



Development of direct current magnetron sputtered TiO_{2-x} thin films as buffer layers for copper indium gallium diselenide based solar cells

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ABSTRACT

We describe the development and characterization of direct current magnetron sputtered titanium dioxide thin films from ceramic targets mixed with metallic titanium particles. The aim of this article is to assess their suitability for the application as buffer layer in copper indium gallium diselenide (CIGSe) based solar cells. The absorber material is produced in a semi-industrial, roll-to-roll hybrid sputter co-evaporation process. A potential strategy to modify electro-optical properties of TiO_2 thin films by controlling the concentration of defects, such as oxygen vacancies, is investigated by X-ray photoelectron spectroscopy (XPS), transmission/reflection spectroscopy, spectroscopic ellipsometry, and cathodoluminescence. The presence of oxygen in the plasma during the sputter deposition process has a crucial impact on the electron transport mechanism in the studied devices. The source of the changed device characteristic can be found in modified band discontinuities at the absorber–buffer interface and in an oxidized CIGSe surface, indicated by the presence of cationic selenium, as detected by XPS. We sketch a tentative band alignment diagram and outline the range of possible modifications. The harmful effect of oxygen in the plasma forces the omission of oxygen in the process and restricts the possibilities to modify the material properties of the TiO_2 layers, and consequently the prospects for an application on CIGSe. Nevertheless, the results of this work depict the principal eligibility, albeit optimization on both sides of the absorber–buffer interface are inevitable for an improved cell performance.

1. Introduction

Copper indium gallium diselenide (CIGSe) is still one of the most promising absorber materials for thin film photovoltaic (PV) application. Besides the operation as absorber in single junction cells, recently the high potential of CIGSe/perovskite tandem devices on flexible substrates has been demonstrated with a certified power conversion efficiency (PCE) of 24.2% in [1].

Cadmium sulfide (CdS) is a well-proven functional buffer layer that passivates the interface between the *p*-type CIGSe absorber and the *n*-type front contact, improving the solar cell performance. However, the high toxicity of cadmium and parasitic absorption, due to its relatively low bandgap energy (E_g) (2.4–2.5 eV), still drives research towards the substitution of CdS buffer layer by alternative low-cost, nontoxic materials. Also, the low thermal stability of CdS is one reason for the degradation of CIGSe based PV, as recently reported in [2]. Many scientific institutions and also the industry invested considerable

efforts to find suitable materials to replace CdS. The most commonly used materials, such as $\text{Zn}(\text{O,S})$, $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, In_xS_y or $\text{Zn}_{1-x}\text{Sn}_x\text{O}_y$ and the corresponding deposition techniques are summarized by reviews in [3,4]. The current world record CIGSe solar cell with an energy conversion efficiency of 23.35% as presented in [5] is fabricated with a Cd free $\text{Zn}(\text{O,S,OH})_x/\text{Zn}_{0.8}\text{Mg}_{0.2}\text{O}$ double buffer layer deposited with a combination of chemical bath deposition and atomic layer deposition (ALD), respectively.

Although roll-to-roll (R2R) application of atmospheric spatial ALD, allowing for large area deposition has been demonstrated [6], magnetron sputtering is still a preferred process in the industry, especially in DC operation mode. Properties of buffer layers, particularly at the interface to the absorber and the resulting cell performance, not only depend on the buffer material itself. For instance, the deposition technique can affect the bulk properties of the thin film and also can change the CIGSe surface, e.g. by sputter damage. In general, the nature of the CIGSe surface is decisive. The hybrid sputter co-evaporation process for

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CIGSe absorber production by Sunplugged GmbH has a specific feature: a process pressure in the range of 0.1 Pa and the presence of argon (Ar) during absorber synthesis, which results in unique CIGSe growth conditions when compared to conventional thermal co-evaporation. The morphology of Sunplugged's absorber layer is characterized by rather small crystals and a rough surface.

The application of magnetron sputter deposited buffer layers to Sunplugged's absorber is purpose of the present investigation. Our approach is the use of direct current (DC) sputtered titanium dioxide (TiO_{2-x}) from conductive TiO_2 targets mixed with additional metallic titanium (Ti). DC sputtering enables a higher process stability and less complex instrumentation in comparison to radio frequency (RF) sputtering, which is required for insulating oxidic target materials. ALD deposited TiO_2 was already demonstrated as an electron selective layer for CIGSe solar cells, where a conversion efficiency of 9.9% was reached [7]. TiO_2 was also used as an intermediate buffer layer in combination with CdS, which allowed to reduce the thickness of CdS without losses in the open circuit voltage (V_{OC}) and fill factor (FF) [8]. Magnetron sputtered TiO_2 could therefore be an interesting nontoxic, low-cost candidate for CIGSe photovoltaic application, especially for industrial production.

2. Experimental and methods

2.1. TiO_{2-x} thin films

TiO_{2-x} thin films are deposited by DC magnetron sputtering from ceramic TiO_2 targets, mixed with additional metallic Ti. TiO_2 powder is mixed with additional (5 vol%) metallic Ti powder and hot pressed (in vacuum) to circular targets bonded to a 2 mm thick copper base plate (produced by RHP Technology GmbH). The TiO_x targets have a diameter of 7 cm and a thickness of 3 mm (copper plate excluded). The thin films are produced with and without introducing oxygen to the Ar process gas. The pre-process vacuum in the deposition chamber was generally in the range $< 2 \cdot 10^{-4}$ Pa. Process conditions are the following: The gas flow was kept constant resulting in a process pressure of 0.32 Pa and a constant DC power of 50 W was applied to the magnetron, which is equivalent to a power density of 2.2 W/cm^2 . The substrates were rotating over the target with a planetary movement while the distance from the target surface to the substrates was 50 mm. The samples referred to as $\text{TiO}_2|4\%$ were produced with $F_{O_2}/(F_{O_2} + F_{Ar}) = 4\%$ (with gasflow F) and the samples referred to as $\text{TiO}_{2-x}|0\%$ without adding oxygen to the process gas. A total gas flow of 68 sccm was used for all samples investigated in this study.

The applied analytical methods require an adaption of substrates and film thickness. This inevitably insists on the assumption that material properties on different substrates and varying thickness are comparable, which might not be clear a priori but the results generally commend it. Table 1 summarizes the sputter conditions for the respective samples and indicates the applied analytical methods.

Optical spectra acquisitions were performed with highly transparent Corning Eagle XG glass substrates ($24 \times 24 \text{ mm}^2$ and 1.1 mm thick; provided by Präzisions Glas & Optik GmbH) with TiO_{2-x} films of a nominal thickness of 60 nm. Transmission/Reflection experiments were performed with a Perkin Elmer Lambda 1050 with integrating sphere. A calibrated mirror was used as a reflection standard. Ellipsometric spectra were recorded at incident angles of 50° , 60° , and 70° in the spectral region from 190 nm to 950 nm using a Sentech 850 DUV. For data analysis we use the code RIG-VM developed at Fraunhofer IST [9], which enables the simultaneous evaluation of ellipsometric, transmission and reflection spectra. Data analysis was performed from 250 nm to 2400 nm as optical properties of the glass substrate are well known in this spectral range.

Samples for Cathodoluminescence (CL) and grazing incidence X-ray diffraction (GI-XRD) were prepared on polished Mo sheets ($20 \times 20 \text{ mm}^2$ and 3 mm thick; provided by Plansee GmbH) with a nominal

Table 1

Summarized sputter conditions.

Sample	Substrate	P (W)	p (Pa)	t (min)	Analytics
$\text{TiO}_2 4\%$ 18 nm	CIGSe	50	0.32	60	XPS/SEM/j-V
$\text{TiO}_2 4\%$ 3 nm	CIGSe	50	0.32	10	XPS
$\text{TiO}_2 4\%$ 60 nm	EAGLE XG	50	0.32	200	UV-VIS/Ellips.
$\text{TiO}_2 4\%$ 250 nm	Mo sheet	50	0.32	833	CL/GI-XRD
$\text{TiO}_{2-x} 0\%$ 18 nm	CIGSe	50	0.32	6.5	XPS/SEM/j-V
$\text{TiO}_{2-x} 0\%$ 3 nm	CIGSe	50	0.32	1	XPS
$\text{TiO}_{2-x} 0\%$ 60 nm	EAGLE XG	50	0.32	21.5	UV-VIS/Ellips.
$\text{TiO}_{2-x} 0\%$ 250 nm	Mo sheet	50	0.32	93	CL/GI-XRD

TiO_2 film thickness of 250 nm. The increased film thickness is necessary to maximize the detection volume of the actual sample layer and to minimize sampling signal of the substrate. CL collection was done in a Jeol JSM-7610F field emission scanning electron microscope (SEM) at room temperature. The acceleration energy of the incident electron beam was set to 5 keV in order to minimize the penetration depth, and hence to increase the surface sensitivity and still being able to record sufficient CL. CL spectra were recorded by a Delmic SPARC CL System equipped with an Kymera 193i spectrometer, an iDus InGaAs 491 infrared (IR) camera, and a Zyla 5.5. CMOS detector for the visible (VIS) and near infrared (NIR) spectral region. Diffraction gratings with 300 lines/mm blazed at wavelengths of 1200 nm and 500 nm, respectively were chosen.

GI-XRD was performed with a Panalytical Empyrean with parallel beam optics and a $\text{Cu K}\alpha$ X-ray source (wavelength = $1.54056 \text{ \AA}$) to determine crystallinity. The $\text{TiO}_2|4\%$ and $\text{TiO}_{2-x}|0\%$ samples are investigated on a height adjustable stage in high vacuum (Anton Paar HTK 16N). A fixed angle of incidence (ω) of 2° was chosen for the 2θ -scan.

2.2. CIGSe/ TiO_{2-x} : Interface and devices

2.2.1. Interface and device fabrication

At Sunplugged GmbH the CIGSe absorber is deposited to a flexible stainless steel foil coated with a glass layer and a multilayer back contact consisting of titanium, sodium doped molybdenum (Mo), and pristine molybdenum. The absorber layer is produced in a semi-industrial, R2R, hybrid sputter co-evaporation process, which combines magnetron sputtering and thermal evaporation. A detailed description of the semi-industrial process developed by Sunplugged GmbH, DePro Control GmbH, University of Innsbruck, and University of Milan-Bicocca can be found in [10]. Recently, it was presented that a double graded Ga profile can be realized with this setup [11]. Also, the Ga content, close to the CIGSe surface can be controlled, which is a very important parameter to optimize the band alignment at the absorber buffer interface.

X-ray photoelectron spectroscopy (XPS) was performed on bare CIGSe and TiO_{2-x} films deposited on CIGSe absorbers, with a nominal TiO_{2-x} film thickness of each 3 nm and 18 nm. Device characterization was done on full layer stacks with 18 nm TiO_{2-x} films covered by a 100 nm layer of indium-tin-oxide (ITO) front contact.

2.2.2. Material-, interface- and device characterization

Characterization of the surface chemistry and electronic properties of the bare CIGSe and the TiO_{2-x} thin films deposited on CIGSe was done by means of XPS. XPS experiments were performed with a commercial laboratory-based SPECS NAP-XPS system. The system is comprised of a μFOCUS 600 NAP monochromatic small spot ($300 \mu\text{m}$) Al $\text{K}\alpha$ X-ray source and a hemispherical energy analyzer (SPECS PHOBIOS 150 NAP equipped with 1D delay line detector). The samples were mounted on a sample holder with conductive copper adhesive tape, in order to reduce charging. Additionally, an electron floodgun was used to compensate potential charging effects in XPS experiments. XPS was used to determine the surface-near composition of the CIGSe absorber

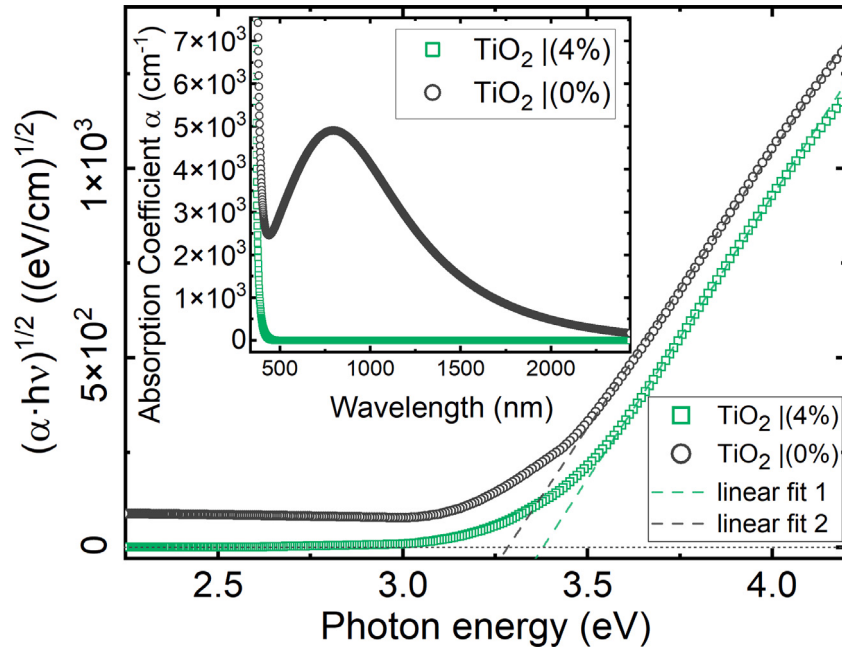


Fig. 1. Absorption coefficient of TiO_{2-x} thin films, extracted from optical transmission/reflection and ellipsometric spectra are presented in a Tauc plot assuming an indirect bandgap. The inset shows the wavelength dependent absorption coefficient.

and to probe the valance band offset (ΔE_v) at the absorber–buffer interface. Due to the changed charge distribution at an interface, the positions of all energy bands generally deviate from those in the bulk. Therefore, the determination of valence band (VB) discontinuity at the absorber–buffer interface was done by a method described in [12,13]. The essential assumption, that the band bending length (typically a few hundred nm) is significantly greater than the sampling depth of XPS (a few nm) is valid. Accordingly, the presence of interface states will shift the energy bands in the same way on both sides of the interface. Following [13] and Fig. 4(a), ΔE_v at the interface of material x and y is given by

$$\Delta E_v = (E_b^x - E_v^x) - (E_b^y - E_v^y) - \Delta E_b, \quad (1)$$

where $\Delta E_b = (E_b^x - E_b^y)$ is the difference of core level positions at the interface. In our case ΔE_b is determined by XPS on samples with a nominal thickness of 3 nm of TiO_{2-x} (material x) deposited on CIGSe (material y), so that both layers can be probed. The binding energy differences $(E_b^x - E_v^x)$ respectively $(E_b^y - E_v^y)$ between core level and valence band maximum (VBM) are determined on bare CIGSe ($y = \text{CIGSe}$) and on 18 nm TiO_{2-x} ($x = \text{TiO}_{2-x}$) on CIGSe. Therefore, two deposition processes for each oxygen setting with different deposition duration are performed for this analysis. For CIGSe, we selected the In $3d^{5/2}$ and for TiO_{2-x} the Ti $2p^{3/2}$ core level peaks. As only binding energy differences are used, it is obvious that the reference energy can be chosen arbitrarily. We used a common Fermi energy (E_F) as a reference by calibrating the binding energy scale ($E_F = 0$) of the spectra with the adventitious carbon peak (C1s) at 284.80 eV. As band bending effects shift all energy bands of each individual semiconductor, the determination of the core level position with respect to the VBM ($E_b - E_v$) is invariant to band bending. The knowledge of ΔE_v , the surface-near bandgap energy of CIGSe, and the optical bandgap energy of TiO_{2-x} layers allows for a rough estimation of the conduction band discontinuity (ΔE_c) at the absorber buffer interface by

$$\Delta E_c = E_g^{\text{TiO}_{2-x}} - \Delta E_v - E_g^{\text{CIGSe}}. \quad (2)$$

While XPS experiments target the investigation of surface and interface properties, wavelength-dispersive X-ray fluorescence (WD-XRF) was acquired with a Rigaku Primus III+ to determine the bulk composition of the CIGSe absorber.

Top-view and cross section SEM imaging is used to characterize the morphology of absorber and buffer layers. Imaging was done with a Jeol JSM-7610F field emission SEM. The preparation of cross sections of a complete layer stack is performed by Ar-plasma etching. CL spectra of the bare CIGSe were recorded with the same system described in Section 2.1.

For device characterization, full layer stacks with a sample size of $5 \times 5 \text{ cm}^2$ were prepared and 25 cells ($0.5 \times 0.5 \text{ cm}^2$) were laser scribed for device individualization and subsequently, characterized by 4-point j - V (current density–voltage) in the dark and under illumination. A Keithley 2420 3A was used as a source meter and the voltage was scanned from -0.5 V to 0.9 V . For illumination a halogen lamp (HL120SA, 220–240 V, 50 Hz, max. 150 W, R7's) was used at a distance of 13.5 cm to the sample, resulting in an irradiance of 785 W/m^2 .

3. Results and discussion

In the following section, we present and discuss the obtained results. In the first part we focus on the material characterization of TiO_{2-x} thin films grown on glass and Mo substrates. Followed by the second part, where the application of TiO_{2-x} thin films on CIGSe absorber is investigated.

3.1. TiO_{2-x} thin films characterization

First of all, GI-XRD experiments (data not shown) do not show any crystalline peaks, except the ones of the Mo substrate, for the as prepared $\text{TiO}_2|4\%$ and $\text{TiO}_{2-x}|0\%$ thin films. This means that we deal with X-ray amorphous thin films.

The absorption coefficient α of the films, as obtained from fitting ellipsometric and photometric measurements simultaneously, is shown in Fig. 1(inset). The optical properties of the TiO_{2-x} films were modeled using four Tauc–Lorentz oscillators. Two oscillators are used to model the absorption onset at the bandgap and higher energy absorption, one oscillator is used to model a tail behavior and one to model the defect absorption where needed. A Bruggeman surface roughness was used for increased accuracy, which yielded reasonable roughness values of 3 to 4 nm for the TiO_{2-x} layers deposited on glass. The optical absorption of the films vary with oxygen addition to the sputtering

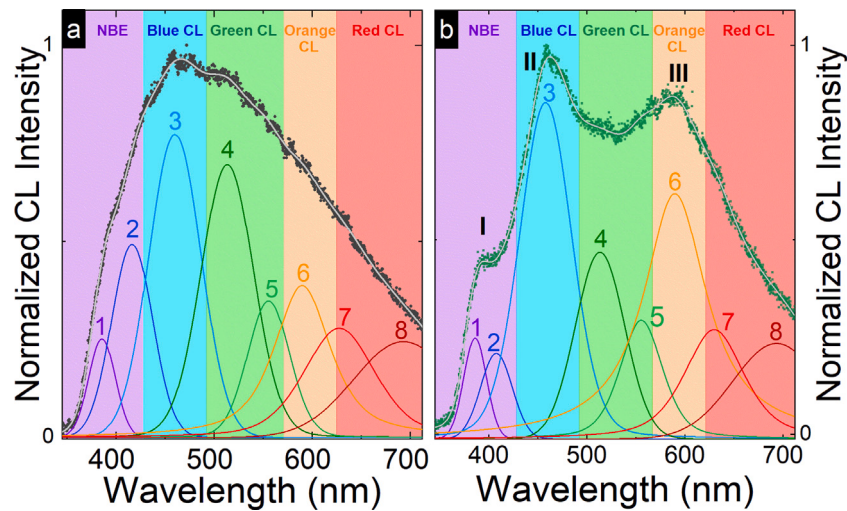


Fig. 2. Normalized CL spectra of (a) $\text{TiO}_{2-x}|0\%$ and (b) $\text{TiO}_2|4\%$; Fitting with Pseudo-Voigt functions is used to deconvolute the spectra. The spectra are divided in five regions: NBE, Blue-CL, Green-CL, Orange-CL, and Red-CL.

process. The film sputtered without oxygen shows a broad absorption feature centered around 800 nm, while for the film sputtered with 4% oxygen no defect absorption peak is evident. It is also important to note, that the observed feature is not a free carrier, Drude-like absorption, which could also be present in the film, but likely further in the IR spectral region. In Fig. 1, Tauc plots for $\text{TiO}_{2-x}|0\%$ and $\text{TiO}_2|4\%$ samples are presented. Assuming an indirect bandgap for both samples, we identify a slightly reduced bandgap energy of 3.28 eV for $\text{TiO}_{2-x}|0\%$ in comparison to 3.38 eV for $\text{TiO}_2|4\%$.

In Fig. 2 the normalized (to the respective intensity maximum of each spectrum) CL spectra of TiO_{2-x} layers are presented. Both samples exhibit a broad emission in the visible region ranging into the near infrared (NIR), whereas the $\text{TiO}_2|4\%$ sample shows a tendency towards more separated features. Here, we observe near band edge emission (NBE) (380 nm–420 nm) and emission in the blue range (Blue-CL) peaking at around 460 nm. A further feature can be identified in the orange at around 590 nm. Therefore, we used the three distinctive single features I, II and III of the spectrum in Fig. 2(b) for an initial peak fitting. In a next step we added a peak in between of features II and III at around 530 nm in the green and a further one in the red wavelength region at around 650 nm. In total, we divide the spectrum in five regions as shown in Fig. 2: NBE, Blue-CL, Green-CL, Orange-CL, and Red-CL. For better assignment of emitting wavelength to possible transitions, we decided to use two peaks each, for regions NBE, Green-CL, and Red-CL. In order to compare both spectra, we calculated the proportional area contributing to the total area for each of the peaks, summarized the values in Table 2, and assigned the emission peaks to presumably involved states/transitions. From that we can see a significant rise of Peak 2 and 4 in the $\text{TiO}_{2-x}|0\%$ sample, while we observe a distinct reduction of Peak 6. The remaining peaks show only minor differences.

Even though, an assignment of the respective CL contribution to specific emitting transitions is still remaining a complex challenge, there are probable emission mechanisms suggested in literature for observed photoluminescence (PL) and CL [18–20]. Considering the obtained optical bandgap energies of 3.28 eV (378 nm) and 3.38 eV (367 nm) for $\text{TiO}_2|4\%$ and $\text{TiO}_{2-x}|0\%$, respectively, the emission spectra of both TiO_{2-x} layers are dominated by defect transitions and surface effects, with energies lower than band to band transition.

Generally, undercoordinated Ti^{3+} is a likely cause for formation of sites that act as electron (e^-) traps, while surface hydroxyls have been implicated as sites for trapping holes (h^+) [21]. In literature, the reported energetic position of respective defect states and also bandgap energies vary, and among other properties, strongly depend

Table 2
CL peak positions and contribution to total area.

No.	$\text{TiO}_2 4\%$		$\text{TiO}_{2-x} 0\%$		Involved states
	Pos. (nm)	Area (%)	Pos. (nm)	Area (%)	
1	386	2.9	386	3.4	recomb. of NBE and tail states with h_{VB}^+ [14]
2	408	3.4	416	10.3	
3	458	23.9	460	20.3	6-fold coord. Ti^{3+} associated with surface hydroxyls recomb. with h_{VB}^+ [15]
4	514	11.6	513	19.2	e^- trapped at oxygen vac. recomb. with h_{VB}^+ [15] or mobile e^- in CB recomb. with trapped h^+ [16]
5	556	7.6	555	7.8	e^- trapped at Ti^{3+} interstitial recomb. with h_{VB}^+ [16]
6	590	29.5	590	15.0	trapp. e^- and h_{VB}^+ [16,17]
7	630	10.4	628	11.8	5-fold coord. Ti at surface recomb. with VB h^+ [14]
8	693	10.6	693	12.3	

on present crystallinity (e.g. phase and crystal size) and surface environment. In [14] it is suggested, that NBE emission as observed by Peaks 1 and 2 in Fig. 2 originates from radiative recombination of near band-edge or band-tail states of amorphous TiO_2 . The relative weight of Peak 2 (peak center at 416 nm) is three times higher in the $\text{TiO}_{2-x}|0\%$ sample compared to the $\text{TiO}_2|4\%$ sample (see Table 2 and Fig. 2), which we therefore interpret as an increase of defect states just below the conduction band. In [15], calculated values of defect states associated with Ti^{3+} are reported from 2.7 eV (460 nm) to 2.2 eV (560 nm) above VB. Whereat, six-fold coordinated Ti^{3+} associated with surface hydroxyls, are reported at around 2.7 eV (460 nm) above VB, and hence, we assign Peak 3 to the recombination of those surface states with VB holes. It is very feasible that surface hydroxyls are formed on both of the TiO_{2-x} surfaces. Therefore, it is consistent that Peak 3 is one dominating emission line in both samples. Whereas, defects with undercoordinated Ti^{3+} , such as oxygen vacancies and Ti^{3+} interstitials are located at 2.3 eV (539 nm) and 2.2 eV (563 nm) above VB, respectively. Those values are in the range of the observed peaks in the Green-CL at 514/513 nm and 556/555 nm, i.e. associated with Peak 4 and 5, respectively. The increased contribution of Peak 4 (see Table 2 and Fig. 2 in the $\text{TiO}_{2-x}|0\%$ sample therefore is a strong argument for an elevated number of oxygen vacancies. Further, in [16] it is reported that green PL at around 530 nm can be assigned to

Table 3
Surface and bulk composition.

	Cu (at%)	In (at%)	Ga (at%)	Se (at%)	CGI [Cu] [Ga+In]	GGI [Ga] [Ga+In]
XPS (surface)	9	33	2	56	0.27	0.04
WD-XRF (bulk)	23	20	6	51	0.87	0.24

the recombination of mobile electrons with trapped holes. The authors in [16] explain an increased green PL emission by an increased number of mobile electrons, i.e. n-donors, such as oxygen vacancies introduced by vacuum annealing. It seems that the absence of oxygen in the plasma during the deposition process, shows a similar effect. The emission band at around 590 nm, Peak 6, we assign to the recombination of trapped electrons with valence band holes, which is also reported in literature [16,17]. In the $TiO_{2-x}|0\%$ sample this emission might be suppressed by the enhanced green PL due to a higher concentration of mobile electrons. Emission of red luminescence from 1.7 eV (729 nm) to 2.0 eV (619 nm) is also reported to originate from trapped electrons at five-fold coordinated Ti atoms at the surface recombining with valence band holes [14], to which we attribute the observed Red-CL (Peak 7 and 8), which is again feasible that those defect states are present at the surface of both samples. The interpretation of the CL emission is summarized in Table 2.

We want to point out again that the CL spectra shown in Fig. 2 are normalized to their respective intensity maximum. The absolute intensity of the respective spectra and therefore the absolute peak area cannot be compared quantitatively because signal optimization (e.g. mirror positioning and beam alignment) is done individually for each sample. However, a significantly higher emission can be observed for the $TiO_{2-x}|0\%$ sample expressed by a shorter acquisition time for the spectrum and a smaller entrance slit. This indicates a higher defect concentration in the $TiO_{2-x}|0\%$ sample, which is consistent with the observed absorption in the optical experiments. Especially the strong intensity of Peak 4 indicates a higher concentration of oxygen vacancies. The CL emission spectra and the low absorbance of the $TiO_2|4\%$ sample might seem contradictory, but one has to consider that CL is highly sensitive to defect emission, especially when a material with an indirect bandgap is investigated. The high sensitivity of CL cannot be compared to the detection of defect absorption in transmission spectroscopy. Also the CL is very sensitive to surface defects, such as surface hydroxyls, which are not visible in the investigated spectral range of transmission/reflection and ellipsometric experiments. For instance, O-H oscillations are far in the infrared. Those surface defects are present in both samples, observed by a similar relative intensity of Peak 3 in the spectra.

3.2. TiO_{2-x} application on CIGSe

This study was designed to investigate material properties of DC magnetron sputtered TiO_{2-x} thin films for an application as a buffer layer in CIGSe solar cells. Hence, we continue with some considerations and comments regarding the CIGSe absorber layer. For a start, Table 3 compares the CIGSe composition, as well as the [Cu]/[Ga+In] (CGI) and [Ga]/[Ga+In] (GGI) ratios at the surface and in the bulk, as obtained by XPS and WD-XRF respectively. The data sets in this table obviously show distinct copper and gallium depletion at the surface, which is expressed by a very low surface- CGI of 0.27 compared to a bulk- CGI of 0.87 and a low surface- GGI of 0.04. We can also observe a slight selenium rich surface.

The absorber material used in this study should be seen as an example layer, which can be used to pigeonhole the suitability of the investigated TiO_{2-x} layers. Controlling the character of CIGSe, especially at the surface or surface near region is a significant handwheel to modify the absorber-buffer interface. This is not part of this work, but should significantly contribute to the demonstration of improved device

characteristics. Nevertheless, in view of the R2R hybrid deposition, we discuss some typical properties. We have seen copper depletion at the surface and an overall CGI of 0.87 (see Table 3). For high efficiency solar cells, a CGI close to, but smaller than 1 is required. A $CGI < 0.9$ is often used in large area deposition to compensate for potential inhomogeneity in spatial distribution of composition in order to prevent secondary phase formation in regions with $CGI > 1$, which can cause shunting paths in the cell [11]. Notwithstanding, local defects with copper enrichment cannot completely be avoided and remain a serious problem in the described CIGSe fabrication process. Consequences of a low CGI , which may be correlated with formation of vacancy compounds, are discussed in [10].

The top view image of bare CIGSe in Fig. 3(c) shows a granular surface structure with pronounced pits and partly sharp dips, which is typical for CIGSe produced with Sunplugged's hybrid-process. This can be challenging when full coverage is required while using a directional deposition technology for buffer layer fabrication. Fig. 3(a) and (b) show cross-sectional SEM images of an 18 nm thick $TiO_{2-x}|0\%$ layer deposited on CIGSe, covered by a 100 nm thick layer of ITO front contact, imaged with a secondary electron (SE) and a backscatter electron (BSE) detector, respectively. The thin TiO_{2-x} layer is deposited quite homogeneously all over the rough CIGSe surface and the coverage seems to be complete, even at sharp and steep dips. However, at very deep pits in the CIGSe, coverage cannot be assured unambiguously by the cross-sectional images. This can be critical, may affect the cell performance and hence, must be taken into account for the interpretation of the presented results, as they could be electronically active.

In Fig. 3(d), a representative CL spectrum of the CIGSe, recorded from the same area as shown in the top view image in Fig. 3(c), is drawn. We observe a broad and asymmetrically shaped CL peak, where two different dominating emission lines are identified. The spectrum could be fitted satisfactorily with two Gauss-Lorentz peaks, centered at 1165 nm (1.06 eV) and 1239 nm (1.00 eV), respectively. Based on an empirical equation, presented in [22], the CIGSe bandgap energy can be calculated in dependence on the GGI using the following relation

$$E_g^{CIGSe}(GGI) = (1 + 0.564 \cdot GGI + 0.116 \cdot GGI^2) \text{ eV}. \quad (3)$$

With a surface GGI of 0.04 and Eq. (3) we calculate a bandgap energy of 1.02 eV, which is in the range of the observed emission lines. We suggest that the Ga gradient within the excited volume is responsible for the different emission lines. For this reason, we used both values (one in brackets) as the surface near bandgap energy of the CIGSe and to calculate ΔE_c .

Comparing the XPS spectra in the Ti 2p region of the two TiO_{2-x} samples (film thickness of 18 nm) deposited on CIGSe in Fig. 4(f) and (g), we recognize only Ti^{4+} states for the $TiO_2|4\%$, while the $TiO_{2-x}|0\%$ exhibits about 7% of Ti^{3+} . The fact that only Ti^{4+} states contribute to the 2p region of Ti for the $TiO_2|4\%$ sample indicates a stoichiometric TiO_2 surface. This is also consistent with the observed optical properties in Section 3.1. Considering the low absorption of the $TiO_2|4\%$ sample, a layer with lower defect concentration can be assumed (absorption coefficient shown in inset of Fig. 1). In contrast, the $TiO_{2-x}|0\%$ sample has an additional Ti^{3+} contribution (about 7%) in the XPS spectrum and shows enhanced absorption in the VIS and NIR range, which we assign to defect absorption. Additionally, this is consistent with the significantly enhanced CL emission at Peak 4, which is associated with oxygen vacancies. At this point it has to be mentioned that the samples were exposed to air during the transport from the deposition chamber to the XPS. Not only the native oxidation of the surface but also the adsorption of water at the surface can distort the XPS results. To get rid of this surface contamination, normally Ar⁺ sputter cleaning is used in XPS experiments, but in case of TiO_2 preferential sputtering can occur, which leads to a reduction of Ti^{4+} to Ti^{3+} [23]. Consequently, this technique could not be applied here. In [24], we demonstrated a method for an indirect proof of the existence of Ti^{3+} contribution in the bulk, even for samples with stoichiometric surface composition.

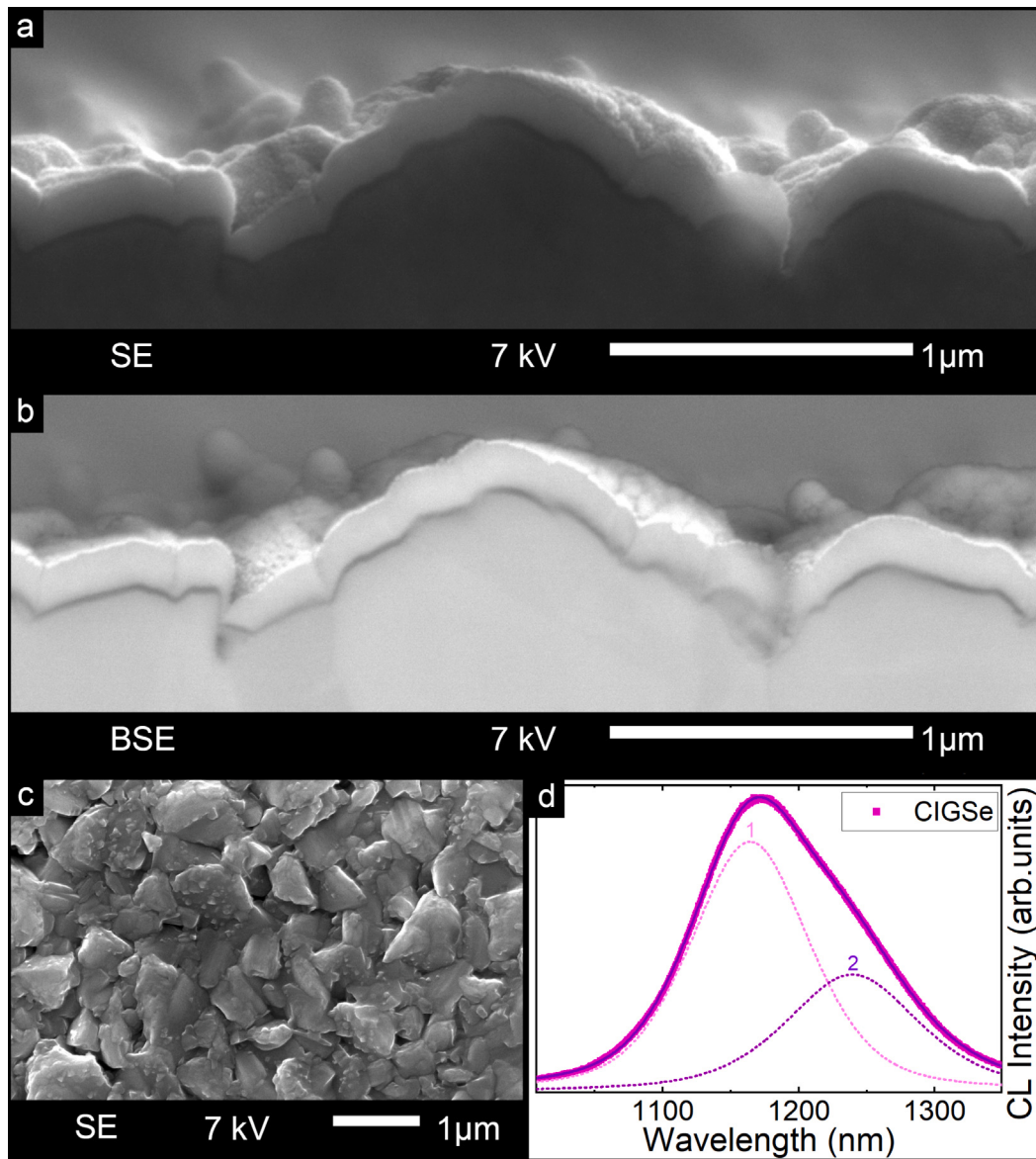


Fig. 3. (a) and (b) cross-sectional SEM images of an 18 nm TiO_{2-x} layer deposited on CIGSe, covered with indium-tin-oxide (ITO), recorded with (a) secondary electron detector (SE) and (b) backscatter electron detector (BSE). (c) SE top view image of bare CIGSe and (d) CL spectrum of CIGSe, recorded from the same area as shown in the top view image (Fig. 3(c)).

Therein, we demonstrate significantly higher percentage of Ti^{3+} in XPS depth profiles for samples prepared with oxygen deficiency, when compared to samples prepared with oxygen. To sum up so far, the results of XPS, CL, and transmission/reflection experiments suggest that the defect concentration in TiO_{2-x} layers can be modified by the presence/absence of oxygen in the plasma.

Now we continue with the determination of the valence band discontinuities at the CIGSe/ TiO_{2-x} interface. For the 18 nm samples, the position of the $\text{Ti } 2p^{3/2}$ (Ti^{4+}) peak is 458.62 eV and 458.57 eV for $\text{TiO}_2|4\%$ and $\text{TiO}_{2-x}|0\%$, respectively (see Fig. 4(f) and (g) and Table 4). The spectra of 3 nm $\text{TiO}_2|4\%$ and $\text{TiO}_{2-x}|0\%$ thin films on CIGSe are plotted in the region of the $\text{Ti } 2p$ and $\text{In } 3d$ in Fig. 4(b) and (c). Therein, the peak positions of the $\text{Ti } 2p^{3/2}$ and $\text{In } 3d^{5/2}$ core levels are determined and hence, the difference of core level positions is calculated. $\Delta E_b^{\text{TiO}_2|4\%}$ is 13.76 eV and $\Delta E_b^{\text{TiO}_{2-x}|0\%}$ is slightly higher with a value of 14.19 eV. In Fig. 4(e) the XPS spectra in the VBM region are shown. Both background and onset regions are fitted with a linear function, and their intersection determines the valence band onset (i.e. E_v^λ). All energy values extracted from XPS experiments and

resultant differences are summarized in Table 4. Using Eq. (1), ΔE_v is calculated to -1.98 eV and -2.68 eV for the $\text{TiO}_2|4\%$ and $\text{TiO}_{2-x}|0\%$ sample, respectively. The negative sign (on the used binding energy scale with $E_F = 0$) means a cliff from the CIGSe valence band to the TiO_{2-x} valence band, as indicated in the tentative band diagram in Fig. 4(a) which summarizes the just presented results graphically.

Using ΔE_v , the peak center position of the CL spectrum in Fig. 3(d) at 1.06 eV (and 1.00 eV) as the bandgap energy of CIGSe and the optical bandgap energies of the TiO_{2-x} layers, extracted in Section 3.1, we calculate conduction band discontinuities with Eq. (2) and we get values of 0.34 eV (0.40 eV) for the $\text{TiO}_2|4\%$ and -0.46 eV (-0.40 eV) for the $\text{TiO}_{2-x}|0\%$. The positive sign for $\text{TiO}_2|4\%$ means a spike, whereas the negative sign for $\text{TiO}_{2-x}|0\%$ means a cliff at the interface, as is also indicated in Fig. 4(a). Additionally, with the determination of secondary electron cutoff energy ($E_{\text{SE-cutoff}}$) as shown in Fig. 4(d) and the valence band onset of the CIGSe, we calculate the position of the VBM with respect to the vacuum level by

$$E_{\text{VBM}} = E_{\text{Al-K}\alpha} - (E_{\text{SE-cutoff}} - E_v). \quad (4)$$

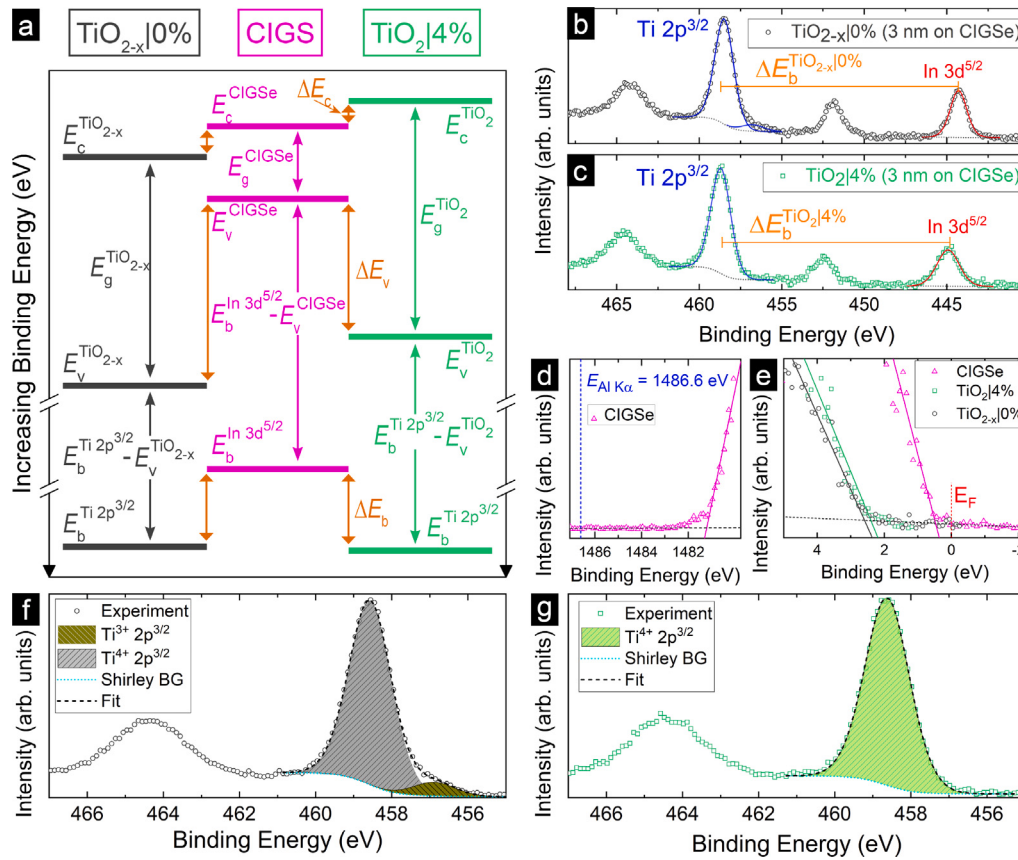


Fig. 4. Summary of XPS results for the determination of valence band discontinuities (ΔE_v). (a) Tentative band diagram in view of the CIGSe/ TiO_{2-x} interface. XPS spectra in the Ti 2p and In 3d region of 3 nm (b) $\text{TiO}_{2-x}|0\%$ and (c) $\text{TiO}_2|4\%$, both deposited on CIGSe. (d) XPS spectrum of bare CIGSe in the SE-cutoff region and (e) XPS spectra of bare CIGSe, 18 nm $\text{TiO}_{2-x}|0\%$ and $\text{TiO}_2|4\%$ (both on CIGSe) in the valence band onset region. XPS spectra in the Ti 2p region of 18 nm (f) $\text{TiO}_{2-x}|0\%$, and (g) $\text{TiO}_2|4\%$ on CIGSe.

With the energy of X-rays from the used Al-K α source ($E_{\text{Al-K}\alpha} = 1486.6 \text{ eV}$), we estimate the position of the CIGSe valence band to $E_{\text{VBM}} = 5.41 \text{ eV}$ below the vacuum level.

To complete the observations of XPS experiments, the Se 3p region of the spectra are presented in Fig. 5. We identify a significant shift of the main contribution of the Se peaks to higher binding energy for the $\text{TiO}_2|4\%$ (3 nm) (Fig. 5(c)) sample. The positions of the Se 3p^{3/2} peaks are again given in Table 4. It is also conspicuous, that on the 18 nm $\text{TiO}_2|4\%$ sample the Se peak is still visible, while this is not the case for the oxygen deficient sample (Fig. 5(d)), even though both samples have approximately the same film thickness. Here we want to point out that the In 3d peaks (and also Cu and Ga) are not present in both samples (18 nm TiO_{2-x}), even though, the relative sensitivity factor (R.S.F.) is almost ten times higher for the In 3d peak than the one for Se 3p. The position of the Se 3p^{3/2} peak of the 18 nm $\text{TiO}_2|4\%$ sample at 165.48 eV is in good agreement with literature values of oxidized Se^{4+} in SeO_2 [25,26]. This means the Se shows, at least partly a cationic character (peak for anionic Se is still present). Whether the Se^{4+} is located in an oxidized CIGSe phase or is incorporated in the TiO_{2-x} cannot be clarified from XPS experiments. In any case there must be a missing Se anion in the CIGSe structure which is very likely replaced by an oxygen anion.

Finally, in order to demonstrate principle transport mechanisms across the TiO_{2-x} /CIGSe interface and to highlight the distinctively different behavior, j - V curves have been recorded for devices completed from Sunplugged's absorber with the two different TiO_{2-x} buffer layers (18 nm) and an ITO front contact, which are shown in Fig. 6. The magnitude of the current densities are plotted on a logarithmic scale in order to emphasize a current blocking in the $\text{TiO}_2|4\%$ sample. The linear region of the $\text{TiO}_2|4\%$ sample indicates a diode characteristic, but no photocurrent is present. On the contrary, we detect a shunting

behavior in the $\text{TiO}_{2-x}|0\%$ sample, marked by a sharp slope in the low bias region, primarily influenced by the shunt resistance response. Furthermore, there is an illumination-dependent change in resistivity under reverse bias conditions for the $\text{TiO}_{2-x}|0\%$ sample. The flat region in the $\text{TiO}_{2-x}|0\%$ sample originates from the current limit used to protect the measurement setup. For comparison the CdS reference cell is included in Fig. 6, which shows a characteristic diode behavior.

We demonstrated a way to modify the defect concentrations and hence, to manipulate the electronic properties, resulting in a distinctively different j - V behavior of the devices. Considering the estimated conduction band offset at the absorber-buffer interface (Fig. 4(a)) for $\text{TiO}_2|4\%$, a spike of 0.34 eV (0.40 eV) sounds convenient at first, but if the density of mobile charge carriers (electrons) is low, it could already account for a barrier for electrons, resulting in a blocked (photo)current across the interface, the buffer layer or both. On the other hand, we observed the Se 3p^{3/2} peak shifting about 4.79 eV to higher binding energies (see Fig. 5) after $\text{TiO}_2|4\%$ deposition on CIGSe. As already discussed, there is a changed surface/interface chemistry, which normally causes a deviation of electro-optical properties. This would be another possible explanation for the observed different valence band offset and also the drastic change in j - V behavior, when oxygen is present in the plasma. Additionally, the fact that the Se 3p^{3/2} (Se^{4+}) peak is also visible on the 18 nm $\text{TiO}_2|4\%$ layer on CIGSe, while no other XPS signal of the CIGSe was detected, could indicate a diffusion or incorporation of Se^{4+} into the $\text{TiO}_2|4\%$ layer. This would change the opto-electrical properties of TiO_{2-x} , as reported in [27]. For example in [28] a significantly enhanced absorbance of visible light, resulting in an increased photo catalytic activity is demonstrated and in [29] a lowered bandgap energy was observed for Se^{4+} doped TiO_2 .

Another point to discuss is the position of the Fermi level with respect to the VBM. On the bare CIGSe the Fermi level is 0.34 eV above

Table 4
Summary of extracted energy parameters.

CIGSe	Cu 2p ^{3/2} (eV)	Ga 2p ^{3/2} (eV)	In 3d ^{5/2} (eV)	Se 3p ^{3/2} (eV)	E _v (eV)	$(E_b^{\text{In } 3d^{5/2}} - E_v^{\text{CIGSe}})$ (eV)
	932.09	1117.81	444.88	160.69	0.34	444.55
3 nm on CIGSe	Ti 2p ^{3/2} (eV)	Cu 2p ^{3/2} (eV)	In 3d ^{5/2} (eV)	Se 3p ^{3/2} (eV)	E _v (eV)	$(E_b^{\text{In } 3d^{5/2}} - E_b^{\text{Ti } 2p^{3/2}})$ (eV)
TiO ₂ 4%	458.69	934.57	444.93	165.48	–	13.76
TiO _{2-x} 0%	458.49	931.54	444.30	160.04	–	14.19
18 nm on CIGSe	Ti 2p ^{3/2} (eV)	Cu 2p ^{3/2} (eV)	In 3d ^{5/2} (eV)	Se 3p ^{3/2} (eV)	E _v (eV)	$(E_b^{\text{Ti } 2p^{3/2}} - E_v^{\text{TiO}_2})$ (eV)
TiO ₂ 4%	458.62	–	–	165.49	2.30	456.32
TiO _{2-x} 0%	458.57	–	–	–	2.51	456.05

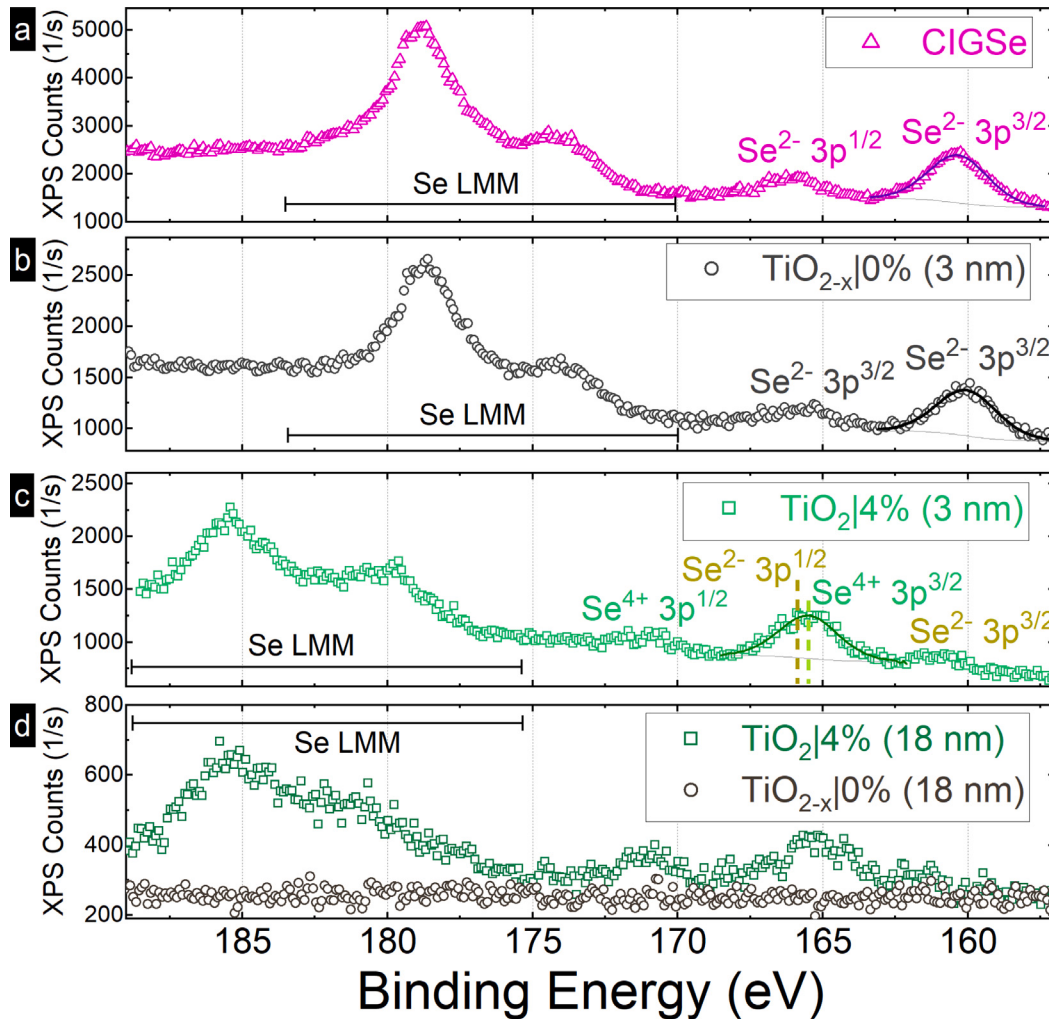


Fig. 5. XPS spectra in the Se 3p and Se LMM region of (a) bare CIGSe and (b)–(d) TiO_{2-x} deposited on CIGSe. (b) 3 nm of TiO_{2-x}|0%, (c) 3 nm of TiO₂|4% and (d) 18 nm of TiO_{2-x} on CIGSe.

the VBM. For the 18 nm TiO₂|4% sample on CIGSe, the Fermi level is 2.30 eV above VBM and the VB offset at the interface is −1.98 eV. This means that the Fermi level position of the CIGSe and TiO₂|4% are very close together, consequently there is hardly a band bending due to interface formation to be expected. This affects the formation of the space charge region after front contact deposition. On the other hand, the VB offset is −2.68 eV for the TiO_{2-x}|0% sample and $E_v^{\text{TiO}_{2-x}|0\%} = 2.51$ eV. This implies that the Fermi level of TiO_{2-x}|0% is lower than the valence band maximum of CIGSe. This would consequently lead rather to a flow of electrons from the CIGSe into the TiO_{2-x} when forming an interface. This suggests an upwards bending of the CIGSe,

making the CIGSe more *p*-type. This could lead rather to an ohmic contact than a diode junction. Further, potential shunt paths due to copper rich growth defects in the CIGSe in combination with a feasible higher conductivity of the TiO_{2-x}|0% cannot be ruled out to be jointly responsible for the observed shunted *j*-*V* behavior shown in Fig. 6. Also a possible incomplete coverage of the TiO_{2-x} layer at deep pits cannot be excluded, however, the fact, that those deep pits are present in both TiO_{2-x} samples, makes them unlikely to be the source of the observed shunted device characteristic.

However, we have to discuss some limits of the applied characterization techniques. It is common practice, to use the position of the

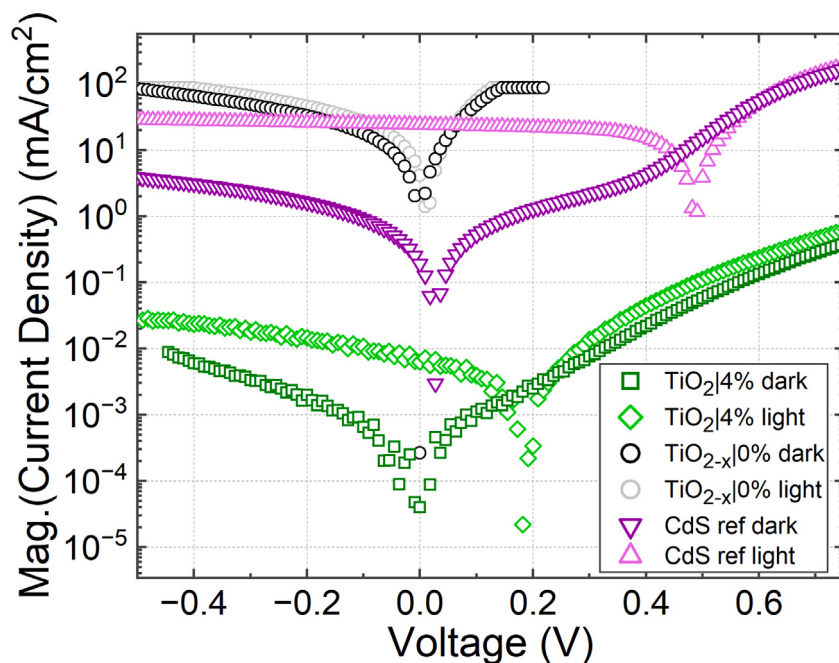


Fig. 6. Dark and illuminated j - V curves of 0.25 cm^2 sized cells completed from Sunplugged's absorber with $\text{TiO}_2|4\%$ (green squares) and $\text{TiO}_{2-x}|0\%$ (gray circles) buffer layers, and ITO front contact and CdS reference cell (purple triangles) plotted on a logarithmic scale.

Fermi-level with respect to the VBM after calibration of the binding energy scale. But the Fermi-level position may not be precisely determined due to factors like band bending at the interface with vacuum and chemical bonding variations of the adventitious carbon used for calibration. Even though, it is common practice [30,31], the estimation of ΔE_c by just using the bandgap energies and the valence band offset has its limits, and therefore, should only be used to approximate the band alignment. The main problem is that the position of the conduction band minimum of the materials are determined separately and not at the actual interface.

In contrast, the determination of ΔE_v is done by measuring the actual interface, and therefore includes possible effects due to interface formation (e.g. a shift of Fermi-level position). And as already mentioned the determination is invariant to potential charging effects or calibrating to a reference energy. Hence the different values for ΔE_v confirm different interface properties and band alignment at the interface for the two TiO_{2-x} samples and depicts the potential of modification to improve the resulting device's performance.

So far, the interpretation of the j - V characteristics is not completely clarified. Anyhow, the presence of oxygen in the plasma during buffer deposition process seems to be harmful for the electron transport mechanism across the device. For instance, besides the discussed potential explanations, it is also conceivable, that the j - V curves contain a transition from an ohmic to a Schottky contact at the TiO_{2-x} /ITO interface, due to a modified position of the Fermi level in the TiO_{2-x} . The fact, that also the TiO_{2-x} /ITO interface is involved, requires further detailed investigation, including a separate characterization of the buffer/TCO interface.

4. Summary, conclusion and outlook

In this work, we presented a comprehensive material investigation of DC magnetron sputtered TiO_{2-x} layers from ceramic TiO_{2-x} targets mixed with metallic Ti particles. We focused on the effect of oxygen presence/absence during the deposition process on the electrical and optical properties. The study was construed in view of an application as a buffer layer in CIGSe based solar cells. With reference to all our

findings, we can summarize, that we are able to modify the quantity of defects within the deposited TiO_{2-x} thin films, such as oxygen vacancies by the oxygen content in the process gas, which of course, has an impact on the opto-electrical properties. We detected a decrease of the optical bandgap from 3.38 eV to 3.28 eV and significant defect absorption and emission for the sample prepared without oxygen, in comparison to the sample sputtered with 4% oxygen. We presented a tentative band diagram in view of the CIGSe/ TiO_{2-x} interface, in which the effect of oxygen in the plasma process on the band discontinuities are apparent. Besides the strongly modified band discontinuities for the two TiO_{2-x} samples, the changed interface chemistry due to the deposition conditions is additionally responsible for the different device characteristic. We show, that the application of oxygen reactive sputtering of TiO_{2-x} thin films is not feasible for buffer layer deposition. Consequently, the options to modify the interface properties are restricted, but still, this study demonstrates, that it is possible to overcome the barrier by oxygen deficiency. The identified harmful impact of oxygen presence in the deposition process on the electron transfer mechanism at the absorber-buffer interface might also concern other magnetron sputtered, oxodic alternative buffer materials. There is the possibility to optimize the TiO_{2-x} layers by reducing the metallic Ti concentration in the mixed sputter targets. Additionally, doping with e.g. niobium (Nb) or $\text{Nb}_2\text{O}_{5-x}$ is a potential way for band alignment optimization as it tends to induce defect states just below the conduction band and to shift the Fermi level closer to the conduction band minimum. Besides the optimization of TiO_{2-x} layers, also the CIGSe surface can be modified, e.g. by post deposition treatments or bandgap tuning.

Other than that, compact TiO_{2-x} based thin films can be used as transparent electron-selective or electron-transport layers in other PV application, such as organic solar cells, silicon heterojunction solar cells, dye-sensitized solar cells, perovskite based solar cells or tandem devices. Another field of application can be found in organic light emitting diodes (OLED), likewise as an electron selective layer. The used approach with conductive ceramic targets and the consequential possibility of DC magnetron sputtering, provides an attractive, easily scalable and stable industrial process for large area deposition.

CRediT authorship contribution statement

David Stock: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft. **Nikolaus Weinberger:** Project Administration, Visualization, Writing – review & editing. **Florian Ruske:** Investigation, Writing – review & editing. **Leander Haug:** Investigation. **Martina Harnisch:** Investigation. **Roman Lackner:** Resources, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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