The sputter deposition of broadband transparent and highly conductive cerium and hydrogen co-doped indium oxide and its transfer to silicon heterojunction solar cells

Leonard Tutsch1,2 | Hitoshi Sai2 | Takuya Matsui2 | Martin Bivour1 | Martin Hermle1 | Takashi Koida2

Abstract
Indium oxide doped with tin (ITO) is the most commonly used material for lateral transport window layers in silicon heterojunction (SHJ) solar cells, as it currently offers the best combination of physical properties, industrial deposition capability, and module reliability. However, typically applied ITO layers by far do not exploit the full electro-optical potential of the indium oxide material class, resulting in optical and electrical losses limiting the solar cell efficiency. In this work, cerium and hydrogen co-doped indium oxide thin films are developed for their application as high-performance transparent conductive oxide layers in SHJ devices. Amorphous In2O3:Ce,H layers are fabricated via radio frequency magnetron sputtering, before being crystallized during post-deposition thermal treatments compatible with the SHJ temperature stability. The resulting excellent electro-optical film properties are on par with values so far solely reported for reactive plasma deposited films. It is shown that the surface morphology of the substrate (planar or textured) has a strong impact on the film properties, and further, the critical role of the atmosphere present during post-deposition annealing is elucidated. Finally, the large potential of an optimally processed In2O3:Ce,H window layer in SHJ cells is demonstrated, quantified by a gain in short circuit current density of 0.6 mA/cm² without impairing the resistive losses in comparison to the usage of a baseline ITO layer.

KEYWORDS
cerium-doped indium oxide, electron mobility, silicon heterojunction solar cells, solid phase crystallization, transparent conductive oxide

1 | INTRODUCTION

Transparent conductive oxides (TCOs) are elementary layers for highly efficient silicon heterojunction (SHJ) solar cells, as they have to meet several physical requirements simultaneously. They have to form a good contact to the doped hydrogenated amorphous Si (a-Si:H) layers and to the metal fingers, have a high lateral conductivity, and at the same time, have a low optical absorption. Due to its decent properties, its stability and the benefit in manufacturing costs since being applied in other photovoltaic (PV) and non-PV mass production...
technologies, tin-doped indium oxide (ITO) is still the predominantly used material for this purpose both in research labs and in SHJ production lines. Even though there is currently no fundamental shortage of indium, its comparatively uncertain supply and rather high cost strive for a reduction of the latter in SHJ cells. There exist several indium-free alternatives. Recently, the replacement of ITO by low-cost aluminum-doped zinc oxide (AZO) on the cell’s rear side or on both sides, taking advantage of the wafers contribution to the lateral current transport in the case of a rear emitter cell design, showed promising results, even though capping layers might be required to solve the module stability issue of zinc oxide-based TCOs.

Exploiting the superb electro-optical properties inherent for the indium oxide material class, another approach to reduce the indium consumption of an SHJ cell can be the reduction of the film’s thickness. Further, the potentially low film resistivity enables the application of a metal grid with comparatively large finger spacing, reducing the amount of Ag, while further improving front contact transparency. However, indium oxide-based materials with properties outperforming conventional ITO have been discovered and extensively studied in the past years. Here, the usage of other metal dopants (e.g., Zr, W, Ti, and Mo) than tin and/or the incorporation of hydrogen resulted in enlarged electron mobility, being an important parameter for the conductivity–transparency trade-off. In general, enabling low resistivity of TCOs via n-type doping is typically accomplished by (i) a substoichiometric, oxygen-poor deposition leading to donor-type oxygen vacancies within the films; (ii) the substitution of indium cations by extrinsic metal atoms; and/or (iii) the incorporation of hydrogen atoms into the film. While by these means, the electron density in the conduction band (N) can be increased, charged impurities remain, which limit the electron mobility with a related scattering cross section showing a square law dependence on the impurity charge state. Oxygen vacancies in In₂O₃ are often present as doubly charged impurities; hence, using solely them to achieve a substantial doping level is not favorable for maximizing the mobility. In the case of inserting extrinsic metal atoms to act as singly charged donors in In₂O₃, several aspects are considered important for a proper selection thereof. The energy level of the respective donor state needs to be high enough to effectively donate electrons to the In₂O₃ conduction band, while hybridization between both should be avoided in order not to affect the band curvature, which might result in an increased electron’s effective mass and hence a lowered . When incorporated into the In₂O₃ lattice structure, the effective radius of the ionized dopant should be close to the one of indium in order to avoid microstrain around the dopant site. Further, a large oxygen affinity of the metal cation can help to decrease the density of unfavorable oxygen vacancies within the TCO. Moreover, in recent years, several studies showed that the addition of hydrogen during the film growth can support high and N within the films simultaneously. This was attributed to the appearance of hydrogen atoms as singly charged donors, their ability to passivate defects at the grain boundaries of polycrystalline films, as well as their beneficial role in the crystallization process of solid phase crystallized (spc) TCOs. Regarding the latter, hydrogen can promote amorphous film growth such that during a post-deposition thermal treatment, high-quality polycrystalline TCO layers with low strain and large crystal grains can emerge, which allow for an exceptional high electron mobility.

Kobayashi et al. recently discovered the co-deposition of In₂O₃ with cerium and hydrogen to facilitate values of up to 145 cm²/Vs when grown via reactive plasma deposition (RPD). Similarly, Koida et al. extensively characterized the microstructure and bulk properties of high RPD In₂O₃:Ce,H layers when deposited polycrystalline or after crystallization from the amorphous phase. However, an equivalent film quality for this material deposited via magnetron sputtering has not been reported yet. Hence, in this work, the electro-optical properties of sputter-deposited and spc In₂O₃:Ce,H are studied dependent on the cerium, oxygen, and hydrogen content within the films. Further, the activation energy/temperature budget required for crystallization is attached importance in order to be compatible with the SHJ thermal stability.

While there are various reports on the successful fabrication of high-mobility TCOs, in several cases, it was difficult for those films to outperform ITO when applied in SHJ cells. Reasons for this were, for instance, a too low electron density in the TCO, being problematic for the contact formation to the adjacent a-Si:H layers, or an excessive hydrogen concentration, which can degrade the contact to the metal finger during the sintering of the metal paste. Another issue is that some reported high-mobility TCO results are achieved on planar substrates like glass or (SiO₂-coated) Si for an unsophisticated TCO characterization. However, the deposition on textured surfaces and/or hydrogen-containing a-Si:H layers present in SHJ devices can lead to different TCO bulk properties. Thus, we investigated the influence of the substrate type on the TCO properties and, further, the influence of the annealing atmosphere (with or without oxygen). Eventually, as a proof of principle, we applied the optimized In₂O₃:Ce,H films on SHJ devices to observe the potential of this material contrasted to the ITO baseline layer.

2 | EXPERIMENTAL DETAILS

Approximately 105 nm thick In₂O₃:Ce,H films were deposited without intentional substrate heating via radio frequency (RF) magnetron sputtering onto planar substrates (glass and SiO₂-coated Si) as well as onto SHJ precursors with random upright pyramidal surface texture. For the SHJ substrates, this leads to an effective In₂O₃:Ce,H thickness (measured perpendicular to the lateral faces of the pyramids) of around 75 nm (the factor of ~1.4 for this surface texture was obtained, e.g., via electron microscopy). The cerium content within the films was adjusted by varying the individual power applied during co-sputtering from ceramic targets of pure In₂O₃ and another one containing 2 wt% of CeO₂. Ar, O₂, and H₂ gas was introduced to the sputtering process. The partial pressure of H₂O was optimized and then fixed at 10⁻⁴ Pa using a variable leak valve, while the O₂ to Ar ratio was varied in the experiments. The films were post-annealed at around 200 °C either within a furnace containing pure N₂ or on a hotplate in ambient air. While for the hot plate, annealing a 10-min step was sufficient for complete crystallization, several TCO
films annealed in the nitrogen furnace still showed a mixed phase after 10 min, which is possibly due to a slightly lower effective substrate temperature. The annealing time in the nitrogen furnace for the samples shown in Figures 2–5 was thus prolonged to 30 min, which ensured complete crystallization for all films, except where stated otherwise.

Monofacial 270 μm thick n-type SHJ cells with random pyramid surface texture and the a-Si:H (i/p) contact on the front side (Figure 8) were fabricated to test the In2O3:Ce:H performance on device level. More information about the SHJ cell fabrication process can be found elsewhere.30,31

The charge carrier mobility and density of the thin films grown on different substrate types were determined via Hall effect measurements in the van der Pauw configuration. In order to additionally evaluate the temperature dependence of these parameters, measurements were performed every 10°C during heating and subsequent cooling processes in vacuum or ambient air between 40 and 200 or 250°C. The optical properties were investigated for around 105 nm thick films deposited on SiO2-coated Si substrates via spectroscopic ellipsometry (SE). Here, the optical constants were calculated for each wavelength by means of inverting the SE spectra under application of the Fresnel equations. For the optical analysis of the charge carrier mobility and density, SE spectra recorded in the ultraviolet–visible and infrared range were combined. The dielectric function of the In2O3:Ce:H films was then modeled with a Tauc–Lorentz oscillator, representing interband absorption, together with the Drude term, which addresses the contribution of the conduction band electrons.32

The J-V characteristics of SHJ cells were evaluated using a solar simulator under AM1.5 and 100 mWcm−2 illumination. The cells were additionally characterized in open circuit condition via the SunsVoc method,33 and for selected cells, external quantum efficiency (EQE) spectra were recorded. The TCO sheet resistance on cell level was measured via the four-point probe (4PP) technique on cell structures without metal grid. Due to the finite cell area (1 × 1 cm2), the sheet resistance obtained from 4PP was overestimated to some extent. In order to take this into account, the transfer length method (TLM) was additionally applied for some wafers possessing dedicated TLM pattern.

3 RESULTS AND DISCUSSION

3.1 Electro-optical film properties and crystallization dynamics

Based on the promising reports on RPD In2O3:Ce:H,20,22 we RF co-sputtered this material type from a pure In2O3 target together with a target containing In2O3 mixed with 2 wt% of CeO2 in order to investigate the impact of the Ce dopant and its concentration. Here, without the intentional addition of water (water partial pressure \( P_{H2O} < 10^{-5} \) Pa), we consistently obtained quite resistive In2O3:Ce films in the as-deposited, polycrystalline state, which became even more resistive after post-annealing, similar to what was reported for In2O3:H films.21 Hence, at first, the impact of the water partial pressure \( 10^{-4} < P_{H2O} < 10^{-3} \) Pa) on the electrical properties of sputter-deposited amorphous In2O3:Ce2wt%,H films and their crystallization dynamics was studied by temperature-dependent Hall effect measurements performed in vacuum (Figure 1). Generally, the introduction of water ensured a substantial doping level in the as-deposited films, but \( N \) in turn decreased from 2.6 to 1.4 × 1020 cm−3 for \( P_{H2O} > 10^{-4} \) Pa. The \( N \) boost (compared to films deposited without water introduction) is attributed to reduced lattice defects by forming an amorphous structure. The decrease in \( N \) with more \( P_{H2O} \) is potentially due to carrier compensation by weakly bonded acceptor-type excess oxygen and/or a reduced doping efficiency of oxygen vacancy-type defects owing to large open spaces34 existing in comparatively porous films when deposited with excess \( H2O \). \( \mu_{as-dep} \) was constant at 40 cm2/V/s for the investigated \( P_{H2O} \) range. \( N \) and \( \mu \) showed weak temperature dependence during the vacuum heat up (squares) to 160°C, indicating the degenerate doping of the films. At \( T > 160°C \), a jump in both Hall parameters occurred, which is related to an increase in crystalline fraction within the layers.32 The mobility

---

**FIGURE 1** Carrier mobility \( \mu \) (a) and density \( N \) (b) as a function of specimen temperature for In2O3:Ce:H films deposited on glass substrates under varying water background pressure. Samples were heated in vacuum from 40 to 250°C before being cooled down again. The step duration at each temperature point amounts to around 30 min before the Hall effect measurement is performed. The individual temperature range where solid phase crystallization occurred is indicated [Colour figure can be viewed at wileyonlinelibrary.com]
increased for all films upon crystallization; however, a clear downward trend in the post-crystallization values exists for increasing $P_{H2O} > 1 \times 10^{-4}$ Pa. Concurrently, $N$ decreased during crystallization within the film deposited at $P_{H2O} = 1 \times 10^{-4}$ Pa, which can be related to the elimination of oxygen vacancies during the film reorganization. For higher $P_{H2O}$, $N$ went rapidly up just before crystallization. Here, it was reported from thermal desorption spectroscopy on similar films that an enhanced water effusion occurs before crystallization. This finding is of particular importance for the application in SHJ cells, since the temperature range around 200°C coincides with the upper limit for the thermal stability of interface passivation and contact resistivity of typical a-Si:H-based contacts. A more in-depth experimental analysis about the crystallization kinetics of H-doped In$_2$O$_3$ was reported by Wardenga et al. Now, in order to both maximize the mobility and reduce the activation energy for spc In$_2$O$_3$:Ce:H films, the water partial pressure was fixed to $P_{H2O} = 1 \times 10^{-4}$ Pa in the following. On the basis of former investigations on pure In$_2$O$_3$:H, a more detailed screening of the $P_{H2O}$ range between $10^{-5}$ and $10^{-4}$ Pa was not expected to yield further improvements.

In Figure 2, the influence of cerium content and the oxygen partial pressure on the electrical film properties ($\mu$ vs. $N$) is shown for as-deposited films and after solid phase crystallization at 200°C in nitrogen atmosphere. In the as-deposited films (open symbols), a broad range in charge carrier density ($1.3 - 5 \times 10^{20}$ cm$^{-3}$) was producible. $\mu_{as-dep}$ was between 35 and 60 cm$^2$/Vs and showed a rather weak dependence on $N$. After annealing (filled symbols), an increasing Ce content resulted in a shift to higher $N$, indicating the enhanced Ce doping efficiency within a crystalline In$_2$O$_3$ lattice. The mobility in the pure In$_2$O$_3$:H films peaked at 147 cm$^2$/Vs, decreasing slightly with Ce addition to 129, 127, 127, and 114 cm$^2$/Vs for 0.5, 1, 1.5, and 2 wt%, respectively. Also, the optimum oxygen flow leading to these mobility temperature demonstrates that the scattering on phonons became a dominant mechanism limiting the electron relaxation time in the crystallized In$_2$O$_3$:Ce$_{2wt\%}$H films. More detailed investigations on the transport-limiting mechanism in such high-quality polycrystalline In$_2$O$_3$-based TCOs can be found elsewhere. The impact of $P_{H2O}$ on the grain size of In$_2$O$_3$:H films fabricated under very similar conditions was investigated in a previous study.

Besides reducing $\mu$ and $N$, an excess introduction of water vapor moreover increased the activation energy for the crystallization process. The temperature related to the completion of the $\mu$ enhancement can be read out to increase from about 193 to 200, 206, and 215°C for $P_{H2O} = 1, 2, 5, 10 \times 10^{-4}$ Pa, well agreeing with the reports on the nucleation and crystallization hampering behavior of hydrogen.

### FIGURE 2

Relationship between Hall parameters in the amorphous state and after crystallization in nitrogen for around 105 nm thick In$_2$O$_3$:Ce:H films deposited on glass. The symbol type indicates the $O_2/Ar$ ratio varied during sputtering between 0% and 0.5% and the color represents the CeO$_2$ content. Dashed lines of equivalent resistivity are drawn [Colour figure can be viewed at wileyonlinelibrary.com]

### FIGURE 3

Relation between carrier mobility and density determined electrically via Hall effect measurements (a) and optically (b) from the Drude absorption spectra. In$_2$O$_3$:Ce:H films deposited under $O_2/Ar$ ratios equidistantly varied between 0% and 0.5% were compared after crystallization in nitrogen or ambient air. The film deposited with 0% $O_2/Ar$ still showed substantial amorphous fraction after N$_2$ annealing, and thus, $\mu$ and $N$ could not be extracted reliably from SE data [Colour figure can be viewed at wileyonlinelibrary.com]
maxima decreased with Ce content. Here, it is important to note that with an increased percentage of CeO₂ also, the relative number of oxygen atoms in the deposited layer possibly increased due to the large oxygen affinity of Ce and the higher oxygen to metal atomic ratio in the stoichiometric oxide (CeO₂: 2, In₂O₃: 1.5). Owing to the very moderate decrease in mobility and the effective doping, the addition of Ce enabled a very low sheet resistance (Rₛ) < 25 Ω□ for 105 nm thick films after solid phase crystallization. An important fact is that the addition of Ce results in N > 2 × 10²⁰ cm⁻³, which is a critical factor for device integration, in particular for the formation of low-ohmic contacts to charge carrier selective layers and to the metal.⁵,²⁴⁻²⁵,²⁹

As shown in Figure S1, the crystallization kinetics was affected by the incorporation of Ce. The onset temperature thereof significantly increased from around 155°C to 163°C when 0.5 wt% CeO₂ was added but then only slightly rose further (to ~165°C) for a CeO₂ increment ≥ 1 wt%. The influence of the oxygen stoichiometry was separately depicted in Figure S2. Here, either a large oxygen excess or deficiency (as obtained by varying the O₂ flow) hampered the crystallization process, while around the optimum oxygen content, the crystallization temperature was marginally changing.

Note that the electrical properties of the here investigated sputter-deposited In₂O₃:Ce:H films in the amorphous and spc state as well as the related crystallization behavior strongly resembled the RPD counterparts²⁰,²² and a comparably high electrical film quality could be achieved. Hence, for a deeper structural analysis, it can be referred to the studies on the RPD films.²²

3.2 | Impact of the annealing atmosphere on In₂O₃:Ce:H layer properties on flat substrates

During the post-deposition temperature treatments, the TCO films applied on test structures or on solar cells are in exchange with the present environment. While for annealing in vacuum or nitrogen atmosphere, as performed for Figures 1 and 2, mostly the effusion of species like hydrogen, oxygen, or water out of the layers³² is important, and also, the diffusion of atmospheric species like O₂, H₂O, or CO₂ into the layers has to be considered for ambient air annealing. The penetration of these species into In₂O₃:H films during solid phase crystallization in air was related to poorer electrical properties in comparison to when annealed in vacuum.⁴⁰ Hence, as a next step, the sensitivity of the In₂O₃:Ce₂wt%:H layers to the ambient during solid phase crystallization was addressed. For this purpose, around 105 nm thick 2 wt% CeO₂-doped films were sputter-deposited onto planar SiO₂-coated Si substrates. Samples at different oxygen partial pressures were produced and after substrate fragmentation exposed to ~200°C in either nitrogen or air. Figure 3a depicts the charge carrier density and mobility obtained via Hall effect measurements for films deposited at different oxygen partial pressure (different symbol type). The layers crystallized in nitrogen (red symbols) showed a μₜ₄all versus Nₜ₄all trend typical for this material class. Here, together with the scattering on phonons, μₜ₄all is presumably mostly limited by grain boundaries⁴¹ and/or excess oxygen within the films for Nₜ₄all < 2.2 × 10²⁰ cm⁻³. The oxygen-poor film with Nₜ₄all ~2.5 × 10²⁰ cm⁻³ still showed a mixed phase (confirmed by SE analysis), and here, the mobility was likely reduced further by the enhanced density of ionized impurities.¹⁶ Nₜ₄all was significantly lower for the same oxygen flow when the temperature step was performed in oxygen-containing ambient air. Hereby the μₜ₄all of the two films deposited at low oxygen partial pressure could be improved, most likely due to the reduction of oxygen vacancy scattering centers. On the other hand, the mobility of the oxygen-richer films was reduced significantly. This could be due to the increase of excess oxygen and/or the enhanced contribution of grain boundaries, which according to the Sato model⁴² become a more dominant electron transport barrier for lower Nₜ₄all in the case of highly doped semiconductors. Additionally, it appears that the rising function of μₜ₄all was sharper for the air-annealed films. This emphasizes the role of the grain boundaries and possibly indicates the degradation of their chemical composition during air annealing. In order to separate the electronic transport inside an In₂O₃:Ce₂wt%:H crystallite from the impact of the grain boundaries, charge carrier density and mobility were determined optically. For this purpose, the same samples which were used for the Hall effect measurements were characterized via SE. Here, the charge carriers are accelerated by an ac electric (and magnetic) field, and the resulting range of motion in the classical point of view for the applied frequency range is much smaller than the typical grain size of the spc In₂O₃:Ce:H films. Thus, the electronic motion is less affected by the grain boundaries, and μopt can be related to the intragrain mobility. In Figure 3b, the Nopt and μopt values were extracted from the dielectric function.²² For the nitrogen-annealed films, these values show a rather similar trend as the Hall parameters. The slight decrease of μopt for lower Nopt can most likely be explained by excess oxygen present in this regime leading to acceptor-type scattering centers and carrier compensation, impairing the intragrain transport. However, for the oxygen richly deposited and air-annealed

**FIGURE 4** Refractive index (n) and extinction coefficient (k) of In₂O₃:Ce:H films deposited under different oxygen partial pressure after crystallization at 200°C in N₂ or air. Optical constants for the ITO reference (Section 3.4) are added [Colour figure can be viewed at wileyonlinelibrary.com]
In$_2$O$_3$:Ce,H films (blue circle and star), $\mu_{\text{opt}}$ is significantly higher than $\mu_{\text{Hall}}$. This indicates the dominant role of the grain boundaries in this range and their resistive behavior after crystallization in air.

In Figure 4, the refractive index ($n$) and extinction coefficient ($k$) of films deposited under an O$_2$/Ar ratio of 0%, 0.13%, and 0.25% (corresponding to squares, pentagons, and triangles in Figure 3, respectively) obtained from ellipsometry spectra are depicted. Both layers deposited without oxygen addition showed significant absorption in the sub-band gap range, likely caused by highly oxygen-deficient regions within the films. For the film annealed in N$_2$, the large charge carrier density simultaneously led to enhanced free carrier absorption (FCA) for lower energy radiation. While for the under 0.13% O$_2$/Ar deposited film, slightly enhanced absorption in both regions was observed when crystallized in N$_2$, and the air-annealed counterpart as well as both films deposited with 0.25% O$_2$/Ar showed first-rate optical properties. These are a comparatively large band gap due to (i) their polycrystalline nature (forbidden fundamental interband transition$^{45}$) and (ii) their relatively large $N$ (Burstein–Moss), negligible absorption within the band gap and a moderate FCA (<2%) in the infrared due to their high mobility.$^5$

### 3.3 Transfer of In$_2$O$_3$:Ce,H films to SHJ solar cell substrates

As a next step, the transfer of In$_2$O$_3$:Ce,H films from flat substrates (glass or SiO$_2$-coated Si) to SHJ solar cell devices with a random upright pyramid surface texture was addressed with a focus on the substrate dependence of the electrical TCO thin film properties. In order to calculate the Hall mobility and charge carrier density via the van der Pauw method, one necessary assumption is to study a flat film order to calculate the Hall mobility and charge carrier density via the van der Pauw method, one necessary assumption is to study a flat film (corresponding to squares, pentagons, and triangles in Figure 3, respectively) obtained from ellipsometry spectra are depicted. Both layers deposited without oxygen addition showed significant absorption in the sub-band gap range, likely caused by highly oxygen-deficient regions within the films. For the film annealed in N$_2$, the large charge carrier density simultaneously led to enhanced free carrier absorption (FCA) for lower energy radiation. While for the under 0.13% O$_2$/Ar deposited film, slightly enhanced absorption in both regions was observed when crystallized in N$_2$, and the air-annealed counterpart as well as both films deposited with 0.25% O$_2$/Ar showed first-rate optical properties. These are a comparatively large band gap due to (i) their polycrystalline nature (forbidden fundamental interband transition$^{45}$) and (ii) their relatively large $N$ (Burstein–Moss), negligible absorption within the band gap and a moderate FCA (<2%) in the infrared due to their high mobility.$^5$

In the as-deposited state as well as after solid phase crystallization in pure N$_2$, $\mu^*$ and $N^*$ behave very similar as in the case of the flat glass substrate (Figure 2). However, for the both films deposited under an O$_2$ to Ar ratio of 0.13% and 1 wt% (red) or 2 wt% (green) of CeO$_2$, the electrical properties became significantly worse after crystallization in ambient air at 200°C. In comparison to flat substrates, this deterioration now already occurred for In$_2$O$_3$:Ce,H films grown under oxygen-poorer conditions. Therefore, achieving high conductivity (and large $\mu^*$) for films deposited on textured SHJ substrates after crystallization in ambient air was only possible when selecting very oxygen-poor growth conditions (black bars in Figure 5). However, since these films showed a significant absorption in the visible range (Figure 4), the simultaneous realization of high conductivity and low absorption seemed to be non-trivial for the combination of textured substrate and ambient air annealing.

In order to study the evolution of the electrical film properties in more detail, the behavior of $\mu$ ($\mu^*$) and $N$ ($N^*$) is compared for annealing in ambient air and vacuum via temperature-dependent Hall effect measurements for films (2 wt% CeO$_2$, 0.13% O$_2$/Ar) deposited either on flat glass or on textured SHJ precursors (Figure 6). Prior to the sputter deposition, the SHJ substrates were exposed to 280°C for 2 h to reduce the impact of hydrogen otherwise later effusing from the a-Si:H into the TCO (this effect will be elucidated afterwards). For both In$_2$O$_3$:Ce,H layers deposited on glass (black curves), the mobility sharply increased at temperatures $>150$°C, representing the onset of the film crystallization, also connected with a decrease in charge carrier density. This decrease was slightly enhanced in the presence of ambient air (black open symbols), indicating the incorporation of external oxygen into the films. The properties of the In$_2$O$_3$:Ce,H layers annealed in vacuum showed a qualitatively similar trend when deposited on the textured SHJ substrate (red filled symbols) with $\mu^*$ doubling after crystallization. However, for the combination of SHJ substrate and air annealing (red open symbols), a significant drop in $N^*$
was observed already at a temperature of around 130°C, indicating the film’s enhanced vulnerability for species (e.g., oxygen) penetrating from the ambient. After crystallization, this resulted in a highly resistive film with both low $\mu^*$ and $N^*$, in accordance to what was observed in Figure 5.

It was reported that the post-deposition crystallization of amor phously grown $\text{In}_2\text{O}_3$-based layers can lead to polycrystalline thin films with very low compressive strain and exceptionally large crystal grains. While this allows for an electron mobility above 100 cm²/Vs, the lack of compressive strain was suggested to yield grain boundaries less sealed than in the case of their polycrystalline grown counterparts. One hypothesis is that this becomes particularly visible when deposited on rough surfaces. Similarly, degraded electrical properties of $\text{In}_2\text{O}_3$-based films were reported when grown on rough layers for the application within Cu (In,Ga)Se₂ solar cells. Here, they observed formation of crack-shaped voids inside $\text{In}_2\text{O}_3$-based thin films, particularly in regions where the substrate layers underneath exhibited ridges or valleys. However, no such degradation was found when textured glass was used as substrate. This was explained by the larger feature size of the glass texture, which corresponds to a lower local slope of the height profile, in turn allowing for a sufficiently undisturbed TCO growth. Apart from this, it was shown that also the microstructure of the hydrogenated silicon thin films underneath can considerably influence the TCO film properties. Here, they observed a more irregular initial ITO growth when comparing nanocrystalline (nc) with amorphous Si layers, which was related to the enhanced surface roughness of the nc-Si films.

Besides the surface texture of the non-planar substrates, also the effusion of hydrogen into the TCO during post-deposition thermal treatments was considered important, and the extent thereof can depend on the type of Si thin film underneath (e.g., a-Si:H (p) vs. nc-Si: H(n)). For our samples, the impact of hydrogen effusing from the a-Si:H layers on the electrical properties of $\text{In}_2\text{O}_3$:Ce,H films was investigated by comparing SHJ substrates, which prior to this were exposed to 280°C for 2 h, with counterparts not having received this predetermination hydrogen effusion treatment. In Figure 7, the resistivity evolution of $\text{In}_2\text{O}_3$:Ce,H films deposited in the same run on conventional (green curves) and hydrogen-poor (red curves) SHJ precursors is shown during their exposure to temperatures increasing from 40 to 200°C before subsequently cooling down to 40°C again. Open and filled symbols represent annealing in air and vacuum, respectively. For both samples crystallized in vacuum, the final $\text{In}_2\text{O}_3$:Ce,H film resistivity is around half of the initial, mostly due to the doubled mobility, as shown above (Figure 6). In particular, for increasing temperatures between 100 and 200°C, the film resistivity was lower when deposited on the hydrogen-rich substrate, which could indicate a doping effect of hydrogen effusing from the a-Si:H layer. In the case of the ambient air exposure, the resistivity of both films degraded continuously for increasing temperatures above 130°C and then during the whole cooling process. However, also here, a significant shift towards lower resistivity values for the $\text{In}_2\text{O}_3$:Ce,H layer on top of the hydrogen-richer SHJ precursor was observed. Hence, even though the impact of effusing hydrogen should be considered, this effect is potentially not substantial for the final electrical properties of optimized high-conductivity $\text{In}_2\text{O}_3$:Ce,H films applied in SHJ devices.

### 3.4 | Potential of $\text{In}_2\text{O}_3$:Ce,H window layers for an improved SHJ cell performance

Finally, selected TCO layers were applied on monofacial SHJ cells (device structure sketched in Figure 8). The aim of this first and rather rudimentary batch was to study whether the trends of the electrical and optical film properties observed on test structures are reflected in the cell’s resistive losses and quantum efficiency, respectively. The parameters under investigation were the oxygen (and cerium) content as well as the annealing atmosphere (N₂ or air). To highlight the trade-off between optical transparency and efficient electrical current transport, cells with varying number of metal fingers and thus varying finger spacing were fabricated for the individual TCO front layers. On the rear side, 75 nm thick $\text{In}_2\text{O}_3$:Ce,H layers with 1 wt% CeO₂ and 0.25% O₂/Ar or 2 wt% and 0.07% were applied for the N₂- and air-annealed cells, respectively. As reference, cells with ITO ($\text{In}_2\text{O}_3$:SnO₂ = 90: 10 wt%) on both sides were included. For the rear side ITO, the oxygen content was increased compared to the layer on the front side. For the ITO reference, the oxygen content of the front and rear side layer together with the annealing process (2 h at 160°C in air) belong to the baseline process sequence for these SHJ cells.

While the optical constants of the front side ITO are shown in Figure 4, the electrical transport properties (both measured for
by the modest passivation quality (open circuit voltage \( V_{oc} \) measured (in house) to amount to 22.2% and was considerably limited.

The maximum conversion efficiency of the fabricated cells was measured (in house) to be 710 ± 5 mV, pseudo fill factor \( pFF \): 83 ± 1%, which did not show a significant dependence on the applied TCO films. While the detailed \( J-V \) parameters are depicted in Figure S3, the TCO-dependent optical and electrical transport properties are quantified in Figure 9 by the short circuit current density \( J_{sc} \) and the difference between \( pFF \) and actual \( FF \).

The blue, magenta, and red squares represent cells with In\(_2\)O\(_3\):Ce\(_{1\%}\)H front TCO layers deposited under increasing oxygen partial pressure (O\(_2\)/Ar ratio of 0.13%, 0.25%, and 0.38%) before being annealed in N\(_2\) atmosphere. Compared to reference cells using the baseline ITO process, a significant improvement in \( J_{sc} \), of around 0.6 mA/cm\(^2\), could be observed. For the widest finger spacing (least metal shading), the In\(_2\)O\(_3\):Ce\(_{1\%}\)H film deposited with 0.25% O\(_2\)/Ar allowed a \( J_{sc} \) of 39.6 mA/cm\(^2\). Pure In\(_2\)O\(_3\):H was included as further reference (black circles). Here, the oxygen flow of 0.25% O\(_2\)/Ar was selected in order to match the film resistivity of the highly conductive In\(_2\)O\(_3\):Ce\(_{1\%}\)H layers (those with 0.13% and 0.25% O\(_2\)/Ar). The resulting \( J_{sc} \) was on a similar level as for the In\(_2\)O\(_3\):Ce\(_{1\%}\)H windows but slightly lower than the optically best performing Ce-doped counterpart.

For the cell structures, which later received annealing in ambient air, a reduced oxygen partial pressure (O\(_2\)/Ar ratio of 0.05% and 0.08%) was used during In\(_2\)O\(_3\):Ce\(_{1\%}\)H deposition, in order to account for the degradation of the electrical In\(_2\)O\(_3\):Ce\(_{1\%}\)H film properties during air annealing, as discussed in the previous section. For these cells, the \( J_{sc} \) was limited to values only slightly above the ITO reference, which is potentially due to oxygen-deficient regions in the In\(_2\)O\(_3\):Ce\(_{1\%}\)H films, which remain after crystallization and cause parasitic absorption.

From quantum efficiency measurements (not shown), it was observed that the main advantage of the In\(_2\)O\(_3\):Ce\(_{1\%}\)H (and In\(_2\)O\(_3\):H) films compared to the ITO reference was in the short wavelength range, due to the larger band gap of the polycrystalline films (cf. Figure 4), together with an improved response in the near-infrared (NIR). Here, an exact quantification of the NIR absorption losses in the front side TCO is not possible with the investigated cell structures, as the TCO at the rear side is not the same for all cells. However, the used rear side TCOs have nominally low FCA owing to their moderate carrier concentration. To extract the exact FCA of the investigated TCOs, a dedicated experiment will be required to accurately quantify the NIR gain enabled by applying the In\(_2\)O\(_3\):Ce\(_{1\%}\)H films either on the front and/or the rear side.

As a measure of the resistive losses within the solar cell, the gap between pseudo fill factor \( pFF \) (determined in open circuit conditions via the SunsVoc method\(^{23} \)) and the actual \( FF \) is plotted in Figure 9b. The legend shows the related sheet resistance of the TCOs on the SHJ structure determined via 4PP and/or TLM. The In\(_2\)O\(_3\):Ce\(_{1\%}\)H layers deposited under 0.13% and 0.25% O\(_2\)/Ar show very low \( R_{sh}^{4PP} \) of 45 and 65 Ω/sq, respectively (slightly overestimated via 4PP due to finite area TCO windows). For these layers, the \( pFF-FF \) difference is of the same range or even lower than for the ITO reference (\( R_{sh}^{4PP} \) ~80 Ω/sq). The application of the oxygen-richer (O\(_2\)/Ar: 0.38%) In\(_2\)O\(_3\):Ce\(_{1\%}\)H film, with increased \( R_{sh}^{4PP} \) of 220 Ω/sq, led to noticeable resistive losses, which increased with larger finger spacing. For the cells annealed in air (\( R_{sh}^{TLM} \) of 135 and 220 Ω/sq, for lower and higher oxygen content, respectively), the FF loss was larger than for the ITO reference and increased with finger spacing. This, together with the simultaneously moderate \( J_{sc} \), is in accordance with the
A thorough analysis of the growth conditions and important aspects for the successful device integration of highly conductive and broadband-transparent In$_2$O$_3$:Ce,H layers was presented. With respect to the deposition conditions, a proper adjustment of the cerium content as well as H$_2$O and O$_2$ partial pressure present during the sputter deposition yielded amorphous In$_2$O$_3$:Ce,H layers, which turned into TCO thin films with high electro-optical quality after crystallization at temperatures compatible with the stability of SHJ contacts. The annealing atmosphere (with or without oxygen in the ambient) was shown to have a strong influence on the film properties. Films deposited on SHJ precursors with a random pyramid surface morphology were particularly vulnerable to the interaction with the environment. When exposed to ambient air, the charge carrier density in such films started to drop severely already at temperatures around 130 °C. In this case, the simultaneous realization of both high conductivity and transparency turned out to be far more difficult. In contrast, the nitrogen-annealed In$_2$O$_3$:Ce,H window layers allowed on SHJ device level a gain of 0.6 mA/cm$^2$ compared to the reference ITO front electrode. At the same time, the doping level of the In$_2$O$_3$:Ce,H films is high enough to allow an effective current transport and the very low sheet resistance enabled the usage of metal grids with a finger spacing clearly above 2 mm without significantly increasing the cell’s series resistance. For these lab-type cells, the In$_2$O$_3$:H reference showed a similar performance. However, regarding the transfer to a more production-like process sequence (screen printed metal contacts, annealing performed after metallization), the limited $N_e$ of pure In$_2$O$_3$:H, which is moreover strongly relying on optimized hydrogen and oxygen management, can be a major issue. Furthermore, due to its brittleness, no established techniques are known for the sintering of pure In$_2$O$_3$ on rotatable targets. For In$_2$O$_3$:CeO$_2$ (98.5:1.5 wt%), the development of such sintering processes is now part of ongoing work. A further next step will be to make use of the low film resistivity and reduce the In$_2$O$_3$:Ce,H layer thickness in combination with the addition of a dielectric layer on top (e.g., SiN$_x$ or a-SiO$_x$) to ensure an anti-reflective coating. Besides improving the light incoupling and reducing the indium consumption, this capping layer potentially hinders species from entering the films during post-deposition annealing and could thus facilitate a metallization procedure more established for industrial production.

4 | CONCLUSION

A thorough analysis of the growth conditions and important aspects for the successful device integration of highly conductive and broadband-transparent In$_2$O$_3$:Ce,H layers was presented. With respect to the deposition conditions, a proper adjustment of the cerium content as well as H$_2$O and O$_2$ partial pressure present during the sputter deposition yielded amorphous In$_2$O$_3$:Ce,H layers, which turned into TCO thin films with high electro-optical quality after crystallization at temperatures compatible with the stability of SHJ contacts. The annealing atmosphere (with or without oxygen in the ambient) was shown to have a strong influence on the film properties. Films deposited on SHJ precursors with a random pyramid surface morphology were particularly vulnerable to the interaction with the environment. When exposed to ambient air, the charge carrier density in such films started to drop severely already at temperatures around 130 °C. In this case, the simultaneous realization of both high conductivity and transparency turned out to be far more difficult. In contrast, the nitrogen-annealed In$_2$O$_3$:Ce,H window layers allowed on SHJ device level a $J_{ic}$ gain of 0.6 mA/cm$^2$ compared to the reference ITO front electrode. At the same time, the doping level of the In$_2$O$_3$:Ce,H films is high enough to allow an effective current transport and the very low sheet resistance enabled the usage of metal grids with a finger spacing clearly above 2 mm without significantly increasing the cell’s series resistance. For these lab-type cells, the In$_2$O$_3$:H reference showed a similar performance. However, regarding the transfer to a more production-like process sequence (screen printed metal contacts, annealing performed after metallization), the limited $N_e$ of pure In$_2$O$_3$:H, which is moreover strongly relying on optimized hydrogen and oxygen management, can be a major issue. Furthermore, due to its brittleness, no established techniques are known for the sintering of pure In$_2$O$_3$ on rotatable targets. For In$_2$O$_3$:CeO$_2$ (98.5:1.5 wt%), the development of such sintering processes is now part of ongoing work. A further next step will be to make use of the low film resistivity and reduce the In$_2$O$_3$:Ce,H layer thickness in combination with the addition of a dielectric layer on top (e.g., SiN$_x$ or a-SiO$_x$) to ensure an anti-reflective coating. Besides improving the light incoupling and reducing the indium consumption, this capping layer potentially hinders species from entering the films during post-deposition annealing and could thus facilitate a metallization procedure more established for industrial production.

ACKNOWLEDGEMENTS

The authors would like to thank Y. Sato, M. Tanabe, T. Oku, and M. Lozach for sample preparation and technical support. Part of this work was funded by the German Federal Ministry for Economic Affairs and Energy under contract numbers 03EE1031A (PaSoDoble) and 03EE1032 (CUSTCO).

Open access funding enabled and organized by Projekt DEAL.

ORCID

Leonard Tutsch https://orcid.org/0000-0001-6698-5541
Hitoshi Sai https://orcid.org/0000-0002-2938-551X
Takuya Matsui https://orcid.org/0000-0003-1589-7052
Takashi Koida https://orcid.org/0000-0001-8496-9166

REFERENCES

1. Senaud L-L, Christmann G, Descoeudres A, et al. Aluminium-doped zinc oxide rear reflectors for high-efficiency silicon heterojunction
14. Macco B, Verheijen MA, Black LE, Barcones B, Melskens J, Buckeridge J, Catlow CRA, Farrow MR, et al. Deep vs shallow nature of oxygen vacancies and consequent-type carrier concentrations in transparent conducting oxides. Phys Rev Materials. 2018;2(5):054604-1-15. https://doi.org/10.1103/physrevmaterials.2.054604

15. Xu J, Liu J-B, Liu B-X, Li S-N, Wei S-H, Huang B. Design of n-type transparent conducting oxides: the case of transition metal doping in In$_2$O$_3$. Adv Electron Mater. 2018;4(3):1700553-1-7. https://doi.org/10.1002/adem.201700553

16. Kobayashi E, Watabe Y, Yamamoto T, Yamada Y. Cerium oxide and hydrogen co-doped indium oxide films for high-efficiency silicon heterojunction solar cells. Sol Energy Mater Sol Cells. 2016;149:75-80.

17. Koida T, Fujisawa H, Kondo M. Hydrogen-doped In$_2$O$_3$ as high-mobility transparent conductive oxide. Jpn Appl Phys. 2007;46(28):L685-L687. https://doi.org/10.1143/jap.46.1685

18. Koida T, Ueno Y, Shibata H. In$_2$O$_3$-based transparent conducting oxide films with high electron mobility fabricated at low process temperatures. Phys Status Solidi (a). 2018;215(7):1700506-1-14. https://doi.org/10.1002/pssa.201700506

19. Tutsch L, Feldmann F, Polzin J, et al. Implementing transparent conducting oxides by DC sputtering on ultra-thin SiOx / poly-Si passivating contacts. Sol Energy Mater Sol Cells. 2019;200:109960-1-5. https://doi.org/10.1016/j.solmat.2019.109960

20. Dimer M, Cruz A, Wang E, et al. 35th European PV Solar Energy Conference and Exhibition. 2018. https://www.euipvsec-proceedings.com/proceedings?paper=46791

21. Messmer C, Bivour M, Luderer C, Tutsch L, Schon J, Hermle M. Influence of interfacial oxides at TCO/Doped Si thin film contacts on the charge carrier transport of passivating contacts. IEEE J Photovoltaics. 2020;10(2):343-350. https://doi.org/10.1109/jphotov.2019.2957672

22. Barraud L, Holman ZC, Badel N, et al. Hydrogen-doped indium oxide/inium tin oxide bilayers for high-efficiency silicon heterojunction solar cells. Solar Energy Materials and Solar Cells. 2013;115:151-156.

23. Erfurt D, Koida T, Heinemann MD, et al. Impact of rough substrates on hydrogen-doped indium oxides for the application in CIS devices. Sol Energy Mater Sol Cells. 2020;206:110300-1-10. https://doi.org/10.1016/j.solmat.2019.110300

24. Cruz A, Ruske F, Eljarat A, et al. Influence of silicon layers on the growth of ITO and AZO in silicon heterojunction solar cells. IEEE J Photovoltaics. 2020;10(2):703-709. https://doi.org/10.1109/jphotov.2019.2957665

25. Bavitzau K-U, Behrendt T, Palaferr D, Bivour M, Hermle M. Hydrogen doping of indium tin oxide due to thermal treatment of heterojunction solar cells. Thin Solid Films. 2016;599:161-165.

26. Sai H, Umishio H, Matsu T, et al. Impact of silicon wafer thickness on photovoltaic performance of crystalline silicon heterojunction solar cells. Jpn J Appl Phys. 2018;57(8S3):08RB10-1-10. https://doi.org/10.7567/jjap.57.08Rb10

27. Sai H, Oku T, Sato Y, Tanabe M, Matsu T, Matsubara K. Potential of very thin and high-efficiency silicon heterojunction solar cells. Prog Photovolt Res Appl. 2019;27(12):1061-1070.

28. Koida T, Kondo M, Tsutsuji K, Sakaguchi A, Saito Y, Fujisawa H. Hydrogen-doped In$_2$O$_3$ transparent conducting oxide films prepared by solid-phase crystallization method. J Appl Phys. 2010;107(3):033514-1-11.

29. Sinton R, Cuevas A. 16th European PV Solar Energy Conference. 2000. https://openresearch-repository.anu.edu.au/handle/1885/71035?mode=full

30. Kamiya T, Nomura K, Hosono H. Electronic structure of the amorphous oxide semiconductor a-InGaZnO$_4$-x: Tauc–Lorentz optical model and origins of subgap states. Phys Status Solidi (a). 2009;206(5):860-867.

31. Koida T. Amorphous and crystalline In$_2$O$_3$-based transparent conducting films for photovoltaics. Phys Status Solidi (a). 2017;214(2):1600464-1-15. https://doi.org/10.1002/pssa.201600464
36. Haschke J, Lemerle R, Aissa B, et al. Annealing of silicon heterojunction solar cells: interplay of solar cell and indium tin oxide properties. *IEEE J Photovoltaics*. 2019;9(5):1202-1207.

37. Luderer C, Messmer C, Hermle M, Bivour M. Transport losses at the TCO/a-Si:H/c-Si heterojunction: influence of different layers and annealing. *IEEE J Photovoltaics*. 2020;10(4):952-958. https://doi.org/10.1109/jphotov.2020.2983989

38. Wardenga HF, Frischbier MV, Morales-Masis M, Klein A. In situ hall effect monitoring of vacuum annealing of In2O3:H thin films. *Materials (Basel, Switzerland)*. 2015;8(2):561-574.

39. Schube J, Tutsch L, Fellmeth T, et al. Low-resistivity screen-printed contacts on indium tin oxide layers for silicon solar cells with passivating contacts. *IEEE J Photovoltaics*. 2018;8(5):1208-1214.

40. Erfurt D, Heinemann MD, Körner S, Szyzka B, Klenk R, Schlatmann R. Improved electrical properties of pulsed DC magnetron sputtered hydrogen doped indium oxide after annealing in air. *Mater Sci Semicond Process*. 2019;89:170-175.

41. Sommer N, Hüpkes J, Rau U. Field emission at grain boundaries: modeling the conductivity in highly doped polycrystalline semiconductors. *Phys Rev Appl*. 2016;5(2):024009-1-22. https://doi.org/10.1103/physrevapplied.5.024009

42. Seto JYW. The electrical properties of polycrystalline silicon films. *J Appl Phys*. 1975;46(12):5247-5254.

43. Walsh A, Da Silva JLF, Wei S-H, et al. Nature of the band gap of In2O3 revealed by first-principles calculations and X-ray spectroscopy. *Phys Rev Lett*. 2008;100(16):167402-1-4.

**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of this article.

---

**How to cite this article:** Tutsch L, Sai H, Matsui T, Bivour M, Hermle M, Koida T. The sputter deposition of broadband transparent and highly conductive cerium and hydrogen co-doped indium oxide and its transfer to silicon heterojunction solar cells. *Prog Photovolt Res Appl*. 2021;29:835–845. https://doi.org/10.1002/pip.3388