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Combinatorial Search for New Solar Water Splitting Photoanode Materials in the Thin-Film System Fe–Ti–W–O

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Abstract: In order to identify new solar water splitting photoanodes, Fe–Ti–W–O materials libraries were fabricated by combinatorial reactive co-sputtering and investigated by high-throughput characterization methods to elucidate compositional, thickness, and structural properties. In addition, photoelectrochemical measurements such as potentiodynamic photocurrent determination and open circuit potential measurements were performed using an automated scanning droplet cell. In the thin-film library, a quaternary photoactive region $\text{Fe}_{30-49}\text{Ti}_{29-55}\text{W}_{13-22}\text{O}_x$ was identified as a hit composition region, comprising binary and ternary phases. The identified region shows a distinct surface morphology with larger grains (~ 200 nm) being embedded into a matrix of smaller grains (~ 80 – 100 nm). A maximum photocurrent density of $117 \mu\text{A}/\text{cm}^2$ at a bias potential of 1.45 V vs. RHE in NaClO_4 as an electrolyte under standard solar simulating conditions was recorded. Additional samples with compositions from the hit region were fabricated by reactive co-sputtering and spin coating followed by annealing. Synchrotron X-ray diffraction of sputtered $\text{Fe}_{32}\text{Ti}_{52}\text{W}_{16}\text{O}_x$ thin-films, annealed in air (600°C , 700°C , 800°C) revealed the presence of the phases FeTiO_3 and $\text{Ti}_{0.54}\text{W}_{0.46}\text{O}_2$. The composition $\text{Fe}_{48}\text{Ti}_{30}\text{W}_{22}\text{O}_x$ from the hit region was fabricated by spin coating and subsequent annealing for a detailed

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investigation of its structure and photoactivity. After annealing the spin-coated sample at 650 °C for 6 h, X-ray diffraction results showed a dominant pattern with narrow diffraction lines belonging to a distorted FeWO_4 (ferberite) phase along with broad diffraction lines addressed as Fe_2TiO_5 and in a small fraction also, $\text{Fe}_{1.7}\text{Ti}_{0.23}\text{O}_3$. In hematite, Fe can be substituted by Ti, therefore we suggest that in the newfound ferberite-type phase, Ti partially substitutes for Fe leading to a small lattice distortion and a doubling of the monoclinic unit cell. In addition, Na from the substrate stabilizes the new phase: its tentative chemical formula is $\text{Na}_x\text{Fe}_{0.33}\text{Ti}_{0.67}\text{W}_2\text{O}_8$. A maximum photocurrent density of around 0.43 mA/cm² at 1.45 V vs. RHE in 1M NaOH (pH ~ 13.6) as an electrolyte was measured. Different aspects of the dependence of annealing and precursor solution concentration on phase transformation and photoactivity are discussed.

Keywords: combinatorial materials discovery; magnetron co-sputtering; photoelectrochemistry; solar water splitting; spin-coating.

1 Introduction

Energy harvesting from sunlight is one of the most promising and challenging approaches towards a sustainable energy future. Photoelectrochemical (PEC) cells are of interest due to their ability to reduce water to hydrogen at a photocathode in aqueous electrolyte solution by solar irradiation [1–3]. However, PEC oxidation of water on the photoanode is a major challenge due to the involvement of a four-electron transfer process which requires high overpotentials [4, 5]. In order to perform the oxygen evolution reaction (OER), photoanodes should have an appropriate bandgap to absorb light in the solar spectrum, enhanced charge separation and charge transport from bulk to the surface. However, efficiencies of PEC photoanodes can be limited by poor electronic conductivity leading to charge recombination and slow carrier transport [5, 6].

Several ternary transition metal oxides systems (M1–M2–O) have been investigated for PEC water oxidation due to their earth abundance, chemical stability, and suitable bandgap energies [6–9]. Meyer et al. [10] investigated the Fe–W–O system using a combinatorial thin-film materials library (MLs) approach and reported a promising PEC multiphase material consisting of the WO_3 , W_5O_{14} and Fe_2WO_6 phases at the metal composition of 15 at.% Fe and 85 at.% W. Similarly, Slizoberg et al. [11] investigated the Ti–W–O system revealing maximum photocurrent density at ~94 at.% Ti and 6 at.% W. Kalanur et al. [12] fabricated 1.16 at.% Ti-doped WO_3 thin films using hydrothermal methods and reported 3.5 times higher photocurrent density as compared to undoped WO_3 thin films. Another

photoanode system with promising PEC activity is Fe–Ti–O [13–15]. Multinary metal oxides (M–O) systems allows to tune their properties in various ways such as changing their composition and/or doping with other metals which may result in improved PEC performance. Apart from numerous investigations on M–O systems for solar water splitting, not much is known about the quaternary oxide system Fe–Ti–W–O. So, this system was explored using combinatorial synthesis of MLs and high-throughput characterization in order to derive correlations between composition, structure, morphology and PEC properties across the fabricated composition space. MLs comprise a large quantity of well-defined and well-comparable samples [16–19], from which a “hit” region with the most promising functional property can be identified, e.g. a region of maximum photocurrent density. Such hit composition(s) should be further verified and optimized by alternative fabrication routes, e.g. wet-chemical processes like spin coating or hydrothermal processes.

Here, we report on combinatorial materials discovery in the system Fe–Ti–W–O using high-throughput characterization methods. The structural and functional properties of the identified promising compositions were further investigated in terms of bandgap energy, crystal structure, photocurrent density, and energy conversion efficiency.

2 Experimental section

2.1 Synthesis of Fe–Ti–W–O thin-film materials libraries and the hit composition sample

Three Fe–Ti–W–O MLs were synthesized using combinatorial reactive co-sputtering in a commercial magnetron sputter system (AJA International ATC2200V). The deposition was performed using Fe (purity 99.95%), Ti (purity 99.95%) and W (purity 99.99%) metallic targets (4-inch diameter) on 4-inch diameter Si/SiO₂ wafers (1.5 μm SiO₂ diffusion barrier) as a substrate and base pressure $<1.7 \times 10^{-4}$ Pa with reactive gas flow of Ar (30 sccm) and O₂ (3 sccm) at a deposition pressure of 0.66 Pa. To achieve continuous composition and thickness gradients, the sputter target positions were such that Fe was in between W and Ti (180° angle between W and Ti), see Figure 1a. W and Ti was sputtered using direct current (DC) while Fe was sputtered by using radio frequency (RF) power supply. Table 1 lists the process parameters used to fabricate ML A, ML B, and ML C.

Two different sets of each ML were prepared at identical parameters to enable different high-throughput characterization methods. For PEC measurements, a 100 nm thick Pt conducting back electrode layer was fabricated onto the Si/SiO₂

Fig. 1: Schematic representation (not to scale) of (a) combinatorial reactive co-sputtering for the synthesis of thin-film materials libraries (top view) and, (b) spin coating-annealing protocol to deposit Fe–Ti–W–O thin films.

Tab. 1: Process parameters for combinatorial reactive co-sputtering of MLs A, B, and C and the homogeneous hit sample.

Materials library [ML]	Deposition power (W)			Deposition time (s)
	RF _{Fe}	DC _{Ti}	DC _W	
ML A	120	180	36	2100
ML B	80	300	36	1800
ML C	60	350	36	1800
Hit sample (homogeneous)	132	180	42	2500

wafer prior to the thin-film deposition. Another set of MLs was prepared on Si/SiO₂ wafers with photoresist patterns in order to perform thickness measurements. The as-deposited MLs were annealed in ambient air at 500 °C for 8 h. The temperature ramp rate was set to 15 °C/min, followed by natural cool down.

Furthermore, after identification of the region with the highest photocurrent, a homogeneous sample was prepared using reactive magnetron co-sputtering and was subsequently annealed at 600 °C, 700 °C, and 800 °C for 8 h in air with a ramp rate of 15 °C per min and natural cool down, see Table 1.

2.2 Synthesis of Fe–Ti–W–O hit compositions via spin coating

To deposit Fe–Ti–W–O films from the hit region, spin coating followed by annealing was used. FTO substrates (TEC 7, Pilkington) were pre-cleaned using ultrasonication in DI water, ethanol and finally in isopropanol for 15 min in each

solution. The substrates were blow-dried with Ar. Precursor solutions for spin coating were prepared by dissolving Fe (III) acetylacetonate, Ti (IV) isopropoxide and W (VI) ethoxide in isopropanol at 50 °C for 2 h. Two sample series with different precursor concentrations were prepared by spin coating (Figure 1b): SP1 was deposited with a concentration ratio Fe:Ti:W = 24 mM:15 mM:11 mM and SP2 with Fe:Ti:W = 48 mM:30 mM:22 mM. The SP1 solution was spin-coated at 1000 rpm for 30 s, and the modified sample was subsequently annealed on a hot plate at 150 °C for 2 min. This sequence is one cycle of the deposition-annealing process, which was repeated 3, 6, and 9 times to vary film thickness. SP2 solution was used with 9 such cycles. The volume of both the solutions was taken as 75 μ L for each cycle, which was just enough to cover the whole substrate. All samples were annealed in a box furnace first at 600 °C and afterwards for 6 h at 650 °C. In a first experiment series, spin coated films were also prepared on Pt-coated Si substrates identical to the combinatorial sputter parameters, and annealed under the same conditions as described above, but only low photoactivities were noticed in PEC experiments with these electrodes. Surprisingly, a different phase, namely $\text{NaFe}_{0.33}\text{Ti}_{0.67}\text{W}_2\text{O}_8$, was observed employing FTO substrates. The formation of this phase can be explained by the diffusion of Na from the FTO glass into the film. This finding demonstrates that the use of different substrates and deposition techniques significantly influence the phase formation in the films.

2.3 High-throughput characterization of MLs

High-throughput characterization methods were used on the MLs for investigation of composition, thickness, crystal structure, and PEC properties on 342 measurement areas (MAs) segmented in a 4.5 mm $\times$ 4.5 mm matrix. The elemental compositions were determined using automated energy dispersive X-ray (EDX, INCA X-act detector, Oxford instruments) analysis in a scanning electron microscope (SEM, JEOL 5800) performed at an acceleration voltage of 20 kV in the center of each MA. Annealed MLs were examined by SEM (Leo 1530VP at 5 kV acceleration voltage). Surface morphologies were obtained by SEM from selected MAs on the MLs. *Image J* software was used to analyze the microstructures. Film thickness measurements were performed on the MLs with photoresist lift-off patterns using a tactile profilometer (Ambios XP2). High-throughput X-ray diffraction (XRD) patterns from the MLs were obtained in Bragg–Brentano geometry (PANalytical X'Pert PRO system) equipped with PIXcel detector and $\text{CuK}\alpha$ radiation. Synchrotron XRD data were recorded at a Beam Line 9 of the DELTA Synchrotron (Technical University Dortmund) to obtain high-quality diffraction data for the highest photocurrent samples annealed at different temperatures (600 °C, 700 °C, 800 °C). Details of the synchrotron diffraction experiments can be found

elsewhere [20]. Identification of the phases for the diffraction patterns obtained from conventional and synchrotron XRD, respectively was performed using Pearson Crystal Data database. High-throughput PEC measurements were performed using an automated optical scanning droplet cell (OSDC) [18, 21]. The OSDC design and its working functionalities are reported elsewhere [11]. The droplet cell has a three-electrode configuration: counter electrode (Pt wire), reference electrode (Ag/AgCl, 3 M KCl) and a working electrode (with MAs having $\sim 0.785 \text{ mm}^2$ surface area). The MAs positions for PEC screening were identical to that of EDX, profilometry, and XRD which allows to correlate all high-throughput characterization results easily. An aqueous solution of 0.5 M NaClO_4 (pH 4.5) acts as a supporting electrolyte, while an optical fiber with 150 W Xe lamp (Hamamatsu Photonics) was used as light source. The light intensity of 100 mW/cm^2 illuminated the MAs. The potentiostat photocurrents were recorded at 1.475 V versus reversible hydrogen electrode (RHE). The photocurrent densities were calculated as a difference between current under illumination and the dark current per unit area on the MA. The delta open circuit potential (ΔOCP) was determined as the difference between the OCP under illumination (at 100 mW/cm^2) and OCP in dark measured at a scan rate of 1 mV/s. OCP current measurements allow the determination of n- or p-type semiconductor behavior. The applied potential (E_{appl}) was converted to RHE using the equation:

$$E_{\text{RHE}} = E_{\text{appl}} + 210 \text{ mV} + (59 \text{ mV} * \text{pH}) \quad (1)$$

2.4 Characterization of spin-coated films

Surface morphologies were analyzed by field emission scanning electron microscopy (FESEM) (ZEISS LEO GEMINI 1530). XRD measurements were performed using a Panalytical diffractometer, with $\text{Cu K}\alpha$ radiation, in a grazing incidence geometry (angle of incidence 0.5°) with a step size of 0.02° and a step time of 7 s. Ultraviolet – visible spectroscopy (UV-vis) measurements were performed using a PerkinElmer spectrometer (Lambda 950S): each sample was placed on an integrating sphere with an offset of $\sim 7.5^\circ$ with respect to the incident light and the trans-reflectance (TR) was measured. TR is the sum of transmittance and reflectance exhibited by the films. The absorption (A) of the film was determined using the expression:

$$A = -\ln(\text{TR}) \quad (2)$$

All PEC measurements were performed in a custom-made Teflon cell in a 3-electrode system with a Ag/AgCl reference electrode (Radiometer Analytical, 3 M

KCl, $E_{\text{Ag}/\text{AgCl}} = 0.210$ V vs. normal hydrogen electrode, NHE), a Pt wire counter electrode and the photoelectrodes as the working electrode. The illuminated MA (~ 0.24 cm²) is in contact with the electrolyte. All measurements were performed under back illumination using 1 M NaOH (pH 13.6) as a support electrolyte. A solar simulator (WACOM, model WXS-505–5H, AM1.5, Class AAA) and a potentiostat (EG&G Princeton Applied Research, Model 273A) were used for PEC measurements. Incident photon-to-current efficiency (IPCE) measurements were performed with an Acton Research monochromator coupled with a Xe lamp (LOT, LSH302). An electronic shutter (Uniblitz LS6) was used for chopping the light, and a long-pass colored filter (Schott, 3 mm thick) was placed between the monochromator and the sample to remove higher-order diffracted light. The calibration of the light intensity was performed by placing a bare FTO substrate in the PEC cell and measuring the transmitted light with a calibrated photodiode (PD300R-UV, Ophir). The formula for calculating the IPCE is:

$$\text{IPCE}(\lambda) = (J(\lambda) \times 1240) / P_{\text{light}}(\lambda) \times \lambda \quad (3)$$

where $J(\lambda)$ is the photocurrent density at the wavelength λ . $P_{\text{light}}(\lambda)$ is the intensity of the monochromator light at respective wavelengths.

3 Results and discussion

3.1 Results of high-throughput characterization of thin-film libraries

The results of the high-throughput EDX analysis show that a large part of the composition space of the Fe–Ti–W–O system was fabricated. The three thin-film MLs comprise compositions from 3–56 at.% Fe, 29–93 at.% Ti, and 4–28 at.% W. The overall thickness in the MLs ranges from 257 to 720 nm. Figure 2 shows color-coded ternary maps of (a) composition and (b) thickness for the three Fe–Ti–W–O MLs. ML A [$\text{Fe}_{(22-56)}\text{Ti}_{(29-72)}\text{W}_{(5-28)}\text{O}_x$] covers a thickness range from 325 to 624 nm. ML B has a composition spread of [$\text{Fe}_{(9-31)}\text{Ti}_{(52-87)}\text{W}_{(4-24)}\text{O}_x$] and film thicknesses from 338 to 720 nm. ML C (257–575 nm film thickness) covers a composition range of [$\text{Fe}_{(3-24)}\text{Ti}_{(63-93)}\text{W}_{(4-27)}\text{O}_x$] and has the maximum Ti content of all three MLs.

ΔOCP allows determining the type of semiconductor: p- or n-type. In a single junction PEC device for water splitting, the type of semiconductor enables one to decide which bias potential must be applied. In other words, the type of semiconductor defines whether an oxidation or a reduction process should be performed on the surface of the working electrode. The n-type semiconductor – here addressed as a photoanode – is used for the oxygen evolution reaction (OER),

Fig. 2: Color-coded ternary (a) composition map of Fe, Ti and W in atomic percentage (at.%) from the three MLs and (b) thickness map with corresponding scale bar for the three MLs.

while a p-type semiconductor can be applied as a photocathode which is used for the hydrogen evolution reaction (HER). Figure 3a shows a color-coded ternary diagram of ΔOCP for the three MLs. Within the composition spread of ML A, ΔOCP values range from -0.074 V to -0.024 V indicating n-type semiconductor properties. For Ti contents < 81 at.% in ML B, no change in ΔOCP values were recorded. Correspondingly, a more negative ΔOCP value up to -0.16 V was observed in ML C towards the Ti-rich region. However, a small region in ML B and ML C showed positive ΔOCP values (0.13 V) suggesting p-type behavior. The visualization of the PEC behavior over the ternary composition spread of the MLs is presented in Figure 3b. A global maximum photocurrent density of $117 \mu\text{A}/\text{cm}^2$ was recorded at the composition $\text{Fe}_{46}\text{Ti}_{34}\text{W}_{20}$, highlighted in Figure 3b. A local maximum photocurrent

Fig. 3: Color-coded ternary plot of (a) ΔOCP and (b) photocurrent density maps of ML A, B, and C for the Fe–Ti–W–O system and corresponding color scale.

density $>80\text{ }\mu\text{A}/\text{cm}^2$ was recorded for compositions ranging between 29 and 50 at.% Ti within the investigated composition space. MLs B and C, with increased Ti content of 92 at.%, showed the lowest PEC performance at the investigated conditions.

Figure 4a shows the XRD patterns of 10 selected MAs from ML A. The MAs follow the photocurrent variation (Figure 4b) and the Ti composition gradient (Figure 4c). Throughout the investigated region, four Fe–Ti–W–O binary

Fig. 4: (a) XRD patterns of selected MAs through the center of ML A along with the (b) photocurrent variation and (c) Ti composition gradient (direction marked with black arrow). K_β appears from the W-filament in the XRD Cu cathode and ‘S’ symbol indicates Pt (back electrode) reaction with substrate.

and ternary phases along with the substrate peaks (marked with *) were identified. The diffraction peaks of the four phases (hexagonal WO_3 , trigonal FeTiO_3 , orthorhombic Fe_2TiO_5 , and tetragonal $\text{Ti}_{0.54}\text{W}_{0.46}\text{O}_2$, matching to 1250681, 1616028, 313424, and 1709821 files, respectively of the Pearson's Crystal database) are marked with different symbols. The MA ($\text{Fe}_{46}\text{Ti}_{34}\text{W}_{20}$) with the highest photocurrent density ($117 \mu\text{A}/\text{cm}^2$) comprises all identified phases. Towards low 2θ values (from 25° to 40°), the WO_3 (200), the FeTiO_3 (104) & (006) and, the $\text{Ti}_{0.54}\text{W}_{0.46}\text{O}_2$ (200) phases match to the diffraction peaks at $2\theta = 28.14^\circ$, 32.06° , 38.63° , and 38.20° , respectively. For diffraction patterns with $2\theta > 40^\circ$, the Fe_2TiO_5 phase is recorded to have (113) and (043) reflection at 46.04° and 46.32° 2θ values, respectively. Another diffraction peak of the $\text{Ti}_{0.54}\text{W}_{0.46}\text{O}_2$ phase is observed at 55.50° 2θ with the (220) reflection. Therefore, no distinct changes in the position and intensity of the diffraction peaks were observed with change in composition as well as from low to the maximum photocurrent region (see Figure 4a–c).

However, surface morphology seems to influence the PEC behavior. Figure 5 shows selected SEM images of ML A, B, and C at different compositions,

Fig. 5: Selected SEM images from the Fe–Ti–W–O MLs A, B, and C at different compositions marked with black arrows in the ternary color-coded (composition-photocurrent) plot. The Ti content is labeled top left and photocurrent density top right.

highlighted with black arrows in the ternary color-coded plot. The surface morphology of ML A shows mixed microstructures throughout the composition spread from 30 to 72 at.% Ti. The larger grains with an average size of ~ 200 nm form chain-like structures that are embedded in a matrix of smaller grains with ~ 80 – 100 nm size. However, in ML B with increased Ti concentration (52–87 at.%), the average grain size decreased to ~ 60 nm. The grain size in ML C reduced to ~ 40 nm for 63–93 at.% Ti. These results underline the importance of identifying both composition and morphology to estimate their impact on PEC behavior.

3.2 Analysis of hit compositions of the Fe–Ti–W–O system

The high-throughput structural and functional investigation of the Fe–Ti–W–O system revealed the composition space ($\text{Fe}_{30-49}\text{Ti}_{29-55}\text{W}_{13-22}\text{O}_x$) to be promising for PEC solar water splitting. Therefore, homogeneous Fe–Ti–W–O samples were prepared from the highest photocurrent region using two different fabrication methods: reactive magnetron co-sputtering and spin coating to investigate the hit region further. For magnetron sputtering, $\text{Fe}_{32}\text{Ti}_{52}\text{W}_{16}\text{O}_x$ was selected as one end of the composition range and for spin coating, the other end, $\text{Fe}_{48}\text{Ti}_{30}\text{W}_{22}\text{O}_x$ was chosen.

3.2.1 Reactive magnetron co-sputtered sample from the hit composition region

The homogeneous sputtered $\text{Fe}_{32}\text{Ti}_{52}\text{W}_{16}\text{O}_x$ sample, annealed at 600 °C, 700 °C, and 800 °C for 8 h in air was characterized using synchrotron XRD demonstrating that the film contains a mixture of two phases (Figure 6): FeTiO_3 and $\text{Ti}_{0.54}\text{W}_{0.46}\text{O}_2$ (Pt was used as a back contact for PEC measurements). The crystallinity and lattice planes of both the crystal structures change with an increase in annealing temperatures. The (104) and (102) lattice planes of the FeTiO_3 phase disappeared after annealing at 800 °C. This might be due to the change of grain orientation from a film with highly ordered grains. The (110) and (205) lattice planes of the FeTiO_3 phase are oriented parallel to the substrate. Moreover, a small shift of the (110) peak position is observed towards a lower 2θ value with an increase in temperature from 600 °C to 800 °C. This shift is likely due to the substitution of Fe atoms by Ti atoms in the lattice structure. For the $\text{Ti}_{0.54}\text{W}_{0.46}\text{O}_2$ phase, the crystallinity increases with an increasing temperature from 600 °C to 800 °C as observed from the (110) and (211) lattice planes. Also, a small signal of the (200) lattice plane of $\text{Ti}_{0.54}\text{W}_{0.46}\text{O}_2$ is only recorded in the diffraction pattern of the 800 °C annealed film.

Fig. 6: Results of the synchrotron XRD on the $\text{Fe}_{32}\text{Ti}_{52}\text{W}_{16}\text{O}_x$ after annealing at 600 °C, 700 °C and 800 °C in air.

3.2.2 Spin-coated samples from the hit composition region

To investigate if the hit composition exists as a novel phase or as a set of different phases, XRD was performed in grazing incidence geometry on spin-coated $\text{Fe}_{48}\text{Ti}_{30}\text{W}_{22}\text{O}_x$ sample. From subsequent PEC characterizations it was obvious that the sample did not change mechanically or electrochemically during the PEC measurements; XRD patterns performed after the electrochemical measurement were similar to the pristine ones. Two typical results are presented in Figure 7. Film SP1, annealed at 650 °C for 6 h, shows broad peaks indexed as $\text{Fe}_{1.698}\text{Ti}_{0.228}\text{O}_3$ (JCPDS # 04-009-6569) in addition to the peaks from the FTO substrate. Low-intensity peaks, corresponding to the orthorhombic Fe_2TiO_5 phase (JCPDS # 00-041-1432), were also observed. Since the observed peaks were probably limited by the lateral dimension of the films, a subsequent batch of samples was prepared with higher precursor concentration (named SP2) to allow better detection of the phase constitution. The XRD patterns for the SP2 film in comparison with SP1 possessed higher crystallinity. This could be either due to Ostwald ripening resulting in bigger grain size or due to the formation of a thicker film with improved stacking of particles. In order to explain the sharp new XRD peaks of SP2, we assume the possibility of the formation of a new phase. The first five peaks have similar FWHM values at $2\theta \sim 15.39^\circ, 17.89^\circ, 23.64^\circ, 31.12^\circ$, and 36.16° . The broad peaks in the diffractogram of SP2 can be assigned to the phases $\text{Fe}_{1.698}\text{Ti}_{0.228}\text{O}_3$, orthorhombic Fe_2TiO_5 , and TiO_2 rutile (see shoulders at $2\theta = 27.27^\circ, 35.79^\circ$, and 53.93°).

Fig. 7: XRD patterns of spin-coated $\text{Fe}_{48}\text{Ti}_{30}\text{W}_{22}\text{O}_x$ synthesized with different precursor concentrations, annealed at 650 °C for 6 h in air.

The grains corresponding to the phase Fe_2TiO_5 are in the range of 10 nm particle size. The new phase identified by the diffraction pattern using PDF database is crystallizing in a distorted ferberite structure, isostructural to $\text{NaCr}_{0.5}\text{Fe}_{0.5}\text{W}_2\text{O}_8$ (JCPDS # 04-017-5992). It needs a certain amount of Na to form. This might be the reason why it first appears at higher temperatures, as Na has to diffuse from the glass substrate via the FTO layer into the Fe–Ti–W–O layer to form this new phase. The lattice parameters together with the lattice constants of the FeWO_4 are given in Table 2. The introduction of Na and the substitution Fe and Ti for Fe atoms in pure ferberite are leading to a small change of the lattice constants b and c of the monoclinic phase but to a doubling of the lattice constant a . Further investigations are needed to elucidate the crystal structure of the new phase in detail.

In a simplified picture, the metal composition of the film of originally Fe:Ti:W = 48:32:22 can now be explained by the formation of two oxide phases

Tab. 2: Lattice parameters of ferberite-type phases.

	a	b	c	β	
FeWO_4	4.73	5.71	4.97	90°	P2/c
JCPDS # 00-012-0729					
$\text{NaCr}_{0.5}\text{Fe}_{0.5}\text{W}_2\text{O}_8$	9.87	5.72	4.96	90.54°	P2/c
JCPDS # 04-017-5992					
$\text{NaFe}_{0.33}\text{Ti}_{0.67}\text{W}_2\text{O}_8$					
New phase					

appearing in the ratio $\text{NaFe}_{0.33}\text{Ti}_{0.67}\text{W}_2\text{O}_8:\text{Fe}_2\text{TiO}_5 = 1:2$. The presence of the phases such as Ti-alloyed hematite can be considered as an intermediate which reacts with detected TiO_2 in the film under the formation of further pseudobrookite Fe_2TiO_5 grains. In case of sputtered thin films on Pt-coated Si wafers, the formation of the new ferberite-type phase could not be observed, since no Na, which stabilizes this structure, was present.

Figure 8 shows FESEM images of SP1 and SP2 films. There is no visible difference in the porous grain distribution with particle diameter in the order of 20 nm on average for both films. The morphology was mainly a porous network of nanoparticles fused together due to high-temperature annealing. EDX analysis was performed and yielded a metal composition of $\text{Fe}_{47}\text{Ti}_{33}\text{W}_{20}$ for SP1 and $\text{Fe}_{47}\text{Ti}_{32}\text{W}_{21}$ for SP2 films.

The optical absorption spectra for the Fe–Ti–W–O films with a different number of deposition-annealing cycles are shown in Figure 9a. The band cut-off edge for all films remained at around 600 nm ($E_g \sim 2.11$ eV). For 3 cycles, the absorption was the lowest and with higher number of cycles, the absorption intensity increased which is attributed to the thick, but still porous films. The absorption remained lower than unity which suggests that thicker films would ensure even higher absorption and higher performance. The brownish-yellow color of the films corroborates the presence of Fe_2TiO_5 and $\text{NaFe}_{0.33}\text{Ti}_{0.67}\text{W}_2\text{O}_8$ in crystalline form as observed from the XRD results. In Figure 9b, the absorption spectra for samples prepared with higher precursor concentration showed higher absorption intensity due to their different thicknesses. Two broad absorption features are located at 415 nm and 470 nm in Figure 9b. They could be explained as d-d transitions of Fe 3d or Ti 3d states at the edge of the valence band to empty W 3d states in case of ferberite phase or as a transition from Fe 3d states to empty Ti 3d states in case of pseudobrookite.

Fig. 8: FESEM image of sample annealed at 650 °C with (a) Fe 24 mM, Ti 15 mM and W 11 mM, and (b) Fe 48 mM, Ti 30 mM and W 22 mM precursor concentration.

Fig. 9: Absorption spectra of SP samples (a) with a different number of deposition-annealing cycles, and (b) with different precursor concentrations for 9 cycles, annealed at 650 °C for 6 h in air.

To evaluate the photoactive response from the Fe–Ti–W–O based electrodes deposited by spin coating, PEC characterization was performed on samples prepared by varying the cycles of the deposition-annealing process. As shown in Figure 10a, the photocurrent density with respect to increasing bias potential showed differences with different thicknesses of the samples under chopped solar simulated light of AM1.5G in 1 M NaOH electrolyte. Early-onset was achieved at around 0.8 V vs. RHE and the photocurrent increased with increasing potential. A photocurrent of around 0.12 mA/cm² at 1.23 V vs. RHE and 0.17 mA/cm² at 1.45 V

Fig. 10: (a) Photocurrent density (*j*) vs. potential (*V*) plot for samples deposited with varying cycles of the deposition-annealing, and (b) deposited with varying precursor concentration for optimized 9 cycles, all annealed at 650 °C for 6 h.

vs. RHE was observed for samples deposited with 9 cycles. Interestingly, the films grown under 3 and 6 cycles showed very similar photocurrent profiles even though the absorption by the 6-cycle film was higher as shown earlier in Figure 9a. This could be due to a balancing mechanism between the particle size and light absorption. With thinner films, the charge separation could be better even with lower absorption, whereas with thicker films, the increase in absorption may not be able to compensate for an increased charge recombination owing to a longer path of excited electrons and holes. It must be noted that the films were measured without any co-catalyst or passivating layer or hole scavenger.

To enhance the absorption and the bulk charge transport by increasing the coverage on FTO substrates, a higher precursor concentration solution was used to make similar cycles while keeping other conditions like spin coating parameters and annealing profile same. Since the phase crystallization already occurs at 650 °C, as shown by XRD, it was used as the annealing temperature for both kinds of films.

The photocurrent density vs. potential curves, as presented in Figure 10b, shows enhancement in photocurrent density for samples synthesized with increased precursor concentration. At 1.45 V vs. RHE, a photocurrent density of 0.43 mA/cm² was achieved for SP2, an improvement by a factor of 2.4 compared to SP1. However, the photocurrent increased only marginally from 0.12 mA/cm² for SP1 to 0.15 mA/cm² for SP2 electrodes at 1.23 V vs. RHE. Since photocurrent densities at lower potential bias reflect primarily the rate constant of holes reacting with OH⁻ groups at the semiconductor-electrolyte interface, it appears that the surface and band bending remained similar but the bulk conductivity improved significantly for SP2. This effect could be explained after the formation of the ferberite-type phase in the film. The latter is apparent from the photocurrent trend after 1.3 V vs. RHE where SP2 samples showed no plateau current and increased almost linearly with increasing potential bias. Even higher precursor concentration was tried but the precursor solution was vulnerable to rapid precipitation which leads to non-uniform films with additional phases and their segregation which are detrimental for electrochemical photoactivity.

Figure 11 shows IPCE as a function of incident light wavelength for photoanodes deposited with different precursor concentrations, measured at an applied bias potential of 1.23 V (a) and 1.45 V vs. RHE (b) in 1 M NaOH. Both curves show a similar trend with a cut off onset at around 550 nm and a similar efficiency profile at 1.23 V vs. RHE. This is supported by the photocurrent density which remained similar for both films. Whereas at 1.45 V vs. RHE, the efficiency profile changed, with the wavelength <400 nm showing a higher increase for SP2 samples, than the wavelength with 400 nm to 500 nm.

Fig. 11: IPCE spectra at (a) 1.23 V vs. RHE and (b) 1.45 V vs. RHE, for photoanodes annealed at 650 °C for 6 h.

4 Conclusions

A large part of the system Fe–Ti–W–O was investigated using combinatorial synthesis and high-throughput characterization to identify suitable materials for solar water splitting. Three thin-film Fe–Ti–W–O MLs were fabricated using reactive magnetron co-sputtering and air annealing at 500 °C for 8 h. High-throughput characterizations enabled the identification of a photoactive region within the MLs consisting of >1000 MAs on the MLs in the composition range $\text{Fe}_{3-56}\text{Ti}_{29-93}\text{W}_{4-28}\text{O}_x$. The MLs have thicknesses in the range from 257 to 720 nm. The screening revealed ML A [$\text{Fe}_{(22-56)}\text{Ti}_{(29-72)}\text{W}_{(5-28)}\text{O}_x$] to exhibit promising PEC behavior compared to other two MLs consisting of mixed Fe–Ti–W–O binary and ternary phases. The ΔOCP identified is typical for n-type photoelectrodes. Moreover, surface morphology influences the PEC activity of the system. Grains with an average size of ~ 200 nm forming a chain-like structure embedded into the matrix of smaller grains (~ 80 – 100 nm) appear in the films with highest photoactivity. In the ‘hit region’, i.e. the composition range $\text{Fe}_{30-49}\text{Ti}_{29-55}\text{W}_{13-22}\text{O}_x$, a maximum photocurrent density of $117 \mu\text{A}/\text{cm}^2$ was observed. Therefore, this region was investigated in greater detail: two hit samples, $\text{Fe}_{32}\text{Ti}_{52}\text{W}_{16}\text{O}_x$ and $\text{Fe}_{48}\text{Ti}_{30}\text{W}_{22}\text{O}_x$, were fabricated by reactive magnetron co-sputtering and spin coating, respectively. The $\text{Fe}_{32}\text{Ti}_{52}\text{W}_{16}\text{O}_x$ sample was prepared for crystal structure investigation, which was subsequently annealed in air at 600 °C, 700 °C, and 800 °C. Synchrotron XRD revealed the presence of the phases FeTiO_3 and $\text{Ti}_{0.54}\text{W}_{0.46}\text{O}_2$. The second set of the hit region films with a composition of $\text{Fe}_{48}\text{Ti}_{30}\text{W}_{22}\text{O}_x$ was synthesized by simple and low-cost spin coating. PEC characterization and efficiency

measurement revealed the importance of annealing temperature and precursor concentration on photoactivity. At 1.45 V vs. RHE, a photocurrent density of around 0.24 mA/cm^2 was attained in pH 13.6 (1 M NaOH) electrolyte under standard illumination conditions. By changing the precursor concentration of the solution, the photocurrent density improved to 0.43 mA/cm^2 at 1.45 V vs. RHE while keeping the annealing temperature to 650°C , 6 h. A new oxide of composition $\text{NaFe}_{0.33}\text{Ti}_{0.67}\text{W}_2\text{O}_8$ was identified by XRD together with the pseudobrookite phase Fe_2TiO_5 . The size of the grains of this new phase is in the range of 50 nm while the grains of pseudobrookite in the films are substantially smaller (10 nm). It is assumed that Na which is necessary to stabilize the new ferberite-type phase is diffusing from the glass substrate into the Fe–Ti–W–O layer during annealing. Sputtered layers also showed a remarkable chemical and mechanical stability under slightly acidic conditions employing a NaClO_4 electrolyte at a pH 4.5. To further improve these photoelectrodes, co-catalysts should be deposited on the electrode surfaces. The fact that the oxide films also show stability under acidic conditions enables the possibility for light-induced water splitting under acidic conditions where non-noble metal co-catalyst for HER can be used at the counter electrode.

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