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Resistance Temperature Detector (RTD) Application: Temperature Coefficient of Resistance (TCR) of TiO_2 Thin Film Via Spin Coating Technique

Nurul Shakira Bakri, Puteri Sarah Mohamad Saad*, Rosfariza Binti Radzali, Mohd Faizul Bin Md Idros

NANO-ElecTronic Centre, School of Electrical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.

Abstract

In the newest technology, thin-film types of RTDs are now replacing temperature measurement devices in industrial applications. However, there are fewer studies reported for semiconductor materials as thin film RTD sensing-based elements. Therefore, in this study, TiO_2 thin films were deposited on a glass substrate via the spin coating technique to study the effects number of deposition layers on the structural properties of TiO_2 thin films by means of X-ray diffraction (XRD), surface morphology by field-emission scanning electron microscope (FESEM) and investigate the temperature coefficient resistance (TCR) behavior as one of the main characteristics of RTD. The number of TiO_2 deposition layers varied from 1, 3, 5, and 7 layers fabricated by the spin coating technique and data collected for resistance change while the temperature increased from 10°C to 100°C. The XRD analysis confirms that an anatase peak was obtained at 25.32° at plane orientation (101) for 7 layers of deposited sample while the other 1, 3, and 5 layers of deposited samples show an amorphous phase structure. By increasing the number of deposition layers, the porosity decreases. However, the FESEM image shows the thin film crack for 5 deposited layers hence degrading the operating temperature due to interference of the pore formation structure. We found that from 40°C to 100°C, a linear TCR was observed in 1, 3, and 7 deposited layer samples, and a linear TCR was found from 60°C to 100°C for 5 deposited layers sample with TCR value of 3284 ppm/°C, 394 ppm/°C, 9494 ppm/°C, and 4490 ppm/°C for 1, 3, 5, and 7 deposited layers samples respectively. Therefore, in this study, 7 layers of the deposited sample show a linear correlation between 40°C to 100°C operating temperature with a large TCR value, 4490 ppm/°C potentially suitable for RTD application.

Keywords: TiO_2 thin films, Spin coating, TCR, RTD.

Full length article **Corresponding Author*, e-mail: *puterisarah@uitm.edu.my*

1. Introduction

RTD sensors made of thin film are available in a variety of sizes, forms, and tolerances to imply that they can be used to measure a wide variety of temperatures. Thin film sensors are appropriate RTD sensors for many high tolerance industrial applications such as refining and petrochemical industries, analytical and medical equipment, aerospace technology, automotive industry, power and energy generation, HVAC (Heating, Ventilation and Air Conditioning) as well instrumentation because of their design and temperature adaptability, as well as their ruggedness and endurance [1-2]. Platinum (Pt) is commonly used as they are extremely thermally stable and resistant to corrosion and oxidation [3]. When the temperature was less than 700°C, the resistance showed a good linear correlation with it.

However, at temperatures above 800°C, the resistance deviated due to evaporation and oxidation on the Pt film surface at high temperatures [4]. It was discovered that the Pt film surface oxidized at 900°C, which contributed to the increased initial resistance of the Pt annealed at 900°C film. RTDs have also been made from other materials such as nickel (Ni). Ni had low thermal tolerance but achieved a linear relationship between resistance-temperature at low temperatures [5]. At room temperature, the Ni thin film RTDs have a temperature coefficient of resistance (TCR) of about 3000 ppm/°C and excellent repeatability under cycling temperatures. Therefore, Ni thin film is still a promising material for RTD but only for low operating temperatures.

The ITO thin film RTD demonstrated promising application above 600°C due to the film's high TCR and a linear relationship between resistance and temperature. However, as the temperature rises from room temperature to 400°C, electrons from oxygen vacancies caused by substitution and the initial rapid increase in grain size increase the electrical conductivity of ITO film [6]. For a positive change in temperature, all metals produce a positive change in resistance. Of course, this is the primary function of an RTD sensor. When the nominal value of the RTD resistance is large, system error is minimized. This implies a high-resistance metal wire. The lower the metal's resistivity, the more quantity needed. TiO_2 has a number of well-defined properties that make it appropriate for a wide range of applications for its great tensile strength, as well as its lightweight, corrosion resistance, and ability to tolerate extreme temperatures. TiO_2 is n-type semiconductor material. At high temperatures, the resistivity decreases due to charge carrier mobility increasing, caused by external thermal energy, high temperature. The number of active surface sites would be determined by the surface roughness. The lower roughness value indicates that the TiO_2 particles on the surface are homogeneous.

The resistivity of TiO_2 on glass substrate increases with annealing time, which could be attributed to extra oxygen interstitial redistribution within TiO_2 film, which prevents anatase nuclei from crystallizing under high-temperature conditions [7]. To improve the resistivity of thin film, the thickness parameter will be analyzed and utilized by layering up to optimize its resistivity value. Research conducted by Aneta Kania, by increasing the thickness of the TiO_2 films, the corrosion resistance was slightly improved [8]. The corrosion resistance of the 200 nm thick TiO_2 film was higher than that of the thicker film. This was due to the thinner TiO_2 film's grain refinement. This result is supported by other conducted studies, in the light of AFM and SAM results the increase in thickness value for each material generates an extra resistance to the material, which is desirable for RTD applications [9]. M. I. Khan stated that by multilayering 1, 2, 3, and 4 stack layers of TiO_2 were deposited on a glass substrate, and the anatase phase of TiO_2 is confirmed by XRD. According to four-point probe results, increasing the number of layers reduced electrical resistivity. This decrease was caused by the formation of a sub valence band in TiO_2's forbidden band [10].

Hence, the gap will be overcome by varying annealing temperatures in this research. Anatase, rutile, and brookite are the three distinct crystalline phases of TiO_2. Rutile is the most stable phase material and when heated at high temperatures, rutile easily transforms [11]. The structural phase can be revealed using X-ray Diffraction (XRD). Therefore, to achieve this stable structural phase, thin films shall deposit at high annealing temperatures. When the TiO_2 thin film was heated to 500°C, the anatase crystalline phase was seen [12]. With the growing circumstances, the roughness and crystalline phase of TiO_2 thin films altered dramatically. Surface roughness improves as temperature rises, indicating the merging of smaller crystallites, according to AFM and FESEM image analysis. Smaller grains contribute to larger grain boundaries as well as represent high resistivity.

However, as the temperature increases too high, even though a stable structural phase can be achieved, the resistivity has the possibility to drop due to electron-hole pairs affected by external thermal energy from high temperature lowering the band gap edge. The band gap was reduced as the annealing temperature increased, demonstrating the effect of annealing temperature on TiO_2 thin films [13]. Annealing was discovered to have a significant impact on the structural, morphological, and optical properties of nanocrystalline TiO_2 thin films. M. I. Khan claimed that thin film has the highest average roughness at 573 K and the lowest roughness at 723 K. The low roughness has high homogeneity, indicating good interaction of TiO_2 particles in different layers of films; as a result, a good film is formed [14]. Many researchers have looked into TiO_2 because of its numerous applications in various industries. TiO_2 is used in a variety of applications due to its numerous electrical, optical, and chemical. properties, including catalysis, optical coatings, sensors, and many more [15].

TiO_2 films can be made using a variety of deposition methods, including spin coating, sol-gel, chemical vapor deposition, electrophoretic, and sputtering. Among all, spin coating is one of the most preferred techniques due to several advantages such as the wide range of film properties that can be varied, the low process cost, and the ease with which large areas can be coated [16]. The temperature coefficient of resistance (TCR) is a physical and electrical property of the material that describes the average resistance change per unit of temperature. There are no limits or standards to the TCR that is achievable but the higher the TCR value indicates the higher the precision of the device. For RTD applications, the resistance change per unit of temperature should have good linearity to minimize error in measurement. The testing temperature may have a specified range, but this is not to say that the resistance to temperature curves is truly linear over the specified temperature range. Therefore, in this study, the TCR behavior of TiO_2 Thin Film was investigated for RTD application by varying the number of deposition layers.

2. Materials and Methods

2.1. Materials

Cleaning a 2 cm by 1.5 cm area while submerged in a chemical solution in a beaker was the first step in preparing the glass substrate. Acetone, methanol, and deionized water (DI) are successively sonicated with an ultrasonic cleaner. Each step took ten minutes to complete. After that, they were dried using nitrogen gas to remove any remaining particles from the substrates. TiO_2 solution using sol-gel method was prepared by Sigma Aldrich, Merck (Darmstadt, Germany) titanium isopropoxide, Ti [OCH(CH3)2]4 (97%) as precursor in absolute ethanol (99.8%) from SYSTERM as solvent, glacial acetic acid (GAA) (98%) from Frien-demann Schmidt as stabilizer, Triton X-100 (98%) from R&M Chemicals as surfactant and deionized water (DI).

2.2. Methods

TiO_2 solution was prepared by dissolving the sol-gel solutions under constant stirring of 200 rpm for 1 hour at room temperature. The thin films were prepared by the spin coating technique. TiO_2 solution was deposited onto cleaned glass substrates at 3000 rpm for 1 minute. Then, the samples were dried at 100°C for 10 minutes before being annealed at 500°C for 1 hour. The process of deposition and drying was then repeated to achieve 3, 5, and 7 layers of coating.

2.3. The characterization of TiO_2 thin films

The phase composition and the structure of the film were studied by X-ray diffraction analysis (XRD). The surface morphology was examined by field-emission scanning electron microscope, FESEM by JEOL (JSM- J600F). The relationship between temperature and resistance was studied and the temperature coefficient of resistance (TCR) was measured by using a 2-point probe method by Keithley 2400 with a temperature controller ESPEC (SH- 261) (Temperature & Humidity Chamber). To testify the temperature sensitivity of the TiO_2 thin film, vary-temperature I-V measurement was conducted at a variable temperature. The TCR value is defined as the ratio of resistance changes between different temperatures. The resistance data were collected every 10s while the temperature increased from 10°C to 100°C for 1, 3, 5, and 7 deposited layers of TiO_2 thin films. The TCR value was calculated by the following formula:

$$\boldsymbol{TCR = \alpha = \frac{R_1 - R_0}{R_0(T_1 - T_0)} \times 10\text{^}4}$$

Where R_1 is the resistance at temperature T_1, R_0 represents reference electrical resistance at reference temperature T_0 (defined at 10°C), α is the temperature coefficient of resistance (TCR), and T_1 is the actual measured temperature. For 1 deposited layer, 394 ppm/°C for 3 deposited layers, 9494 ppm/°C for 5 deposited layers and 4490 ppm/°C for 7 deposited layers sample. The higher absolute value of TCR represents a greater change amount with temperature. All samples show a linear TCR. This confirms that the sensor can be used to make precise measurements. **Fig. 1** shows the schematic diagram of calibration for temperature dependence testing. The humidity function at the temperature controller was turned off for this measurement and on a thin film of TiO_2, a silver (Ag) contact with a 99.9% purity was deposited with a thickness of 100nm. The metal sputter coater was used to carry out the deposition. $1\text{x}10^{-1}$ mbar of argon gas was purged into the chamber.

3. Results and Discussions

3.1. Structural properties

The phase composition and the structure of the film were studied by X-ray diffraction analysis. XRD analysis was characterized by radiation (Cu Kα radiation, 40 mA, 40 kV) with a step size of 0.02°/5s in the range 2θ= 10° to 90°. **Fig. 2** shows the measured and fitted XRD spectra of the TiO_2 thin film. From **Fig. 2**, the anatase peak was obtained at 25.32° at plane orientation (101) for TiO_2 films prepared at 7 deposited layers on glass substrates via spin coating. The other 1, 3, and 5 layers of the deposited sample show an amorphous, indicating low crystallinity. According to the research that is currently accessible, this orientation is TiO_2 material. According to the International Centre for Diffraction Data (ICDD card no. 01- 086-1156), the peaks were associated with the anatase phase. By varying the number of the TiO_2 solution-coated process onto the substrate, the thickness of the nanostructured TiO_2 thin film can be adjusted. The anatase peak of TiO_2 can be more clearly seen in XRD spectra as the number of deposited layers increases. At 7 deposited layers, the crystallinity of TiO_2 was most clearly observed.

3.2. Morphological properties

The sensing element thin film surface morphology has a big impact on how well it senses. Thus, using a JEOL (JSM-J600F) field-emission scanning electron microscope (FESEM) with an operating voltage of 5 keV and a magnification of 30 k, the surface morphology of the thin film was examined. The morphology of the TiO_2 thin film is shown in **Fig. 3**. The FESEM images show that the presence of TiO_2 nanoparticles combined together and formed a thin film. By increasing the number of deposition layers, the porosity decreases. However, for 5 deposition layers of TiO_2 thin film, it can be seen that the thin film crack affects the arrangement of nanoparticles. TiO_2 thin film observed peaks at about 0.5 and 4.5 keV in these EDX spectra, which are assigned to oxygen and titanium respectively. Such an analysis can be confirmed by the presence of titanium dioxide as shown in **Fig. 3**.

3.3. Temperature coefficient resistance, α (TCR)

TCR results are shown in **Fig. 4**. We found that from 40°C to 100°C a linear TCR was observed in 1, 3, and 7 deposited layer samples, and a linear TCR was found from 60°C to 100°C for 5 deposited layers sample; 3284 ppm/°C measurements, the operating temperature was lesser than the other 1, 3, and 7 deposited layers of TiO_2 thin film. The improvement in TCR value might be due to carrier mobility of recombination in the TiO_2 thin films which we will focus on in our next work.

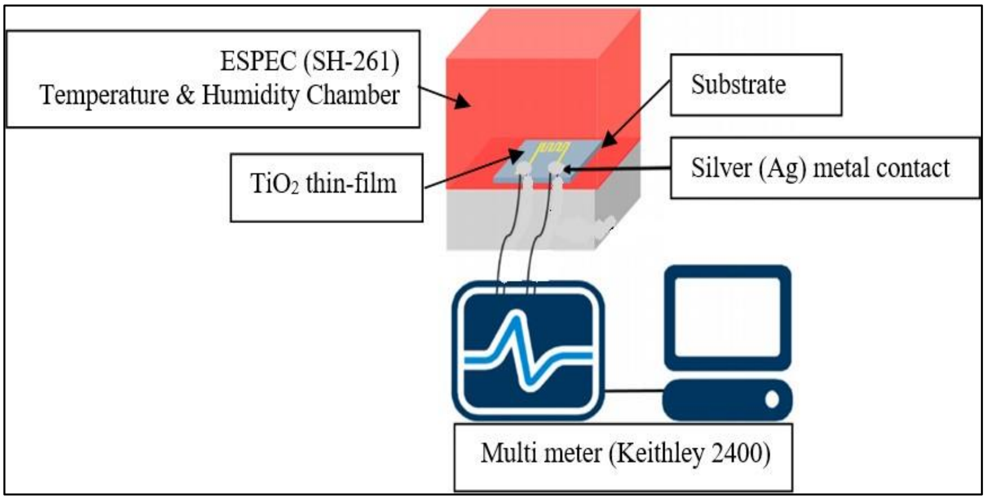


Fig. 1. The schematic diagram of calibration for temperature dependence testing.

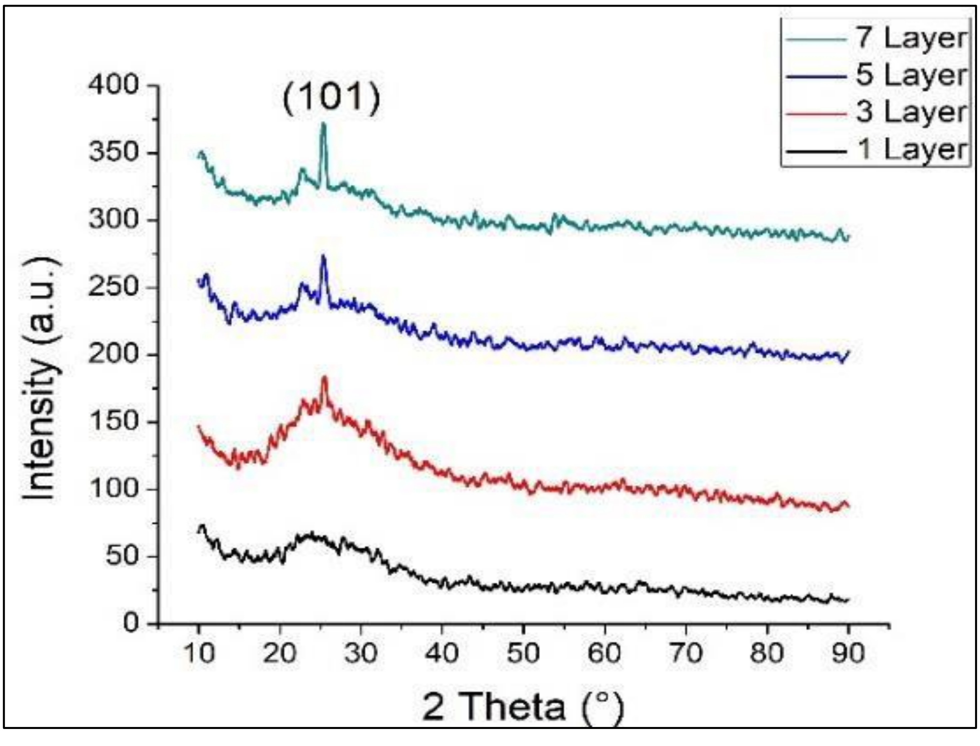


Fig. 2. XRD spectra of 1, 3, 5, and 7 deposited layers of nanostructured TiO_2 thin film.

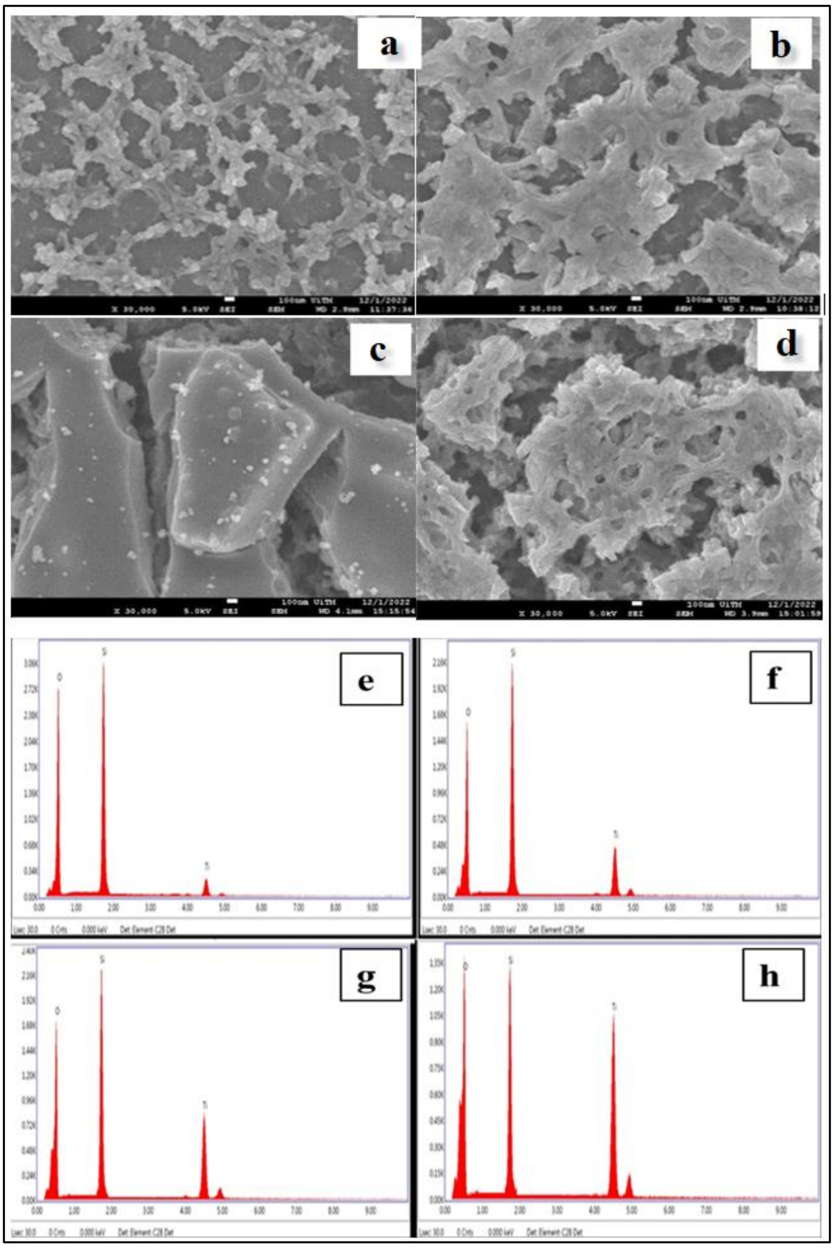
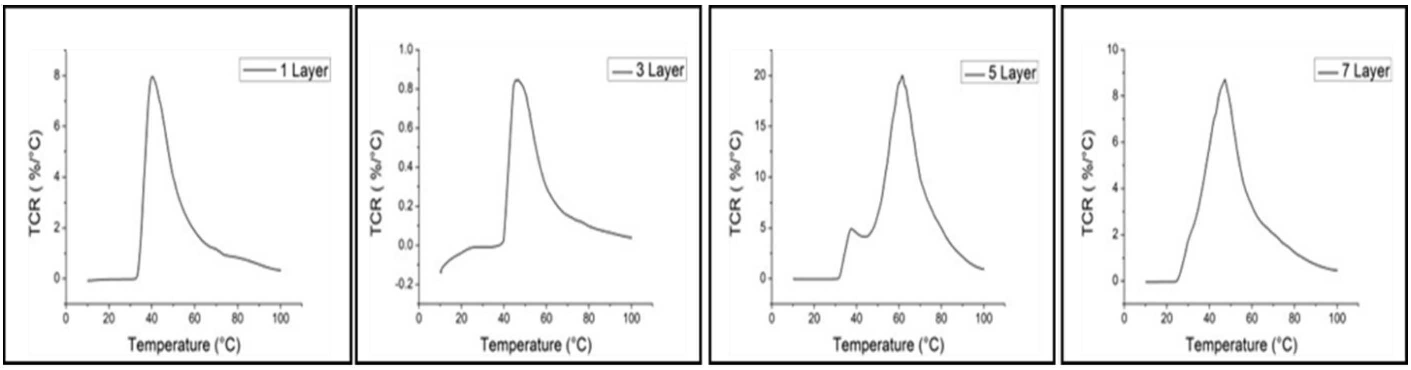


Fig. 3. FESEM images and EDX spectra of the surface morphology of TiO_2 thin films deposited at different numbers of deposited layers. **(a, e)** 1 Layer; **(b, f)** 3 Layers; **(c, g)** 5 Layers; **(d, h)** 7 Layers.



(a) **(b)** **(c)** **(d)**

Fig. 4. The TCR test results of TiO_2 thin films with different numbers of deposited layers. (a) 1 layer (b) 3 layers (c) 5 layers (d) 7 layers.

4. Conclusions

In conclusion, we have successfully fabricated TiO_2 thin films on a glass substrate via the spin coating technique at various deposited layers to study the physical properties and investigate the TCR behavior for RTD application. Results showed that an anatase phase of a nanostructured TiO_2 thin film could be seen in the XRD spectra, uniform nanoparticles across the thin film examined by FESEM, a linear correlation between resistance and temperature, and a large TCR value at 4490 ppm/°C with an operating temperature of 40°C to 100°C for 7 deposited layers TiO_2 thin films. The influence of the number of deposition layers studied has an effect on the values of TCR and operating temperature. The TiO_2 thin film's TCR behavior showed a promising result for RTD application in the fact that they had a large TCR value and there was a linear correlation between resistance and temperature.

Acknowledgments

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