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Deposition and Characterization of Cobalt doped Titanium Dioxide Thin Films using Sol-gel Method

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Abstract: Thin films become more importance and a lot of research and studies have been done toward the improvement and achievement. In this study, the new finding of deposition Cobalt (Co) doped TiO_2 thin films have been prepared by sol-gel method onto a glass substrate at room temperature for enhancement of optical properties. The effect of Co doped TiO_2 thin films have been studies. The different concentration of Co was varied from 1 wt %, 2 wt % and 3 wt % dopant. The deposition of Co doped TiO_2 was prepared by using sol-gel method and spin coating technique on the glass substrate. The obtained films have been annealed at 400 ºC, 500 ºC, and 600 ºC for 2 hours and were investigated. X-ray diffraction (XRD) peaks revealed that the films exhibit showed that Co:TiO_2 films are anatase crystalline structure at orientation (101). The surface morphologies of the Co:TiO_2 thin films were evaluated by Field Emission Scanning Electron Microscopy (FESEM) and Atomic Force Microscopy (AFM). The calcination temperature and content of Co dopant gave a different size of particle and grain boundary. Root Mean Squared (RMS) roughness values increase by increasing the molar ratio of dopant. While, as the calcination temperature increases, the RMS also increasing. The optical properties were studied by using UV-visible spectroscopy (UV-Vis) with a wavelength range of 300 nm to 1000 nm. The calculated optical band gap decreases with increasing of Co doping.

Keyword: Thin films; TiO_2; Co doped TiO_2; Sol gel method.

1. Introduction

Nowadays nanotechnology becomes more interests for the scientists and academicians as the size is very tiny [1]. Nanomaterials are known to have unique mechanical, thermal, biological, optical and chemical properties, and suitable for versatile industrial applications [1,2]. The thin films has received major research and engineering emphasis with a consistent change of the process for deposition and patterning over the last few decades [3]. The appearing of a material layer with a thickness between fractions of a single and multiple micrometers or thin films are obviously can be found everywhere [4]. The application and the used of thin films such as eyeglasses [5], microelectronics [6], drill bits and cutting tools [7], solar cells [8], mirrors [9], flat screens and windows [4]. Mechanical properties, optical properties, electrical properties [10] and heat transport are the functional properties that influenced by the microstructure of thin films [4]. Titanium dioxide (TiO_2) thin films is commonly studied as it has to appeal of photocatalytic properties [11]. Photocatalysis [2,12], photovoltaics [13], water purification [14] and thin films transistors [15] are the prospective of applications from TiO_2 thin films [16]. Instead of dye-sensitized solar cells [1] and photoelectrolytic cells [17], TiO_2 also being used in water treatment membranes because of the biocompatible [18] and photocatalytic [19]. Hence, in this study Co-TiO thin films had been synthesized using sol-gel method with spin coating technique on glass substrates and enhancement the structural and optical properties of the thin films.

2. Experimental Detail

Co:TiO_2 thin films was prepared using a sol-gel method where the Titanium butoxide

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($C_{16}H_{36}O_4Ti$) as the starting materials was added with butanol and stirrer for 30 minutes. Then, distilled water (H_2O) also being added into the mixture and stirrer again for 30 minutes. After the solutions have been stirrer for 30 minutes, glacial acetic acid as the stabilizer was added and stirrer for 30 minutes. Lastly, the cobalt hexahydrate was added into the solution to form Co-doped TiO_2 solutions. Then the mixer was stirred using hot plate magnetic stirrer at room temperature for 60 minutes. The sol-gel was aging for 24 hours before being coated into glass substrate. The thin films were deposited onto a glass substrate using sol-gel spin coated method. The Co-doped TiO_2 sol-gel on top of the substrate and the glass substrate will be coated as the coater wheel rotate. The speed of running process for the initial is 1000 rpm for 10 second and then 3000 rpm for 40 seconds for each layer. After five layers, the glass substrate being heated at 100 °C for 10 minutes by using oven. Then, another five layers on glass substrate to complete 10 layer for each thin films. To make sure the layer completely dry, the glass substrate was heated for 10 minutes at 100°C by using oven. The remaining solvent from Co:TiO_2 thin films was eliminated as the process of drying and calcination finished. The drying process using the conventional oven for 3 minutes at a temperature of 227 °C. The calcination process takes place using furnace box at 400 °C, 500 °C and 600 °C for 2 hours for each sample. From the observation, there is no effect on thin film such as crack or defect before the characterisation. The characterisation of Co:TiO_2 thin films was undergo several steps of analytical instruments which are X-ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), Atomic Force Microscope (AFM) and UV-Visible Spectroscopy (UV-Vis)

3. Results and Discussion

Structure of TiO_2 doped Cobalt thin film

The growth of Co:TiO_2 thin films were studied using XRD as shown in Fig. 1, Fig. 2, and **Error! Reference source not found.**. The XRD spectra of the thin films of TiO_2 after annealing at 400 °C, 500 °C and 600 °C for 1 wt%, 2 wt% and 3 wt% of Co respectively. Diffraction pattern observed from XRD machine matched with reference spectra JCPDS 01-086-1157 (structure: a = 3.78300 Å and c = 9.497Å). XRD analysis confirmed that the TiO_2 are present as the Co:TiO_2 thin films have an anatase phase located at peak at $2\theta = 25.322$ corresponds to anatase (101) crystal plane. Similar with the studies by Boutlala et.al (2016) [20], the (121) peak intensity increases with increasing concentration of cobalt. No peak has been detected corresponding to the brookite and rutile phase of TiO_2. However, the presence of Co was not shown in XRD analysis. Co cannot be detected by XRD analysis due to the small amount of doping. The EDS analysis was used to confirm the existence of Co. Studies by Boutlala [20] and Rengasamy et al [21] also cannot detect the present of Co by using XRD machine but by using Energy Dipersive Spectroscopy (EDS) the Co existed as the wt % is more than 10 wt %. Therefore, Co cannot be seen as the wt % is less than 10 wt % by using XRD or EDS**.**

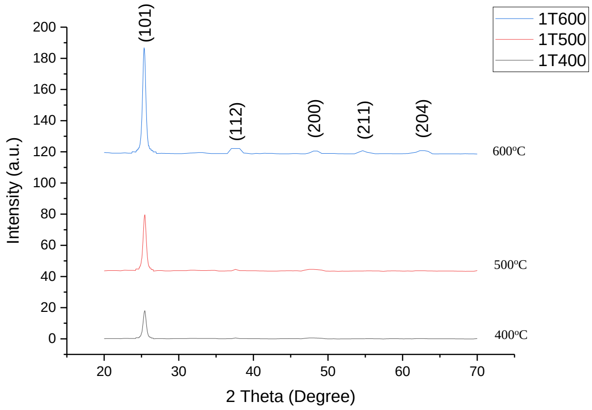


Fig. 1 XRD patterns of Co:TiO_2 thin film (1 wt% of Co) with different calcination temperature.

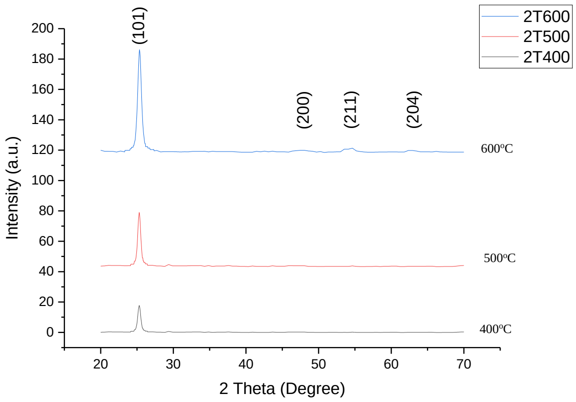


Fig. 2 XRD patterns of Co:TiO_2 thin film (2 wt% of Co) with different calcination temperature.

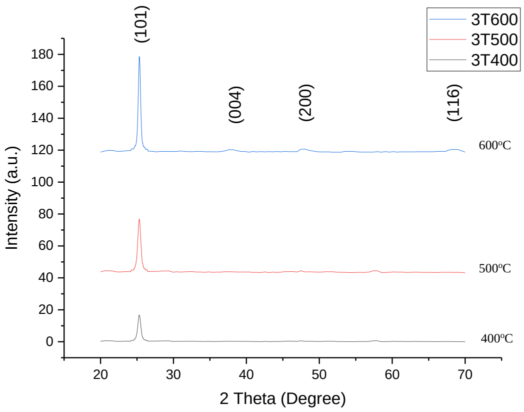
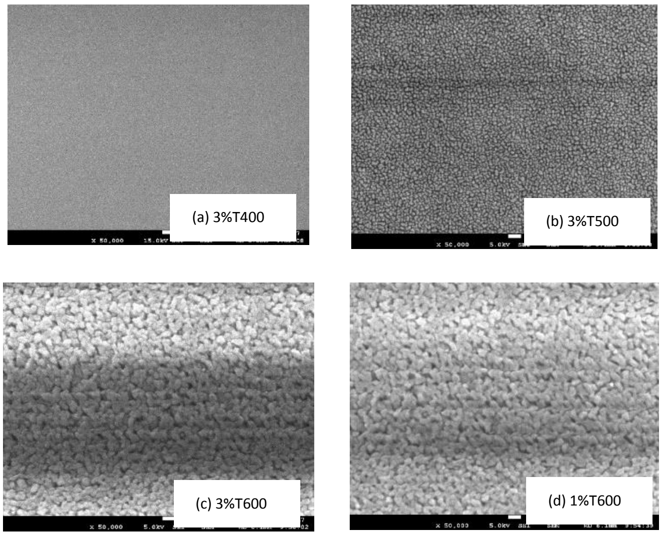


Fig. 3 XRD patterns of Co:TiO_2 thin film (3 wt% of Co) with different calcination temperature.

Nanostructure analysis

The nanostructure of Co:TiO_2 thin film was studied using FESEM. The images capture with scale of 100 nm and magnification of 50 000x as shown in **Error! Reference source not found.**. From the Fig. 4, as the calcination temperature increases, the particle and boundary are clearly can be seen. Using SEM micrograph shows the increases of the Co doping concentration, the particle growth bigger and the grain boundary size become smaller similarly with the studies by Rengasamy et.al. [21].



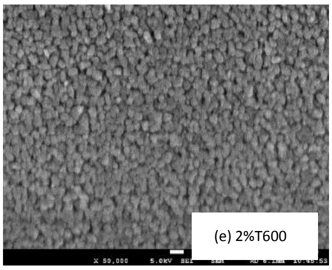
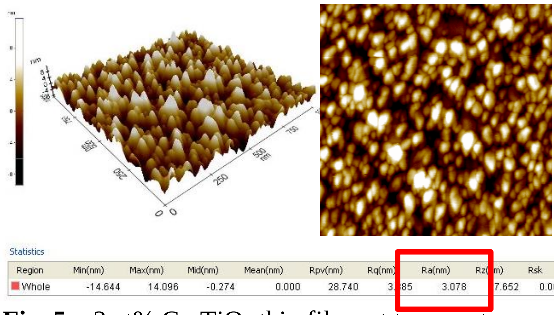


Fig. 4 FESEM micrograph at (a) 3 wt % with temperature 400 ºC, (b) 3 wt % with temperature 500 ºC, (c) 3 wt % with temperature 600 ºC, (d) 1 wt % with temperature 600 ºC and (e) 2 wt % with temperature 600 ºC

Morphology and roughness

The surface of Co:TiO_2 thin films was characterized by using AFM. Fig. 5 shows the 3D and 2D view of AFM images of surface morphology Co:TiO_2 thin films prepared on glass substrates and indicates a porous and fine structure with small size grains in anatase phase. From the studies by Boutlala et.al (2016) [20] also mentioned that the value of surface root means square (RMS) roughness of the Co:TiO_2 thin films shows the presence of small crystalline grains with spaces, the appearance of grains making the films to have higher surface roughness. Similarly with the study by Rengasamy et al. [21], the summary of the RMS shown in Table 1 shows that the RMS roughness values increases from 1.543 nm to 3.078 nm by increasing the molar ratio of dopant from 0 wt% to 3 wt%. While, as the calcination temperature increasing from 400 ºC to 600 ºC, the RMS also increasing from 0.236 nm to 3.078 nm.



Statistics

Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(m)	Rsk
Whole	-14.644	14.096	-0.274	0.000	28.740	3. 85	3.078	7.652	0.0

Fig. 5 3wt% Co:TiO_2 thin films at temperature 600ºC

Transmittance of Co:TiO_2 thin films

From Table 1, the optical transmittance is improved by increasing the value of Co dopant. The Co:TiO_2 thin films result as enhancement of the optical properties. The calcination temperature also give an influence of the increment of transmittance value as it formed better crystallite. From the research from A Boutlala et.al (2016) [20] with the increases the percentage of transmittance, this can be attributed on the one hand to the structural change and the increase in grain size to increase the values of extinction coefficient K with the rise in temperature.

As the calcination temperature increases, the band gap values also increase. The optical band gap is determined from the plotting of $(\alpha h\nu)^2$ versus photon energy (eV), the extrapolation intercepting the photon energy axis given the optical band gap (Eg) It varied between 3.32 eV to 3.16 eV. From Table 2, it is easy to notice that the gap value decreases with increasing temperature treatment. At this stage, the annealing temperature contributes to the reorganization of the structure and impurities that come to their sites more easily occupied when it rises and the decrease of band gap energy can be correlated with the grain size, which increases with temperature.

Table 1 Summary of the RMS value of Co:TiO_2 thin films

Calcination Temperature	Molar ratio of Co dopant	RMS (nm)
400°C	3%	0.236
500°C	3%	1.543
600°C	0%	1.127
	1%	2.491
	2%	2.345
	3%	3.078

Table 2 Summary of value of transmittance and band gap

Calcination Temperature	Molar ratio of Co dopant	Transmittance	Band Gap (eV)
400°C	1%	72	3.32
	2%	85	3.30
	3%	92	3.28
500°C	1%	70	3.30
	2%	75	3.26
	3%	83	3.22
600°C	1%	75	3.26
	2%	88	3.21
	3%	88	3.16

4. Conclusion and Recommendation

As the conclusion the XRD results obtained shows that the TiO_2 anatase structure found but Co cannot be detected using XRD as well as the EDS as the content of Co dopant is little. From the XRD result, it shows that by increasing the calcination temperature the intensity also increases but the intensity decreases as the content of Co dopant increasing. Therefore, the intensity affected by the calcination temperature and content of Co dopant. From the FESEM results, the calcination temperature and content of Co dopant gave a different size of particle and grain boundary. While the RMS from the analysis by AFM increases with calcination temperature and content of Co dopant increases.

References

[1] Devi, M. and Panigrahi, M.R. “Synthesis and Characterization of Mg Doped TiO_2 Thin Film For Solar Cell Application,” in *Int. J. Eng. Appl. Sci.*, (2015) pp. 1–7.

[2] Khataee, A. and Mansoori, G. A. Nanostructured Titanium Dioxide Materials: Properties, Preparation and Applications.. World Scientific Publishing Co. (2011)

[3] Henini, M. Handbook of Thin-Film Deposition Processes and Techniques, Vol. 31. No. 3 (2000).

[4] Magnfält, D. Fundamental Processes in Thin Film Growth (2014).

[5] Fujishima, A., Rao, T. N. and Tryk, D. A. “Titanium Dioxide Photocatalysis,” in *J. Photochem. Photobiol. C Photochem. Rev*., Vol. 1. No. 1 (2000) pp. 1–21.

[6] Mondal, S. and Kumar, A. “Tunable Dielectric Properties of TiO_2 Thin Film Based MOS Systems for Application in Microelectronics,” *Superlattices Microstruct*., (2016) pp. 1–10.

[7] Thampi, V. V. A., Bendavid, A. and Subramanian, B. “Nanostructured TiCrN Thin Films by Pulsed Magnetron Sputtering for Cutting Tool Applications,” *Ceram. Int*., vol. 42, no. 8, (2016) pp. 9940–9948.

[8] Yuan, C., Zhang, L., Liu, W. and Zhu, C. “Rapid Thermal Process to Fabricate Sb2Se3 Thin Film For Solar Cell Application,” *Sol. Energy,* Vol. 137 (2016) pp. 256–260.

[9] Yamada, Y. Miura, M. Tajima, K. Okada, M. Tazawa, M. and Yoshimura, K. “Optical Indices of Switchable Mirrors based on Mg-Y Alloy Thin Films in the Transparent State,” *Thin Solid Films*, Vol. 571, No. P3, (2014) pp. 712–714.

[10] Fallis, A. The Materials Science of Thin Films, Vol. 53, No. 9 (2013).

[11] Bensouici, F., Bououdina, M., Dakhel, A. A., Tala-Ighil, R., Tounane, M., Iratni, A., Souier, T., Liu, S., Cai, W., “Optical, Structural and Photocatalysis

Properties of Cu-doped TiO_2 Thin Films," *Appl. Surf. Sci.*, Vol. 2 (2016).

[12] Qin, H. L. Gu, G. B. and Liu, S. "Preparation of Nitrogen-doped Titania using Sol-gel Technique and its Photocatalytic Activity," *Mater. Chem. Phys*., Vol. 112, No. 2 (2008) pp. 346–352.

[13] Chen, C.-C. Chang, S. H. Chen, L.-C.,. Cheng, H.-M., Tseng, Z.-L. and Wu C.-G., "Manipulating Multicrystalline Grain Size in $CH_3NH_3PbI_3$ Thin Films for Application in Photovoltaics," *Sol. Energy*, Vol. 139 (2016) pp. 518–523.

[14] Arcadipane, E., Sanz, R., Miritello, M., Impellizzeri, G., Grimaldi, M. G., Privitera, V., and Romano L. "TiO_2 Nanowires on Ti Thin Film for Water Purification," Mater. Sci. Semicond. Process., Vol. 42 (2016) pp. 24–27.

[15] Liau, L. C.-K. and Lin, Y.-G. "Fabrication of Assembled ZnO/TiO_2 Heterojunction Thin Film Transistors using Solution Processing Technique," *Solid. State. Electron*., Vol. 103 (2015) pp. 54–58.

[16] Juma, A., Oja Acik, I., Oluwabi, A.T., Mere, A., Mikli, V., Danilson, M., and Krunks M. "Zirconium Doped TiO_2 Thin Films Deposited by Chemical Spray Pyrolysis," *Appl. Surf. Sci.*, Vol. 387 (2016) pp. 539–545.

[17] Kowalski, J. M. "Ceramic Electrodes for Photoelectrolytic Decomposition of Water," Vol. 7 (1981).

[18] Roy, P. Berger, S. and Schmuki, P. "TiO_2 nanotubes: Synthesis and applications," *Angew. Chemie - Int. E*d., Vol. 50, No. 13 (2011) pp. 2904–2939.

[19] Kim, J., Suh, D., Kim, C., Baek, Y., Lee, B., Kim, H. J., Lee, J. C., Yoon J. "A High-performance and Fouling Resistant Thin-film Composite Membrane Prepared via Coating TiO_2 Nanoparticles by Sol-gel-derived Spray Method for PRO Applications," Desalination, Vol. 397 (2016) pp. 157–164.

[20] Boutlala, A. Bourfaa, F. Mahtili, M. and Bouaballou, A. "Deposition of Co-doped TiO_2 Thin Films by Sol-gel Method," *IOP Conf. Ser. Mater. Sci. Eng.*, Vol. 108 (2016) pp. 12048.

[21] Renugadevi, R. Venkatachalam, T. Narayanasamy, R. and Dinesh Kirupha, S. "Preparation of Co Doped TiO_2 Nano Thin Films by Sol Gel Technique and Photocatalytic Studies of Prepared Films in Tannery Effluent," *Optik (Stuttg)*, Vol. 127, No. 20 (2016) pp. 10127–10134.