様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　３ 年　 ６ 月 １４ 日現在

機関番号：１２１０２
研究種目：基盤研究(C)（一般）
研究期間：2018～2020
課題番号：１８Ｋ０５０１０

研究課題名（和文）Study of group-IVB metal doped BiVO4 thin-films for development of a highly efficient Z-Scheme photocatalyst

研究課題名（英文）Study of group-IVB metal doped BiVO4 thin-films for development of a highly efficient Z-Scheme photocatalyst

研究代表者
ＩＳＬＡＭ　ＭＯＮＩＲＵＬ（Islam, Monirul）

筑波大学・数理物質系・助教

研究者番号：３０７３９７１９

交付決定額（研究期間全体）：（直接経費）　　2,900,000円

研究成果の概要（和文）：将来のエネルギー源として期待される水素の生成を目指し、BiVO4 酸素 (O2) 発生光触媒の研究を行ってきました。 特に、光学特性、結晶構造、および光触媒性能に対する、BiVO4 材料へのジルコニウム (Zr) のドーピングの影響を研究しました。 n型伝導性を高めるBiVO4のBiサイトにZrが置換されていることを確認しています。 BiVO4 中の Zr の最適化されたドーピングは、Mo ドープ サンプルと比較してより多くの O2 を生成することにより、より良いパフォーマンスをもたらします。 さらに、スパッタリング法を使用して、Zr ドープ BiVO4 薄膜を作製することに成功しました。

研究成果の学術的意義や社会的意義
Understanding of doping mechanism of Zr in BiVO4 has academic interest for the enhancement of photo-catalytic performance. Development of BiVO4 photocatalyst will pave way to reduce dependence of carbon-di-oxide-emitting fossil fuels, and open path for the establishment of hydrogen society.

研究成果の概要（英文）：We have studied BiVO4 oxygen (O2) evolution photocatalyst in aiming for the production of hydrogen, which is considered as future source of energy. In particular we have studied effect of zirconium (Zr), molybdenum (Mo) and titanium doping in BiVO4 materials on the optical properties, crystal structure and photocatalytic performance. We have confirmed that Zr is substituted on Bi site in BiVO4 enhancing n-type conductivity. Optimized doping of Zr in BiVO4 results in better performance by generating more O2 comparing to Mo-doped samples. In addition, We have confirmed and made a model for the recombination mechanism in the BiVO4 crystals. Furthermore, we have successfully used sputtering methods to fabricate Zr and Mo-doped BiVO4 thin films from a single BiVO4 target. Thus scalable production of BiVO4 in industry level should be possible for photocatalytic application.

研究分野：Energy Materials and devices, Defect Study

キーワード：Photocatalyst　oxygen evolution　Hydrogen society　Photocarrier dynamics　zirconium doping　Defect study

１．研究開始当初の背景

Bismuth vanadate ($BiVO_4$), an *n*-type metal oxide semiconductor is a potential photoanode for oxygen (O_2) production through water splitting due to its suitable band-gap of ~ 2.4 eV. However, actual solar-to-hydrogen (STH) conversion of $BiVO_4$ is below the theoretical limit. This is mainly due to recombination losses, poor electron transport properties, and slow hole transfer kinetics in this material, which result in lower extraction of photo-generated electron-hole pairs in the $BiVO_4$ based system. Doping with group IV element, *e.g.*, with zirconium (Zr), thereby, enhancing conductivity are among some options to enhance performance.

２．研究の目的

In our study we aim to understand photocarrier dynamics and recombination mechanism in **$BiVO_4$ (BVO).** We also have investigated the doping mechanism of Zr in $BiVO_4$ host crystals as well as_mechanism of how Zr enhance photocatalytic activities in BVO. Results were compared with other dopant like molybdenum (Mo). In addition, to reduce photo corrosion, and also to make hetero structure, we have fabricated vacuum deposited BVO in thin films doped with Zr. Finally, to complete Z-scheme photocatalyst structure with BVO we also deposited suitable p-type thin films like $Cu(In,Ga)Se_2$.

３．研究の方法

BVO powders were prepared via liquid−solid reaction, whereas BVO thin films were deposited through electrodeposition as well as sputtering methods. Crystal structure was studied by x-ray diffraction method (XRD). Photo-carrier recombination in BVO was studied using steady-state photoluminescence (PL) and time-resolved photoluminescence measurements (TRPL) using a femtosecond Ti: sapphire laser with 400 nm of wavelength in continuous wave and pulsed wave with width of ~80 fs, respectively. X-ray absorption spectra (XANES) around the Zr K-edge (~17,998 eV) and extended X-ray absorption fine structure (EXAFS) were conducted using at 12C beamline at Photon Factory (PF) in Tsukuba, Japan.

４．研究成果

a) **Photocatalytic activity of Zr doped and Undoped BVO:**

Photocatalytic activity increases with an increase of Zr doping level until an optimum amount of 0.1 mol.% keeping the monoclinic crystal structure as observed from XRD. Higher Zr doping beyond 0.1 mol.% deteriorate the activity, mainly due to phase transition to the tetragonal structure [1,2].

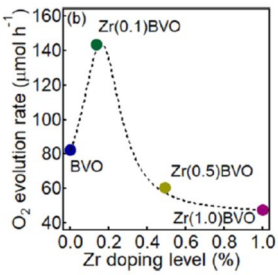

Fig. 1. Photocatalytic O_2 evolution of undoped and Zr doped BVO with different dopant level in mol% inside parenthesis.

b) **Photocarrier recombination in BVO:**

Carrier recombination dynamics in BVO was investigated using temperature-dependent, steady-state, and time-resolved PL. We developed a model showing that radiative recombination in BVO occurs through donor-to-acceptor transition (DAP), associated with shallow acceptor levels around 35 and 115 meV, above the valence band, and donor levels around 655 and 575 below the conduction band. Effective lifetimes (τ) of minority carrier were found in the

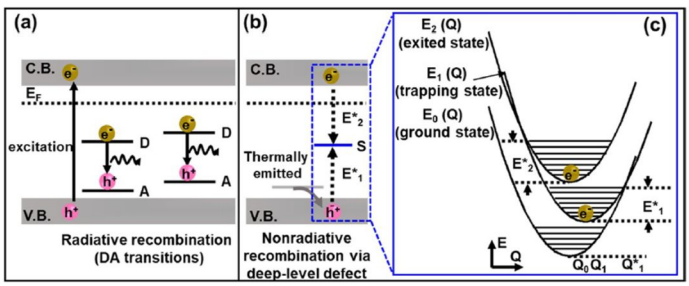

Fig. 2. Photocarrier dynamics in BVO. (a) The radiative recombination via DAP, (b) Thermal quenching of PL due to escape of holes from the shallow acceptor-levels, (c) Configuration Coordinate diagram showing capture process of the photocarrier by a deep-level defect.

order of nanoseconds, which is far behind the ideal radiative lifetime of 6 µs, calculated theoretically. This phenomenon suggests that the photocarrier recombination in BVO occurs predominantly through multiphonon nonradiative recombination, via deep level defects [3].

c) **Mechanism of Zr incorporation in BVO host crystal:**

Extended X-ray absorption fine structure (EXAFS) along with X-ray absorption near edge structure (XANES) at Fig. 3 suggests that Zr is incorporated as a substitute on Bi site in BVO enhancing n-type conductivity (until optimum amount of 0.1 mol. %) [1].

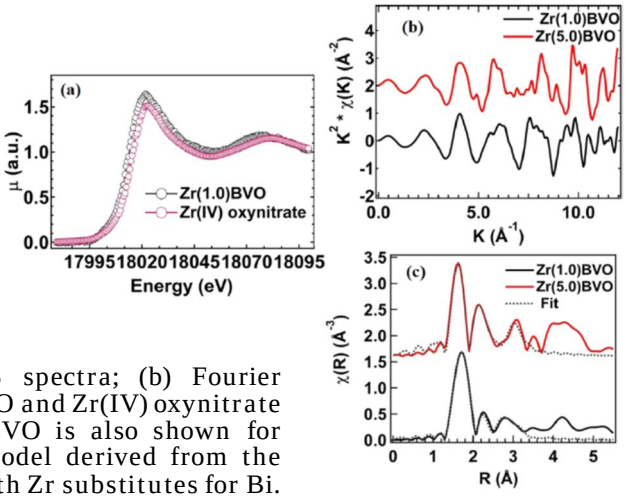

Fig. 3. (right): (a) Zr k-edge XANES spectra; (b) Fourier transformed K^2 Zr EXAFS of Zr(1.0)BVO and Zr(IV) oxynitrate reference samples. EXAFS of Zr(5.0)BVO is also shown for comparison. The data were fit to a model derived from the monoclinic scheelite structure of BVO with Zr substitutes for Bi.

d) Effect of Zr on the photoexcited carrier recombination in BVO:

Although incorporation of optimum amount of Zr at Bi-sites in improved activity, due to ionic radius difference, Zr incorporation causes local distortion, leading to large formation of O_{vac} and possibly ZrBi-O_{vac} defect complexes ⇒ low donor efficiency (self compensation), increased nonradiative recombination and small hole diffusion length. Sub-gap absorption in the Fig. 4 is associated with Zr-oxygen vacancy defect complexes [1].

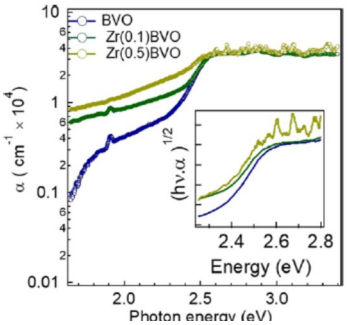

Fig. 4.: Absorption coefficients as functions of incident photon energy for undoped BVO and Zr(0.1)BVO powders, calculated from reflectance and transmittance measurements. The inset is Tauc plot derived from absorption spectra.

e) Sputtering of BVO from single target:

We have done Monte Carlo simulation to study effect of RF Power on the ratio of Bi and V in $BiVO_4$ Films sputtered from single target. BVO films with monoclinic scheelite crystal structures were obtained at high RF power and found to exhibit comparable photocatalytic performances as shown in Fig. 5 [4].

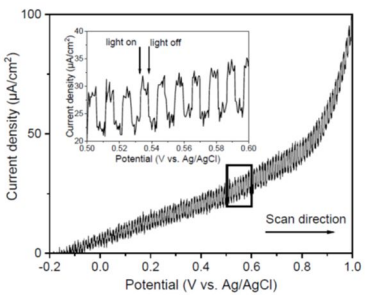

Fig. 5. Chopped LSV of BVO film deposited on FTO at 200 W in an electrolyte containing 0.02 mol/L Na_2S and 0.02 mol/L Na_2SO_3 hole scavengers under simulated sunlight (AM 1.5G).

References:

[1] I. Abdellaoui, **M. M. Islam**, et al. *Mechanism of Incorporation of Zirconium into $BiVO_4$ Visible-Light Photocatalyst*, J. Phys. Chem. C 125 (2021) 3320.

[2] Imane Abdellaoui, Doctoral Thesis, *Study on Optoelectronic Properties of BiVO4 for Photocatalytic Applications,* March 2021, Graduate School of Pure and Applied Sciences, University of Tsukuba.

[3] I. Abdellaoui, **M. M. Islam et al.**, *Photocarrier Recombination Dynamics in $BiVO_4$ for Visible Light-Driven Water Oxidation*, The Journal of Physical Chemistry C, 124 (2020) 3962.

[4] J. Liu, K. Tajima, I, **M. M. Islam et al.**, *Effect of Radio-Frequency Power on the Composition of $BiVO_4$ Thin-Film Photoanodes Sputtered from a Single Target*, Energies 14 (2021) 2122.

５．主な発表論文等

〔雑誌論文〕　計9件（うち査読付論文　9件／うち国際共著　8件／うちオープンアクセス　1件）

１．著者名 I. Abdellaoui, M.M. Islam, M. Remeika, Y. Higuchi, T. Kawaguchi, T. Harada, C. Budich, T. Maeda, T. Wada, S. Ikeda, and T. Sakurai	４．巻 124
２．論文標題 Photocarrier Recombination Dynamics in BiVO4 for Visible-Light Driven Water Oxidation	５．発行年 2020年
３．雑誌名 J. Phys. Chem. C	６．最初と最後の頁 3962-3972
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.jpcc.9b10621	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Alban Lafuente-Sampietro, Jingdong Chen, Shenghao Wang, Xia Hao, Muhammad Monirul Islam, Takuya Kato, Hiroki Sugimoto, Katsuhiro Akimoto, and Takeaki Sakurai	４．巻 12
２．論文標題 Wavelength-dependent I-V characteristics of CuIn1-x Ga x (S,Se)2 solar cells and carrier recombination	５．発行年 2019年
３．雑誌名 Applied Physics Express	６．最初と最後の頁 061001-(1-6)
掲載論文のDOI（デジタルオブジェクト識別子） 10.7567/1882-0786/ab1ad8	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 Ikeda Shigeru、Kawaguchi Takato、Higuchi Yui、Kawasaki Naoto、Harada Takashi、Remeika Mikas、Islam Muhammad M.、Sakurai Takeaki	４．巻 6
２．論文標題 Effects of Zirconium Doping Into a Monoclinic Scheelite BiVO4 Crystal on Its Structural, Photocatalytic, and Photoelectrochemical Properties	５．発行年 2018年
３．雑誌名 Frontiers in Chemistry	６．最初と最後の頁 266 (1-6)
掲載論文のDOI（デジタルオブジェクト識別子） 10.3389/fchem.2018.00266	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

１．著者名 Islam Muhammad Monirul、Wang Shenghao、Ishizuka Shogo、Shibata Hajime、Niki Shigeru、Akimoto Katsuhiro、Sakurai Takeaki	４．巻 57
２．論文標題 Deep level emission in polycrystalline CuGaSe2 thin-films observed by micro-photoluminescence	５．発行年 2018年
３．雑誌名 Japanese Journal of Applied Physics	６．最初と最後の頁 08RC02～08RC02
掲載論文のDOI（デジタルオブジェクト識別子） 10.7567/JJAP.57.08RC02	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 Islam Muhammad Monirul、Ishizuka Shogo、Shibata Hajime、Niki Shigeru、Akimoto Katsuhiro、Sakurai Takeaki	4．巻 10
2．論文標題 Characterization of Defect Properties in Wide-Gap CuGaSe2 Thin-Film Solar-Cells	5．発行年 2018年
3．雑誌名 Nanoscience and Nanotechnology Letters	6．最初と最後の頁 559～564
掲載論文のDOI（デジタルオブジェクト識別子） 10.1166/nnl.2018.2672	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 Abdellaoui Imane、Islam Muhammad Monirul、Sakurai Takeaki、Hamzaoui Saad、Akimoto Katsuhiro	4．巻 179
2．論文標題 Impurities removal process for high-purity silica production from diatomite	5．発行年 2018年
3．雑誌名 Hydrometallurgy	6．最初と最後の頁 207～214
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.hydromet.2018.06.009	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 Ando Yuta、Ishizuka Shogo、Wang Shenghao、Chen Jingdong、Islam Muhammad Monirul、Shibata Hajime、Akimoto Katsuhiro、Sakurai Takeaki	4．巻 57
2．論文標題 Relationship between bandgap grading and carrier recombination for Cu(In,Ga)Se2-based solar cells	5．発行年 2018年
3．雑誌名 Japanese Journal of Applied Physics	6．最初と最後の頁 08RC08～08RC08
掲載論文のDOI（デジタルオブジェクト識別子） 10.7567/JJAP.57.08RC08	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

1．著者名 Wang Shenghao、Hao Xia、Islam Muhammad Monirul、Kato Takuya、Sugimoto Hiroki、Akimoto Katsuhiro、Sakurai Takeaki	4．巻 57
2．論文標題 Influence of potassium treatment on electronic properties of Cu(In1-xGax)(Se1-ySy)2 solar cells studied by steady state photo-capacitance and admittance spectroscopy	5．発行年 2018年
3．雑誌名 Japanese Journal of Applied Physics	6．最初と最後の頁 08RC13～08RC13
掲載論文のDOI（デジタルオブジェクト識別子） 10.7567/JJAP.57.08RC13	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

１．著者名 後藤 彩子 原田 隆史 中西 周次; Islam Muhammad Monirul, 櫻井 岳暁 , 池田 茂	４．巻 65
２．論文標題 水の光電気化学的酸化分解に活性な BiVO4薄膜光電極への Zr 添加効果	５．発行年 2018年
３．雑誌名 甲南大学紀要．理工学編	６．最初と最後の頁 11~16
掲載論文のDOI（デジタルオブジェクト識別子） なし	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 －

〔学会発表〕　計12件（うち招待講演　1件／うち国際学会　6件）

１．発表者名 Muhammad Monirul Islam
２．発表標題 Study of BiVO4 photocatalysts for application as anodes in photoelectrochemical water splitting system
３．学会等名 Tunisia-Japan Symposium on Science, Society and Technology (TJASSST 2019), Nov- 29- Dec 2, 2019（招待講演）（国際学会）
４．発表年 2019年

１．発表者名 Imane Abdellaoui
２．発表標題 Recombination Mechanism in BiVO4 Photocatalyst Studied by Photoluminescence
３．学会等名 The 80th JSAP Autumn Meeting 2019, September 18th -21th, 2019, Sapporo Campus, Hokkaido University, Japan
４．発表年 2019年

１．発表者名 田島 和哉
２．発表標題 RF スパッタリング法による BiVO4薄膜成長法の検討
３．学会等名 第67回応用物理学会春季学術講演会
４．発表年 2020年

１．発表者名
Muhammad Monirul Islam

２．発表標題
Study of Si-layers on graphite-substrates obtained through electrochemical reduction of silica powder

３．学会等名
2019 International Conference on Solid State Devices and Materials (SSDM 2019), Sep 2-5, 2019（国際学会）

４．発表年
2019年

１．発表者名
Said Hajer

２．発表標題
Microstructural investigation of Silicon films electrochemically deposited on carbon materials

３．学会等名
Tunisia-Japan Symposium on Science, Society and Technology (TJASSST 2019), Nov- 29- Dec 2, 2019（国際学会）

４．発表年
2019年

１．発表者名
A. Imane, Kazuya Tajima, Mikas Remeika, Shigeru Ikeda, Takato Kawaguchi, Muhamed Islam Monirul, Takeaki Sakurai

２．発表標題
Relationship between synthesis temperature and the photocatalytic activity of BiVO4

３．学会等名
2019年第66応用物理学会 春季学術講演会

４．発表年
2019年

１．発表者名
K. Tajima, I. Abdellaoui, M. Remeika, S. Ikeda, T. Kawaguchi, M.M. Islam, T. Maeda, T. Kusumoto, T. Wada, C. Budich, T. Sakurai

２．発表標題
Enhanced photocatalytic activity of monoclinic BiVO4 via Zr doping.

３．学会等名
甲南学園100周年記念国際科学シンポジム

４．発表年
2019年

１．発表者名
I. Abdellaoui, K. Tajima, M. Remeika, S. Ikeda, T. Kawaguchi, M.M. Islam, T. Maeda, T. Kusumoto, T. Wada, C. Budich, T. Sakurai

２．発表標題
Structural and Electrical Properties of Zr doped ms-BiVO4.

３．学会等名
多元系化合物・太陽電池研究会　年末講演会

４．発表年
2018年

１．発表者名
I. Abdellaoui, M. Remeika, S. Ikeda, T. Kawaguchi, M.M. Islam, T. Maeda, T. Kusumoto, T. Wada, C. Budich, T. Sakurai

２．発表標題
Effect of zirconium doping on the structural and optical properties of BiVO4

３．学会等名
2018年第79応用物理学会 秋季学術講演会

４．発表年
2018年

１．発表者名
Takato Kawaguchi, Yui Higuchi,a Naoto Kawasaki, Takashi Harada, Mikas Remeika, Muhammad Monirul Islam, Takeaki Sakurai, and Shigeru Ikeda

２．発表標題
Photocatalytic and photoelectrochemical properties of zirconium-doped bismuth vanadate

３．学会等名
The 8th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT8) (国際学会)

４．発表年
2018年

１．発表者名
Muhammad Monirul Islam, Shenghao Wang, Takuya Kato, Hiroki Sugimoto, Katsuhiro Akimoto, Takeaki Sakurai

２．発表標題
Photoluminescence Study of Alkali-doped Cu(In,Ga)(S,Se)2 materials

３．学会等名
Conference: 21st International Conference on Ternary and Multinary CompoundsAt: Boulder, Colorado, USA (国際学会)

４．発表年
2018年

１．発表者名 Takeaki Sakurai, J. Chen, Shenghao Wang, Muhammad Monirul Islam, Katsuhiro Akimoto, Yoshiaki Hirai, Takuya Kato, Hiroki Sugimoto,
２．発表標題 Study of Defects in Cu(In,Ga)(S,Se)2-based Solar Cells
３．学会等名 International Conference on Electronic Materials 2018, Daejeon, Korea（国際学会）
４．発表年 2018年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

―

６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考
研究分担者	櫻井　岳暁 (Takeaki Sakurai) (00344870)	筑波大学・数理物質系・准教授 (12102)	
研究分担者	池田　茂 (Shigeru Ikeda) (40312417)	甲南大学・理工学部・教授 (34506)	

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関