Does Sb$_2$Se$_3$ Admit Nonstoichiometric Conditions? How Modifying the Overall Se Content Affects the Structural, Optical, and Optoelectronic Properties of Sb$_2$Se$_3$ Thin Films

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ABSTRACT: Sb$_2$Se$_3$ is a quasi-one-dimensional (1D) semiconductor, which has shown great promise in photovoltaics. However, its performance is currently limited by a high $V_{oc}$ deficit. Therefore, it is necessary to explore new strategies to minimize the formation of intrinsic defects and thus unlock the absorber’s whole potential. It has been reported that tuning the Se/Sb relative content could enable a selective control of the defects. Furthermore, recent experimental evidence has shown that moderate Se excess enhances the photovoltaic performance; however, it is not yet clear whether this excess has been incorporated into the structure. In this work, a series of Sb$_2$Se$_3$ thin films have been prepared imposing different nominal compositions (from Sb-rich to Se-rich) and then have been thoroughly characterized using compositional, structural, and optical analysis techniques. Hence, it is shown that Sb$_2$Se$_3$ does not allow an extended range of nonstoichiometric conditions. Instead, any Sb or Se excesses are compensated in the form of secondary phases. Also, a correlation has been found between operating under Se-rich conditions and an improvement in the crystalline orientation, which is likely related to the formation of a MoSe$_2$ phase in the back interface. Finally, this study shows new utilities of Raman, X-ray diffraction, and photothermal deflection spectroscopy combination techniques to examine the structural properties of Sb$_2$Se$_3$, especially how well-oriented the material is.

KEYWORDS: quasi-1D semiconductors, chalcogenides, photovoltaics, Sb$_2$Se$_3$, MoSe$_2$, material characterization, emerging materials

INTRODUCTION

In recent years, thin-film chalcogenide-based photovoltaic (PV) technologies have emerged as one of the most attractive complementary pathways to silicon-based solar cells, opening the door to greater versatility and implementation opportunities for photovoltaics, including flexible and semitransparent devices. Among these innovative absorbers, CdTe and Cu(In,Ga)(S,Se)$_2$ (CIGS) have accomplished remarkable improvements in their power conversion efficiency (PCE), exceeding the 20% barrier. However, the potentially unstable supply of scarce elements such as In, Ga, and Te and the toxicity of Cd raise doubts about the ability of CIGS and CdTe to meet the necessary industrial demands to transition toward a 100% renewable energy system. Consequently, thin-film chalcogenide-based photovoltaics free of critical raw materials remain a highly active research field, generating relevant scientific and technological awareness. For instance, Cu$_2$SnZn(S,Se)$_4$ (CZTSSe) has aroused great interest as a successful sustainable alternative to CIGS, achieving PCE values of up to 12.6%. However, its chemical complexity makes it difficult to overcome the current limitations, mostly regarding the high number of native defects and secondary phases.

In contrast, antimony selenide (Sb$_2$Se$_3$) is constituted by earth-abundant and low-toxicity components and possesses a number of highly appealing properties for photovoltaic implementation, such as binary stoichiometry, an optimal band gap (1.2–1.3 eV), a large absorption coefficient, and a quasi-one-dimensional (Q-1D) crystal structure. In addition, solar cells made with this compound can be fabricated in both substrate and superstrate configurations at comparatively...
low temperatures, thus panning the way for alternative substrates and architectures. Furthermore, Sb$_2$Se$_3$ has shown great promise not only for photovoltaics but also for energy storage, achieving a high reversible capacity of 312.03 mAh/g at a current density of 1000 mA/g for potassium-ion batteries.\textsuperscript{14,15} The Q-1D structure of Sb$_2$Se$_3$ consists of (Sb$_2$Se$_{3n}$)$_m$ covalently bonded ribbons along one crystallographic direction, while they are stacked by weak van der Waals forces in the other two directions,\textsuperscript{16} conferring strong anisotropic optoelectronic properties, such as preferential carrier transport in the [001] direction (along the covalently bonded ribbons according to \textit{Pbnm} \#62).\textsuperscript{16} Hence, by tuning the crystalline orientation of the Sb$_2$Se$_3$ film, it is possible to increase the minority carrier mobility and collection and thus improve the photovoltaic (PV) performance of the device.\textsuperscript{17}

Thus far, it has been reported that the substrate on which the Sb$_2$Se$_3$ is grown has a significant influence on the ribbon alignment, along with the temperature at which the material is subjected during synthesis (with a reported optimal \(T\) range of 300–330 °C).\textsuperscript{18–20} However, the effect of the relative amount of Se/Sb on the film’s crystalline orientation is yet to be thoroughly investigated.

In a very short time, Sb$_2$Se$_3$ has shown steady improvements in the PV performance, achieving record cell efficiencies of 9.2% (nanorod arrays) and 8.5% (planar heterojunction solar cells), prepared by close-spaced sublimation,\textsuperscript{11,21} and 6.84% by magnetron sputtering.\textsuperscript{22,23} However, devices are still mainly limited by a high \(V_{oc}\) deficit, suggesting that recombination processes involving deep defects might be a limiting factor.\textsuperscript{24,25} Indeed, despite being a relatively simple binary compound, it has been shown by first-principles calculations that the intrinsic defects in Sb$_2$Se$_3$ are unexpectedly complicated and unconventional, with up to three different \(V_{Se}\) and two \(V_{Sb}\) components due to several nonequivalent atomic sites, in addition to substitutional and intrinsic defects and other uncommon defects, such as 2Se replacing one Sb antisite (2SeSb).\textsuperscript{26} There is consequently a clear interest in exploring novel strategies that make it possible to control the emergence of these defects and to offer new conditions to unlock the whole potential of the absorber.

In particular, modulating the relative amount of Se/Sb by moving away from the stoichiometric conditions could offer an opportunity to compensate defects, while modifying the electronic properties of the material, without adding new components (i.e., complexity) to the system. For instance, according to Huang et al.,\textsuperscript{26} the electrical conductivity could be tuned from p-type to n-type by modulating the Se chemical potential through transitioning from Se-rich to Se-poor conditions. Moreover, it has been reported by theoretical studies that deep defects have a higher concentration under Sb-rich conditions, suggesting that a hypothetical strategy to enhance the performance of the device could be by favoring a Se-rich synthesis.\textsuperscript{24} However, it is still unclear whether Sb$_2$Se$_3$ allows an extended off-stoichiometric range or, on the contrary, grows forming a single phase highly resilient to compositional variations. Indeed, off-stoichiometric film composition has been a key element in the past success of mature thin-film chalcogenide absorbers such as CIGS or CZTSSe, especially in terms of control of the minority carrier concentration.\textsuperscript{27–29} For example, it has been shown that the shallow defect \(V_{Cu}\) in kesterites becomes dominant under Cu-poor conditions, contributing to an enhanced p-type conductivity.\textsuperscript{30,31}

Considering these relevant characteristics of chalcogenide absorbers such as CIGS and CZTSSe, it is extremely important to investigate the tolerance of Sb$_2$Se$_3$ to intrinsic doping and compositional variations, moving toward a broader understanding of this material with the goal of developing improvement strategies based on verifiable empirical knowledge.

Remarkably, recent experimental evidence has revealed that moderate Se excess increases the PV performance of Sb$_2$Se$_3$/CdS p-n junction-based devices.\textsuperscript{32,33} Nonetheless, whether this excess has been incorporated into the structure or segregated in the form of additional phases is still unclear.

Here, we have used a sequential process based on the selenylation of thermally evaporated Sb to synthesize a series of Sb$_2$Se$_3$ thin films with different Se/Sb relative contents, ranging in a wide spectrum of nominal compositions. By forcing the incorporation of different Se amounts, we expected to elucidate whether the Se and Sb excesses had been incorporated into the Sb$_2$Se$_3$ structure and thus determine whether Sb$_2$Se$_3$ is a highly stoichiometric single-phase semiconductor in the same manner as in CdTe or it admits an extended compositional range as it occurs in CIGS or CZTS. Also, we have identified all the phases that appear under the different conditions studied, with which we have been able to develop a phase diagram as a function of the overall Se content. Interestingly, we have detected a correlation between the amount of the self-generated MoSe$_2$ phase and the preferential crystalline orientation of Sb$_2$Se$_3$, proving that the presence of such a phase is critical to obtain good-quality devices with an optimal orientation. Finally, prototype solar cells have been fabricated and characterized to assess the effect of varying the Se content in the absorber on the PV performance of the device.

### EXPERIMENTAL METHODOLOGY

**Material and Device Preparation.** Sb$_2$Se$_3$ layers were manufactured on Mo-sputtered SLG substrates (SLG/Mo), using a two-step sequential process consisting of the deposition of a 250 nm Sb layer followed by reactive annealing under a Se atmosphere. Sb coating was performed by thermal evaporation (Oerlikon Unives, 250), from Sb shots (Alfa Aesar, 1–3 mm), using a base vacuum of 10$^{-7}$ mbar and an evaporation rate of 1 Å/s. Then, the SLG/Mo/Sb precursors were subjected to Se reactive annealing in a tubular furnace, using a semiclosed graphite box (23 cm$^3$). Accordingly, samples were heated up to 320 °C (with a 20 °C/min heating ramp) at 500 mbar and then cooled naturally (45 min approximately). To explore different compositions, different annealing durations were applied between 15 min (Se-poor) and 30 min (Se-rich). Likewise, the Se availability was modulated by changing the amount of Se powder placed in the graphite boxes, without any condition below the threshold required to achieve a saturated atmosphere. To synthesize Sb-rich films (Se contents below its stoichiometric amount), 10–15 mg of Se powders was used (Alfa Aesar, Se powder 200 mesh). On the other hand, to synthesize Se-rich samples, approximately 25 mg was placed in the boxes. The appropriate contents in each case were determined through previous optimization processes. Importantly, graphite boxes are subjected to high-temperature cleaning (650 °C, 2 h) beforehand to eliminate any possible selenium excess in between each sample processing.

To characterize the optoelectronic properties, some of the Sb$_2$Se$_3$ layers prepared in accordance with the previous procedures were converted into solar cells. The heterojunction was completed with an n-type CdS buffer deposited by chemical bath deposition, followed by i-ZnO + indium tin oxide (ITO) deposition by direct current (DC) pulsed magnetron sputtering (Alliance Concept C100), as reported elsewhere.\textsuperscript{34}
Material and Device Characterization. The nominal composition and thickness of the as-synthesized Sb₂Se₃ absorbers were determined by X-ray fluorescence (XRF) with Fischerscope XVD equipment, which was previously calibrated by inductively coupled plasma mass spectrometry (ICP-MS). Cross-sectional morphology and thickness of complete devices were characterized by scanning electron microscopy (SEM), using a Zeiss Series Auriga field-emission microscope, with an acceleration voltage of 5 kV and working distances ranging between 3 and 5 mm. Composition profiles were studied by X-ray photoelectron spectroscopy (XPS) in the CCGiTB with a PHI 5500 multitechnique system from Physical Electronics, using a monochromatic X-ray source Al Kα line of 1486.6 eV. X-ray diffraction (XRD) data were obtained using a PANalytical X’Pert PRO MPD alpha1 Bragg-Brentano powder diffractometer, with a Cu tube operating at 45 kV and 40 mA, a Johansson-type Ge (111) primary focusing monochromator, and a solid-state strip 1D PIXcel³D detector. High-resolution, high-statistics, full-angular range primary focalizing monochromator, and a solid-state strip 1D tube operating at 45 kV and 40 mA, a Johansson-type Ge (111) using a monochromatic X-ray source Al Kα with a PHI 5500 multitechnique system from Physical Electronics, studied by X-ray photoelectron spectroscopy (XPS) in the CCiTUB with the fundamental parameters approach. Raman spectroscopy measurements were performed with an optical probe in the backscattering configuration developed at IREC facilities coupled to a FHR640 Horiba Jobin Yvon spectrometer, where the signal is acquired with a liquid nitrogen-cooled (140 K) CCD detector. The excitation wavelength employed was 633 nm and was focused on a macrospot (≈50 μm) to avoid sample inhomogeneity. The laser power was kept under 25 mW/cm² to avoid degradation of the films.

Additionally, the optical absorption of glass (Corning1737)/Sb₂Se₃ samples was characterized by photothermal deflection spectroscopy (PDS). This technique was used to determine the absorbance of the Sb₂Se₃ films in the sub-band gap region. A single-slab model was applied to compute the absorption coefficient (see the Supporting Information for a more detailed description of the procedure). The transverse PDS setup used in this work consists of a 100 W tungsten halogen lamp, PTI 01-0002 monochromator (two-grating monochromator, spectral range of 400–2000 nm), and Thorlabs MC1000 optical chopper (4 Hz light modulation frequency). A Signal Recovery 7265 lock-in amplifier was connected to a Hamamatsu C10442-02 PSD position-sensitive detector to measure the deflection of a MC6520C 10 mW laser probe beam. Samples were put in a quartz cell filled with Fluorinert TM FC-40. A personal computer was used to control the monochromator, change the order filters, and store the PDS signal read from the lock-in amplifier.

RESULTS

Compositional and Structural Analysis of Sb₂Se₃ Nonstoichiometric Thin Films. SLG/Mo/Sb₂Se₃ thin films were prepared following the aforementioned experimental methodology. The XRF analysis of the samples revealed that the suggested two-step process allowed us to obtain Sb₂Se₃ thin films with the Se amount ranging from 0.36 to 0.55 (2[Se]/(2[Se] + 3[Sb])), where 0.50 corresponds to the

Figure 1. XPS in-depth profiles of samples with a nominal composition of 2[Se]/(2[Se] + 3[Sb]): (a) 0.36, (b) 0.48, (c) 0.53, and (d) 0.54, (e, f) distribution of Se out of the stoichiometry for the 0.53 and 0.54 samples, respectively.
stoichiometric conditions. Thus, it was proved that sequential thermal evaporation and reactive annealing synthesis, with control over Se vapor pressure and annealing time, allowed us to incorporate different amounts of Se into the thin films. However, XRF indicated the elemental content in the sample, regardless of whether it forms a single phase or several secondary phases.

To determine the elemental distribution of the films and to elucidate whether the material admits an extended non-stoichiometric range, in-depth XPS analysis was performed for the different compositions, as shown in Figure 1. In all the cases, it is observed that after a certain sputtering time, the Mo signal increases abruptly, denoting the back Mo/Sb$_2$Se$_3$ interface. Also, atomic concentrations of Se$^{−2}$ (black spots) and Sb$^{+3}$—(blue spots)—evolve correlatively, indicating that the Sb$_2$Se$_3$ composition remains steady throughout the film thickness, regardless of the overall Se content as measured by XRF. This suggests that Sb$_2$Se$_3$ is a single-phase stoichiometric material, whereby any Se or Sb excess in the sample is compensated as secondary phases, rather than forming off-stoichiometry Sb$_2$Se$_3$. Indeed, for Sb-rich conditions (see Figure 1a,b), an Sb$_2$O$_3$ phase has been detected at the front of the cell, the amount of which increases as the nominal Se content decreases, indicating that unreacted Sb on the surface of the film has been oxidized following the annealing process, once the material came in contact with air. Interestingly, it is observed that Se has a lower concentration near the surface than in the deeper region of Sb-rich samples (0.36 and 0.48, respectively). A possible hypothesis would be that during the heating ramp, there exists a Se flux toward Mo, before the Sb$_2$Se$_3$ crystallizes upon reaching its formation temperature around 320 °C. Under Se-deficit conditions, most Se element will have diffused to the back, leading to the aforementioned Sb$_2$Se$_3$ profile. Recent experiments with interrupted growth processing have shown similar trends; however, more experiments are required to unequivocally confirm the hypothesis. Finally, Figure 1a shows a high amount of metallic Sb at the back of the absorber, suggesting that the very low Se amount in such a sample is insufficient to react with the Sb precursor throughout its entire thickness. On the other hand, in the samples with 0.53 and 0.54 Se amounts (see Figure 1c,d), an offset between the Se$^{−2}$ and Sb$^{+3}$ signals, overlapping the Mo curve, is observed. This may indicate that a Se-rich phase has appeared in the back contact interface. To observe more clearly the distribution of Se under these circumstances, the amount of Se in excess (beyond stoichiometry) has been plotted as a function of the sputtering time; see Figure 1e,f. Interestingly, it can be noticed that the Se excess remains fairly low for most of the layer (within the noise range), while significantly increasing in the rear interface. The fact that the amount of Se excess at the back interface increases as the film becomes Se-richer supports the hypothesis that under Se-excess conditions, a Mo–Se phase appears, whose content increases as the overall Se content increases. This phase is likely to be MoSe$_2$, as consistently reported for chalcogenide films grown on the Mo substrate.41

To study the structural properties of the Sb$_2$Se$_3$ phase in either of the previous cases, SEM cross-sectional images of the
completed devices are acquired; see Figure 2a. Images have been obtained from complete devices (including buffer and window layers)—see Figure S1 for a complete energy dispersive X-ray analysis (EDX) profile and mapping compositional analysis of the layers constituting a sample. Interestingly, the Se-rich films (I and II) have large grains all developed alongside the entire thickness of the layer, while the Sb-rich samples (III and IV) exhibit smaller grains scattered throughout the thickness of the layer (see Figure S2 for lower magnification images). Moreover, the shape of the grains appears much more random in these samples, whereas I and II show well-oriented grains in the growth direction. To delve deeper into the crystalline orientation and structure of nonstoichiometric Sb$_2$Se$_3$, a detailed XRD full-profile Rietveld analysis was performed; see Table S1. The average crystal size (Lorentzian) shows a clear threshold around stoichiometric conditions (0.50), from which the crystal size increases significantly as the overall Se amount increases, whereas by shifting toward Sb-rich conditions, it drops abruptly and the slope becomes much less pronounced; see Figure 2b. Importantly, this diverging behavior between Se-rich and Sb-rich conditions clearly implies a change in the growing conditions that favors a more orderly and controlled formation of the grains; one of the goals of this work is to determine the cause. As shown below, this trend is consistently repeated with the other material properties under analysis.

Figure 3a shows the X-ray diffractograms of samples in each of the compositional ranges of interest for this study, i.e., Sb-rich (2[Se]/(2[Se] + 3[Sb]) = 0.36), slightly Sb-rich/near stoichiometry (0.48), and moderately Se-rich (>0.54), focusing on the selected 20 ranges; see Figure S3 for the complete 10–140° diffractograms, the Rietveld-calculated patterns, and the difference between the experimental and theoretical patterns. Since the XRD analysis was performed on Mo/Sb$_2$Se$_3$ samples, the main crystalline phases include Mo (back contact layer) and Sb$_2$Se$_3$ (absorber). Also, for the Se-rich films, a certain amount of MoSe$_2$ and Se secondary phases have been detected, which increase as the overall concentration becomes Se-rich (see Table S1 for the main Rietveld refinement analysis parameters including the phase amount, crystal size, and cell volume). In contrast, for Sb-rich thin films, these phases are not observed; however, important amounts of $\alpha$-Sb$_2$O$_3$ (0.48, 0.36) and m-Sb (0.36) are detected, whose content also increases as the composition becomes Se-poorer. The presence of the Se and $\alpha$-Sb$_2$O$_3$ phases in each group of the samples is directly corroborated from the diffractograms; see Figure 3a. Although with very weak and wide peaks, which are difficult to identify, reflections corresponding to MoSe$_2$, mainly oriented in the (001) direction, have been detected and quantified in the Se-rich samples by Rietveld analysis (Table S1); see Figure S4 for the enlarged diffractogram in the 11–15° region, where the MoSe$_2$ peak (003) appears. Moreover, a change in the Sb$_2$Se$_3$ crystallinity depending on the Se content in the films can also be observed. Overall, Sb$_2$Se$_3$ layers show a complex multiaxial crystallinity, with a [001]-preferred orientation (also in the $[hk]1$ and $[h0]1$ directions), which is manifested by the intense and sharp peaks observed at 45.6° (002), 29.2° (211), 31.2° (221), and 32.2° (301). Interestingly, as the Se content decreases, these reflections become broader and their intensity declines, until no preferential texture is visibly discerned for the sample with the lowest Se amount. Therefore, it is shown that despite a single-phase stoichiometric material, the crystalline orientation and structure of Sb$_2$Se$_3$ are indeed affected by the overall Se content of the film, exhibiting a good [001]-preferred orientation for Se-rich samples and deteriorated randomized texture in the Sb-rich range. To quantitatively assess the differences in the crystalline orientation between samples with a distinct Se concentration, the texture coefficient (TC) of the selected Bragg reflections was calculated based on eq 1, where $N$ is the number of reflections considered for the calculation, $I_{hkl}$ is the measured empirical intensity of a diffraction peak, and $I_{0,hkl}$ corresponds to the intensity value in the standard XRD pattern (ICDD 04-003-0715 Powder Diffraction File patterns).

$$\text{TC}_{hkl} = \frac{I_{hkl}/I_{0,hkl}}{\sum_{i=1}^{N} I_{hkl}/I_{0,hkl}}$$

The results of the TC calculations from a series of selected Sb$_2$Se$_3$ samples are illustrated in Figure 3b. Notably, samples with Se excess and most especially those with 0.54 Se are primarily dominated by the (002) reflection. Since the $h$ and $k$ Miller indices are both 0, this indicates that $(Sb_4Se_6)_n$ ribbons grow perpendicular to the substrate surface, proving that Se-rich conditions help enhance the orientation of Sb$_2$Se$_3$ grains. On the other hand, as we shift toward Sb-rich conditions, the (231), (141), and (221) peaks become dominant. In this case, $h$ and $k$ values are greater or equal to 3, indicating that the angles between the $(Sb_4Se_6)_n$ ribbons and substrate are small, revealing an Sb$_2$Se$_3$ lateral growth deemed detrimental to the electrical properties of the material. Finally, we observe that the sample with 0.36 Se has a virtually arbitrary crystalline orientation, with all TC presenting very small, similar values between 0 and 1. However, we note that this sample has the smallest value of TC$_{002}$ and the largest value of TC$_{230}$, indicating a total loss of the preferred orientation in the (002) direction.

In addition, the XRD—Rietveld analysis has showed a connection between the cell volume and the overall Se amount; see Figure S5. First, it is noticed that the cell volume of Sb$_2$Se$_3$ thin films is smaller than that of the bulk monocrystals. This reduction of the volume could be associated with a decrease of Se$_{\alpha}$ and 2Se$_{\alpha}$ defects and an increase of $V_{Se}$ vacancies, allegedly reducing the Fermi level splitting (which could affect negatively the $V_{Se}$, since $Se_{\alpha}$ is responsible for p-type conductivity). Interestingly, near stoichiometry, this compressive effect is larger, with samples having a cell volume of 54.3 Å$^3$ against that of 54.6 Å$^3$ of a single crystal, while for the Se(Sb)-richer films, a sequential increase is observed as the nominal composition moves away from stoichiometry, the cell volume becoming more similar to that of the single crystal. It is possible that an increase in the overall Se content compensates the detrimental $V_{Se}$ defects, lessening the compressive strain, hence the volume enlargement.

Complementing the previous study of structural properties by XRD and now paying special attention to the characterization of interfaces (both the surface and back interface), a complete Raman spectroscopy analysis was performed. The average Raman spectra of bare Sb$_2$Se$_3$ thin films (surface) with a nominal composition in the range of 0.36 < $2[Se]/(2[Se] + 3[Sb])$ < 0.54 are shown in Figure 4a. The formation of the $\alpha$-
Sb$_2$O$_3$ secondary phase, which appears only on the surface of Sb-rich samples (peak at 254 cm$^{-1}$), is also detected. On the other hand, elemental Se phases (t-Se) have been detected in the Se-richer samples; see Figure S6. Furthermore, the following trends in some areas of the Raman peaks associated with the Sb$_2$Se$_3$ phase are also observed (boxed areas in Figure 4a):

1. The area of the Sb$_2$Se$_3$ peak at 101 cm$^{-1}$ increases as the overall Se amount increases.
2. The area of the Sb$_2$Se$_3$ peaks between 110 and 140 cm$^{-1}$ decreases as the overall Se amount increases.
3. The area of the Sb$_2$Se$_3$ peak at 150 cm$^{-1}$ decreases as the overall Se amount increases.

As previously reported by Fleck et al., an enhanced ribbon alignment in the [001] direction leads to minimization of the Raman signal at 150 cm$^{-1}$, proving that Raman spectroscopy allows us to quickly and easily assess the quality of the crystalline orientation in Sb$_2$Se$_3$ thin films. In addition, it is shown here that the areas defined by the 101 and 110–140 cm$^{-1}$ signals also experience clear variations depending on the 2[Se]/(2[Se] + 3[Sb]) relative concentration of the films increasing and decreasing. The fact that these variations occur in samples where the Sb$_2$Se$_3$ phase is single-phase stoichiometric, as shown with XPS, but with different crystalline orientations (see Figure 3) leads us to think that the area defined by the 101 and 110–140 cm$^{-1}$ signals is also contingent on the loss of the (002)-preferred orientation, which will be discussed later. The probing depth of the Raman measurements is surface-sensitive (∼100 nm), although their consistency with other methods (XRD), the small thickness of the films (∼800 nm), and the relatively large size of grains (Figure 2) allow us to hypothesize that these observations are also valid throughout the entire film thickness.

Further analysis related to the area variations in Raman spectra and their correlation with the Sb$_2$Se$_3$ nominal composition of several samples (including samples with a lateral compositional gradient) has been performed; see Figure 4b. Hence, the areas of the 101, 110–140, and 150 cm$^{-1}$ Raman peaks, normalized to the main Sb$_2$Se$_3$ signal at 190 cm$^{-1}$, have been plotted as a function of 2[Se]/(2[Se] + 3[Sb]). Accordingly, it is clearly noticed that there is a threshold around 0.50 Se, so that for increasing Se amounts,
the areas of signals at 150 and 110–140 cm\(^{-1}\) stop decreasing at the same rate, and the slope becomes more pronounced. Significantly, these behaviors present similarities with the trends in the crystal size (Figure 2b) and texture coefficient, TC (Figure 4e), where TC\(_{002}\) also shows a continuously decreasing slope that becomes more pronounced as the Se amount increases beyond the stoichiometric point. Thus, it is confirmed that both the 110–140 cm\(^{-1}\) band and 150 cm\(^{-1}\) peak reflect changes in the crystalline orientation, with their areas decreasing as the (002) direction becomes dominant. Otherwise, the 101 cm\(^{-1}\) signal presents a similar behavior with a positive slope, which is consistent with the opposite symmetry of this peak. The trend may not be as clear as that for the 110–140 and 150 cm\(^{-1}\) signals; however, the area of integration is also smaller, leading to the signal/noise ratio of the measurement affecting more pronouncedly the dispersion of data points.

These observations raise a question: if Sb\(_2\)Se\(_3\) is indeed a stoichiometric material, why does it have an enhanced ribbon alignment when the overall composition is Se-rich? To delve deeper into this behavior, a mechanical lift-off of a series of samples with different [2Se]/([2Se] + 3[SB]) nominal concentrations was performed. See Figure 4c for the lift-off remains on the Mo substrate for samples with the Se concentration ranging from 0.50 to 0.54. Interestingly, a MoSe\(_2\) phase has been identified, whose content increases as the overall Se amount also increases, while for the stoichiometric sample (0.50), Sb\(_2\)Se\(_3\) is observed and only traces of MoSe\(_2\) are detected. Note that this trend coincides with the loss of the (002)-preferred orientation as shown by XRD and Raman. Thus, it is likely that the in situ formation of MoSe\(_2\) plays a crucial role in the growth of well-oriented XRD and Raman. Therefore, modifying the texture of the back contact (from Mo to the Mo/MoSe\(_2\) system) ultimately affects the formation of Sb\(_2\)Se\(_3\) by enhancing its selectively oriented growth in the (001) direction, essential to develop a good quasi-1D structure. This is supported by previous research, according to which the substrate affects all electronic, structural, and crystallographic properties of the absorber.43

Regarding the role of MoSe\(_2\), we can point to two factors that lend weight to our hypothesis about its effect on the oriented growth of Sb\(_2\)Se\(_3\). First, since the enthalpy of formation of MoSe\(_2\) (−234.4 kJ/mol) is negative and smaller than that of Sb\(_2\)Se\(_3\) (−128.7 kJ/mol), i.e., MoSe\(_2\) is thermodynamically favored under our manufacturing conditions; and experimental evidence indicates that there is a Se flux toward Mo during the heating process (see Figure 1), it is plausible to assume that the MoSe\(_2\) layer is formed in the first place, effectively influencing the subsequent Sb\(_2\)Se\(_3\) crystallization.55 Second, the lattice mismatch (see eq 2, where \(\varepsilon\) stands for the mismatch and \(a\) is the lattice parameter of each layer) of the MoSe\(_2\)/Sb\(_2\)Se\(_3\) interface is significantly smaller (8%) than that of Mo/Sb\(_2\)Se\(_3\) (26%) when both the substrate and layer are oriented in the c direction; see the lattice constants and mismatch in Table S3.56–58 This indicates that the strain between MoSe\(_2\) and Sb\(_2\)Se\(_3\) layers with the preferred crystalline orientation is lower than that of the Mo/Sb\(_2\)Se\(_3\) system, which may contribute to a more ordered ribbon growth in the first case. Also, a mismatch larger than 20% inevitably implies the formation of incoherent interfaces, while for \(\varepsilon < 10\%\), the system may be strained but leads to coherent interfaces.59

\[
\varepsilon = \frac{a_{\text{Sb}_2\text{Se}_3} - a_{\text{substrate}}}{a_{\text{substrate}}}
\]

(2)

To sum up, the previous compositional and structural analysis of Sb\(_2\)Se\(_3\) nonstoichiometric thin films has led to the following observations:

- Sb\(_2\)Se\(_3\) is a single-phase compound that does not allow an extended range of nonstoichiometry conditions. Indeed, any Sb or Se excess is compensated in the form of secondary phases: Sb\(_2\)O\(_3\) and m-Sb for Sb-rich conditions and MoSe\(_2\) and amorphous Se for Se-rich conditions.
- Under Sb-rich conditions, the crystal domain is small and grains grow in a disordered manner. In Se-rich films, grains are as thick as the layer itself with only grain boundaries parallel to device thickness.
- The crystalline orientation and structure of Sb\(_2\)Se\(_3\) films are affected by the nominal Se content. A clear tendency toward an improved (002) orientation is maintained until stoichiometry is reached (most likely related to the
increased annealing times and fewer impurity phases when approaching the 0.50 threshold). In contrast, for the increased Se content, the presence of MoSe₂ in the rear contact of the films plays a crucial role in the growth of well-oriented polycrystalline layers, leading to an abrupt enhancement of the (002) reflections.

**Absorption Coefficient.** Finally, photothermal deflection spectroscopy (PDS) was used to study the effect of varying the overall Se amount on the optical band gap and Urbach energy of Glass/Sb₂Se₃ samples. This information is very relevant since it allows us to assess the degree up to which changes in the nominal composition can affect intrinsic properties of the material, such as band gap energy. Also, exponentially decaying density of state (DOS) tails due to low-quality crystalline materials may cause transitions between these energy states inside the band gap (Urbach tails), which are characterized by the Urbach energy (U₀), leading to sub-band gap absorption. It is known that U₀ has an impact on carrier mobility and lifetime, affecting the device performance, especially the open-circuit voltage.⁶³,⁶⁴ Hence, by computing U₀, it is possible to characterize the influence of modifying the overall Se content on the performance of the cell, with regard to the presence of band tails. Also, considering that these observations relate only to the absorber rather than the complete junction, they allow us to decouple the limitations from the films and the limitations from a specific junction, such as interfacial intermixing and band alignment, offering a good approach to characterize the defects of the material itself.

The absorption coefficient α is represented as a function of the energy of the incident (exciting) beam in Figure 5a. It is significant decrease in the sub-band gap absorption may be due to compensation of deep defects. Interestingly, the samples with the lowest subgap α are those with 0.52 and 0.53 Se, whereas those with 0.54 are slightly higher, suggesting that a large Se excess can be detrimental to the absorber, possibly due to the appearance of Sb secondary phases on the surface (see Raman spectra with elemental Se peaks in Figure S6). The effect of Se phases in the front interface could be assessed by comparing as-grown samples with films subjected to selective or complete surface etching (Br₂).⁶₂,⁶₆ Other than that, the larger subgap absorption in Se-richer thin films could also be due to the recently reported abnormal defect behavior in Sb₂Se₃, which causes the density of Se vacancies Vₛ to increase as the material becomes anion-rich, leading to general deteriorated performance in extremely Se-rich films.⁶₅ Tauc plots were computed from the PDS-derived α from which the value of the optical band gap was extrapolated; see the obtained values in Table 1. Note that all values are comparable considering the uncertainty. This confirms our hypothesis that Sb₂Se₃ is a stoichiometric material. Even though different nominal compositions have been explored, the band gap remains unchanged, indicating that no compositional changes of the Sb₂Se₃ phase are expected. Finally, the Urbach energy is determined in accordance with eq 3, where α₀ and U₀ are constants determined by fits to the experiment, h is Planck’s constant, and ν is the incident beam frequency. Therefore, U₀ is obtained from the inverse of the slope resulting from plotting ln(α) as a function of energy; see results in Table 1.¹⁷ In the Se-rich range, U₀ is low (23–24 meV), indicating a good-quality absorber with a small number of absorption centers inside the band gap. Significantly, the Urbach energy in the Se-rich range is lower than other reported U₀ values from Sb₂Se₃-evaporated films.¹⁷,⁶⁶ Nonetheless, values shown here are still above the 20 meV barrier, which has been indicated to be one of the factors contributing to the large Vₛ defect in CIGS and CZTSSe technologies.⁶⁸ On the other hand, when the overall Se amount decreases, the Urbach energy increases steadily. As stated above, all previous measurements point toward a stoichiometric Sb₂Se₃ layer regardless of the synthesis conditions. Hence, variations in U₀ are likely due to increased disorder of the material, resulting from nonoptimal growth conditions, such as the presence of Sb₂O₃ and Sb preventing good crystalline growth (small, randomly oriented grains under Sb-rich conditions; see Figure 2). Changes in Urbach energy can also be connected to modifications in the defect structure of the material, where deep defects are compensated under Se-rich conditions but are prominent under Sb-rich conditions, all included inside the Sb₂Se₃ doping level. Considering both the very low sub-band gap absorption and U₀ of Se-rich Sb₂Se₃ thin films, it is expected that these can lead to better performing devices.

### Table 1. Optical Band Gap (eV) and Urbach Energy (meV) in Relation to the Nominal Se Content in the Samples

| Se content | band gap (eV) | Urbach energy (meV) |
|------------|--------------|---------------------|
| 0.48       | 1.153 ± 0.022| 70.12 ± 0.91        |
| 0.50       | 1.150 ± 0.027| 41.80 ± 1.20        |
| 0.52       | 1.144 ± 0.012| 24.80 ± 0.37        |
| 0.53       | 1.151 ± 0.008| 23.49 ± 0.34        |
| 0.54       | 1.154 ± 0.006| 22.99 ± 0.32        |

Figure 5. Absorption coefficient (α) as a function of photon energy (hv) of glass/Sb₂Se₃ films prepared during the same synthesis process as the SLG/Mo/Sb₂Se₃ corresponding samples with 2[Se] /[2[Se] + 3[3[3b]]]: 0.54, 0.53, 0.50, 0.48, and 0.36. The absorption coefficient obtained from the PDS spectra.
Moving further away from the stoichiometry toward Sb-rich conditions, the amount of unreacted Sb increases. On the other hand, for $2[\text{Se}]/(2[\text{Se}] + 3[\text{Sb}]) > 0.54$, Se elemental phases appear, which could likely be a limitation for electronic transport.

So far, the effect of varying the overall Se concentration in Sb$_2$Se$_3$ on the intrinsic properties of the absorber (structure, composition, morphology) has been considered, regardless of how it might affect its PV performance. To investigate the optoelectronic properties of nonstoichiometric Sb$_2$Se$_3$-based solar cells, $J$-$V$ curves of a selected set of samples have been acquired, which are processed into PV devices with the following architecture: Mo/Sb$_2$Se$_3$/CdS/ZnO/ITO. The results from this study are shown in Figure 6d–g, where the power conversion efficiency (PCE), $V_{oc}$, $I_{sc}$, and fill factor (FF) have been plotted as a function of $2[\text{Se}]/(2[\text{Se}] + 3[\text{Sb}])$. Notice that PCE and $V_{oc}$ follow similar trends (Figure 6d,e), with the devices prepared from absorbers with 0.36 and 0.48 Se showing the lowest $V_{oc}$ (66 and 157 mV, respectively), which could be due to the abundant secondary phases appearing under Sb-rich conditions, the high Urbach energy (see Table 1), and the extremely large sub-band gap absorption (see PDS results in Figure 5a). These secondary phases include an Sb$_2$O$_3$ layer in front of the cell (see XPS profiles in Figure 1), thicker than a few nanometers, and possibly inhomogeneous morphology is likely to disrupt the Sb$_2$Se$_3$/CdS interface, preventing a good performance of the p-n junction. On the other hand, both 0.53 and 0.54 Se films exhibit a good PCE and $V_{oc}$ of around 4% and 400 mV, respectively, with which it is shown that a small deviation toward Se-poor compositions is much more detrimental to the operation of the device than switching toward Se-rich conditions. However, as the Se amount continues to increase, a small reduction in $I_{sc}$ is observed (see Figure 6f), which could result from the appearance of Se elemental phases at the heterointerface with CdS (Figure S6).

More interestingly, the sample with 0.50 Se (strictly stoichiometric) shows low PCE, $V_{oc}$, and FF, when under these conditions of absence of impurity phases, much higher values, or at least similar to those of the 0.53 and 0.54 films (Se-rich), would be expected. On the other hand, the better performance of Se-rich films could be due to the compensation of $V_{oc}$ defects, which might act as effective recombination centers. On the other hand, the reported declining trends in $V_{oc}$ and FF coincide with the loss of a (002)-preferred crystalline orientation when the Se content decreases, as shown by TC$_{002}$ in Figure 6c. Indeed, all optoelectronic parameters in the range of $0.36 < 2[\text{Se}]/(2[\text{Se}] + 3[\text{Sb}]) < 0.54$ present the characteristic double-slope trend of TC$_{002}$, indicating a strong dependence of Sb$_2$Se$_3$ PV performance on the crystalline orientation. A deterioration in the ribbon alignment implies the loss of the enhanced c-axis conductivity due to the anisotropic properties of Sb$_2$Se$_3$, causing a sharp drop in the PV performance.

Furthermore, it is observed that while the MoSe$_2$ content gradually decreases until it stops forming for Sb-rich samples, TC$_{002}$ decreases steeply to values between 1 and 2. Afterward, the (002)-preferred orientation continues dwindling, but with a much lower rate. Therefore, it is likely that the existence of a MoSe$_2$ phase plays a relevant role in the well-oriented growth of quasi-1D Sb$_2$Se$_3$. Thus, a certain amount and good crystalline orientation of MoSe$_2$ can decisively influence the preferential orientation of Sb$_2$Se$_3$, improving its optoelectronic performance.

Discussion of Structural and Optical Characterization and Its Translation to the Optoelectronic Properties of Devices. With the results of the compositional analysis presented above, a phase diagram has been developed; see Figure 6. Accordingly, note that the XRD analysis (Figure 6a) shows different secondary phases depending on whether the material is under Se-rich or Sb-rich conditions, suggesting that Sb$_2$Se$_3$ does not allow an extended off-stoichiometry range. Instead, Sb excesses are either converted into Sb$_2$O$_3$ or remain as unreacted m-Sb, whereas Se excesses diffuse toward the Mo back contact, forming a MoSe$_2$ layer. Nevertheless, XRD tends to underestimate the MoSe$_2$ content, which has been detected in all Se-rich films analyzed by Raman spectroscopy (Figure 6b), demonstrating that MoSe$_2$ appears systematically in the Mo/absorber interface of Se-rich Sb$_2$Se$_3$. Therefore, combining XRD and Raman, it can be inferred that Sb$_2$Se$_3$ is a stoichiometric material, highly resilient to compositional changes, with any Sb or Se excesses compensated in the form of metallic Sb, Sb$_2$O$_3$ (Sb-rich), or MoSe$_2$ (Se-rich).
properties. Certainly, by the XRD–Rietveld analysis, it has been noticed that the MoSe₂ has a preferred crystalline orientation in the (001) direction, confirming its role in enhancing the Sb₂Se₃ grain growth perpendicular to the substrate (see Table S1).

Overall, these results clearly point out in the direction that Sb₂Se₃ is a single-phase material that does not admit significant off-stoichiometric variations, whose crystalline orientation is essential to develop good PV performance, and for which the growing conditions, in particular with regard to the formation of certain phases, can either improve or deteriorate its structural and electronic properties. However, the study presented here has some limitations. For instance, although it confirms previously reported improvements of incorporating a MoSe₂ layer in Mo/Sb₂Se₃ devices⁴⁸ (in this case by in situ formation of MoSe₂ during the Sb₂Se₃ reactive annealing), no specific analysis of the MoSe₂ phase has been performed. Thus, we believe that studying the formation process and properties of the MoSe₂ phase in detail could help to clear up some of the hypotheses raised in this work, such as the specific effect it exerts on the Sb₂Se₃ crystalline growth. Furthermore, results suggest that the Sb₂Se₃ formation by reactive annealing constitutes a dynamic process, in which there is a Se flux through the Sb layer, and then, the absorber crystallizes upon reaching 320 °C, validating the premise that the back contact’s texture has an impact on the Sb₂Se₃ structure. However, the precise formation mechanism should be investigated further—we suggest performing complete characterization analysis of samples acquired by interrupted growth at different annealing times.⁴¹ Also, this work is essentially centered on the standard process for preparing Sb₂Se₃ thin films in the substrate configuration (i.e., Mo/Sb₂Se₃/buffer layer/TCO), leading to the formation of the MoSe₂ layer under Se-excess conditions. Notwithstanding, we believe that it might be interesting to investigate what happens when there is no Mo resource available. Under these circumstances, it may be possible that the Se surplus is effectively incorporated into the Sb₂Se₃ structure or else it accumulates at the front interface in the form of elemental Se, as has been suggested elsewhere.⁶⁷–⁶⁹ Further research and supporting evidence for verification are required.

In this work, we have shown that there is a direct correlation between Raman spectra and (002) crystalline orientation, which so far has been justified based on a comparative study of Raman analysis and XRD (especially TC calculations); however, additional support is required, for example, by studying the Raman spectra of Sb₂Se₃ grown on different substrates or using synthetic routes that give rise to different textures. Otherwise, further study of Sb₂Se₃ in the Se-rich range might be necessary to unequivocally identify the nature of the elemental Se phases that appear under these conditions and hence design strategies to remove or minimize them, such as etching procedures. Finally, we emphasize that this study has been based on investigating the consequences of significantly modifying the nominal concentration of Sb₂Se₃ films; however, focusing on a very small interval around the stoichiometry might shed new light on the effect of intrinsic doping, especially with regard to reducing the amount of VₓSe defects.

### CONCLUSIONS

In this work, it has been confirmed that Mo/Sb₂Se₃ thin films do not allow an extended off-stoichiometric range, whereby any Sb or Se excess is compensated in the form of secondary phases: MoSe₂ and Se elemental phases under Se-rich compositional conditions and Sb₂O₃ and m-Sb in the Sb-rich range. The results presented here illustrate the difficulty of selectively controlling or enhancing the formation of Sb₂Se₃ intrinsic properties (e.g., defects) by modulating the Se chemical potential beyond stoichiometric conditions, unlike CIGS or CZTS. Hence, we suggest that enhancing the many virtues of Sb₂Se₃ (and minimizing its numerous defects) will require exploring new opportunities through extrinsic doping or alloying. For instance, the similar behavior of Sb₂Se₃ to that of CdTe makes us think about the suitability of applying successful recipes in CdTe to unlock the full potential of Sb₂Se₃. Second, it has been shown that despite the fact that Sb₂Se₃ is stoichiometric, it is necessary to operate under Se-rich conditions to develop good devices, primarily to form a MoSe₂ phase—promoting a well-oriented growth in the (002)-crystalline direction and avoiding the appearance of unwanted secondary phases—and also to minimize the number of detrimental VₓSe-type defects, although this aspect needs to be investigated further. We demonstrate that MoSe₂ plays a dual role, as a hole transport layer and as a growth matrix, directing and effectively influencing the structural characteristics of Sb₂Se₃.⁷⁰ Ultimately, this study has shown the power of Raman–XRD-related combined techniques to examine the structural properties of Sb₂Se₃, especially the degree of orientation in the (001) direction, and PDS to obtain the sub-band gap absorption and Uₒ which need to be minimized to develop good absorbers. Overall, this work points out at new strategies to improve Sb₂Se₃ devices, including extrinsic doping approaches rather than intrinsic doping (due to the small gap free of damaging secondary phases when the composition shifts away from stoichiometry) and etching treatments for Se-rich samples (to take advantage of the MoSe₂ formation, while eliminating the surface elemental Se disruptive phases).

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmi.1c20764.

Description of the procedure to obtain the absorption coefficient by PDS; additional XPS, XRD, Raman, and SEM figures; and XRD analysis and Rietveld parameters (PDF)

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Author Contributions
L.C. performed the synthesis procedure of samples, analyzed results from XRD, Raman, and PDS techniques, and wrote the article. P.V. performed the PDS measurements and data analysis and contributed to the writing of the article. L.C. conducted the XPS measurements and data analysis. X.A. performed the XRD measurements and Rietveld analysis. J.A. contributed to the article by providing PDS equipment and measurements. S.G. conducted the SEM measurements. Y.S. participated in the synthesis of PV devices (chemical treatments). Z.J., M.P., and E.S. contributed to the conceptualization of research and to the writing of the article (review and editing). J.P., V.I., and E.S. contributed to the conceptualization of research and provided funding and resources. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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