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IMPACT OF SULFURIZATION ON SPUTTERED $BiVO_4$ THIN FILMS

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The sulfurization method has been used to decrease the band gap of the $BiVO_4$ structure, reduce the recombination of electrons and holes, and increase the photoelectrochemical performance of this material. It has been observed that incorporation of sulfur into stoichiometry is variously affected changing of properties of the V-rich $BiVO_4$ structure . Sulfurization can modify V-rich $BiVO_4$ structure rather than stoichiometric $BiVO_4$.

Keywords: $BiVO_4$, sulfurization, S doped $BiVO_4$, sputtering, photocatalyst

ВЛИЯНИЕ СУЛЬФУРИЗАЦИИ НА НАПЫЛЕННЫЕ ТОНКИЕ ПЛЕНКИ $BiVO_4$

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Метод сульфуризации использовался для уменьшения запрещенной зоны структуры $BiVO_4$, уменьшения количества рекомбинации электронов и дырок, и повышения фотоэлектрохимических характеристик этого материала. Обнаружено, что введение серы в стехиометрический и насыщенную ванадием структуры $BiVO_4$ по-разному влияет на изменение свойств материала в целом. Сульфирование может изменить насыщенную ванадием структуры $BiVO_4$, а не стехиометрическую структуру $BiVO_4$.

Ключевые слова: $BiVO_4$, сульфирование, BiVO4 легированный серой, напыление, фотокатализатор

OLTINGUGURTLASH JARAYONINING $BiVO_4$ YUPQA PLYONKASIGA TA'SIRI

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$BiVO_4$ ning ta'qiqlanga soxasini qisqartirish, elektron va g'ovaklar rekombinatsiyasi sonini kamaytirish hamda fotoelektrokimyoviy xususiyatini oshirish maqsadida oltingugurtlash metodi qo'llanildi. $BiVO_4$ ning teng miqdorda hamda V ga boy xolatda kimyoviy elementlar mutanosibligiga ega bo'lishi, oltingugurtning BiVO4 strukturasiga kiritilishida farqli bo'lishi ko'rsatildi. Oltingigurtning kiritilishi V ga boy $BiVO_4$ strukturasini o'zgartirdi, teng miqdorli elementlarga ega $BiVO_4$ strukturasiga ta'siri sezilarli emasligi tadbiq etildi.

Kalit so'zlar: $BiVO_4$, oltingugurtlash, oltingugurt kiritilgan $BiVO_4$, sochilish, fotokatalizator

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Introduction

Bismuth vanadate ($BiVO_4$) exhibits highest photocatalytic performance among metal oxide semiconductors for O_2 production, and also for solar water splitting in Z-Scheme photocatalytic systems, mainly due to excellent chemical stability, and narrower bandgap (2.4-2.5 eV) [1-8]. The conduction band of $BiVO_4$ is mainly composed of V3d, and the VB is formed by the hybrid orbitals of Bi6s and O2p, driving hole transport to the surface of the material [9]. Poor photocurrent in $BiVO_4$ causes fast recombination of photoexcited electrons and holes, and this is main issue of $BiVO_4$ [7, 8]. Unmodified $BiVO_4$ has not yet achieved its best efficiency with the limitation of a relatively wide bandgap. Excited electrons, owned less energy than ~2.48 eV, cannot obtain a conduction band and recombine with holes fast. To circumvent this limitation, various methods have been developed to optimize of $BiVO_4$, most of these studies have been focused on molybdenum and tungsten cation dopants with the goal of substituting vanadium sites [10-13]. Anion doping with sulfur is a possible approach to enhance the charge-carrier mobility by decreasing the $BiVO_4$ bandgap [14, 15]. Sulfur has higher orbital energy comparing with oxygen, and the substitution of oxygen with sulfur in $BiVO_4$ shifts the VB upward, resulting in a decrease in its bandgap. Thus, this study is focused on the impact of S using sulfurization annealing into $BiVO_4$ thin films, deposited by RF sputtering method.

Experimental methods

Thin-film preparation

Monoclinic $BiVO_4$ thin films were deposited by RF sputtering. A $BiVO_4$ target (consisting of Bi_2O_3 and V_2O_5 in a 1:2 molar ratio) was used as the sputtering source. The RF power for sputtering was set to 50 W. The O_2 partial pressure (defined as $O_2/Ar+O_2$) was set at 5% and 25%, while the total pressure was maintained at 0.6 Pa during sputtering to make various property of pure $BiVO_4$. Thin films were deposited on alkaline Earth boro-aluminosilicate glass (Eagle XG, Corning) substrates. The deposited $BiVO_4$ thin films was placed in a gold-coated tubular furnace and annealed at 500 °C for 90 min under an O_2 atmosphere to obtain monoclinic $BiVO_4$ crystal structures.

Sulfurization

Figure 1a shows $BiVO_4$ and Sulfur doped $BiVO_4$ (S-$BiVO_4$) thin films on the glass sustrate. The sulfurization process was used to incorporate sulfur into the $BiVO_4$ thin films, as the schematic illustration shows in Figure 1b. The sulfur powder was placed alongside the $BiVO_4$ samples in a graphite box. Subsequently, a graphite box was introduced into the annealing furnace. The temperature was increased from 20 °C to 350 °C by 10°C min^{-1}. After maintaining the temperature at 350 °C for 60min, the heating was stopped, and the sample was naturally cooled. During sulfurization, 10^5 Pa nitrogen gas flow was maintained in the annealing furnace. The names of the samples were chosen as $BiVO_4$-St (Stoichiometric $BiVO_4$) and $BiVO_4$-V_{rich} according to the atomic ratio of Bi, V and O in the $BiVO_4$ thin films, calculated from the X-ray photoelectron spectroscopy (XPS) results.

The chemical states and compositions of S doped $BiVO_4$ were determined by X-ray photoelectron spectroscopy (XPS) (JPS-9010 series, JEOL). The atomic percentage of S 2s, Bi 4f, V 2p, and O 1s were calculated by the peak area considering sensitive factors. The C1s peak (284.8 eV) was used for calibration. Structural analysis of the $BiVO_4$ and S doped $BiVO_4$ thin films was performed using X-ray diffraction (XRD; X'Pert, Malvern PANalytical) analysis and Raman spectrometer (Nanofinder 30, Tokyo Instruments). Raman spectra were measured using a 532 nm Nd: YAG laser source. Transmittance and reflectance spectra were obtained using a UV−VIS/NIR spectrophotometer (V-670, Jasco).

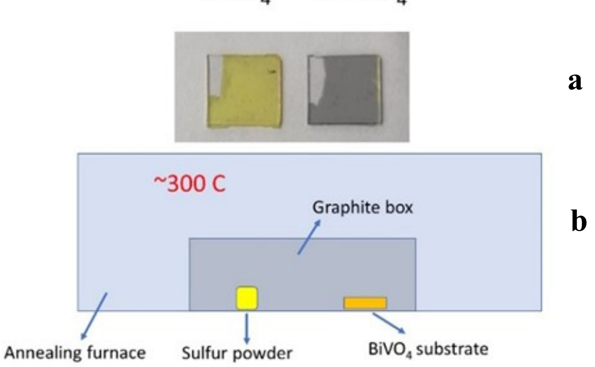

Figure 1. Undoped and sulfur-doped $BiVO_4$ samples (a), schematic of sulfurization process (b).

Results and discussion

X-ray Photoelectron Spectroscopy (XPS) measurements has been done to analyze atomic ratio of elements (Bi, V, O, and S) in $BiVO_4$ and S - $BiVO_4$ samples (Fig. 2a and 2b). XPS results showed that increase of O_2 pressure relative to Ar during the film deposition turns V rich $BiVO_4$ ($BiVO_4$-V_{rich}) film from stoichiometric $BiVO_4$ ($BiVO_4$-St). Optical bandgaps of the S doped stoichiometric $BiVO_4$ (S-$BiVO_4$-St) and S doped V rich $BiVO_4$-V_{rich} (S-$BiVO_4$-V_{rich}) have been estimated as ~2.61 eV and ~2.45 eV, respectively, analyzed by the Tauc plot of transmittance and reflectance data. These values are narrower than bandgap of pure BVO films (2.52 eV and 2.63 eV) (Fig. 3a and Fig. 3b).

Raman spectroscopy is used for sensitive structural analysis of films. Figure 4a shows, that incorporation of S into $BiVO_4$-St less affected to $BiVO_4$ structure. However, S doping more changed V-O interactions from vanadium oxide and impacted to $BiVO_4$-V_{rich}, it turned to clear monoclinic $BiVO_4$ phase (Fig. 4b). Because of lower electronegativity of S than O, the electronic cloud can deviate from the original position in a V –O polyhedron and the bonds between V and O are weakened [14] in S-doped $BiVO_4$ sample. This phenomenon observed in Raman spectra, showed downshift of main peak of $BiVO_4$ and small shift to lower wavenumber side after incorporation of S into $BiVO_4$ (Fig. 4b).

Figure 5 shows magnified X-ray Diffraction (XRD) peaks of (121) plane at approximately 29.06°, for $BiVO_4$-V_{rich} and S-$BiVO_4$-V_{rich} thin films. A slight shift in the XRD peak due to sulfur doping into $BiVO_4$ toward a lower diffraction angle suggests the presence of S^{2-} ions in $BiVO_4$. According to Bragg's law, the diffraction peak shift to a lower angle can be

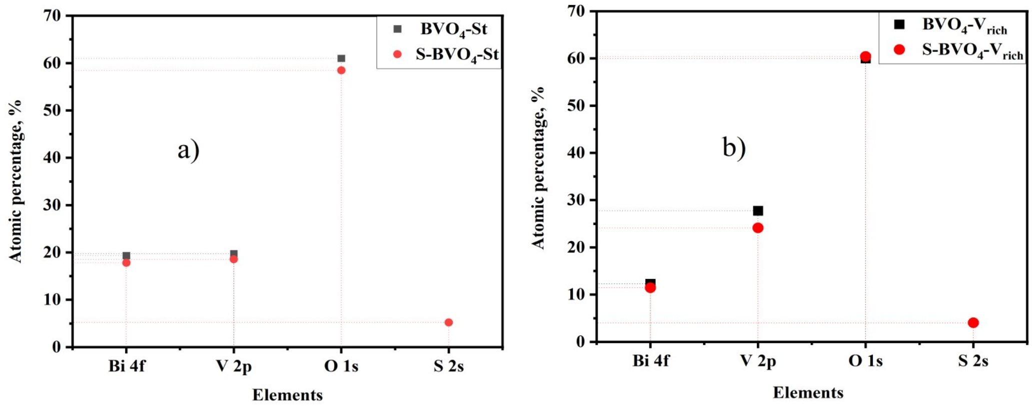

Figure 2. Atomic percentages of $BiVO_4$ and Sulfur doped $BiVO_4$ thin films observed by XPS.

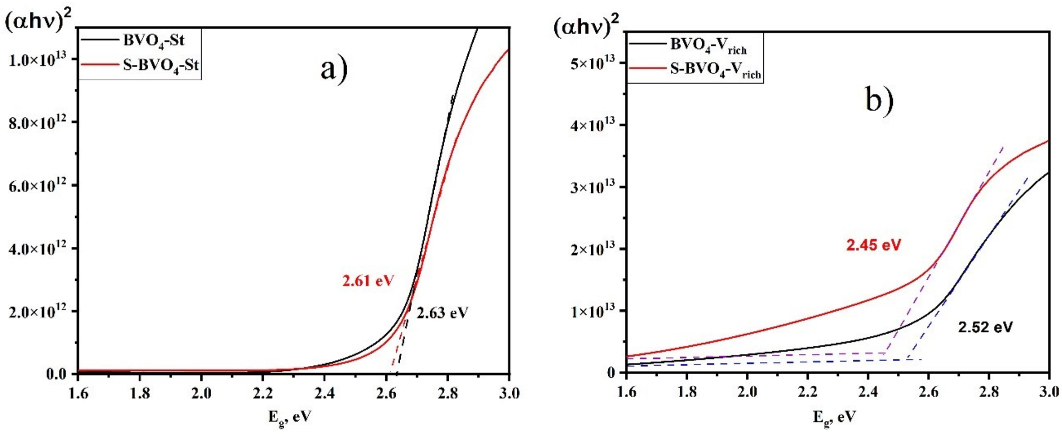

Figure 3. Band gap of $BiVO_4$ and Sulfur doped $BiVO_4$ thin films estimated by Tauc plot method.

attributed to the higher ionic radius (0.184 nm) of sulfur than that of oxygen (0.140 nm).

PL spectra of pure $BiVO_4$ and S- $BiVO_4$ samples at room temperature are shown in Figure 6. Intensity of PL is increased by doping of S into $BiVO_4$-St (Fig. 6a), it is expected cause of changing of $BiVO_4$-St band structure. In this case, number of photogenerated electron-hole pairs which participated in radiative recombination is increased and originates higher PL intensity of S-$BiVO_4$-St than pure $BiVO_4$-St. PL intensity was decreased by doping of S into $BiVO_4$-V_{rich} (Fig. 6b), plausibly due to the increase of defects [16].

Post sulfurization variously affected into $BiVO_4$ structures where it is in stoichiometric and V_{rich} condition. Stoichiometric $BiVO_4$ is structurally equals in whole thin film, that may cause difficulty of Sulfur doping effect. It is supposed, that role of vanadium oxide acts on not only structural properties of pure $BiVO_4$, but also S incorporation into $BiVO_4$ structure. In case of S doped V_{rich} -$BiVO_4$ crystal lattice, probably defects are increased in the band gap, which are responsible for trapping holes and electrons. Therefore, decreased recombination rate [14] would be beneficial for higher photo electrochemical performance of the S-$BiVO_4$-V_{rich} samples.

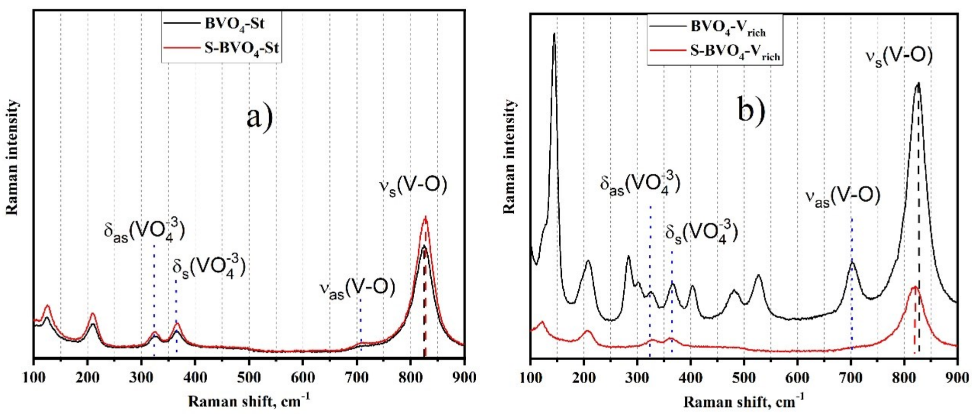

Figure 4. Raman spectra of $BiVO_4$ and Sulfur doped $BiVO_4$ thin films.

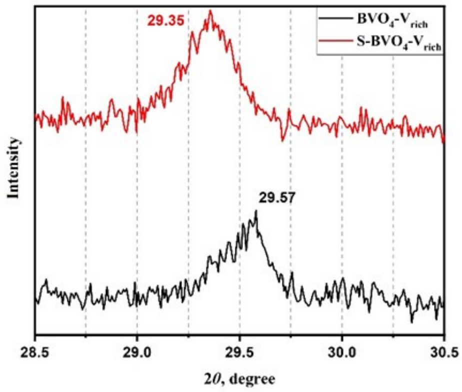

Figure 5. XRD spectra of $BiVO_4$ and Sulfur doped $BiVO_4$ thin films.

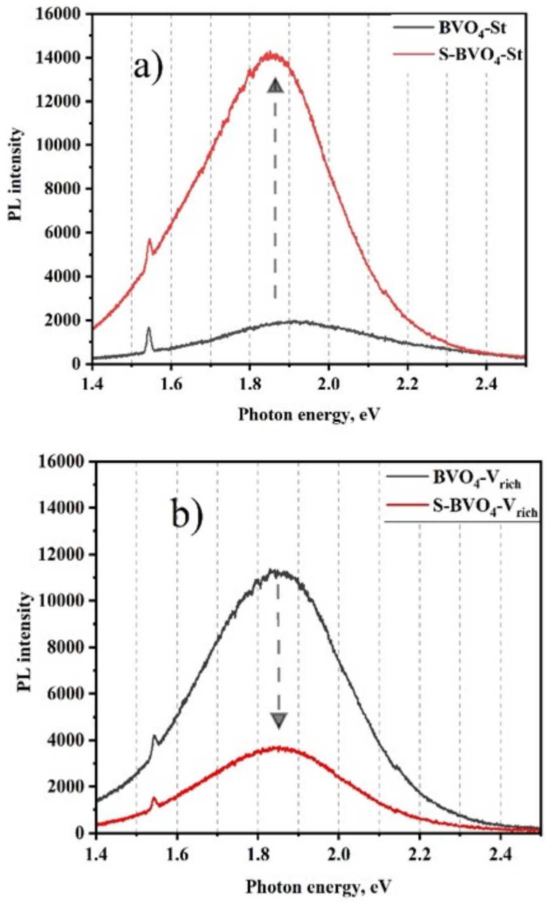

Figure 6. PL spectra of $BiVO_4$ and Sulfur doped $BiVO_4$ thin films.

Conclusion

$BiVO_4$, owned stoichiometric and V_{rich} ratio, showed various properties obtained by structural (XRD, Raman spectroscopy) and optical (UV-Vis, PL) measurements. Doping of S, with aiming to enhance photoelectrochemical properties, varied with placing in $BiVO_4$ structure. Sulfurization can modify V_{rich} surface in $BiVO_4$. However, incorporation of S might not highly effective for stoichiometric $BiVO_4$.

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