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**High-Throughput Characterization of Structural
and Photoelectrochemical Properties of a
Bi–Mo–W–O Thin-Film Materials Library**

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Abstract: A Bi–W–Mo–O thin-film materials library was fabricated by combinatorial reactive magnetron sputtering. The composition spread was investigated using high-throughput methods to determine crystalline phases, composition, morphology, optical properties, and photoelectrochemical performance. The aurivillius phase $(\text{Bi}_2\text{O}_2)^{2+} (\text{Bi}_M(\text{W}_{1-N}\text{Mo}_N)_{M-1}\text{O}_{3M+1})^{2-}$ is the predominantly observed crystal structure, indicating that the thin films in the library are solid solutions. With increasing amounts of Mo $\pm 7\text{--}22\%$ the diffraction peak at $2\theta = 28^\circ \pm [131]$ shifts due to lattice distortion, the photoelectrochemical activity is increasing up to a wavelength of 460 nm with an incident photon to current efficiency (IPCE) of 4.5%, and the bandgap decreases. A maximum photocurrent density of $31 \mu\text{A}/\text{cm}^2$ was measured for $\text{Bi}_{31}\text{W}_{62}\text{Mo}_7\text{O}_z$ at a bias potential of 1.23 V vs. RHE (0.1 M Na_2SO_4).

Keywords: high-throughput characterization; metal oxides; solar water splitting; thin-film materials libraries.

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1 Introduction

Research on photoelectrocatalytically active materials for solar water splitting is important [1] to discover new light-absorbing semiconductors with suitable band gaps in the range from 1.6 to 2.4 eV [2] as a basis for using a large range of the solar spectrum. In addition, the band edge positions need to match the envisaged redox processes of photoelectrochemical (PEC) water splitting and parasitic reactions, e.g. charge carrier recombination, should be minimal [3–6]. Furthermore, the materials should be non-toxic, abundant, low cost, and stable [4]. Due to these requirements, it is challenging to discover suitable semiconductors as photoabsorbers which, in combination with adapted electrocatalysts, exhibit a high conversion of incident photons to electrons for product formation. Bi_2WO_6 [6–9] and Bi_2MoO_6 [10–12] fulfil some of the requirements and were here selected as starting materials for a combinatorial search of new materials suitable for photoelectrocatalytic energy conversion. Bi_2WO_6 exhibits band edges with suitable positions of 1.77 eV for the valence band (VB) and -1.03 eV for the conduction band (CB), which makes Bi_2WO_6 a candidate material for photoelectrocatalytic water splitting without application of an external bias voltage [4, 8, 13]. Bi_2MoO_6 was selected as a starting compound since its absorption edge is red-shifted to a wavelength of about 560 nm, which is a basis for absorbing a wider range of the incident solar spectrum as compared with Bi_2WO_6 . However, Bi_2MoO_6 showed substantially lower photoelectrocatalytic activity than Bi_2WO_6 [14].

Here, we aim to combine the properties of both material systems by fabricating Bi–W–Mo–O compositions-spread materials libraries (MLs) which are subsequently systematically analysed by high-throughput methods [15, 16] with respect to the effects of Mo addition to the Bi–W–O system and its suitability for PEC applications, aiming to reveal correlations of composition, crystal structure and microstructure on the photoelectrochemical properties (PEC) as well as the influence on the bandgap.

2 Experimental and methods

2.1 Fabrication of a thin-film materials library by reactive co-sputtering

The Bi–W–Mo–O thin-film ML was co-deposited using reactive direct current magnetron-sputter-deposition (AJA International ATC 2200J) on a pre-cleaned fluorine doped tin oxide (FTO, TEC8, XOP Glass) substrate with a size of $7.5\text{ cm} \times 7.5\text{ cm}$. The deposition and pre-cleaning steps were started at a base pressure of

2.6×10^{-6} Pa. Mo and W were used as elemental targets (100 mm diameter) with a purity of 99.99%, while Bi_2O_3 with a purity of 99.95% was used as a compound target. The azimuthal angle between the cathodes was 90° with Mo and Bi_2O_3 next to each other and W opposite to the Bi_2O_3 target. Pre-cleaning of the targets was performed to obtain a non-poisoned surface. The applied power during deposition was 100 W at the Bi_2O_3 target, 70 W at the Mo target and 55 W at the W target. An operating pressure of 0.66 Pa and a 40 sccm Ar gas flow was applied. An oxygen gas flow was not applied as an oxide target was used. The ML was annealed after deposition in air for 4 h at 500°C [5, 9] (heating rate: 15 K/min, cooling rate: 4 K/min).

2.2 High-throughput characterization of the materials library

Chemical composition, crystal structure, optical and PEC properties were determined on a rectangular array of 16×16 (256) measurement areas with a distance of $4.5\text{ mm} \times 4.5\text{ mm}$ to each other. For the compositional analysis high-throughput energy-dispersive X-ray spectroscopy (EDX) (JEOL JSM 5800 LV equipped with an Oxford Inca System, measurement accuracy: $\pm 1\text{ at.}\%$) was applied with a $100\text{ }\mu\text{m}$ aperture and an acceleration voltage of 20 kV. For the crystallographic phase analysis of the ML, high-throughput X-ray diffraction (XRD) (Philips XPert, PANalytical, Ni-filter Cu-K_α radiation) in Bragg-Brentano geometry was used. To determine PEC properties, optical scanning droplet cell (OSDC) measurements were performed (for details see [17]). The OSDC contained a $\text{Ag/AgCl}/3\text{ M KCl}$ reference electrode and a Pt wire counter electrode. A polytetrafluoroethylene (PTFE) cone with a surface area of 0.785 mm^2 was pressed on the surface and was connected as working electrode to a potentiostat (Jaissle 1002 PC). The positioning accuracy of the step-motor driven micrometer stages to position the SDC in three-dimensions is about $1\text{ }\mu\text{m}$. The specific PEC properties were determined within the surface area of the capillary over the measurement areas of the complete ML.

3 Results and discussion

Since Bi_2WO_6 exhibits the higher photocurrent of the two base compounds [13], the ML was designed such that it included Bi_2WO_6 for comparison. The results of the EDX composition analysis of the annealed ML is shown in a ternary diagram (Figure 1), where compositions are provided as ternary Bi/W/Mo atomic ratios. The oxygen amount in the ML is shown color-coded. The atomic ratio of oxygen was calculated according to $\left(\frac{\text{O}_{\text{at.}\%}}{\text{M}_{\text{at.}\%} + \text{O}_{\text{at.}\%}} * 100 \right)$. The compositions of the sputtered metals (M) range from 8 to 30 at.% Mo, from 25 to 74 at.% W, and from

Fig. 1: Color-coded ternary Bi–W–Mo–O composition diagram of the thin-film materials library after heat treatment in air at 500 °C for 4 h.

24 to 70 at.% Bi. The oxygen amount determined by means of EDX gives only a rough estimate of the O content in the thin-film library as it was sputtered on FTO substrates and thus contributions to the amount of O from the underlying substrate cannot be excluded. According to the measured O amount, a significant uptake of O occurs in Mo-rich regions which is consistent with the thickness gradient with the thinnest layer being deposited in Bi-rich regions. The O amount is stoichiometric in the Mo-rich and thickest areas, and under-stoichiometric in the thinnest and Bi-rich area of the ML.

Figure 2a shows selected XRD patterns of measurements areas with W-rich to Mo-rich compositions. The XRD patterns reveal that the Aurivillius $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{M-1}\text{B}_M\text{O}_{3M+1})^{2-}$ phase is present in the entire ML. The corresponding phase is $(\text{Bi}_2\text{O}_2)^{2+}(\text{Bi}_M(\text{W}_{1-N}\text{Mo}_N)_{M-1}\text{O}_{3M+1})^{2-}/(\text{Bi}_2\text{O}_2)^{2+}(\text{Bi}_M\text{W}_{M-1}\text{O}_{3M+1})^{2-}$ [9, 12]. For comparison, a diffraction pattern of the Bi_2WO_6 phase is displayed at the bottom of Figure 2a. One of the characteristic peaks ($2\theta = 28^\circ \pm [131]$) [8] shifts to smaller diffraction angles with increasing Mo content in the ML indicating lattice distortion [1]. Additionally, a sharp peak at $2\theta = 32^\circ \pm [002]$ is observed with increasing amount of Mo.

The increasing intensity of these peaks indicates increasing crystallinity of the thin films with higher Mo-content. In addition, the diffraction peak at

Fig. 2: (a) XRD patterns of selected measurement areas of the $\text{Bi}_2\text{Mo}_x\text{W}_{1-x}\text{O}_6$ ML for compositions with x from 0.08 to 0.53. (b) SEM images of three regions exhibiting different Mo content with $x = 0.08, 0.25$ and 0.53 .

$2\theta = 28^\circ$ is getting sharper with higher amount of Mo in the thin film (FWHM minimum in the Mo-rich region: 0.11, FWHM maximum in Bi-rich region: 1.39) which implies that the crystallite domain size is getting larger if Mo is added [1]. Figure 2b shows different morphologies depending on the amount of Mo in the thin film. A high amount of Mo shows small linked grains, a medium amount shows plates and also small linked grains, while the lowest amount of Mo exhibits some large plates, but many more smaller non interlinked plates.

Figure 3 shows color-coded ternary diagrams for (a) the peak width (FWHM), (b) the peak center, and (c) the calculated crystallite domain sizes. The peak width is smaller with either high amount of Bi or high amount of Mo in the thin film. By considering only the quasi-binary cut with a constant Bi amount of 47% no change in the peak width can be seen. Although with low amount of Bi (25%), decreasing amount of W and increasing amount of Mo a change in the peak width can be observed. Hence, it can be concluded that the peak width is increasing with decreasing amount of Mo and is decreasing with an increasing amount of Mo indicating again an increasing crystallinity and crystallite domain size. Furthermore, the peak center shifts to smaller angles with increasing amount of Mo

Fig. 3: Color-coded ternary maps derived from the XRD patterns of the MLs for the [131] plane $2\theta = 28^\circ$: (a) peak width, (b) peak center, (c) crystallite domain sizes calculated by applying the Scherrer equation for the most prominent peak [131].

if the amount of Bi is $<45\%$ indicating a lattice distortion at higher Mo content. The crystallite domain size is correlated with the peak width, as calculated using the Scherrer equation in which the peak width and the peak center are the only variables [18]. The smallest crystallite domain size is visible at a small amount of Bi and Mo and a high amount of W. The biggest crystallite domain sizes were identified for a small amount of Bi and high amounts of W and Mo. The color-coded ternary map of the crystallite domain size supports the conclusion that Mo was successfully incorporated.

Optical transmission measurements were performed at each measurement area of the ML to determine the bandgap. Bandgaps were calculated by semi-automated Tauc-plot analysis (see Figure 4a). The smallest bandgap of 2.0 eV was calculated for a composition area of $\text{Bi}_{31}\text{Mo}_{11-23}\text{W}_{46-58}\text{O}_z$. Another area with comparatively small bandgaps is the Bi-rich region with low Mo and low W amount in the thin film. A high bandgap (2.6–2.8 eV) was found in the region with medium amount of Bi (45–50%), low amount of W (25–35%) and high amount of Mo (22–29%). The area in between shows bandgaps around 2.2–2.4 eV. The difference in the bandgaps seems to be influenced by two parameters, namely (i) the degree of lattice distortion due to substitution of Mo, and ii) the quantity of the Mo 4d to W 5d orbital involved in the conduction band. A similar correlation for the influence of the Mo amount was shown before [1]. Comparing literature values for the bandgap of Bi_2WO_6 (2.7–2.8 eV [1, 4]) it can be noticed that by addition of Mo, the bandgap was systematically decreased for the complete ML.

Figure 5a shows the correlation of the indirect bandgap against the concentration of Mo in the thin film and Figure 5b against the ratio of W:Mo in the ML. It can be seen, that the indirect bandgap is increasing with increasing amount of Mo. With increasing amount of W and decreasing amount of Mo, the bandgap is

Fig. 4: (a) Semi-automated Tauc-plot analysis for indirect bandgap extrapolation. (b) Color-coded ternary map of the calculated bandgaps.

decreasing. This supports the hypothesis that the bandgap seems to be influenced by the degree of lattice distortion due to substitution of Mo and the quantity of the Mo 4d to W 5d orbital involved in the conduction band.

Figure 6a shows a plot of the color-coded photocurrent density in a partial ternary diagram. The highest photocurrent density was measured in the region with a Bi-content of 28–31%, a Mo content of 6–11% and a W content of 61–66%. The corresponding XRD pattern of the region with highest photocurrent density can be seen in Figure 2a with a Mo content of $x = 0.08\text{--}0.14$. The

Fig. 5: (a) XY-diagram of the indirect bandgap vs. the concentration of Mo in the thin film
(b) XY- diagram of the indirect bandgap vs. the ratio of W:Mo.

measurement area of highest photocurrent density (hit region) has a composition of $\text{Bi}_{31}\text{Mo}_7\text{W}_{62}\text{O}_z$ and a photocurrent density of $31 \mu\text{A}/\text{cm}^2$. Another area with relatively high photocurrent density is the region with high Bi amount ($>50\%$) and low amount of Mo ($<12\%$) as well as a low amount of W ($\approx 25\%$). This region has the composition $\text{Bi}_{67}\text{Mo}_9\text{W}_{27}\text{O}_z$ ($\text{Bi}_{1.7} \text{Mo}_{0.25}\text{W}_{0.75}\text{O}_z$). This correlates with the stoichiometric $\text{Bi}_2 \text{Mo}_{0.25}\text{W}_{0.75}\text{O}_6$ composition of the identified crystal structure. The region in between scarcely shows any photocurrent density.

Fig. 6: (a) Color-coded map of the photocurrent density measured with the OSDC in 0.1 M Na_2SO_4 , $\text{pH} = 5.8$ at an applied bias voltage of 1.23 V vs. RHE at an illumination of 100 mW/cm^2 . (b) Measured IPCE values in the region of highest photocurrent density with low Mo-concentration in comparison with Bi_2WO_6 (sputtered reference ML).

The IPCE values in the region of highest photocurrent ($\text{Bi}_{31}\text{Mo}_7\text{W}_{62}\text{O}_z$) and a Bi_2WO_6 sample were compared in Figure 6b. $\text{Bi}_{0.45}\text{Mo}_{0.11}\text{W}_{0.89}\text{O}_z$ is photoelectrochemically active up to a wavelength of 460 nm while Bi_2WO_6 is photoelectrochemically active just up to a wavelength of 420 nm. By comparing Bi_2WO_6 and

$\text{Bi}_{0.45}\text{Mo}_{0.11}\text{W}_{0.89}\text{O}_z$ it can be concluded that the bandgap was decreased due to the insertion of the Mo in the lattice which is supported by the calculated bandgap values presented in Figure 4b.

Focusing on a quasi-binary cut, for example from 12–24% Mo, 25% Bi and 55–65% W (Figure 6a), it can be supposed that a high concentration of Mo (4d element) decreases the photocatalytic efficiency for water oxidation which is most likely due to the exchange of W (5d element) by Mo which leads to a change in electronegativity. The effective electronegativity of a 4d element is higher and one can anticipate that it forms more covalent bonds with oxygen and will thus lead to a possibly improved delocalization of charge carriers. Furthermore, the change in electronegativity leads to a smaller curvature of the conduction band (CB). The smaller curvature because of the more covalent bonds with oxygen are not effective for the movement of photogenerated electron-hole pairs and will thus lead to a decreasing photocatalytic efficiency [19]. On the other hand, just a minute content of Mo in the lattice resulted in a decrease of the bandgap, shifting the absorption spectra to higher wavelength, and also improving the IPCE values as compared to Bi_2WO_6 (cf. Figure 6b) suggesting an improved electron transport due to lattice distortion analogous to BiVO_4 [20].

4 Conclusions

A $\text{Bi}_2\text{Mo}_x\text{W}_{1-x}\text{O}_6$ ML was synthesized using reactive magnetron co-sputtering. The ML shows maximum photocurrent density and IPCE values in the composition region $\text{Bi}_2\text{Mo}_{0.07}\text{W}_{0.93}\text{O}_6$ as compared with Bi_2WO_6 . Addition of Mo decreases the bandgap to a value of around 2.2 eV providing the basis for light absorption to higher wavelengths. Moreover, Mo is increasing the crystallite domain size if the Bi amount in the thin film is low. It is shown that the crystallite domain sizes influence the photocurrent density such that an increased crystallite domain size leads to a lower photocurrent density for the case of low Bi-concentrations. The decreased photocurrent density is probably due to a smaller space charge layer, an increased travelling length for the electrons to reach the surface within their lifetime, which also correlates with the increased grain size [21].

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