Electrical Properties of Niobium Doped Titanium Dioxide Thin Films by Spin Coating Technique

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***Abstract*—Undoped TiO_2 and Niobium (Nb)-doped TiO_2 thin films have been successfully prepared and deposited on glass substrate by spin coating technique. The effect of annealing temperature on electrical properties using I-V measurement of Titanium Dioxide thin films was studied. TiO_2 thin films were annealed at 300°C to 550°C. The results indicated that the conductivity increased while resistivity decreased with the increasing of annealing temperatures. Using 450°C as an optimum annealing temperature that has been examined, the effect of Nb doping concentrations on electrical properties was investigated. As the doping concentration of Nb was increased, the resistivity decreased and conductivity was increased. Optical properties of TiO_2 thin films were investigated using UV-vis-NIR spectrophotometer and indicated that the optical band gap increased with increasing Nb doping concentration. The FESEM investigation showed that the thin films consist of nanometer-sized grain particles.**

Keywords-Titanium Dioxide Thin Film; Nb doping; Electrical Properties; Optical Properties; Structural Properties

I. INTRODUCTION

TiO_2 is well known as a metal oxide semiconductor, has been extensively studied in many applications such as it is used for dye-sensitized solar cells (DSSC) [1], photo-electrodes and photocatalysts, and applications with high performance due to its fine physical, chemical and optical properties [2]. TiO_2 thin films can be prepared by many techniques such as sol-gel, chemical vapour deposition and spray pyrolysis.

Many researchers have studied, and found that the properties of transition metal oxides can be enhanced by doping, which widen their potential applications. In order to be easily applied to electronic devices fabrication such as DSSC application, TiO_2 needs to be able to be deposited into thin films structure. Nb doping is the one of transition metal oxide that can be modified the microstructure of TiO_2, introduces electronic defects at the surface or in the bulk of grains, controls grain growth mechanisms, and so modifies TiO_2 conductivity [3]. This experiment of TiO_2 thin films present sol-gel spin coating technique due to low preparation cost [4], simple technique and large area deposition, good optical properties and have the ability to produce thin and uniform films on large substrate area [5].

M.K. Ahmad et. al, [6] examined the effects of annealing temperatures and found that the electrical properties of the TiO_2 thin films were changed with the increasing of the annealing temperature. The porosity at 500ºC is the highest among the sintered temperatures.

A.V.Manole et. al, [7] conducted studied optical properties of pure and Nb-doped TiO_2 synthesized using a sol–gel method and deposited as thin films by spin-coating followed by annealing in air at 500°C for 1h and vary between 1.8 and 4.3 at%. From doping TiO_2 with Nb modified the surface morphology of the samples; the grain size is increasing while the surface roughness decreases with the increase in Nb content.

In this paper, undoped TiO_2 and Nb-doped TiO_2 thin films were analyzed at different annealing temperature and atomic percent of doping concentration of niobium in terms of electrical properties, optical properties and the structural.

II. METHODOLOGY

The glass substrates cleaned with acetone, followed with methanol and the last step is rinsed using deionized water for 10 minutes each step. The cleaned substrates are blown by Nitrogen gas after being rinsed with deionized water.

The solution was prepared by mixing the Titanium (IV) isopropoxide as a precursor, glacial acetic acid as the stabilizer, and absolute ethanol solvent. All these methods are mixed in a beaker A. Then, deionized water was added into absolute ethanol solvent and two drops of Triton X-100 as surfactant in a beaker B. The deionized water is to increase the hydrolysis rate.

The solution of both beakers is stirred for 30 minutes at 50°C using a magnetic stirrer on a hot plate separately. After 30 minutes stir, the solution of both beakers was mixed together into one beaker and it was continuously heated and stirred for 30 minutes at 50°C. The heating increased the reaction process between the materials in the solution.

The next process is the TiO_2 thin films were deposited on glass substrate by spin coating technique. It was set at a 2000 rpm for one minute of time. The TiO_2 solution was dropped which is 10 drops and then the TiO_2 thin films underwent the drying process in closed furnace at 150°C for 10 minutes. The dropping and drying process were repeated for 5 times onto the same substrate. Then, the thin films were annealed at 300°C -550°C for 30 minutes.

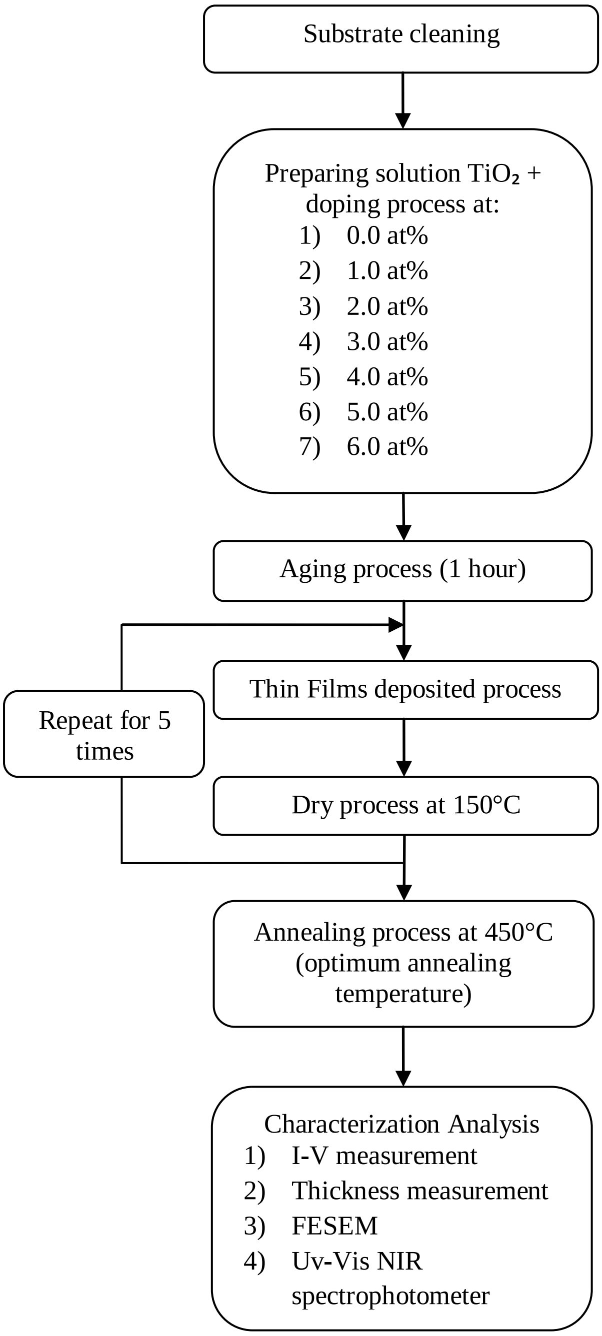

Figure 1. Flowchart for Nb-doped TiO_2 thin films

For doping part using the best annealing temperature result as a reference (0 at.%), niobium (Nb) was added in beaker A at doping concentration of 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 at.%. The amount of niobium was calculated to produce these doping concentrations. All the processes were repeated as preparation of undoped TiO_2 thin films.

Au was deposited on thin films using thermal evaporator and it was used as electrode for Current–voltage (I-V) measurement for all samples. The thickness of thin film was characterized using surface profiler (VEECO DEKTAK 150). The optical properties were characterized using ultraviolet-visible-near infrared (UV-vis-NIR spectrophometer). The surface morphology on the TiO_2 thin films were analysed by field emission scanning electron microscope (FESEM, JEOL JSM- J600F). Experiment process flow is summarized in Figure 1.

Au(gold) was used as the standard for metal contact because of their low resistivity and their ease of application by standard manufacturing processes such as sputtering [4]. This is due to it forms a good ohmic contact with materials. The ohmic contact is very important due to minimize leakage current.

III. RESULTS AND DISCUSSIONS

A. Electrical Properties of TiO_2 Thin Films

The electrical properties of undoped and Nb-doped TiO_2 thin films were characterized by performing I-V measurement to the thin films.

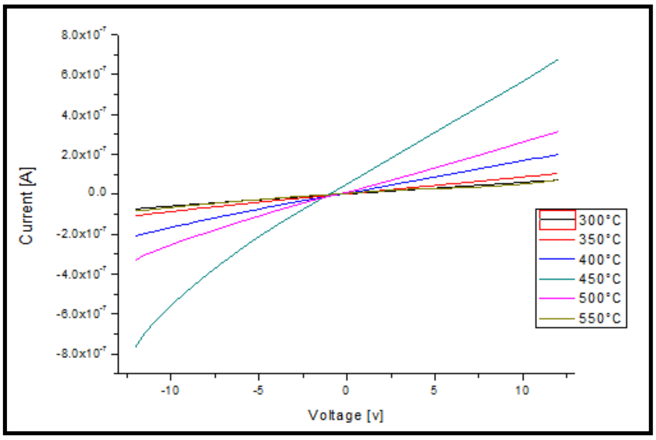

Figure 2. I-V curves for undoped TiO_2 thin films at different annealing temperature

Figure 2 represent current-voltage (I-V) properties of undoped TiO_2 thin films. All the samples show linear curve, indicating an ohmic behavior between the thin films and Au (gold) metal contact.

Figure 3 shows the relation between resistivity and annealing temperature. From the results obtained, the resistivity decreased with the increasing of annealing temperatures up to 450˚C and the resistivity at 500˚C and 550˚C annealing temperature are slightly increased. This is due to the grain size. When the grain size becomes larger, electron pass through from particles to other particles improves [6,8] which will in turn decrease the electrical resistivity after annealing process was done.

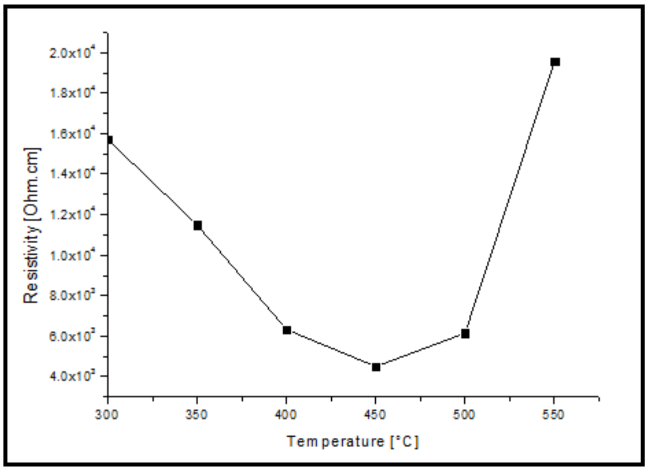

Figure 3. Resistivity for undoped TiO_2 thin films at different annealing temperature.

The resistivity of the thin films was calculated using equation (1).

$$\rho = R[\frac{wt}{L}] \quad \text{in unit } \Omega \text{ cm} \qquad (1)$$

Where:
ρ = resistivity
R = resistance
w = width of metal contact
t = thin film thickness
L = distance between metal contact

The thickness of the films increases with Nb concentration due to addition of niobium pentaethoxide, as the dopant source, to the Titanium (IV) isopropoxide (TTIP) solution [7] and the thickness of the thin films was about 125-360nm. The thickness of the thin film can affect resistivity and conductivity. It is because the movements of the electron will be difficult if the thin film is too thick [9].

The conductivity was obtained using the calculation in the equation of (2) as follows:

$$\sigma = 1/\rho \text{ in unit S.cm}^{-1} \qquad (2)$$

Figure 4 shows the conductivity for undoped TiO_2. The conductivity increased with increasing in annealing temperature. From the figure it shows the most conductive sample is 450˚C. At temperature 500˚C and 550°C, the conductivity decreased.

I-V plots of the thin films of Nb-doped TiO_2 thin films at different doping concentration with annealed at the optimum temperature which is 450°C that has been obtained from undoped TiO_2 thin films experiment are shown in Figure 5. All Nb-doped TiO_2 sample shows linear and symmetrical curve represented a good ohmic behavior between thin film and Au metal contact.

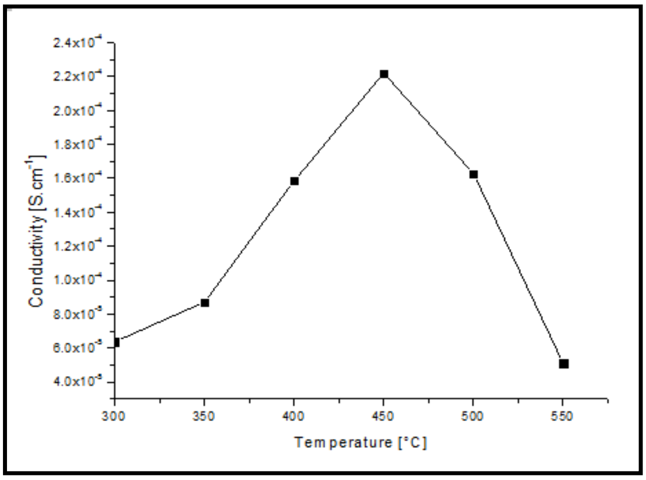

Figure 4. Conductivity for undoped TiO_2 thin films at different annealing temperature.

Table 1: Electrical properties

Nb Doping concentration	Thickness (nm)	Resistivity (ohm.cm)	Conductivity (ohm.cm)
Undoped	155	4.51E+03	2.22E-04
1 at%	200	4.28E+03	2.34E-04
2 at%	218	4.25E+03	2.35E-04
3 at%	273	3.95E+03	2.53E-04
4 at%	309	3.65E+03	2.74E-04
5 at%	353	2.95E+03	3.39E-04
6 at%	435	2.63E+04	3.80E-05

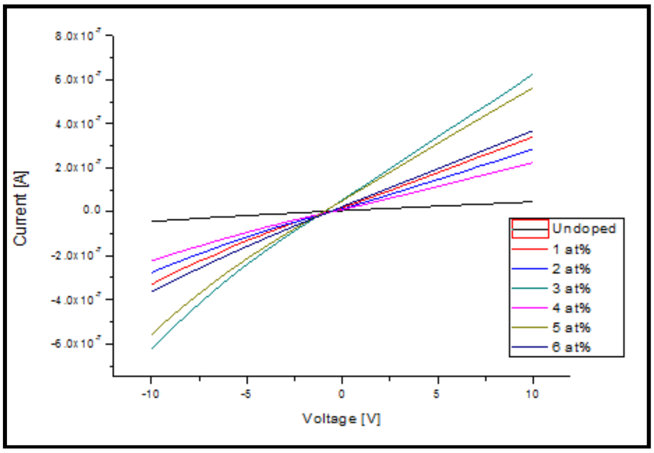

Figure 5. I-V curve for Nb-doped TiO_2 thin films at different doping concentration.

The relationship between resistivity value and Nb-doping concentration is shown in Figure 6. Resistivity of the thin films decreased with the increase of Nb doping concentration until a minimum point at 5.0 at.%. The resistivity is then increased at 6.0 at.%. Thus, the sample of 5.0 at.% is most conductive. This result is in agreement with previous result reported [10]. Another possible explanation is as study conducted by M.Z Musa et al. resulted in the same trend but the minimum resistivity was achieved at 8.0 at.% Nb doping concentration [11]. This discrepancy may be caused by preparation of solution or deposition process.

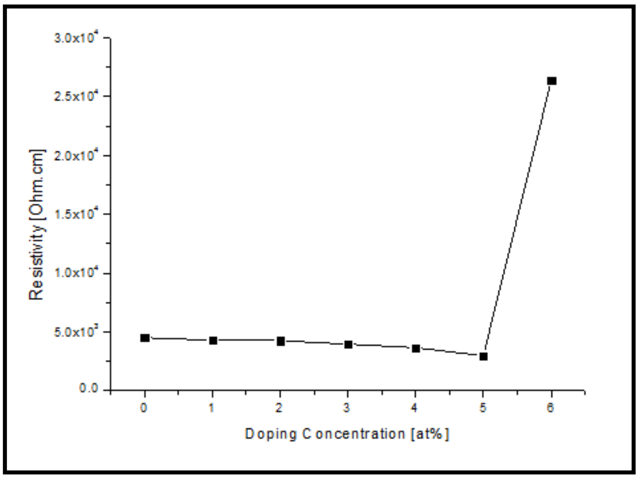

Figure 6. Resistivity for Nb-doped TiO_2 thin films at different doping concentration.

B. Optical Properties of TiO_2 Thin Films

Figure 7 present the transmittance spectra for undoped and Nb-doped TiO_2 thin films with different Nb doping concentration in the wavelength 300-800 nm. From Figure 7 it can be seen that all the films show high transmittance and exhibit 58-90% transmittance in the UV region and it starts absorbing in between wavelength 300 nm which corresponds to the energy band gap of Nb-doped TiO_2.

Plots of absorption coefficient versus wavelength are shown in Figure 8. The absorption coefficient was estimated from transmittance spectra. The absorption edge shifted towards lower wavelength side indicating the increase in the band gap of the Nb-doped TiO_2 thin films with increasing Nb doping concentration. This result is in agreement with previous result reported [7,12].

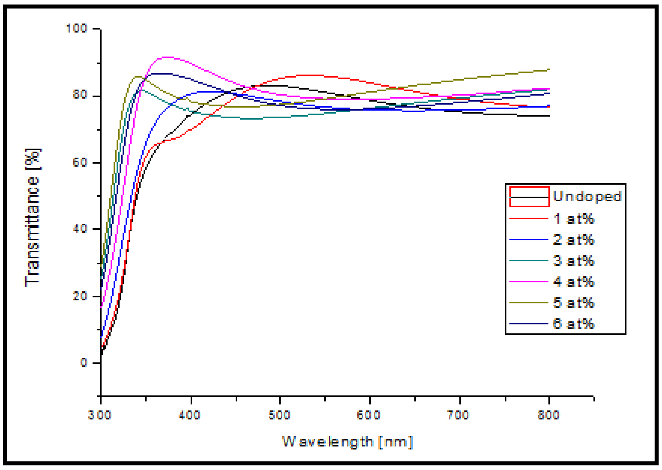

Figure 7. Transmittance spectra for TiO_2 thin films at different Nb doping concentration.

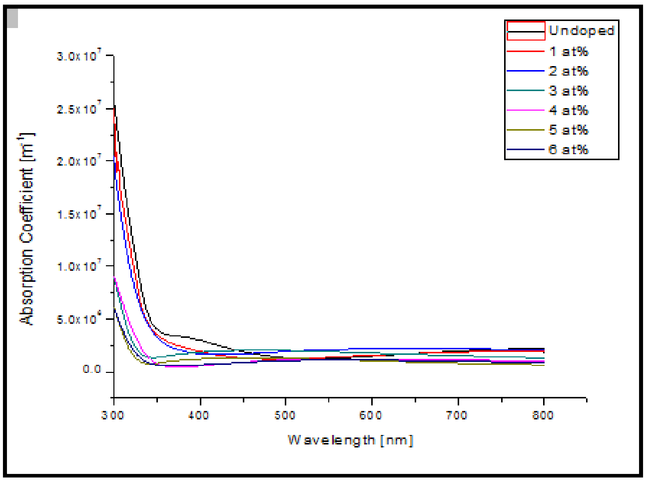

Figure 8. Absorption coefficient for TiO_2 thin films at different Nb doping concentration.

The optical band gap E_g was calculated using the Tauc equation (3).

$$\alpha h v = A(hv - Eg)½ \qquad (3)$$

Where α is an absorption coefficient and is a constant which estimated from the transmittance spectra using Newton Raphson [12]. The optical band gap of TiO_2 thin films is estimated from the energy $(E = hv)$ plot extrapolation of the linear plots of $(\alpha h v)$ ½ versus hv plot.

By increasing in Nb doping concentration band gap were increased from 3.28 to 3.61 eV and reaches the maximum value at 5.0 at.%. The band gap dropped to 3.55 eV at 6.0 at.%. Figure 9 shows band gap estimated for TiO_2 thin films at different Nb doping concentration.

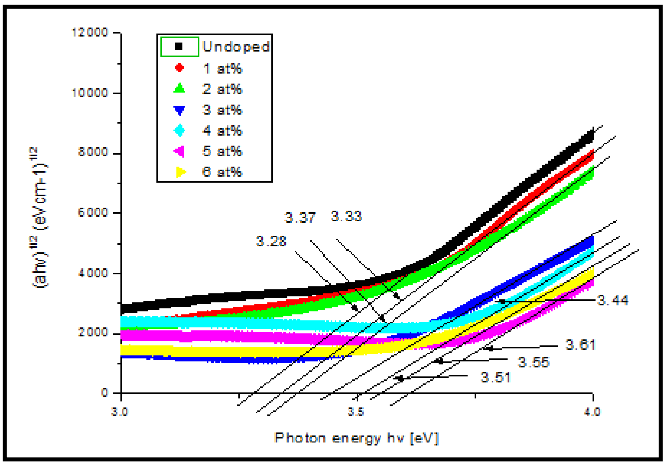

Figure 9. Optical band gap estimated for TiO_2 thin films at different Nb doping concentration.

C. Structural Properties (FESEM)

Figure 10 show FESEM image of different Nb doping concentration revealed that the morphology change with Nb doping. It can be observed that the thin films consist of nanometer-sized grain particles. As previously reported, the particles in Nb-doped TiO_2 thin films appears are more closely attached to each other and tend to agglomerated with increasing in Nb doping concentration compared to undoped TiO_2[11] .

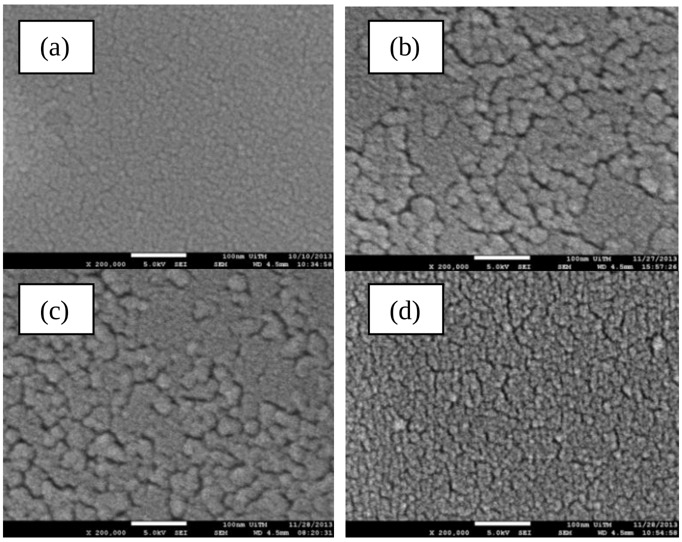

Figure 10. FESEM images at magnifier of 200kx with different Nb doping concentration at: (a) Undoped (b) 1 at. % (c) 3 at. % and (d) 5 at.%

IV. CONCLUSION

Titanium Dioxide thin films and Niobium (Nb)-doped Titanium Dioxide thin films have been successfully deposited on glass substrate by spin coating technique. The electrical properties of undoped TiO_2 thin films were investigated by I-V measurements and it shows that optimum annealing temperature is 450°C. The effect of Nb doping concentration (up to 6.0 at.%) on the I-V measurement, the optical properties and the structural has been examined. Doping at 5.0 at% shows the best doping concentration and higher band gap. All the thin films maintain high transmittance and exhibit 58-90% transmittance in the visible region. Also, as shown by FESEM technique the thin films consist of nanometer-sized grain particles and tend to agglomerated with increasing in doping concentration. All the characteristic of this thin film are favourable for electronic device application such as solar cell (DSSC) which is front layer.

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