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BiVO₄ photoanodes for water splitting with high injection efficiency, deposited by reactive magnetron co-sputtering

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Photoactive bismuth vanadate (BiVO₄) thin films were deposited by reactive comagnetron sputtering from metallic Bi and V targets. The effects of the V-to-Bi ratio, molybdenum doping and post-annealing on the crystallographic and photoelectrochemical (PEC) properties of the BiVO₄ films were investigated. Phase-pure monoclinic BiVO₄ films, which are more photoactive than the tetragonal $BiVO_4$ phase, were obtained under slightly vanadium-rich conditions. After annealing of the Mo-doped BiVO₄ films, the photocurrent increased 2.6 times compared to undoped films. After optimization of the BiVO₄ film thickness, the photocurrent densities (without a catalyst or a blocking layer or a hole scavenger) exceeded 1.2 mA/cm² at a potential of 1.23 V_{RHE} under solar AM1.5 irradiation. The surprisingly high injection efficiency of holes into the electrolyte is attributed to the highly porous film morphology. This co-magnetron sputtering preparation route for photoactive BiVO₄ films opens new possibilities for the fabrication of large-scale devices for water splitting. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4947121]

INTRODUCTION

Photoelectrochemical (PEC) water splitting for hydrogen generation is a promising strategy to capture and store solar energy.¹ There are many material challenges that must be overcome to make PEC water splitting viable on a large scale. In a practical water splitting system, a highly active semiconductor photoelectrode should absorb a large portion of the solar spectrum. Moreover, the photoelectrode materials should be stable in the electrolyte under illumination and consist of earth-abundant elements. For these reasons, many groups have focused on the development of metal oxides as robust and inexpensive photoelectrode materials,² many of which are stable under PEC operating conditions. A large variety of metal oxide-based photoanodes have been studied and several dozen have been found to oxidize water to generate molecular oxygen, albeit with widely varying efficiencies (for a recent review see Ref. 3). Over the last two decades $BiVO_4$ (bismuth yellow) has attracted much attention as an efficient, robust and inexpensive photoanode⁴ and more recently as thin film photoelectrodes.^{5,6} BiVO₄ exhibits three polymorphs: the tetragonal zirconia structure, the monoclinic scheelite and the tetragonal scheelite structures, with the monoclinic polymorph being the most active one for water oxidation.⁷ Monoclinic BiVO₄ (m-BiVO₄) has a bandgap of ~ 2.4 eV, which translates into a maximum theoretical photocurrent of 7.5 mA/cm² under AM1.5G light (100 mW/cm²).⁷ Therefore, the maximum theoretical solar-to-hydrogen (STH) conversion efficiency is 9.2% (based on the lower heating value (LHV of hydrogen of 237 kJ/mol),



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which is close to the entry level efficiency for commercialization (at least 10%).² The valence band of BiVO₄ is located more than 1 V positive of the water oxidation potential, which means that oxygen evolution is thermodynamically possible.⁷ Moreover, its conduction band edge is located close to the reversible hydrogen electrode (RHE) level,^{8–11} which enables water splitting at modest external bias potentials. This makes BiVO₄ attractive for combining with hydrogen-producing photocathodes in a tandem water splitting device.¹⁰

A variety of synthesis techniques have been used to prepare BiVO₄ films. The most widely used methods are based on wet chemistry combined with spin-coating¹¹ or spray pyrolysis.⁶ These methods are cheap and flexible, and have recently made great progress. BiVO₄ photoelectrodes deposited by spray pyrolysis have reached photocurrents as high as 3.6 mA/cm², using blocking layers at the back contact and catalytically active layers.¹² Combining these electrodes with a double-junction thin film amorphous silicon cell resulted in a stand-alone water splitting device with a STH efficiency of 4.9%.¹² Very recently, a combined electrodeposition / metal organic decomposition route developed by Choi et al. has resulted in nanoporous BiVO₄ films that show AM1.5 photocurrents of 4.5 mA/cm² at 1.23 V vs. RHE when covered with a dual-layer FeOOH/NiOOH oxygen evolution catalyst.¹³

Other synthesis method are based on physical vapor deposition, such as reactive ballistic deposition (RBD),⁵ and reactive magnetron sputtering.^{14,15} An important advantage of physical vapor deposition techniques over chemical solution methods is the much higher purity that can generally be achieved. This is not only because the deposition process takes place under high vacuum conditions, but also because no organic ligands or surfactants are involved. Other advantages include a generally superior adhesion and film uniformity, and the ability to make dense films for the evaluation of fundamental properties. The vapor deposition process has been used to deposit metal oxide and nitride thin films such as TiO₂, WO₃, and TaON for photocatalytic and photoelectrochemical applications.¹⁶ RBD and magnetron sputtering are commercially available, highly scalable (up to 20 m² coating area) and widely applied in industry, so physical vapor deposition might offer a convenient way to realize large scale industrial PEC applications. Recent work from Ager's group demonstrated that the photocurrent density of sputter-deposited undoped $BiVO_4$ can reach $0.5 \text{ mA/cm}^{2.14}$ By doping their BiVO₄ films with molybdenum, Chen et al. obtained recently a photocurrent density of 3.5 mA/cm² with a hole scavenger (Na₂SO₃).¹⁵ This is comparable to what can be obtained with wet-chemical methods, and represents a promising first step towards a scalable deposition process for efficient BiVO₄ films based on physical vapor deposition.

For undoped BiVO₄, without additional films (i.e., blocking layers, catalytic films), reported photocurrents for water oxidation with AM1.5 illumination are lower than 1 mA/cm²,⁸ which is less than 15% of the theoretical maximum for a 2.4 eV absorber. Known issues with BiVO₄ include poor electron transport, as evidenced by higher photocurrents for back as opposed to front illumination, and slow water oxidation kinetics.¹⁷ Density functional theory studies have shown that Mo-doping in BiVO₄ can exhibit excellent n-type conductivity and could significantly enhance the PEC activity. Experimental results confirmed this.¹⁸ Incorporation of Mo into BiVO₄ increases the carrier density and distorts the VO₄ tetrahedron, resulting in a local internal electric field.¹⁹ It has also been observed that Mo is better suited than the commonly used W for the n-type doping of BiVO₄.²⁰

In this work, we systematically investigated the deposition of $BiVO_4$ films by a reactive magnetron sputtering process. First, we investigated the effect of the V-to-Bi ratio on the growth of monoclinic $BiVO_4$ films. By comparing the charge carrier injection and separation efficiencies, we find that slow water oxidation kinetics is not a limiting factor for water splitting. Herein, doping and annealing were adopted to improve the charge separation efficiency by increasing the carrier concentration and the conductivity. We also optimized the thickness of the films to establish the optimum thickness *d* with respect to light absorption (high *d*) and separation of the electron-hole pairs (low *d*).

EXPERIMENTAL

The films were deposited in a co-magnetron sputtering system equipped with a load-lock chamber. Metallic bismuth (Bi, 99.9%) and vanadium (V, 99.99%) targets were used for cosputtering



FIG. 1. Scheme of the process chamber for magnetron co-sputtering from separate bismuth and vanadium targets, mounted under an angle of 60 $^{\circ}$. The substrates with a size of 22x22 mm² were fixed on the substrate holder with an electrical heater behind it.

(see Figure 1). A boron nitride encapsulated graphite heater beneath the substrate holder was used to heat the substrates up to temperatures of 450 °C. Because of the much higher sputtering yield of Bi compared to V^{21} to obtain the same deposition rate for Bi and V (necessary to generate stoichiometric films) the distance between the Bi target and the substrate was set to twice the distance between the V target and the sample. The larger distance between the Bi target and the substrate (compared to the V target) leads to a higher number of collisions of the sputtered Bi atoms with the sputtering gas (mostly Ar), thus thermalizing the energetic Bi atoms before arriving at the growing film. Due to the significantly lower mass of the vanadium atoms nearly the same thermalization is achieved despite the lower number of collisions arising from the smaller target-to-substrate distance.²²

Two separate DC power supplies were used to adjust the Bi and V sputtering powers independently. Typical power ranges were $20 \sim 30$ W for the Bi target and $150 \sim 350$ W for the V target. A mixture of Ar and O₂ was used as the sputtering atmosphere. The total pressure was fixed at 1.0 Pa with an O₂ partial pressure of 0.20 Pa. For this O₂ concentration in the sputtering gas, the two target surfaces were completely oxidized, and the Bi and V arrival rates on the substrate were comparable. For molybdenum (Mo) doped BiVO₄ films, a Mo stripe was attached onto the Bi target, so that Mo was sputtered simultaneously with Bi. The BiVO₄ deposition rate was about 12 nm/min.

Prior to deposition, fluorine-doped tin oxide (FTO) coated glass substrates were ultrasonically cleaned for 15 min in isopropanol, rinsed with de-ionized water and dried under a stream of compressed nitrogen. The film thickness was controlled by varying the deposition time. After deposition, the films were annealed in air at 500 °C for 2 h in a muffle furnace using a heating ramp of 10 K/min.

The phase composition was analyzed with a Bruker AXS D8-Advance X-ray diffractometer. The CuK_{α} X-ray tube was operated at 40 kV and 40 mA, and the measurements were carried out in the symmetrical Bragg-Brentano $\theta/2\theta$ diffraction geometry. The morphology of the films was characterized with a LEO GEMINI 1530 field emission scanning electron microscope (FE-SEM), operated at an acceleration voltage of 7 kV. The bulk elemental composition was measured using Rutherford backscattering spectrometry (RBS) on samples deposited onto glassy carbon substrates. The RBS spectra were simulated with the SIMNRA software.²³ The film thickness was measured using a DEKTAK profilometer. The optical transmittance (*T*) and reflectance (*R*) spectra were measured with an UV/Vis double-beam spectrometer (Perkin-Elmer Lambda 950). For the Tauc plots the absorption coefficient (α) was determined from $\alpha = -\ln T/d$, where *d* is the film thickness.

Photoelectrochemical (PEC) measurements were carried out in a quartz-windowed electrochemical cell with the BiVO₄ films as the working electrode, an Ag/AgCl reference electrode, and 045108-4 Gong et al.

a platinum mesh counter electrode. An EG&G Princeton Applied Research 273A potentiostat was used for all experiments. White-light photocurrent measurements were performed under simulated AM1.5 solar illumination (100 mW/cm²) with a Voss Class AAA solar simulator (WXS-50S-5H). The electrolyte used for all measurements was 0.5 M Na₂SO₄ in 0.1 M potassium phosphate buffer solution (pH = 7). All potentials were converted to the reversible hydrogen electrode (RHE) scale using the Nernstian relation: $V_{RHE} = V_{Ag/AgCl} + 0.0591$ pH + 0.1976 V (1).

The charge separation (η_{sep}) and injection efficiencies (η_{inj}) were estimated by using H₂O₂ as a hole scavenger, using the following equations:²⁴

$$\eta_{sep} = \frac{J_{ph}(H_2O_2)}{J_{abs}} \tag{1}$$

$$\eta_{inj} = \frac{J_{ph}(H_2O)}{J_{ph}(H_2O_2)}$$
(2)

Here, $J_{ph}(H_2O_2)$ and $J_{ph}(H_2O)$ are the measured photocurrent densities with and without H_2O_2 in the electrolyte, respectively. J_{abs} is the photon absorption rate expressed as the photocurrent density by integrating the overlapped area between the UV-Vis absorption spectrum of sample electrode and an AM1.5G solar irradiance. Spectrally resolved photocurrents for incident photon-to-current conversion efficiency (IPCE) determination were measured using a Newport Xe lamp (300 W) and an Oriel Cornerstone 1/8 m monochrometer with 1.0 mm slits. A Thorlabs FDS1010-CAL calibrated Si photodiode was used to monitor the intensity of the monochromatic output during the measurement. The configuration of the photoelectrochemical cell was the same as for the PEC measurements with three electrodes to measure the current of the photoanode. An electronic shutter (model VMM-T1) was used, and a long-pass color glass filter (Schott, 3 mm thick, cut-off wavelength 340 nm) was placed between the monochromator and the sample to block second-order diffracted light.

The IPCE was then calculated according to the following formula:

$$IPCE[\%] = \frac{1240 J_{ph}}{I_{inc}\lambda} \cdot 100\%,$$
(3)

where J_{ph} is the measured photocurrent density in mA/cm², I_{inc} is the incident light intensity in mW/cm², and λ is the incident photon wavelength in nm.

RESULTS AND DISCUSSION

Structure and composition

The V-to-Bi ratio was varied from 0.5 to 2.0 in order to check phase formation, especially with respect to the monoclinic BiVO₄ phase. Because of the arrangement of the two magnetron sputtering sources, the concentration of Bi decreases and the V concentration increases from the Bi-target to the V-target side of the sample. This gives us a convenient tool to investigate the properties of thin films with different chemical compositions on our $22x22 \text{ mm}^2$ sized samples. In this experiment, we performed research on the spots in the center of half V-target side and use these data to represent the whole sample. The RBS data are summarized in Table I.

Figure 2 shows XRD spectra of the BiVO₄ films with different V-to-Bi ratios. Since the films are thin (\sim 90 nm), the most prominent diffraction peaks are due to the FTO substrate, marked by

TABLE I. Elemental composition of four samples with different V-to-Bi ratios.

Sample no.	0	V	Bi	V/B	
1	0.68	0.12	0.20	0.60	
2	0.67	0.15	0.18	0.83	
3	0.683	0.165	0.152	1.09	
4	0.675	0.20	0.125	1.60	



FIG. 2. XRD patterns of as-deposited films with V-to-Bi ratios ranging from 0.60 to 1.60. FTO peaks are marked with asterisks (*). Powder diffraction peaks of monoclinic and tetragonal BiVO₄ are marked with solid and dashed bars, respectively. Deposition parameters: p = 1.0 Pa, $T_{sub} = 350 \text{ °C}$, $P_V = 270 \text{ W}$, $P_{Bi} = 20 \text{ W}$.

asterisks (*). The characteristic diffraction peaks of monoclinic (JCPDS 83-1700) and tetragonal (JCPDS 14-0133) $BiVO_4$ are displayed by solid and dashed bars, respectively.

The film deposited with the lowest V-to-Bi ratio (V/Bi = 0.60) shows, in addition to the FTO peaks, three peaks at $2\theta = 12^{\circ}$, 18.8° , and 28.5° . The broad peak at 12° is assigned to the (020) reflex of the orthorhombic Bi₂VO_{5.5} phase (o-Bi₂VO_{5.5}).¹⁴ The 18.8° peak is the (011) peak of the monoclinic BiVO₄ phase. The peak located at 28.5° is actually composed of a main peak and a shoulder. The main peak at around 28.3° is assigned, to the o-Bi₂VO_{5.5} (131) diffraction peak. We can clearly observe this for the high Bi concentration phase Bi₂VO_{5.5} on the Bi side of this sample., The shoulder located at 28.8° is ascribed to the strongest (-112) reflex of m-BiVO₄. This means, we observe a phase separation at V/Bi = 0.60, which is different from the result of Chen et al.,¹⁴ who obtained by reactive magnetron sputtering primarily the monoclinic crystal structure at this V-to-Bi ratio. This could be caused by their slightly different sputtering conditions; instead of a metallic Bi target they used a Bi₂O₃ target, which was excited by an RF power supply at a total pressure of 0.67 Pa (our total pressure was 1 Pa).

With increasing V-to-Bi ratio (0.83 and 1.09), the bismuth-rich phase o-Bi₂VO_{5.5} disappears completely, and only m-BiVO₄ is left. However, for V/Bi = 0.83, the tetragonal BiVO₄ phase (t-BiVO₄) appears, which is obvious from the splitting of the peak at 18° and the appearance of a new peak at 24.3°. This shows that t-BiVO₄ is prone to nucleate and grow at higher bismuth concentrations,[29] rather than m-BiVO₄. However, we did not find the peaks of t-BiVO₄ for the [V]/[Bi] = 1.09 film. Under vanadium-rich conditions, i.e., when the V-to-Bi ratio reaches 1.60, a tiny peak at 20 = 20° indicates that vanadium oxide (V₂O₅) (JCPDS 089-0611) began to crystallize. The size of the BiVO₄ grains can be estimated with the Scherrer formula: $D = k\lambda/(B \cos \theta)$, where *D* is the average diameter of the grains, *K* is the Scherrer constant (0.89 for cubic grains), λ is the wavelength of the X-rays (0.15418 nm), *B* is the full width at half maximum (FWHM) in radians, and θ is the diffraction angle. The estimated grain size is about 30 nm.

The integrated diffraction peak intensities of m-BiVO₄ (112), t-BiVO₄ (200), and o-Bi₂VO_{5.5} (131) are compared to estimate how the relative amounts of the different phases evolve as a function of the V-to-Bi ratio (Figure 3). The content of the Bi-rich phase o-Bi₂VO_{5.5} is highest at [V]/[Bi] = 0.60, and decreases sharply at higher vanadium contents. For t-BiVO₄, it seems that it



FIG. 3. Diffraction peak intensities of the three phases monoclinic $BiVO_4(112)$, tetragonal $BiVO_4(200)$, and orthorhombic $Bi_2VO_{5.5}(131)$ as a function of the V-to-Bi ratio.

only exists around V/Bi = 0.83. The relative amount of m-BiVO₄ increases sharply for V-to-Bi ratios above 0.83, which is presumably due to the transformation from t-BiVO₄ to m-BiVO₄.

For our molybdenum-doped BiVO₄ films, the concentration of Mo is about 10 at% relative to V, as determined by RBS. This concentration gave the highest photocurrents for the Mo-doped BiVO₄ samples studied by Park et al.²¹ No Mo-related XRD peaks were observed, suggesting that Mo does not segregate out of the BiVO₄ lattice even for a concentration of 10 at% Mo. However, the possibility of small amounts of amorphous or nanocrystalline MoO_x phases cannot be excluded. A shift of the diffraction peaks of BiVO₄:Mo with respect to undoped BiVO₄ was not observed, since there is only a small difference between the ionic radii of Mo⁶⁺ (59 pm) and V⁵⁺ (54 pm), respectively.

A series of BiVO₄ films were also deposited onto bare float glass substrates, using the same deposition conditions that were used for the deposition on FTO. For the glass/BiVO₄ samples, the intensity of the X-ray diffraction peaks is quite weak compared to those of the FTO/BiVO₄ samples. When decreasing the deposition temperature to 250 °C, the BiVO₄ films on FTO still show clear diffraction peaks, whereas the films deposited on glass were X-ray amorphous. These results suggest that fluorine-doped tin oxide supports the nucleation and growth of the BiVO₄. Alternatively, sodium diffusion from the float glass into the BiVO₄ may prevent crystallization at elevated temperatures; this effect is well known for TiO₂ films. The XRD patterns for [V]/[Bi] = 1.09 after annealing at 500 °C for 2h were almost identical with unannealed films, and there are no V₂O₅ peaks. This suggests that excess vanadium is incorporated into the interstitial sites of the films and we can get phase-pure m-BiVO₄ deposited at [V]/[Bi] = 1.09. So, unless otherwise stated, all the following experiments are based on BiVO₄ thin films with a V-to-Bi ratio of 1.09.

Scanning electron microscopy

Figure 4(a) shows that the films consist of island-like features with a size of about 200 nm to 1 μ m. In between the BiVO₄ grains there are holes and crevices, and the FTO crystallites from the underlying substrate can be clearly seen. The crystallite size estimated from the XRD data is much smaller than the observed feature size, which is due to the fact that by XRD in Bragg-Brentano geometry the vertical diffracting domain size is probed. The BiVO₄ crystallite size is larger than the size of the FTO grains showing that a strong surface diffusion occurs during film growth. This is also supported by the morphology of samples deposited at higher substrate temperatures. As the temperature increases to 400 °C (Figure 4(b)), the separated islands join together and grow into



FIG. 4. FESEM images of Mo-doped BiVO₄ deposited at different substrate temperatures and deposition times (thicknesses): (a) 350 °C, (b) 400 °C, and (c) 450 °C for 400 s (90 nm); (d) 600 s (120 nm), (e) 900 s (150 nm), (f) 1800 s (300 nm) at 350 °C (V-to-Bi ratio = 1.09).

irregular worm-like structures longer than 1 μ m, and nearly half of the substrate area is exposed. Further increase of the temperature (as high as 450 °C, in Figure 4(c)) accelerates surface diffusion, and as a result only large, well-separated particles are left. As a consequence, large parts of the FTO are no longer covered with BiVO₄, which is clearly an undesired side-effect. The SEM images in Figure 4(a)-4(c) suggest that the maximum deposition temperature should not be higher than ~350 °C if extensive FTO exposure is to be avoided. We also studied the effect of the film thickness on the surface morphology of Mo-doped BiVO₄. As the deposition time was increased from 400 s to 600 s, the BiVO₄ particles continue to grow and some join with nearby particles to form larger agglomerates. However, it appears that the substrate has not yet been totally covered. For even longer deposition times (Figure 4(e)), although the size of particles doesn't change significantly, we observe that the film is composed of stacked crystallites, through which the FTO surface is no longer visible. As will be shown below, more complete coverage of the FTO has a favorable effect on the PEC performance as it minimizes exposure of the FTO to the electrolyte (internal short circuit).

Optical Properties

UV-VIS transmission and reflection measurements were performed to determine the optical properties of the synthesized films. The absorption data are plotted as $(\alpha hv)^2$ versus the photon energy (Tauc plot, see Figure 5), assuming that the BiVO₄ has a direct band gap. All the samples show a similar absorption spectrum, regardless of annealing and doping. Extrapolation of the curve for the 90 nm undoped BiVO₄ reveals a direct bandgap of 2.60 eV, which is in agreement with other reports.¹² This is somewhat larger than the value of 2.4 eV that is usually reported for the *indirect* bandgap of BiVO₄. However, a proper distinction between a direct and an indirect transition is not so easy to make for BiVO₄, and the smaller value of ~2.4 eV has also been attributed to the presence of point defects in the material. BiVO₄ films doped with Mo consistently show a bandgap of about 2.52 eV, regardless of the amount of Mo; this seems indeed consistent with the notion that point defects may lower the apparent band gap of the material. The absorption tail extending to lower photon energies (<2.4 eV) could be caused by diffuse reflection and scattering from the rough film surface.⁵

Photoelectrochemical properties

Figure 6 shows linear sweep voltammograms (under chopped light) of differently doped and heat-treated BiVO₄ films deposited with [V]/[Bi] = 1.09 in a 0.5 M Na₂SO₄ electrolyte buffered



FIG. 5. Tauc plots of optical absorption curves for doped and undoped BiVO4 thin films.

with 0.1 M potassium phosphate to pH7 under AM1.5 light (1 sun). The photocurrents increase with increasing potential due to the enhanced band bending and hence a reduced electron-hole recombination. Before annealing, all films show a similar photocurrent onset at about 430 mV vs. RHE and a dark current starting at about 1.8 V_{RHE} . The photocurrent densities are similar for all as-deposited films, with the highest value of 0.42 mA/cm² at 1.23 V_{RHE} observed for the 90 nm thick undoped film.

The films, annealed at 500 °C in air show a lower onset potential at about 350 mV, and a 2-3 times higher photocurrent. The lower onset potential could be due to the formation of catalytic sites, which act as active centers that decrease the kinetic barrier for water oxidation. An alternative explanation is that the annealing treatment passivates surface defects, thus reducing surface



FIG. 6. Chopped light linear sweep voltammograms of undoped and doped BiVO₄ electrodes (arranged in the order of decreasing photocurrent at 1.23 V_{RHE}). The measurements were carried out in 0.5 M Na₂SO₄ in 0.1 M potassium phosphate buffer solution (pH = 7) under simulated AM1.5 light, 100 mW/cm², front side illumination. The Mo dopant concentration is 10 at% for all samples. The scan rate was 10 mV/s and the shutter was switched on and off every 5 seconds.

recombination. The much higher photocurrents are tentatively attributed to the improved crystallinity of the material, which reduces the bulk recombination.

Doping of the BiVO₄ films with 10 at% Mo reduced the resistivity by one to two orders of magnitude, but the photocurrent decreased. However, after annealing at 500 °C for 2 hours in air, the thin film showed a current density as high as 1.08 mA/cm^2 . If the film thickness was increased to 150 nm, the photocurrent density increased to 1.2 mA/cm^2 . This thickness of 150 nm was the optimum thickness with respect to absorption and transport of the photogenerated carriers to the back contact and the electrolyte interface, respectively, since the current decreased for a 200 nm thick film. The 150 nm thick, Mo-doped BiVO₄ film, was investigated both for front and back illumination. The observed photocurrent for back illumination is only slightly (a few percent) lower than for front illumination. This shows that charge transport is not limiting the photocurrent of our magnetron-sputtered BiVO₄ films up to thicknesses of about 150 nm.

Figure 7 displays the IPCE curves of the BiVO₄ films at 1.4 V_{RHE} bias potential. For all the films, the IPCE values dropped off rapidly for wavelengths higher than 460 nm and approached 0% at 520 nm, as indeed expected for a material with a band gap of ~2.4 eV (517 nm light). The maximum IPCE values reached about 50% for Mo-doped BiVO₄ after annealing. The increased photocurrent of the annealed films is presumably caused by the reduction of the concentration of point defects, which act as recombination centers. It is noteworthy that although the 300 nm doped thin film after annealing has higher IPCE value at 1.4 V_{RHE}, the corresponding photocurrent is lower than the 90 nm one at 1.23 V_{RHE} bias. This demonstrates that the applied bias could have an effect on the water oxidation kinetics.

To compare the effects of doping and annealing in terms of the charge separation efficiency (η_{sep}) and the efficiency of charge injection into the electrolyte solution (η_{inj}) , the photon absorption rates (expressed as the photocurrent densities, J_{abs}) were estimated by multiplying the absorption spectra of the BiVO₄ with the 100 mW/cm² AM1.5G spectrum followed by integration over the spectral range where the material absorbs light. Linear sweep voltammograms of undoped and doped BiVO₄ were also obtained in the presence of 50 mM H₂O₂ as a hole scavenger to determine J_{ph} (H₂O₂). As shown in Figure 8, η_{sep} increases with increasing bias potential due to the enhanced band-bending and reduced charge recombination. Overall, we found that the annealing at 500 °C has a large effect on the charge separation efficiency, and a much smaller effect on the charge injection efficiency. Moreover, since η_{inj} is already high ($\approx 80\%$), we can conclude that recombination in the bulk, or at surface defects, is the main bottleneck.



FIG. 7. IPCE of undoped and Mo-doped BiVO₄ electrodes measured from front side illumination at 1.4 V_{RHE} bias (The inserted legend is arranged in the order of decreasing photocurrent at 1.23 V_{RHE}).



FIG. 8. The charge injection efficiency η_{inj} (solid lines) and the charge separation efficiency η_{sep} (broken lines) of undoped and Mo-doped BiVO₄ electrodes measured from front side illumination at 1.23 V_{RHE} bias (The inserted legend is arranged in the order of decreasing photocurrent at 1.23 V_{RHE}).

CONCLUSIONS

Reactive co-magnetron sputtering from bismuth and vanadium targets was used to deposit photoactive BiVO₄ photoanodes. Phase-pure monoclinic BiVO₄ films were obtained under slightly vanadium-rich deposition conditions. By optimizing film thickness, Mo-doping and annealing, BiVO₄ photoanodes with photocurrent densities exceeding 1.2 mA/cm² at a potential of 1.23 V_{RHE} under AM1.5 solar irradiation could be prepared. This high photocurrent density (without a catalyst or a blocking layer or a hole scavenger) is due to a high hole injection efficiency (>80%), which we attribute to the porous BiVO₄ film morphology. On the other hand, the separation efficiency, which is on the order of only 25%, has to be significantly improved. Our results demonstrate the suitability of reactive co-magnetron sputtering for the preparation of large-area BiVO₄ photoanodes for water splitting.

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