OHMIC CONTACT CHARACTERISTICS OF NANOSTRUCTURED TITANIUM DIOXIDE (TiO_2) THIN FILMS ANNEAL AT DIFFERENT TEMPERATURE

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***Abstract*—** This paper studied on the ohmic contact characteristics of nanostructured TiO_2 thin films anneal at different temperature. The preparation of TiO_2 solution used the Titanium (IV) butoxide as a precursor at concentration of 0.2M. TiO_2 thin films were prepared by spin-coating technique and derived sol onto glass substrate, followed by an annealing at temperatures ranging from 350◦C to 550◦C. The result will be analyse on the I-V characteristics and observed it to get the ohmic contact by using gold, platinum and palladium as a metal contact. The influence of the annealing temperature on the electrical, structural and surface morphology of the thin film were characterize by using the I-V measurements, scanning electron microscope (SEM) and atomic force microscope (AFM). Due to the observation in electrical measurement at 550ºC, platinum is the best metal contact compared to gold and palladium. This ohmic contact was observed by looking at the capability of metal contact delivering the required current with no voltage drop between the semiconductor and the metal.

***Keywords*—**Titanium Dioxide thin films, Spin coating technique, Electrical measurement, Ohmic contact.

1.0 SCOPE OF WORK

This project was initiated by making some review on the topic related to the Titanium dioxide (TiO_2) thin films. A study focused on the prepararation of TiO_2 thin films at concentration of 0.2M. Spin coating technique is used to deposit TiO_2 thin films on the glass substrates. The TiO_2 thin films is annealed at temperature ranging from 350ºC to 550ºC. Then the I-V measurement were characterized to observe the ohmic contact. Finally, this report has been done after all the information and results have been gathered.

2.0 OBJECTIVE

The project is completed based on the following objectives:

a) To deposit the nanostructured Titanium Dioxide thin films by using spin coating technique.

b) To study the ohmic contact characteristics nanostructured Titanium Dioxide thin films

3.0 INTRODUCTION

Titanium dioxide as a raw material supports industries worth $3 billion annually in the United States alone [1]. The element titanium is finding more and more applications in today's society. The use of titanium metal in aerospace, sports and medicine is well known; in fact, over 96% of the worldwide use of titanium is in the oxide form, TiO_2 (Titanium dioxide), thus creating a high demand. Among the several oxides of metals, titanium dioxide (TiO_2), a high-k dielectric with excellent biocompatibility and good photocatalytic performance has been considered to be a material of great interest due to its wide range of applications in several areas such as photonic materials, dye-sensitized solar cells [2] and a sensing film for gas sensor [3].

Titanium dioxide is a ceramic material, commonly known as titania. Although generally used as a white pigment or opacifier, titania can also be applied in enameling and catalysis [4]. Three polymorphs of titanium dioxide Exist: brookite, anatase, and rutile. All possess the same empirical chemistry, TiO_2, but each has a different crystal structure. Brookite has an orthorhombic crystal structure and spontaneously transforms to rutile around 750°C [4]. The predominant commercial phase of titanium dioxide is anatase, although it is rarely found in ore form. It is metastable with respect to rutile under all conditions of temperature and pressure and reverts spontaneously to rutile at temperatures above 915°C [5]. Among them anatase is the low temperature phase, exhibiting properties which render it interesting for various application such as photovoltaic cell, photocatalysis and for it antimicrobial properties [6]. Recent study by M. K Ahmad found that anatase phase in TiO_2 thin films exist at 250°C until 800°C [7]. TiO2's anatase phase with a band gap of 3.2eV has proven to be TiO2's most active crystal structure, largely because of its favorable energy band positions and high surface area [8]. Anatase has a tetragonal crystal structure in which the Ti-O octahedra share four corners, as shown in Figure 1.

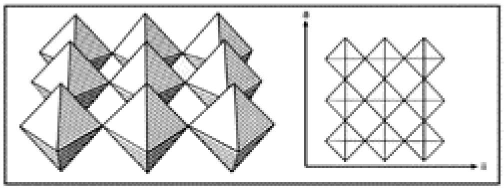


Figure 1: A diagram of the anatase crystal

The stable form of titania is rutile, to which the other forms of titania transform at sufficiently high temperatures. Rutile has a crystal structure similar to that of anatase, with the exception that the octahedra share four edges instead of four corners. This leads to the formation of chains, which are subsequently arranged in a four-fold symmetry, as shown in Figure 2.

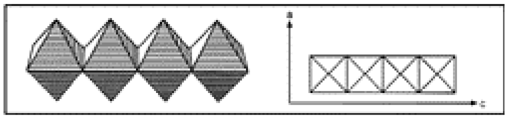


Figure 2: A diagram of the rutile crystal

A comparison of Figure 1 and Figure 2 shows that the rutile structure is more densely packed than anatase. Its refractive index and density also is larger compared to anatase [9]. From the previous research state that the band gap value of rutile is at 3.0 eV [10].

In this research, the type of TiO2 used is anatase. Anatase is used because of the ranging temperature using in this project is between 350°C until 550°C. The recent study by M. K Ahmad also found that anatase phase in TiO_2 thin films exist at 250°C until 800°C [7].

In this research contains the study of ohmic contact characteristics of nanostructured TiO_2 thin film anneal at different temperature. In general, an ohmic contact refers to the contact between a metal and a semiconductor to allow carriers to flow in and out of the semiconductor. There are 3 types of ohmic contact which is different configuration, different distances and different type of metal used. In this project only focused on ohmic contact using the different type of metal used such as gold, platinum and palladium. The discussion also consists of conductivity and resistivity by using different metal contact which is used in I-V measurement. By using different metal contact, the ohmic contact of Au/TiO_2/glass, Pt/TiO_2/glass and Pd/TiO_2/glass in I-V measurement was studied. At the end in this research, the best metal contact to perform good result in I-V measurement is obtained.

4.0 METHODOLOGY

Preparation of nanostructured TiO_2 thin films by using spin coating method

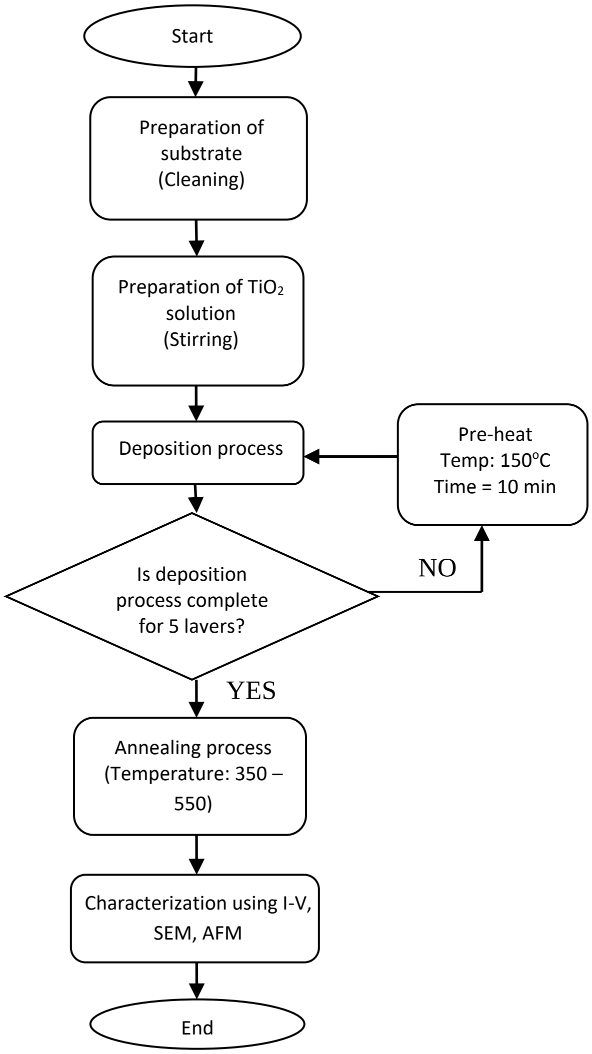


Figure 3: Flowchart for preparation of TiO_2 thin films

In this project, spin coating method is used to prepare and build TiO_2 thin films. Spin coating is a procedure used to apply uniform thin films to flat substrates. The process occurred when a few drop of solution is placed on the substrate, which is then rotated at high speed in order to spread the fluid by centrifugal force. For this research glass was used as substrates. The substrates were cleaned by several steps before went to the deposition process. The substrates were cleaned with acetone, methanol and DI water followed by the drying process using the Nitrogen (N_2) gas.

The starting solutions for the deposition of pure TiO_2 thin films were prepared by mixing 6.8 ml of titanium *n*-butoxide (Ti(C4H9)4) in 100ml of ethanol, 5 ml of glacial acid followed by the addition one drop of Triton X- 100 and deionised water. The amount of deionised water depends upon the molar concentration of precursor used. After mixing all the materials, at the first hour the solution was stirred and heated at 60°C, then another 1hour to stir the solution at room temperature (37°C). Make sure mixed all the material while stirrer.

The TiO_2 thin films were deposited on the glass substrates by using spin coating technique. For this method, spin coater is very important equipment to complete the process. Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved. The applied solvent is usually volatile, and simultaneously evaporates. So, the higher the angular speed of spinning, the thinner the film. The thickness of the film also depends on the concentration of the solution and the solvent. To proceed with this technique, spin coater was set at one speed of 3000rpm, in 1 minutes and Nitrogen (N_2) gas was applied at 4 bars. The TiO_2 solutions were dropped 10 times onto the glass substrate and heated in the furnace at 150°C for 10 minutes. This process was repeated for 5 times to make samples become 5 layers. Then the thin films were annealed at 350°C, 450°C, 550°C for 1 hour. Only six samples were annealed at different temperature and one sample was not applied to any heat treatments which call as deposited.

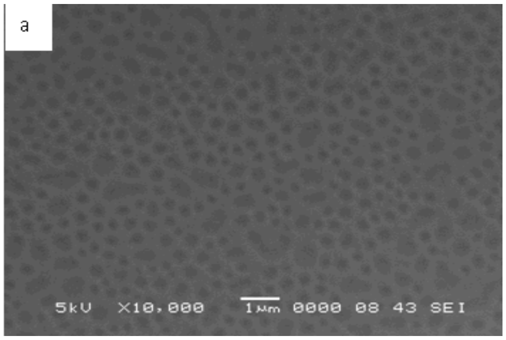
Lastly the samples of TiO_2 thin films was characterize and analyzed using I-V measurement, Atomic Force Microscope (AFM), and Scanning Electron Microscopy (SEM).

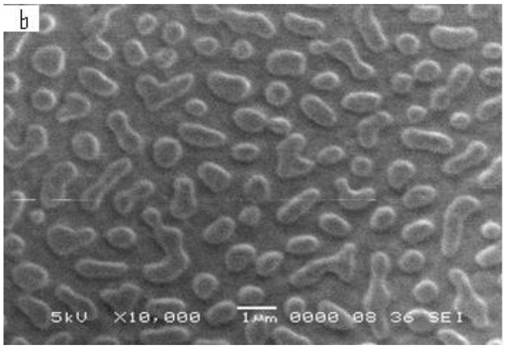
5.0 RESULT AND DISCUSSION

5.1 Surface Morphology of TiO_2 thin films

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. Figure (4) shows the observation of TiO_2 thin films using Scanning Electron Microscopy annealed at 350°C, 450°C, 550°Cand also including the as-deposited sample. The SEM images showed the presence of TiO_2 particle has combined together and formed thin film [14].

It was also observed the formation of thin film cracked during the sample preparation. Due to these samples, the grain sizes of TiO_2 thin films increase when increasing the temperature. So, when the grain sizes increase, it will provide higher surface contact between TiO_2 thin films and electrode [14].





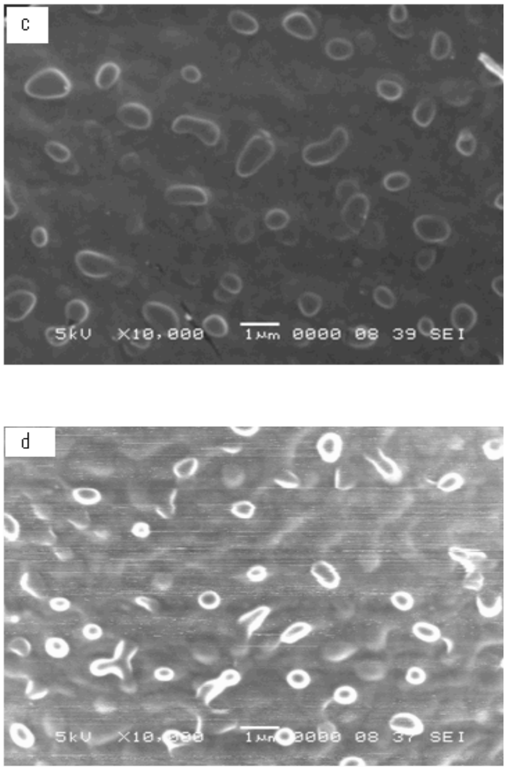


Figure 4: SEM images for TiO_2 thin films deposited onto glass substrate at different temperature (a) as-dep: (b) 350^{o}C: (c) 450^{o}C: (d) 550^{o}C.

5.2 Surface Topography of TiO_2 thin films

The atomic force microscope (AFM) is a very high-resolution type of scanning probe microscopy. This microscope was used to observe the surface topography of thin films. From the figure below shows that the surface topography of TiO_2 thin films depends on the temperature. Due to the temperature at 350^{o}C, the surface topography of the TiO_2 thin films is not uniform and bulky. As annealing temperatures increase, the surface topography of thin films becomes more uniform. The surface topography of TiO_2 thin film becomes uniform at temperature 550^{o}C. This uniform surface can be related with high conductivity at 550^{o}C in the I-V measurement. It is because the current can easily flow during the uniform surface rather than non uniform surface.

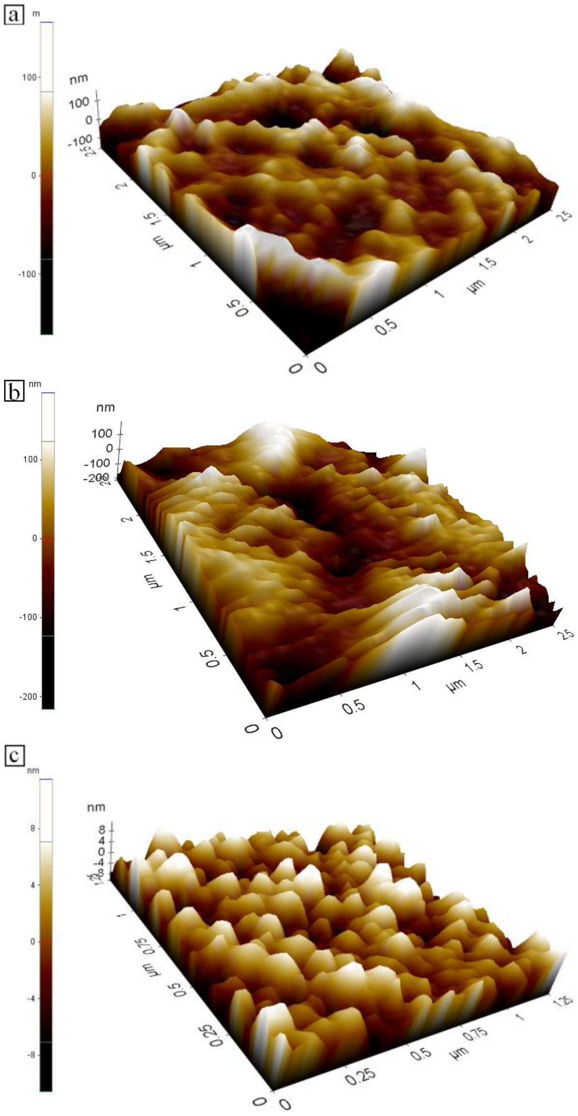


Figure 5: AFM images for TiO_2 thin films deposited onto glass substrate at different temperature (a) 350^{o}C: (b) 450^{o}C: (c) 550^{o}C.

5.3 Electrical properties of TiO_2 thin films

Gold (Au), Platinum (Pt) and Palladium (Pd) deposited onto TiO_2 thin film act as an electrode. The layer of TiO_2 thin films on the glass substrate is as shown in Fig 5. Four probes are tapped on the coated gold, platinum and palladium in order to measure it electrical measurement and also observed the ohmic contact.

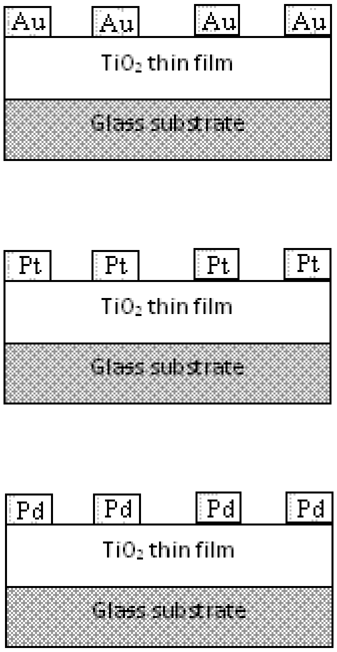


Figure 6: Diagram of electrode (Au, Pt, and Pd) coated on the TiO_2 thin films.

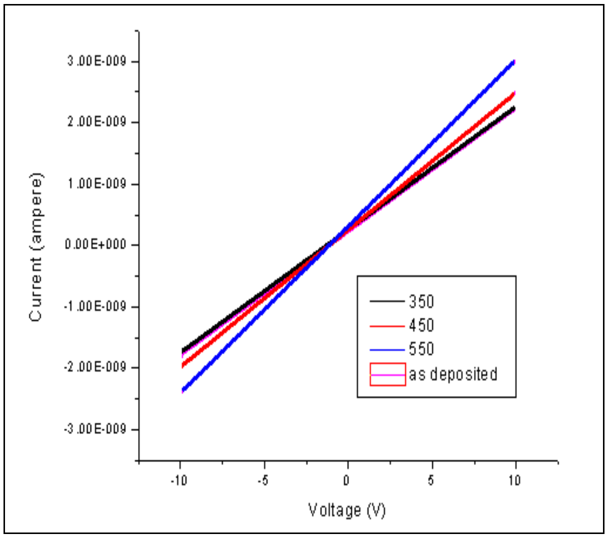


Figure 7: I-V Characteristics for TiO_2 thin films deposited onto glass substrate at various annealing temperature using gold as metal contact.

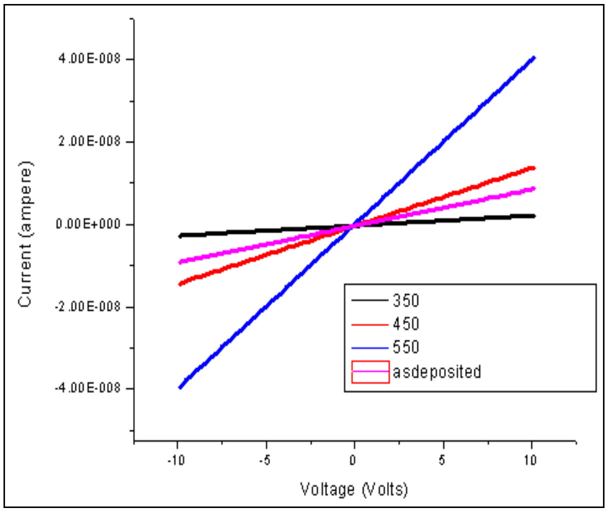


Figure 8: I-V Characteristics for TiO_2 thin films deposited onto glass substrate at various annealing temperature using platinum as metal contact.

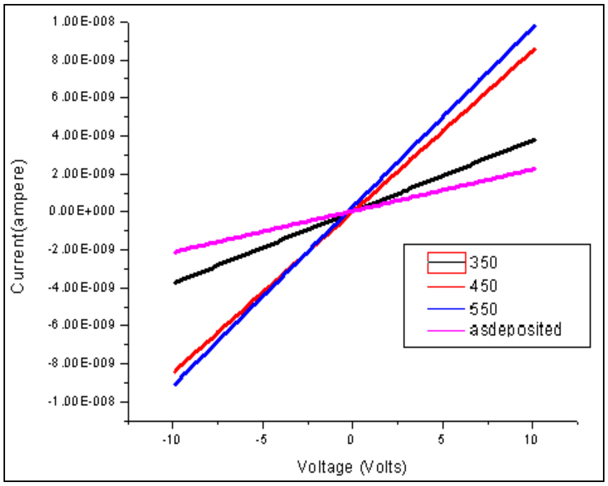


Figure 9: I-V Characteristics for TiO_2 thin films deposited onto glass substrate at various annealing temperature using palladium as metal contact.

Figure 7 and figure 9 above shows the electrical characteristics of TiO_2 thin films annealed at different temperature. I-V characteristic showed that the resistance decreased when the annealing temperature increased. This is the effect of the grain size. When grain size becomes larger, electron migration will improve [14]. Therefore the resistivity of TiO_2 thin films also decreased considerably after the thermal treatment. The thermal treatment produced electronic contacts not only between the particles but also between all the particles of the film [7].

For figure 8, the result shows contradict between as-deposited result and the sample annealed at 350ºC. It is because of the non uniform sample at 350ºC. So, the result gives inconsistence reading at temperature 350ºC.

From observation all graph of the I-V characteristics, it was found that the lowest value is as-deposited. It is because when the sample is as-deposited sample, all electrons are in the valence band, and there are no electrons in conduction band. So, this condition we called it poor conductor [15]. When Increasing in temperature means that the electrons accept energy due to the temperature given. Since the temperature is high, the energy also high. So, when the resultant of increasing temperature to the sample, it can cause an appreciable numbers of electrons are thermally excited from the valence band to the conduction band [15]. Since there are many empty states in the conduction band, a small applied potential can easily move these electrons, resulting in moderate current [15]. Then, the result shows that during the temperature at 550ºC, all the electrons in the valence band have sufficient energy to jump to the conduction band. It shows that the conductivity is at maximum condition during the high temperature. From the research also state that the conductivity is inversely proportional to resistivity of the thin films. The sheet resistivity and conductivity of TiO_2 thin films was calculated according to the following equations. Using the voltage and current readings from the probe:

$$R_s = \rho_{\square} = \frac{\pi}{\ln(2)}\frac{V}{I} \quad .... (1) \quad [8]$$

$\rho_{\square}$ = sheet resistivity (Ω/□)

Table 1: The resistivity of TiO_2 thin films at different annealing temperature using gold, platinum and palladium as metal contact

Temperature	Resistivity, ρ(Ω/□)		
	gold	platinum	palladium
As-deposited	2.01E+10	4.8E+9	2.37E10
350	1.99E+10	1.75E+10	1.32E10
450	1.81E+10	3.46E+9	5.67E9
550	1.49E+10	1.09E+9	5.41E9

Table 2: The conductivity of TiO_2 thin films at different annealing temperature using gold, platinum and palladium as metal contact

Temperature, (ºC)	Conductivity, σ(S-□)		
	gold	platinum	palladium
As-deposited	4.97E-11	2.08E-10	4.21E-11
350	5.02E-11	5.71E-11	7.59E-11
450	5.52E-11	2.89E-10	1.76E-10
550	6.71E-11	9.18E-10	1.85E-10

From result in the resistivity table, it can be discussed that when increasing the temperature, the value of resistivity is decrease. A low resistivity indicates a material that readily allows the movement of electrical charge. Due to the electron mobility, electrons will move around randomly in the absence of an applied voltage. Therefore, if one averages the movement over time there will be no overall motion of charge carriers in any particular direction [16]. However, upon applying voltage, electrons will be accelerated in an opposite direction to the electric field [16]. So, it can make current easier to flow and reduce the number of resistivity. Since the resistivity is proportional to the conductivity, the table state that the value of conductivity increasing when the temperature increase and followed the equation below:

$$\boldsymbol{\sigma = 1/\rho \;...... (2)}$$

σ = conductivity (S-□)
ρ = resistivity (Ω/□)

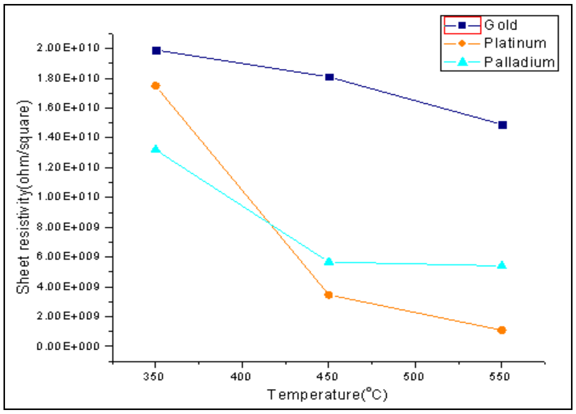


Figure 10: Resistivity of TiO_2 thin films deposited on the glass substrate at different annealing temperature using Au, Pt and Pd as a metal contact

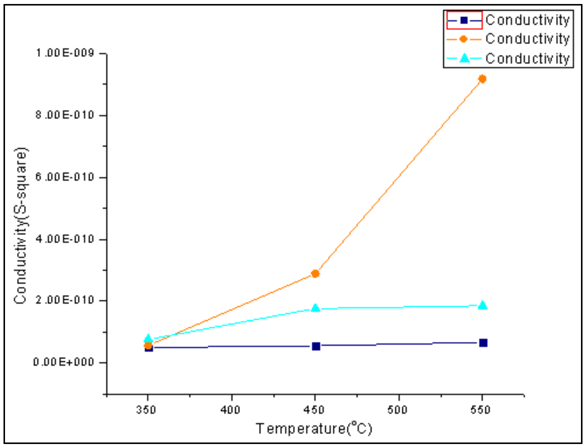


Figure 11: Conductivity of TiO_2 thin films deposited on the glass substrate at different annealing temperature using Au, Pt and Pd as a metal contact

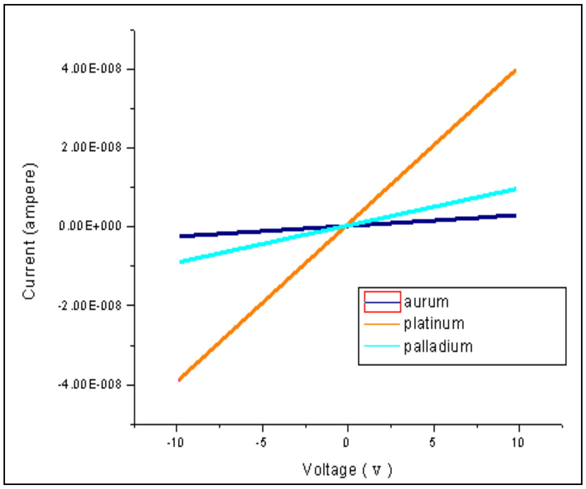


Figure 12: Comparison between highly conductive results using different metal contact

The effect of three kinds of metal contact to the Ohmic contact has been studied. Gold (Au), Platinum (Pt) and Palladium (Pd) have been used to perform the I-V measurement. Three current versus voltage graphs have been plotted and the configurations as follows: Au/TiO_2/Glass, Pt/TiO_2/Glass and Pd/TiO_2/Glass. The graphs in figure 12 shows that Pt/TiO_2/Glass thin film, Pd/TiO_2/Glass thin film and Au/TiO_2/Glass thin film at temperature 550°C give highest current intensity at 0.2M of sol-gel concentration. Due to the observation with three metal contacts refer to figure 12, all three show ohmic from the graph because linear and symmetry and Platinum give the best contact compared to palladium and gold [17]. From the calculation also shows the platinum give high conductivity with the value 1.85E-10 (S-□) compared to palladium and gold. This state can be discuss as when a platinum used as a metal contact, the carriers easier to flow in and out of the semiconductor [17]. It means that the platinum have capability of delivering required current between the semiconductor and the metal.

6.0 CONCLUSION

Titanium dioxide thin films have been successfully deposited using 0.2M precursor solution. The ohmic contact characteristics of nanostructured TiO_2 thin films deposited on glass substrate by using spin coating technique annealed at various temperature is investigated. From a linear graph of I-V curve it can be concluded that all films deposited on glass substrate exhibited ohmic contact and the electrical properties of annealed sample is better than the control sample. I-V curve in figure 7 and figure 9 only show decreased in the resistance as the annealing temperature increased. This indicated that as the annealing temperature increased from 350°C to 550°C the resistivity of TiO_2 films decreased. The value of the resistivity decreased from 1.99E+10(Ω/□) to 1.49E+10(Ω/□) for gold and 1.32E10 (Ω/□) to 5.41E9 (Ω/□) for palladium. Since the conductivity is inversely proportional to the resistivity, the value of conductivity increased as the temperature increases in the sample annealed at 350°C to 550°C. The values of the conductivity are increasing from 5.02E-11(S-□) to 6.71E-11(S-□) for gold and 7.59E-11(S-□) to 1.85E-10(S-□) for palladium. This is influenced by the grain size of the sample that provides the higher surface contact between TiO_2 and electrode to improve the electron migration. The electrons have enough energy to excite to conduction band during increasing in temperature also will cause conductivity increase.

Figure 8 shows that it has some contradict result between as-deposited sample and the sample annealed at 350°C for I-V measurement. It is because of the non-uniform sample gives inconsistence reading at temperature 350°C. This problem occurred during the deposition process of Titanium Dioxide solution deposited onto the glass substrate. This problem can be solve with better deposition process.

7.0 FUTURE DEVELOPMENT

The result can be improved for the future in many ways. Since the pure TiO_2 has wider energy bandgap (3.2eV), it will provide lower photoexcitation process. This problem for titanium dioxide also reported as high as 3.2 eV [9][12-13].

So, to overcome this problem, TiO_2 need smaller bandgap energy that lowers than 3.2eV. It is recommended that the TiO2 can be doped with other material such as Gallium (Ga), Niobium (Nb) and Tantalum (Ta) [14]. Smaller energy band gap can cause the TiO_2 become more conductive. These characteristic shows the electron can easily migrate from valence band to conduction band when has sufficient energy. The accumulation electrons in conduction band affect the TiO_2 become more conductive.

8.0 ACKNOWLEDGMENTS

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