



## ANNEALING EFFECT ON THE PHOTOELECTROCHEMICAL PROPERTIES OF $\text{BiVO}_4$ THIN FILM ELECTRODES

(Kesan Sepuh Lindap terhadap Sifat Fotoelektrokimia Elektrod Filem Nipis  $\text{BiVO}_4$ )

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### Abstract

Monoclinic bismuth vanadate ( $\text{BiVO}_4$ ) thin film electrodes were fabricated on fluorine-doped tin oxide via aerosol-assisted chemical vapour deposition (AACVD). Annealing and without annealing effect of thin films were analysed by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), ultraviolet–visible spectrophotometry (UV-Vis) and current-voltage measurement. All  $\text{BiVO}_4$  thin films showed an anodic photocurrent. The sample of  $\text{BiVO}_4$  annealed at 400 °C exhibited the highest photocurrent density of 0.44  $\text{mA cm}^{-2}$  vs. Ag/AgCl at 1.23 V.

**Keywords:**  $\text{BiVO}_4$  thin film, AACVD, PEC water splitting, annealing

### Abstrak

Elektrod filem nipis monoklinik bismut vanadat,  $\text{BiVO}_4$  telah dianapkan pada substrat fluorin terdop-timah oksida melalui kaedah pemendapan bantuan-aerosol wap kimia (AACVD). Kesan sepuh lindap terhadap filem nipis dianalisis menggunakan pembelauan sinar-X (XRD), analisis mikroskop elektron imbasan pancaran medan (FESEM), spektrofotometer ultralembayung-nampak (UV-Vis) dan pengukuran arus-voltan. Semua sampel yang dihasilkan menunjukkan arusfoto anodik. Sampel  $\text{BiVO}_4$  yang melalui sepuh lindap pada suhu 400 °C menunjukkan ketumpatan arusfoto tertinggi iaitu 0.44  $\text{mA cm}^{-2}$  vs. Ag/AgCl pada 1.23 V.

**Kata kunci:** Filem nipis  $\text{BiVO}_4$ , AACVD, PEC pembelahan air, sepuh lindap

### Introduction

Practical semiconductor photoelectrodes for water splitting application have been receiving attention for several decades. The important aspect to make the photoelectrodes water splitting is the materials. The materials have to exhibit a direct bandgap excitation of visible light which then generates photocharge carriers [1,2]. In addition, the semiconductor materials should be abundant, affordable and have chemical and photochemical stability [2-4]. In order to obtain superior photo-conversion properties, the materials must have good charge mobility of one-dimensional structure thin films [5, 6]. Bismuth vanadate ( $\text{BiVO}_4$ ), which is an *n*-type photoanode with bandgap of 2.4 eV, has a suitable valence band position to photooxidize water and attracted attention as one of the promising photoanodes.

Chemical bath deposition [7], hydrothermal [8] and spin-coating [9] are general methods used to fabricate BiVO<sub>4</sub>. However, these methods frequently lead to non-homogenous coverage. Therefore, Aerosol-Assisted Chemical Vapour Deposition (AACVD) offers an alternative technique to synthesize thin films. Moreover, this method helps to control the porosity, crystallinity, agglomeration and chemical homogeneity by the parameters modification [10]. Furthermore, the films obtained by AACVD will have strong adhesion, owing to the droplet size precursor of the aerosol [11]. In this work, we fabricate BiVO<sub>4</sub> thin films using AACVD, and study the annealing effect on the photoelectrochemical properties of BiVO<sub>4</sub> thin films electrodes.

### Materials and Methods

Fluorine-doped tin oxide (FTO) glass substrates (TEC 8, ~8Ω/sq Pilkington) were used for this experiment. Initially, the FTO glass substrates were cleaned ultrasonically for 10 minutes in deionized water, acetone and isopropanol, and dried. Then, the FTO was placed on a hot plate at temperature 440~450 °C. 0.2 M of precursor was prepared from bismuth nitrate pentahydrate (Bi (NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O) and 0.2 M vanadylacetylacetonate (C<sub>10</sub>H<sub>14</sub>O<sub>5</sub>V) that were dissolved in ethylene glycol and methanol, respectively. Then, these two solutions were mixed homogeneously before the deposition process. To generate the aerosol, 20 ml of the precursor was added to a 50 ml round-bottom flask and immersed in the piezoelectric modulator of an ultrasonic humidifier. Each electrode was deposited for a period of 90 minutes, with a 1.2 cm distance from the nozzle to the substrate. Finally, the films were subjected to the annealing process at 400 °C, 500 °C and 600 °C, for 30 minutes in air.

The phases and crystalline structure of BiVO<sub>4</sub> films were analysed by XRD (model Bruker D8 Advance) in the 2θ range from 20° - 60°. Photoelectrochemical (PEC) measurement was carried out using a potentiostat/galvanostat Autolab PGSTAT 204, connected to a three-electrode configuration of a 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte, an Ag/AgCl (3M KCl) reference electrode and a Pt wire counter electrode, in a quartz container. The electrochemical measurement was conducted under dark and incident light intensity of 100 mWcm<sup>-2</sup>. PEC measurement was performed on a 1.0 cm<sup>2</sup> area of the working electrode. Optical absorbance spectra were performed using a PerkinElmer UV Winlab 6.0.2.0738 / Lambda35 1.27 spectrophotometer.

### Results and Discussion

The structure and crystallinity of BiVO<sub>4</sub> thin films are shown in Figure 1. The BiVO<sub>4</sub> diffraction peaks observed at 2θ = 28.82°, 30.55°, 34.50°, 35.22°, 39.78°, 42.47°, 46.71°, 47.31°, 50.32° and 53.25° affirm the samples have a monoclinic clinobisvanite BiVO<sub>4</sub> structure (JCPDs file No. 00-014-0688). This structure was photocatalytically active and most prevalent under normal conditions [12]. The intensity peak of the plane (-121) was slightly reduced when the annealing temperature was increased in the following order: as-deposited < 600 °C < 500 °C < 400 °C. The less pronounced diffraction peak intensity of FTO at (101) plane in BiVO<sub>4</sub> samples annealed at 400 °C, indicates that high compact films were obtained as the BiVO<sub>4</sub> thin films were overlapped with the FTO peak. The peak pattern for planes (110), (200) and (211) showed similar behaviour for the same reason. In contrast, the sudden increase in the diffraction peak of the (101) plane at 500 °C and 600 °C was caused by the fade yellow of BiVO<sub>4</sub> films formation as the annealing temperatures were increased. The yellowish BiVO<sub>4</sub> thin films started to fade when the annealing temperature was 500 °C, and the films were almost transparent at 600 °C. Hence, diffraction peaks of FTO became dominant at these elevated temperatures. Moreover, the result obtained from XRD can be used to calculate the grain size of BiVO<sub>4</sub> using a Sherrer equation 1 as follows:

$$Grain\ size = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where, λ is the X-ray wavelength of 0.15406 nm, β is the full width at half-maximum (FWHM) of the (-121) diffraction peak, θ is the Bragg angle, and k is a constant. Table 1 shows the increase in grain size with the increase in annealing temperature. Although all samples showed a crystalline monoclinic phase based on the XRD pattern, the half-widths and intensities of the peaks show small variations in the structural parameters of the thin films [13].

Table 1. Crystallite size and photocurrent density of as-deposited, annealed at 500, 550 and 600 °C of BiVO<sub>4</sub> thin films.

Sample	Crystallite size (Å)	J <sub>sc</sub> (mA/cm <sup>2</sup> ) at 1.23 V
As-deposited	211.1	0.20
500 °C	236.4	0.07
550 °C	260.1	0.04
600 °C	293.1	0.01

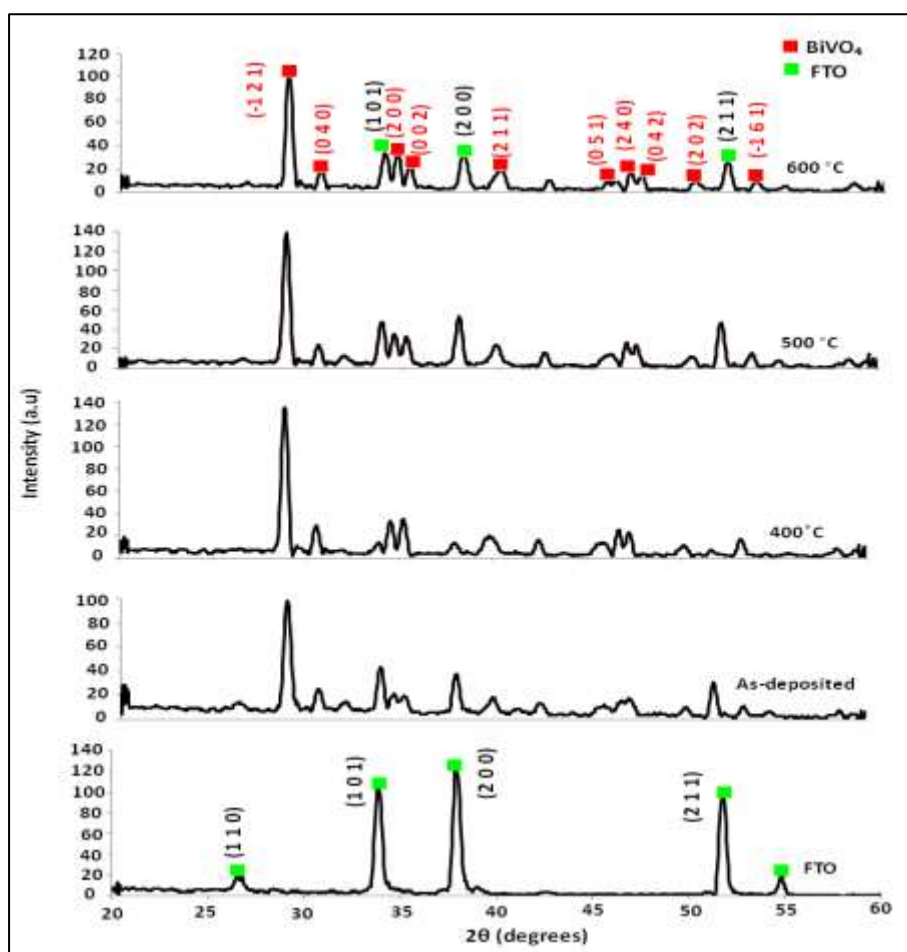


Figure 1. X-ray diffraction (XRD) peaks of FTO and BiVO<sub>4</sub> thin films

The effect of annealing temperature on PEC performance of  $\text{BiVO}_4$  was recorded by a three-electrode configuration, using a 1.5 AM solar simulator. From the plot of the photocurrent density as a function of the applied voltage (Figure 2), the highest photocurrent density was obtained by  $\text{BiVO}_4$  that were subjected to the annealing treatment at 400 °C. As can be seen in Figure 2, the  $\text{BiVO}_4$  shows a good photocatalytic response both under dark and visible light irradiation. The characteristic pattern of the photocurrent clearly shows that  $\text{BiVO}_4$  produced higher anodic potential (n-type). However, the photocurrent density decreased significantly from  $0.07 \text{ mAcm}^{-2}$  to  $0.01 \text{ mAcm}^{-2}$ , when the annealing temperature increased to 600 °C, as shown in Table 1. As discussed earlier, samples annealed at 600 °C produced more transparent films than others. Therefore, less amount of light was absorbed by  $\text{BiVO}_4$  films [14]. In addition, the light screening effect of FTO (owing to the high transparency of samples annealed at 600 °C) also contributed to the photocurrent reduction [15].

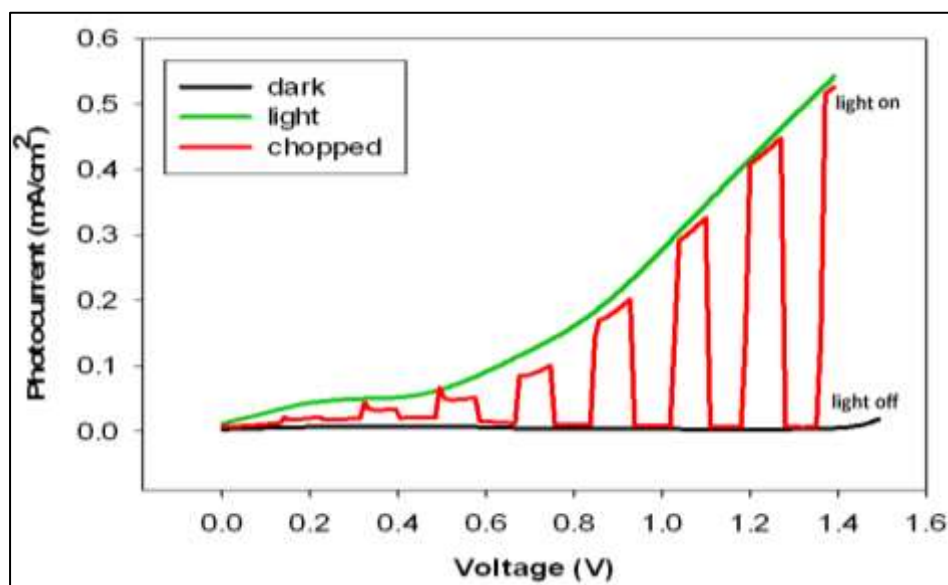


Figure 2. Photocurrent densities under dark, simulated and chopped conditions in 1 M  $\text{NaSO}_4$  vs.  $\text{Ag/AgCl}$  (3M  $\text{KCl}$ ) of  $\text{BiVO}_4$  annealed at 400 °C

The optical characterization of  $\text{BiVO}_4$  thin films was studied using UV-Vis spectroscopy. The absorbance spectra (Figure 3) shows the absorption edge  $\sim 537 \text{ nm}$  of  $\text{BiVO}_4$  thin films annealed at 400 °C. The bandgap estimation was calculated using a Tauc plot derived from UV-Vis absorbance spectra, which corresponds to the bandgap energy of 2.31 eV, as shown in the inset of Figure 3. This value is close to the bandgap energy of  $\text{BiVO}_4$  (2.4 eV) [16].

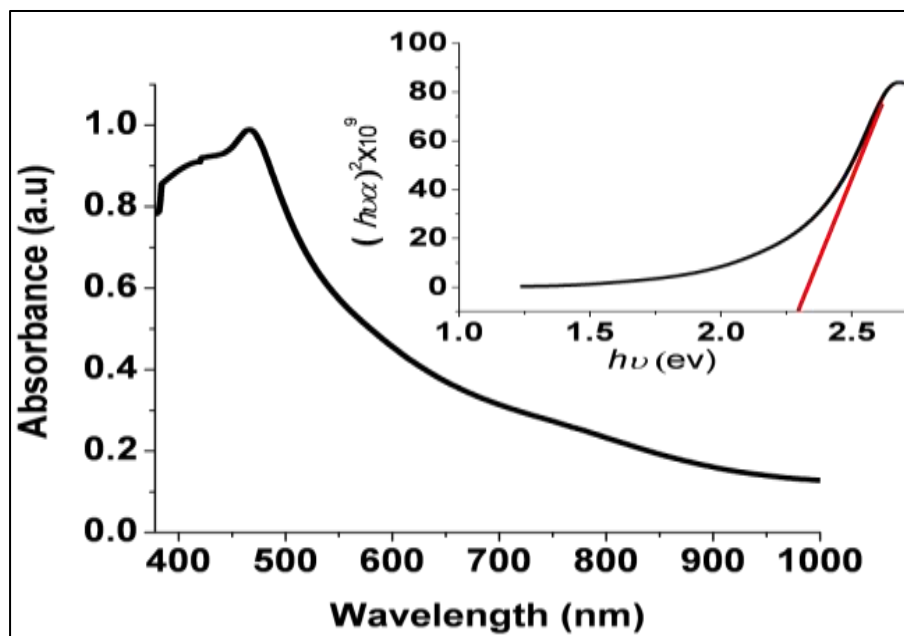


Figure 3. Absorbance of BiVO<sub>4</sub> annealed at 400 °C film and estimation of bandgap by Tauc plot

#### Conclusion

BiVO<sub>4</sub> thin films with a monoclinic structure were prepared successfully using aerosol-assisted chemical vapour deposition (AACVD). The BiVO<sub>4</sub> thin films that were subjected to the annealing treatment in air at different temperature exhibited an anodic photocurrent and were photoelectrochemically active. PEC performance of the samples annealed at 400 °C showed an increased photocurrent density than the samples annealed at 500 °C, 600 °C and as-deposited. It is believed that the photoelectroactivity properties can be improved further by the optimization of various parameters, in order to obtain effective and ideal photoelectrodes.

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#### References

1. Osterloh, F. E. and Parkinson, B. A. (2011). Recent developments in solar water-splitting photocatalysis. *MRS Bull.*, 36 (1): 17 - 22.
2. Lewis, N. S., Walter, M. G., Warren, E. L., McKone, J. R., Boettcher, S. W., Mi, Q. and Santori, E. A. (2010). Solar Water Splitting Cells. *Chem. Rev.*, 110 (11): 6446 - 6473.
3. Chen, Z., Jaramillo, T. F., Deutsch, T. G., Kleiman-Shwarsstein, A., Forman, A. J., Gaillard, N., Garland, R., Takanabe, K., Heske, C., Sunkara, M., McFarland, E. W., Domen, K., Miller, E. L., Turner, J. A. and Dinh, H. N. (2010). Accelerating materials development for photoelectrochemical hydrogen production: Standards for methods, definitions, and reporting protocols. *J. Mater. Res.*, 25 (1): 3 - 16.
4. Turner, J., Sverdrup, G., Mann, M.K., Maness, P-C., Kroposki, B., Ghirardi, M. and Blake, D. (2008). Renewable hydrogen production. *Int. J. Energy Res*, 32(5): 379 - 407.
5. Thimsen, P. B. E., Rastgar, N. 2008. Nanostructured TiO<sub>2</sub> Films with Controlled Morphology Synthesized in a Single Step Process: Performance of Dye-Sensitized Solar Cells and Photo Water splitting. *J. Phys. Chem. C.*, 112 (11): 4134 - 4140.
6. Roel van de Krol, J. S. and Liang, Y. (2008). Solar hydrogen production with nanostructured metal oxides. *J. Mater. Chem.*, 18 (20): 2311 - 2320.

7. Neves, M. C. and Trindade, T. (2002). Chemical bath deposition of BiVO<sub>4</sub>. *Thin Solid Films.*, 406 (1-2): 93 - 97.
8. Zhou, Y., Vuille, K., Heel, A., Probst, B., Kontic, R., Patzke, G. R. 2010. An inorganic hydrothermal route to photocatalytically active bismuth vanadate. *Appl. Catal. A Gen.*, 375(1): 140 - 148.
9. Parmar, K. P. S., Kang, H. J., Bist, A. Dua, P. and Jang, J. S. and Lee, J. S. (2012). Photocatalytic and Photoelectrochemical Water Oxidation over Metal-Doped Monoclinic BiVO<sub>4</sub> Photoanodes. *ChemSusChem.* 5, (10): 1926 - 1934.
10. Swihartm M. T. (2003). Vapor-phase synthesis of nanoparticles. *Curr. Opin. Coll. Int. Sci.*, **8**(1): 127 - 133.
11. Palgrave, R. G. and Parkin, I. P. (2006). Aerosol assisted chemical vapor deposition using nanoparticle precursors: a route to nanocomposite thin film. *J. Am. Chem. Soc.*, 128 (5): 1587 - 1597.
12. Tokunaga, S., Kato, H. and Kudo, A. (2001). Selective Preparation of Monoclinic and Tetragonal BiVO<sub>4</sub> with Scheelite Structure and Their Photocatalytic Properties. *Chem. Mater.*, **13** (12): 4624 - 4628.
13. Thalluri, S. R. M., Virga, A., Russo, N. and Saracco, G. (2013). Insights from Crystal Size and Band Gap on the Catalytic Activity of Monoclinic BiVO<sub>4</sub>. *Int. J. Chem. Eng. Appl.*, **4** (5): 305 - 309.
14. Seabold, J.A., Zhu, K. and Neale, N. R. (2014). Efficient solar photoelectrolysis by nanoporous Mo: BiVO<sub>4</sub> through controlled electron transport. *Phys Chem Chem Phys*, **16**(3): 1121 - 1131.
15. Jeon, T.H. and Park, H. (2011). Cobalt – Phosphate Complexes Catalyze the Photoelectrochemical Water Oxidation of BiVO<sub>4</sub> Electrodes Water Oxidation of BiVO<sub>4</sub> Electrodes. *Phys. Chem. Chem. Phys.*, 13(48): 21392 - 21401.
16. Baoping Xie, Y. X., Zhang, H., Cai, P. and Qiu, R. (2006). Simultaneous photocatalytic reduction of Cr(VI) and oxidation of phenol over monoclinic BiVO<sub>4</sub> under visible light irradiation. *Chemosphere*, **63**(6): 956 - 963.