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A post-deposition annealing approach for organic residue control in TiO₂ and its impact on Sb₂Se₃/TiO₂ device performance

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We report a systematic investigation on the influence of two-step post-deposition treatments (PDTs) on TiO₂ buffer layers deposited by ultrasonic spray pyrolysis (USP) for emerging Sb₂Se₃ photovoltaics. Air annealing is a typical method for recrystallizing chemically deposited TiO₂ films. However, organic residues (such as carbon species) from a precursor solution based on titanium tetraisopropoxide and acetylacetone may still remain on the TiO₂ surface, therefore requiring an additional annealing step. We demonstrate that vacuum annealing can be a suitable technological approach to decrease the concentration of carbon species in TiO₂ films. Vacuum annealing was performed at temperatures at 160–450 °C prior to the 450 °C air annealing step. It was found that vacuum annealing at 160 °C followed by subsequent air annealing led to better device performance. This was explained by achieving an optimal balance between the removal of carbon content during vacuum annealing and the active recrystallization of TiO₂ during air annealing. The decrease of carbon concentration by employing the two-step approach was supported by changes in the lattice parameters of TiO₂ and proven by X-ray photoelectron spectroscopy (XPS). The given study provides experimental evidence on how nanoscale carbon species in the TiO₂ heterojunction partner layer of a Sb₂Se₃ solar cell can affect the device's performance. By this approach, we generate complementary insights on how the quality of the main interface has an impact and can take a key role despite the optimized Sb₂Se₃ grain structure and orientation.

Introduction

The field of thin film photovoltaics (PV) is booming at the moment as it is seeing remarkably fast progress in the development and optimization of new emerging

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semiconductor absorber materials, such as thin sulfides,¹ chalcostibites,² chalcogenide perovskites,³ nitrides,⁴ and antimony chalcogenides.^{5,6} These materials have attracted intensive thin film PV research of late because of the high abundance of their constituent elements in the Earth's crust and the non-toxicity of the chemical elements, which are combined with highly demanded material qualities, such as defect tolerance⁶ and high chemical stability. Among these materials, Sb-chalcogenides, *e.g.*, Sb₂Se₃, Sb₂S₃, and Sb₂(S,Se)₃, have demonstrated great potential with a nascent track record of performance development. Sb₂Se₃ and Sb₂S₃ are both single-phase binary compounds with quasi-one-dimensional crystal structures, absorption coefficients of $>10^4$ cm⁻¹ (for energies above 1.5 eV)^{7,8} and band gap energies of ~ 1.2 eV and ~ 1.7 eV,^{9,10} respectively. Such optoelectronic properties are excellent for developing efficient thin film solar cell devices.

Despite a paucity of research, PV devices based on antimony chalcogenides have already reached cell power conversion efficiencies (PCEs) of around 10%.¹¹ As for Sb₂Se₃, the absorber material in the focus of the current study, absorbers deposited by close-spaced sublimation^{12,13} and vapor transport¹⁴ deposition techniques have produced devices with record PCEs ranging between 7–9%. Despite these achievements, there are several challenges that need to be overcome to harness the full potential of Sb₂Se₃ PV devices. Critical limitations include finding an optimal device structure,¹⁵ optimization of Sb₂Se₃ growth,^{6,12,13} identification of suitable heterojunction partner layers,^{9,15,16} and development of post-deposition treatments and doping strategies.^{17,18} Most of the R&D efforts in recent years have been focused on optimizing Sb₂Se₃ growth, in conjunction with a CdS heterojunction buffer layer, an established partner layer in CdTe,¹⁹ CIGS,²⁰ and CZTS solar cells.²¹ While the CdS buffer layer ($E_g \sim 2.5$ eV)²² has been the preferred choice for a majority of research groups,^{9,14,23} and has shown favorable band alignment with the Sb₂Se₃ absorber,¹⁵ TiO₂ buffer layers ($E_g = 2.8$ – 3.3 eV)²⁴ have emerged as suitable and more stable alternatives to CdS buffer layers. Namely, chemical intermixing at the interface between CdS and Sb₂Se₃ has been reported in superstrate Sb₂Se₃/CdS PV devices, causing the formation of an interface layer, which acts like an electrostatic barrier that obstructs charge transfer and collection.¹³ As for TiO₂ synthesis, spin coating (SC)¹³ and ultrasonic spray pyrolysis (USP)²⁵ are common deposition techniques, especially for superstrate Sb₂Se₃/TiO₂ PV devices. The best superstrate Sb₂Se₃/TiO₂ solar cells have thus far demonstrated PCEs between 5–8%.^{5,12}

Despite these promising results, there is ongoing research into various aspects of how the heterojunction between TiO₂ and Sb₂Se₃ can be improved. Since Sb₂Se₃/TiO₂ PV devices suffer from substantial V_{OC} deficits, developing a strategy for Sb₂Se₃/TiO₂ interface engineering is of extreme importance for giving Sb₂Se₃/TiO₂ solar cells a further boost. One of the aspects in the Sb₂Se₃/TiO₂ interface engineering entails post-deposition treatment of the TiO₂ films after the films have been deposited by either UPS or SC chemical methods. Usually, such a treatment implies thermal annealing in air at 450–500 °C for 20–30 min,¹⁰ with the main purpose of improving the crystallinity of the TiO₂ films. It is mostly accepted that for chemically deposited TiO₂ layers, air annealing at elevated temperatures causes residual organic components, which are inevitably present in the precursor solution, to be easily removed as a result of a pyrolysis process. However, in our recent study, we noticed that the pyrolysis process in the presence



of air at high temperatures might not be enough to purge the TiO₂ films of organic residuals, and to some extent, organic residuals may remain on the TiO₂ surface and could degrade the quality of the Sb₂Se₃/TiO₂ interface and curtail the performance of the device.¹² Hence, this finding served as a hypothesis, forming the basis of the subsequent study with the focus of systematically investigating the effects of different annealing procedures over a wide range of temperatures on the properties of the TiO₂ films and the performance of Sb₂Se₃/TiO₂ solar cells. With this approach, we aimed to screen the evolution of organic residues at the surface of USP-deposited TiO₂ films, gain an understanding of the kinetics of a vacuum annealing process for removing these organic residuals, and assess the overall impact of annealing on Sb₂Se₃/TiO₂ solar cell performance.

Experimental

Fabrication of superstrate configuration glass/FTO/TiO₂/Sb₂Se₃/Au thin film solar cells

The solar cells were fabricated according to the superstrate configuration. FTO-coated 2.3 mm thick glass with a surface resistivity of 7 Ω sq⁻¹ (provided by Sigma-Aldrich) was used as a substrate. USP TiO₂ films were deposited atop FTO at 340 °C using a precursor solution of a 1 : 4 ratio of titanium(IV) isopropoxide (TTIP) and acetylacetone (AcacH). The USP deposition was set in a way to keep a constant controllable TiO₂ thickness of 80–90 nm. In the next step, the TiO₂ films were divided into two sets and subjected to three different annealing procedures, described in the section below. After the annealing of TiO₂, a 1.3–1.5 μm thick Sb₂Se₃ absorber layer was deposited at 460 °C by CSS, following a previously described procedure.²⁶ 5 N granular Sb₂Se₃ (Sigma-Aldrich) was used as the source material for the absorber deposition. To complete the solar cell, an Au back contact was deposited *via* thermal evaporation.

Post deposition annealing of USP TiO₂ films

After the deposition, the TiO₂ sets underwent three annealing procedures: (I) vacuum annealing only (labeled as “Vac”), (II) vacuum and subsequent air annealing (labeled as “Vac+Air”), and (III) air annealing only (labeled as “Air”); vacuum annealing of the USP TiO₂ films was carried out in a closed process tube with a diameter of 55 mm and a volume of 1500 mL. For this procedure, the process tube containing the samples was evacuated at room temperature (RT) and then introduced into a cylindrical furnace set at RT, to allow a slow thermal annealing process. The annealing temperature was varied in the 160–450 °C range in steps of Δ*T* = 50 °C, and the annealing time was fixed at 60 min. The vacuum level in the process tube was maintained at ~10⁻⁵ mbar, using a turbomolecular vacuum pump in a dynamic regime. Air annealing of the USP TiO₂ films was carried out in a pre-heated open process tube at 450 °C. The annealing time was fixed at 30 min, after which the tube was taken out from the furnace for rapid cooling at room temperature.

Material and device characterization

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to analyze the structural and morphological properties of the samples. XRD



characterization was carried out on a Rigaku Ultima IV diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$, 40 kV, 40 mA). Rigaku PDXL software was used to analyze the XRD data. The following data cards were used: JCPDS 01-089-0821 for Sb₂Se₃, JCPDS 00-021-1272 for TiO₂ and JCPDS 01-077-0452 for FTO (SnO₂). A Zeiss HR-SEM MERLIN SEM with the GEMINI II column was used for the top and cross-sectional views of the structures. The XPS spectra were measured with a standard XPS laboratory system based on a nonmonochromatic X-ray source from SPECS with a Mg anode, providing an excitation energy of 1253.6 eV.²⁷ All XPS spectra were measured at room temperature at a pressure of 5×10^{-6} Pa. The energy analyzer was calibrated by fixing the C 1s core level binding energy at 285.0 eV. AUTOLAB PGSTAT 30 and an Oriel class A solar simulator 91159A (100 mW cm⁻², AM1.5) were used for *J*-*V* characteristic measurements. In the EQE measurements, a 300 W xenon lamp and an SPM-2 Carl Zeiss-Jena monochromator were used at 30 Hz.

Results and discussion

XRD and SEM techniques were used to analyze the structural properties of the as-deposited and annealed TiO₂ films. Fig. 1a and b show the XRD patterns of the TiO₂ films which underwent different annealing steps. It is observed that for the as-deposited TiO₂ film, the diffractogram does not show clearly distinguishable peaks related to the TiO₂ crystal structure, indicating that the layers contain a large amount of the amorphous phase. The amorphous phase is kept present in both the Vac+Air and Vac 160–250 °C annealing steps. For Vac+Air and Vac annealing in the range of 300–450 °C, all the TiO₂ films showed an anatase crystal structure (PDF: JCPDS 00-021-1272), with characteristic (101) and (200) peaks at 25.28° and 48.05°, respectively. These peaks are characteristic of anatase TiO₂ and have been previously reported for USP-deposited TiO₂ films.²⁸ To understand

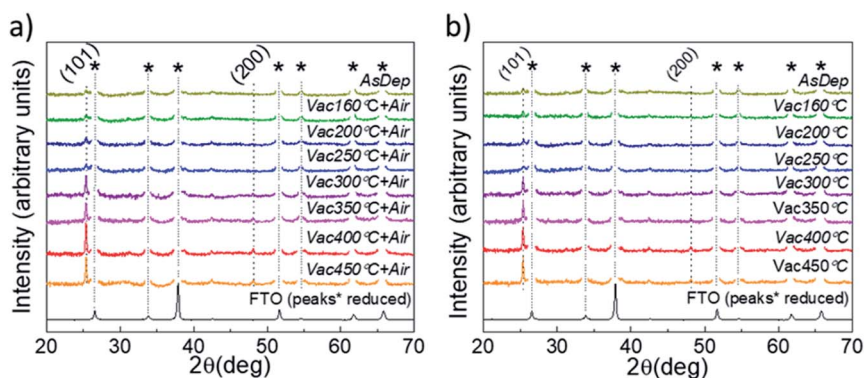


Fig. 1 XRD patterns of TiO₂ thin films (showing the characteristic (101) and (200) peaks of anatase TiO₂) deposited by USP onto FTO/glass substrates, before and after annealing procedures. (a) Vacuum annealing at the temperature range of 160–450 °C for 60 min, and subsequent air treatment at 450 °C for 30 min (labelled as VacT°+Air). (b) Vacuum annealing at 160–450 °C for 60 min (labeled as VacT°). For a better clarity of the diffractograms, the strong peak reflections related to FTO underlayer (marked with star symbols) were artificially reduced.



the effect of annealing conditions on the structural properties of TiO₂ layers, we further analyzed the changes in the crystallite sizes (Fig. 2d, e). As an overall trend, the crystallite size increases with the increase of the Vac+Air and Vac annealing temperatures. For the Vac+Air treatment (Fig. 2d), crystallites were ≈ 30 nm at low-*T* (160–250 °C) annealing and ≈ 50 nm at high-*T* (300–450 °C) annealing. In the case of the Vac annealing, the trend in crystallite size was slightly sharper, with ≈ 20 nm size at low-*T* (160–250 °C) and ≈ 60 nm large crystallites after annealing at 450 °C (Fig. 2e).

Fig. 2a and b show the top-view SEM images of the TiO₂ samples before and after vacuum annealing at 160 °C and subsequent 450 °C air treatment, respectively. The cross-sectional view of the 160 °C vacuum annealed and 450 °C subsequent air treated TiO₂ layer is shown in Fig. 2c. As can be seen in Fig. 2a, the amorphous TiO₂ film consists of small grains and has quite a homogeneous distribution. After annealing, the films are more compact with well-sintered grains (Fig. 2b) and the thickness is reasonably uniform (Fig. 2c). It is important to note that the TiO₂ films kept the same morphology (shown in Fig. 2b) independent of the Vac+Air, Vac, or Air annealing at 450 °C. It is also worth mentioning that from the UV-Vis measurements (Tauc plots, not shown), the band gap value of TiO₂ was determined to be $E_g \sim 3.3$ eV and no changes in this value have been observed, independent of either Vac+Air, Vac, or air annealing at 450 °C.

Based on the above XRD and SEM results, it can be concluded that there were no noticeable differences in the properties of TiO₂ films when annealed with different Vac+Air, Vac, or Air conditions. A systematic increasing trend in the crystallite size with the increase of annealing temperature was expected, however looking from the perspective of the organic impurity incorporation into the lattice of TiO₂ films, the evolution in the lattice parameters of the annealed films was

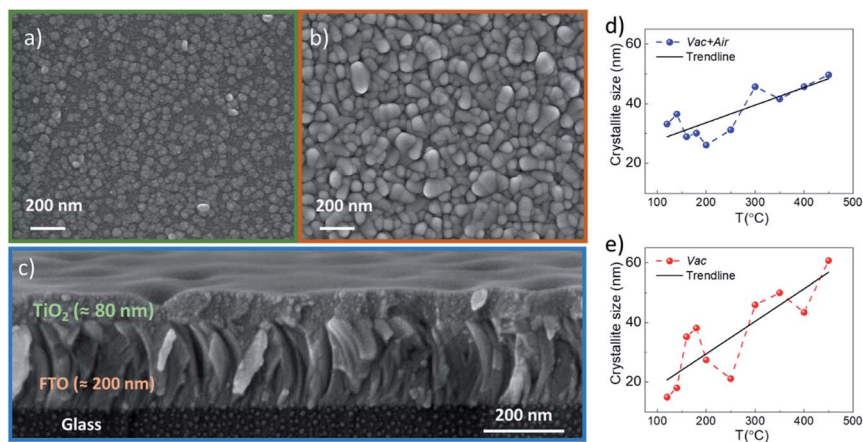
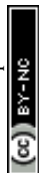


Fig. 2 (a and b) Top view SEM images of USP-deposited TiO₂ after a 160 °C vacuum annealing step (Vac) and after 160 °C vacuum and subsequently 450 °C air annealing steps (Vac+Air), respectively. (c) Cross-sectional view of the TiO₂ layer after 160 °C vacuum and subsequently 450 °C air annealing steps (Vac+Air). (d and e) Evolution of the crystallite size of vacuum and subsequently air annealed (labeled as Vac+Air) and vacuum annealed only (labeled as Vac) TiO₂ films.



analyzed. The lattice parameters of anatase TiO_2 correspond to tetragonal crystal lattice with $a = b \neq c$ and the values for the $\text{Vac}160^\circ\text{C}$ annealed films were between $a = b \sim 3.68\text{--}3.75$ and $c \sim 9.50\text{--}9.52$ Å. A small but systematic gradual decrease of the lattice parameters along all the a , b and c axes, from $a = b \sim 3.75$, $c = 9.51$ Å in the $\text{Vac}160^\circ\text{C}$ annealed films to $a = b \sim 3.80$, $c = 9.55$ Å in the $\text{Vac}450^\circ\text{C}$ treated layers was observed. An explanation for such a phenomenon can be related to the decrease in organic species in the TiO_2 lattice by a gradual increase of the Vac annealing temperature. A plausible hypothesis related to the presence of possible organic species in the TiO_2 lattice is the presence of carbon impurities.^{29,30} Such a scenario is quite possible considering the fact that the USP TiO_2 precursor solution contains TTIP and AcacH in the ratio of 1 : 4, where the AcacH is a good source of carbon contamination. During the USP deposition process at 340°C in air, the carbon from AcacH could incorporate into the TiO_2 lattice. Incorporation of carbon atoms into the lattice of anatase TiO_2 could occur through a substitutional mechanism at the oxygen sites.²⁹ At the same time, the carbon species are present on the surface of the TiO_2 .³¹ The concentration of carbon and related organic species seems to be $\leq 10^{19} \text{ cm}^{-3}$ (*i.e.* ≤ 0.01 at%), which is below the detection limit of classical XRD and EDX techniques. In this direction, employment of the XPS technique can provide a more in-depth analysis of the residual species at the TiO_2 surface. However, the large number of samples processed with various annealing conditions would imply intensive and time-consuming XPS measurement efforts. Thus, as a next stage, a large set of $\text{Sb}_2\text{Se}_3/\text{TiO}_2$ solar cells were fabricated with TiO_2 annealed at various conditions, and the impact of the treatment on the device performance was analyzed. With this approach, we attempted to identify the optimal TiO_2 annealing conditions which would allow reasonable device efficiency and, thus, to select a reasonable set of TiO_2 samples for the analysis of carbon species by XPS. Fig. 3 shows the solar cell parameters for Sb_2Se_3 devices employing a TiO_2 buffer layer that underwent either Air, Vac+Air, or Vac annealing.

It is clear from Fig. 3 that the devices annealed according to the Vac+Air approach gained a significant boost in performance over devices that were subject to just one of the two other annealing procedures. All J - V parameters showed higher values for a combined Vac+Air procedure in the temperature range of $160\text{--}300^\circ\text{C}$, with the Vac+Air procedure carried out at 160°C enabling the best device performance of 4.7%. The J - V characteristics and EQE spectral response of the representative 4.7% efficient device are shown in Fig. 4a and b. The increase of the annealing temperature beyond 160°C in the Vac+Air procedure caused all solar cell parameters to slightly worsen. Also important to note is the fact that the Vac+Air annealing of TiO_2 layers at temperatures in the range of 350 to 450°C causes devices to produce lower J_{SC} values than devices with Vac annealed TiO_2 layers (Fig. 3). Considering the differences in the solar cell efficiencies (Fig. 3), one could emphasize that the grain structure and texture of the Sb_2Se_3 absorber films deposited on either Vac, Vac+Air, or Air annealed TiO_2 should be reflected in the final device performance. Looking at the top- and cross-sectional view SEM images of Sb_2Se_3 absorber films deposited onto $\text{Vac}160^\circ\text{C}+\text{Air}$ (Fig. 5a and b) and $\text{Vac}450^\circ\text{C}+\text{Air}$ (Fig. 5c and d) annealed TiO_2 , no detectable changes in the grain morphology of the absorber were observed. Independent of the TiO_2 annealing procedure, the absorber growth follows a similar morphology of columnar sintered grains (Fig. 5b and d).



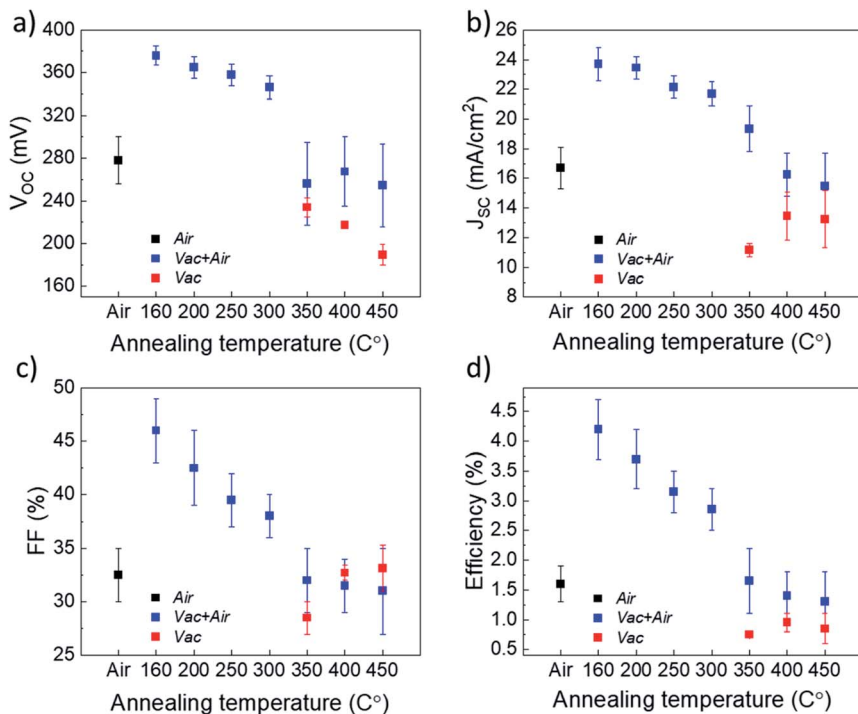


Fig. 3 J - V parameters, including (a) open-circuit voltage – V_{OC} , (b) short-circuit current density – J_{SC} , (c) fill factor – FF and (d) efficiency of $\text{TiO}_2/\text{Sb}_2\text{Se}_3$ devices with different TiO_2 annealing conditions.

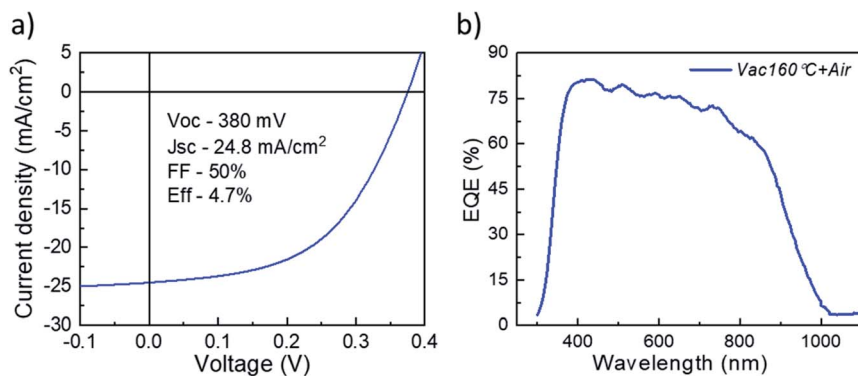


Fig. 4 (a) J - V characteristics and (b) EQE spectral response of the representative 4.7% efficiency device.

Analysis of the XRD patterns of the Sb_2Se_3 absorber deposited onto Vac+Air and Vac annealed TiO_2 layers (Fig. 6a and b) and the related texture coefficients (Fig. 6c and d) reveals that independent of the TiO_2 annealing, the absorber exhibits preferential orientation along the (211), (221) and (002) planes.

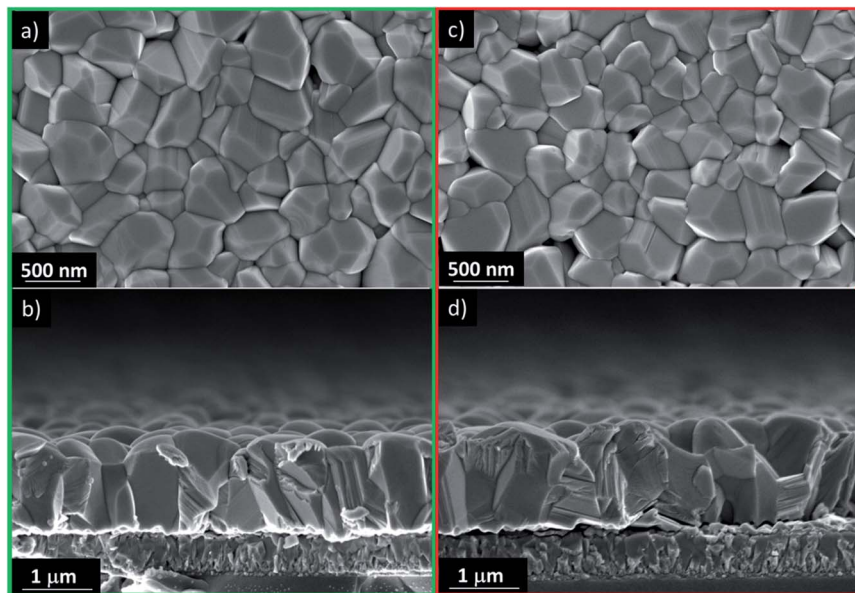


Fig. 5 Top- and cross-sectional view SEM images of CSS Sb_2Se_3 absorber films deposited at 460 °C onto $\text{TiO}_2/\text{FTO}/\text{glass}$ stacked substrates, with (a and b) 160 °C vacuum and consequent 450 °C air annealed TiO_2 and (c and d) 450 °C vacuum and consequent 450 °C air annealed TiO_2 layers.

These peaks are characteristic of the orthorhombic Sb_2Se_3 crystal structure (PDF card no. 01-089-0821) and match well with those reported in the literature for the Sb_2Se_3 absorber deposited by the CSS and VTD techniques.^{32–35} Although there could be other changes at the nanoscale of the absorber (grain interior to grain boundaries), these results indicate that the quality of the main $\text{Sb}_2\text{Se}_3\text{--TiO}_2$ interface (which is determined by the annealing approach of TiO_2) is the main parameter which affects the solar cell performance in Fig. 3. The optimum efficiency point found for 160 °C TiO_2 vacuum annealing may be explained through the combined effect of reduced carbon content in the vacuum annealing step and oxygen-included recrystallization of the film during the following 450 °C air annealing step. A low carbon content at the $\text{Sb}_2\text{Se}_3\text{--TiO}_2$ main interface implies an improved heterojunction formation (and, probably, a lower concentration of the interface defect states), resulting in an increased performance of the solar cell (Fig. 3).

So far, our results indicate that the vacuum annealing of TiO_2 can be a suitable processing step for decreasing the concentration of organic residual species in TiO_2 and, by this, to improve the heterojunction quality and cell efficiency. However, the treatment needs to be performed at a moderate temperature (≤ 200 °C) so as to keep the TiO_2 grain sizes small enough for their active recrystallization in the subsequent air annealing step at 450 °C. On the other hand, the low solar cell efficiency obtained with only Vac annealed TiO_2 (*i.e.*, without subsequent 450 °C air treatment) indicates the necessity of oxygen-rich conditions during the recrystallization of USP deposited TiO_2 .



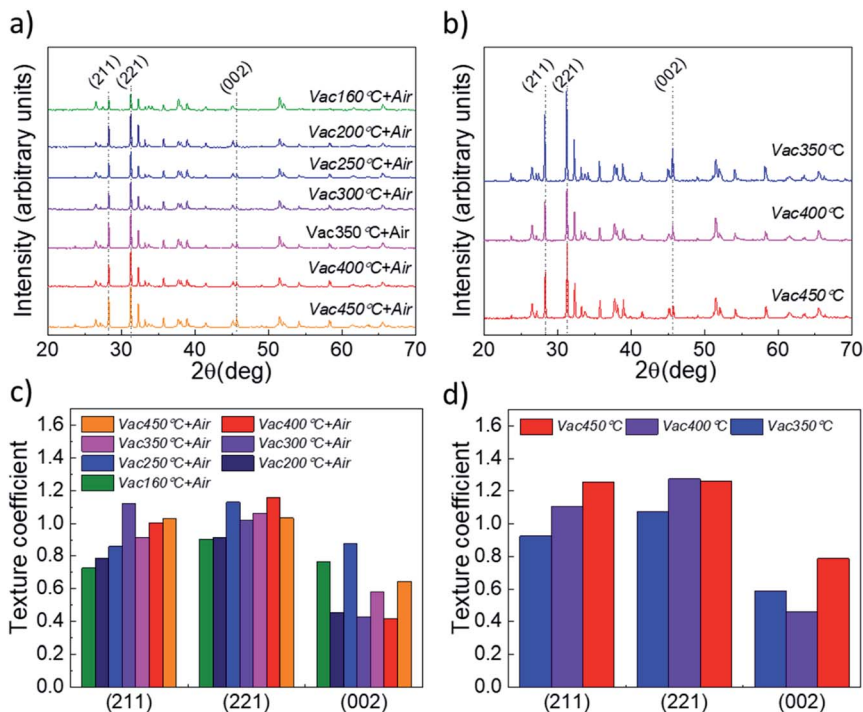


Fig. 6 XRD patterns of CSS Sb₂Se₃ absorber films deposited at 460 °C onto TiO₂/FTO/glass stacked substrates, with (a) vacuum and subsequent air annealed (Vac+Air) TiO₂ and (b) vacuum annealed only (Vac) TiO₂ layers. Related texture coefficients (TC) for (c) vacuum and subsequent air annealed (Vac+Air) and (d) vacuum annealed (Vac) films, calculated from the integrated intensity ratios (using the Harris formula⁴⁶) for the dominant miller planes of Sb₂Se₃.

To provide support for the above statements, especially on the concentration of carbon species at the TiO₂ surface, we further analyzed the annealed TiO₂ films by XPS. The XPS spectra were registered from the surface of ~80 nm thick USP TiO₂ films deposited at 340 °C onto FTO/glass substrates. Since no distinguishable differences were observed between the spectra of the as deposited and annealed TiO₂, only one survey spectrum of the as-deposited TiO₂ film is illustrated in Fig. 7a. The binding energy (BE) values, as well as the shape of the Ti 2p_{3/2} and O 1s core level peaks (not shown here), are characteristics of single-phase anatase TiO₂ films.²⁸ Emission of the Sn 3d_{5/2} core level from the underlying FTO substrate is registered only in the case of the as-deposited film and can be related to the presence of some pinholes in the TiO₂ film. No secondary phases were revealed in any of the as deposited or annealed TiO₂ films, supporting the above-mentioned XRD results (Fig. 1).

To clarify the evolution of carbon impurities at the surface of the annealed TiO₂ films, we analyzed the C 1s core level emission. We cannot quantify the air contamination of the measured surfaces but, keeping in mind that all the TiO₂ samples spent the same time in air from the UPS until the XPS analysis, we assume that a similar amount of carbon species from the air contamination is



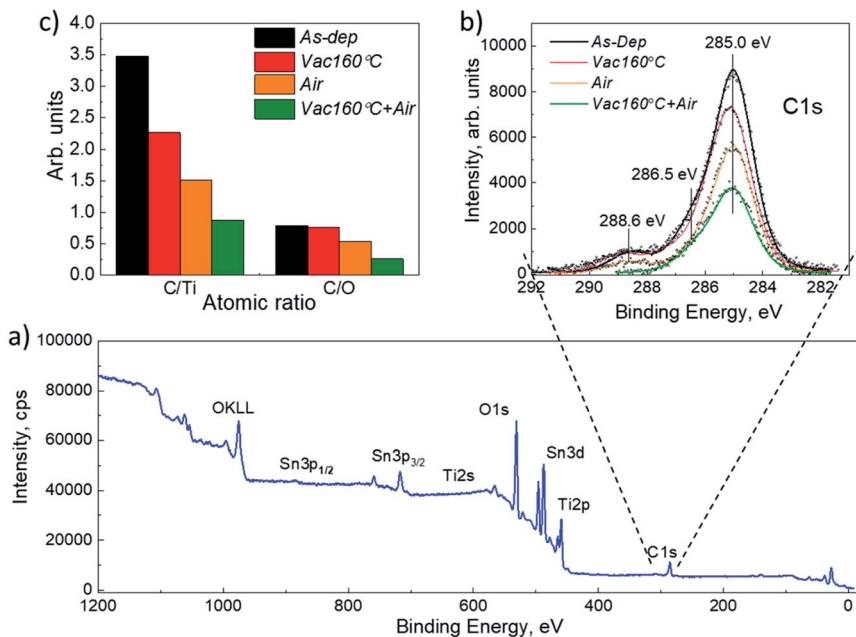


Fig. 7 (a) XPS survey spectrum of TiO_2 films deposited by USP at 340°C onto FTO/glass substrates. (b) C 1s core level from the as deposited (labelled as As-dep), 160°C vacuum annealed (labelled as Vac160°C), 450°C air annealed (labelled as Air), 160°C vacuum and subsequent 450°C air annealed (Vac160°C+Air) TiO_2 films. (c) Calculated atomic ratios C/Ti and C/O for the related samples.

present on all analyzed samples and the differences in the C 1s signal can be attributed to the fluctuation of other carbon species from the near surface bulk of the TiO_2 film. The C 1s peak contains three features at BE values of 285.0 eV, 286.5 eV, and 288.6 eV (Fig. 7b). The highest peak located at 285.0 eV originates from the C=C bond. Peaks with the BE values 286.5 eV and 288.6 eV represent the oxygen-bound species C–O and Ti–O–C bonds, respectively.³⁶ These peaks, and especially the one at 288.6 eV, confirm the incorporation of carbon into the TiO_2 lattice.³⁷ Therefore, we consider the C 1s emission at 288.6 eV as evidence of so-called organic residuals of the USP precursor solution (TTIP complex, together with oxygen, and carbon from AcacH) and analyze how they are affected by the annealing of TiO_2 .

Fig. 7b and Table 1 show that the as-deposited TiO_2 films contain the most intense C 1s emission at 288.6 eV and vacuum (Vac) annealing at 160°C slightly decreased it. Such a low annealing temperature seems to be insufficient for a significant reduction of carbon. An air treatment at 450°C further reduced the concentration of the carbon, however, the lowest intensity of 288.6 eV emission was observed for the combination of the two steps, Vac160°C and subsequent Air 450°C annealing of TiO_2 (Fig. 7). Interestingly, in the case of the Vac+Air treated samples, the concentration of oxygen was found to be much higher compared with those from the Vac annealed samples (63.5 at% vs. 52.5 at%, Table 1).

The XPS results prove that the organic residuals of the USP precursor solution are not easily removed as vapors of H_2O and CO and CO_2 gas at the stage of the



Table 1 Relative atomic concentration of elements (from natural spectra of C 1s, N 1s, O 1s, and Ti 2p_{3/2} core levels) in TiO₂ thin films before and after: 160 °C vacuum, 450 °C air, 160 °C vacuum, and subsequent 450 °C air annealing steps

Sample	C 1s, at%	N 1s, at%	O 1s, at%	Ti 2p _{3/2} , at%
As-dep	38.3	1.8	48.3	11.8
Vac	36	0.6	47.6	15.9
Air	28.2	0.6	52.5	18.7
Vac+Air	16.3	1.5	63.5	18.8

USP deposition at 340 °C and during post-deposition air treatment at 450 °C. A few recent studies from the photocatalysis field have shown the presence of carbon species in USP TiO₂ films after air annealing at temperatures ≥ 500 °C and after additional ultraviolet treatments.³⁸

Moreover, the carbon was found to be beneficial for the photocatalytic performance of TiO₂.³⁹ The same TTIP–AcacH based precursor solution is widely used for the spin coating and USP deposition of planar TiO₂ films as an electron transport layer in perovskite solar cells.^{40,41} In particular, for TiO₂ based perovskites, a single step air treatment at 450–500 °C is a well-established annealing step and there is little to no impact of the AcacH concentration (over a wide range from 1 : 10 to 1 : 20 TTIP : AcacH ratios) on the perovskite device performance.^{42,43} Our results instead bring experimental evidence that the USP precursor and annealing procedures for TiO₂ strongly impact the efficiency of Sb₂Se₃/TiO₂ solar cells. Based on XPS data (and changes in the lattice parameters of TiO₂), we show that the residual carbon species (Fig. 7b) play an important role in the composition of the surface and bulk defects in TiO₂. This effect is then translated into the quality of the Sb₂Se₃–TiO₂ heterointerface formation and subsequently has a great impact on the final device performance. We demonstrate that vacuum annealing could be a suitable technological approach to decrease the concentration of carbon species in TiO₂ films and, by this, to improve the performance of Sb₂Se₃ solar cell efficiency. However, more research efforts are required to understand the correlation between the USP precursor solution, residual organic species, and TiO₂ surface defects and, thus, their impact on the TiO₂–Sb₂Se₃ interface, related interface defect states, and final device performance. In this direction, a combination of advanced characterization methods, such as scanning transmission electron microscopy (STEM)⁴⁴ and transient SPV spectroscopy,⁴⁵ could be suitable techniques to gain in-depth insights into the impact of nanoscale carbon species on GBs electronic properties in TiO₂ and passivation of the electronic traps at the main interface.

Conclusions

In this work, we systematically study the impact of TiO₂ annealing conditions on the performance of Sb₂Se₃/TiO₂ thin film solar cells. The results were compared for three annealing variations: vacuum annealing only at 160–450 °C, two-step vacuum annealing at 160–450 °C followed by a subsequent 450 °C air treatment, and 450 °C air treatment only. XRD and SEM analysis showed improved



structural properties of the TiO_2 when a two-step annealing was applied. We showed that vacuum annealing can be a suitable technological approach to decrease the concentration of organic residues in TiO_2 films. Changes in the lattice parameters of annealed TiO_2 indicated the processes taking place inside the crystalline lattice of the TiO_2 films and were connected with the removal of residual species. The annealing conditions do not affect the grain structure of the Sb_2Se_3 absorber films but significantly impact the final device performance. The employment of one step TiO_2 vacuum annealing has a detrimental impact on the cell efficiency. Vacuum annealing at 160 °C followed by subsequent 450 °C air treatment led to a 4.7% device performance. This was explained by achieving an optimal balance between the removal of carbon content during vacuum annealing and the active recrystallization of TiO_2 during air annealing. The decrease of the carbon concentration by employing the two-step approach was proven by XPS. Our findings pave a solid platform for further research investigations on the impact of organic residues in chemically processed TiO_2 , including optimization of post deposition treatments for efficient Sb_2Se_3 solar cells.

Author contributions

Mykhailo Koltsov: conceptualization, data curation, formal analysis, methodology, software, visualization, writing – original draft. Robert Krautmann: software, visualization, writing – review & editing. Atanas Katerski: formal analysis, writing – review & editing. Natalia Maticiu: formal analysis, writing – review & editing, validation. Malle Krunks: formal analysis, validation. Ilona Oja Acik: validation, project administration, funding acquisition. Nicolae Spalatu: conceptualization, formal analysis, methodology, supervision, visualization, writing – review & editing, validation and funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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