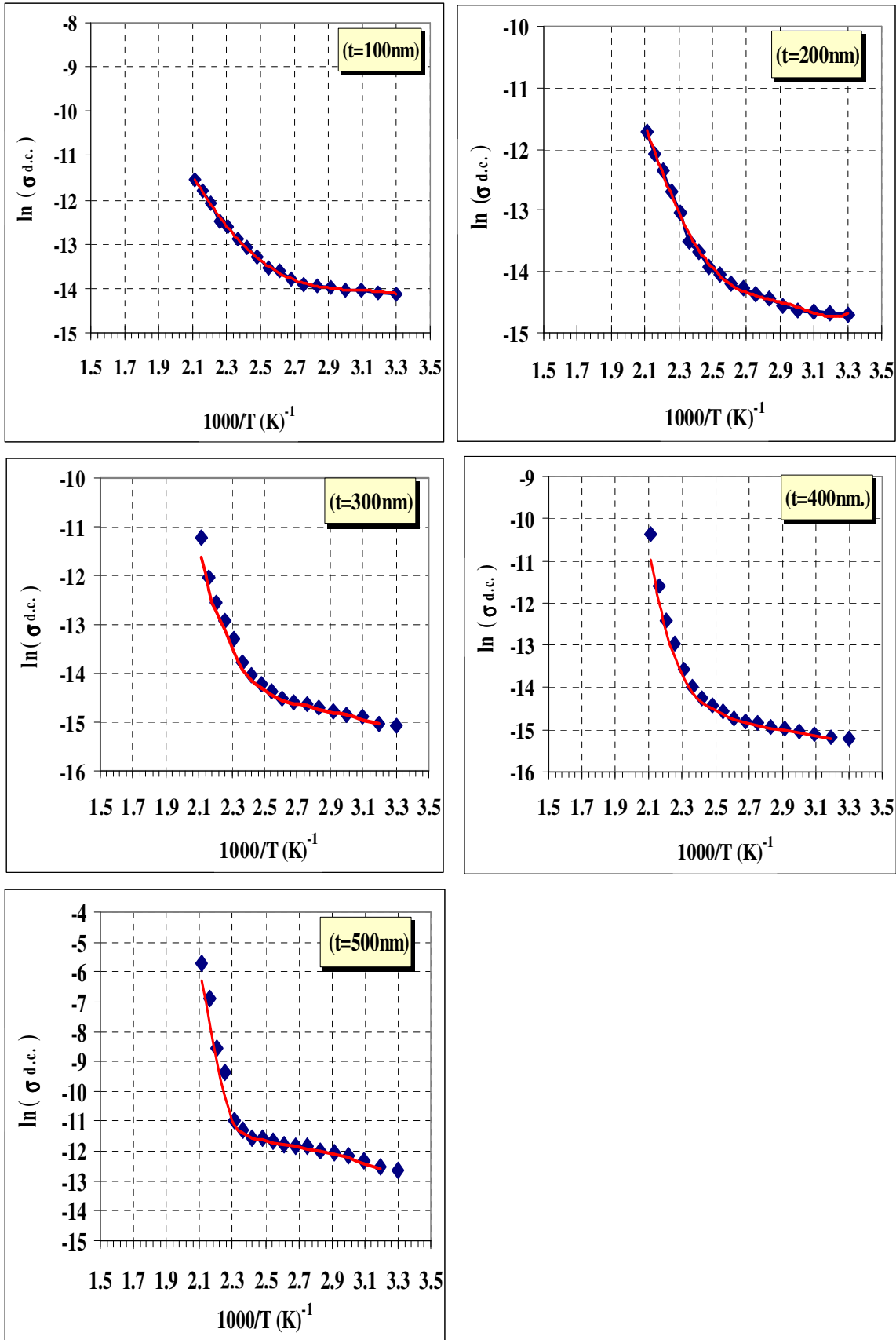
Figure 2. Relation between ln ($\sigma_{d.c.}$) and (1000/T) for TiO$_2$ films for different thickness.

Table 1. Shows activations energies (E_a) for different thickness of TiO_2 films, within thermal range (293-363)K.

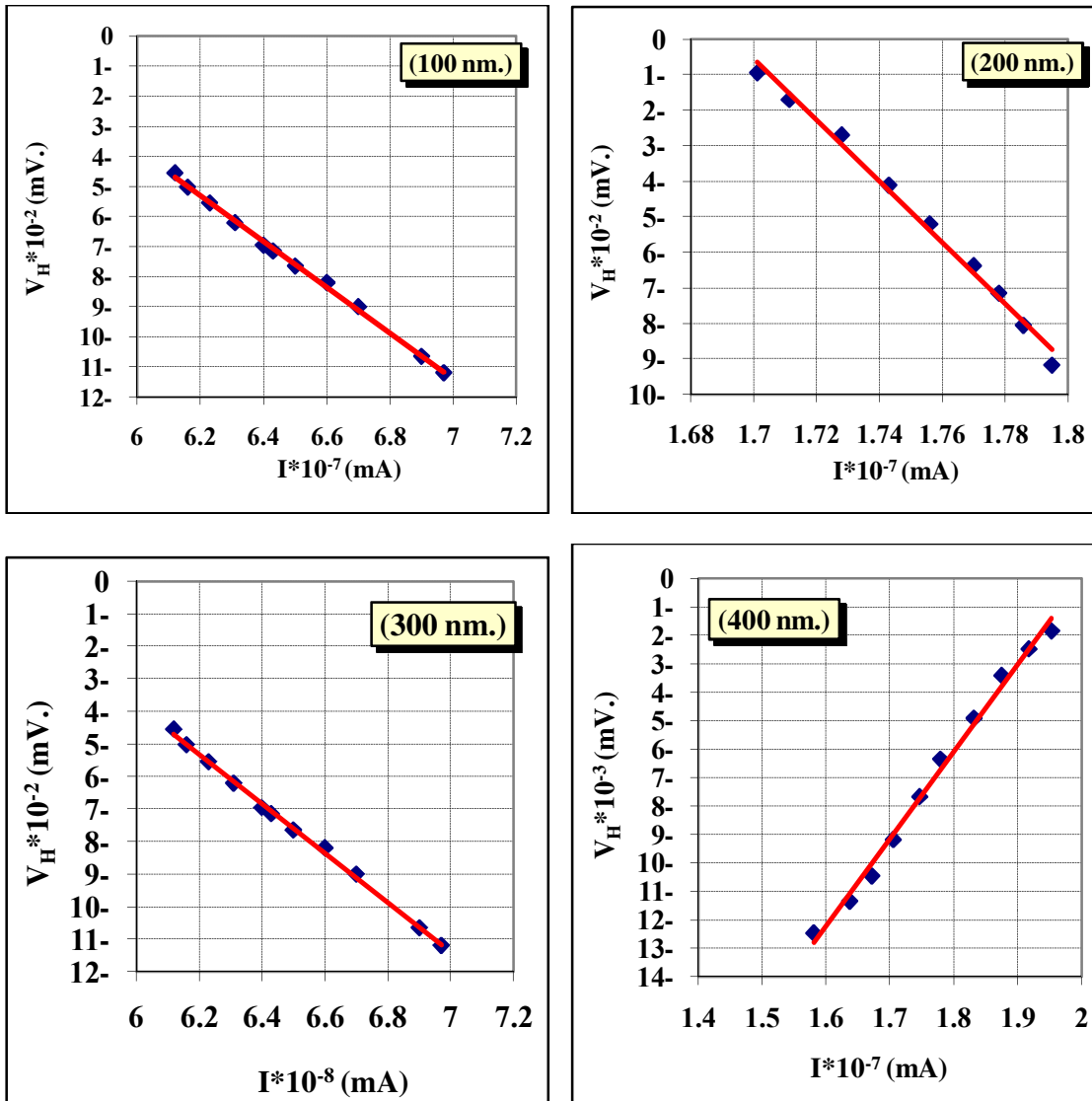| Thickness (nm.)	E_a(eV) (1) at low temperatures	E_a(eV) (2) at high temperatures
100	0.0259	0.609754400
200	0.04378	0.67678015
300	0.0697	0.775672838
400	0.1186	1.226222504
500	0.1465	2.197980847

Figure 3. The relations between Hall voltage and current (TiO_2) films for different thickness.

have been calculated from the relations (1), (2) and (3), and their values is recorded in Table (2).

$$R_H = \frac{V_H}{I} \times \frac{t}{B} \quad \text{..................................... (1)}$$

$$n_H = \pm \frac{1}{q\,R_H} \quad \text{.. (2)}$$

$$\mu_H = \sigma \times R_H \quad \text{.. (3)}$$

Table 2. Shows the hall coefficient and concentration and mobility of charge carriers of TiO_2 films

Thickness (nm)	R_H (cm^3/C)	N_D (1/cm^3)	μ_H (cm^2/V.sec.)
100	4.331808	$1.4428*10^{18}$	0.022265
200	18.371667	$34.019*10^{18}$	0.032747
300	129.954	$480.939*10^{18}$	0.884638
400	1.161767	$5.3797*10^{18}$	0.00344
500	0.13512027	$46.255*10^{18}$	0.0035380

CONCLUSIONS

1. (TiO_2) films have low conductivity, this conductivity increase with thickness increase.

2. All prepare films have two activation energies and their values increases with thickness increase.

3. Hall coefficients results has shown that the conductivity samples of (TiO_2) films was (n-type) for the films at thickness (100-200-300) nm, while (p-type) at the thickness (400-500) nm.

4. The Hall coefficient, mobility and concentration of charge carriers were increase exponentially with increasing films thickness.

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