

# Hollow Cathode Gas Flow Sputtering of Nickel Oxide Thin Films for Hole-Transport Layer Application in Perovskite Solar Cells

Sri Hari Bharath Vinoth Kumar,\* Ruslan Muydinov,\* Natalia Maticiu, Nivin Alktash, Marin Rusu, Bertwin Bilgrim Otto Seibertz, Hans Köbler, Antonio Abate, Thomas Unold, Iver Lauermann, and Bernd Szyszka

Nickel oxide ( $\text{NiO}_{1+\delta}$ ) is a versatile material used in various fields such as optoelectronics, spintronics, electrochemistry, and catalysis which is prepared with a wide range of deposition methods. Herein, for the deposition of  $\text{NiO}_{1+\delta}$  films, the reactive gas flow sputtering (GFS) process using a metallic Ni hollow cathode is developed. This technique is distinct and has numerous advantages compared to conventional sputtering methods. The  $\text{NiO}_{1+\delta}$  films are sputtered at low temperatures (100 °C) for various oxygen partial pressures during the GFS process. Additionally, Cu-incorporated  $\text{NiO}_{1+\delta}$  ( $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$ ) films are obtained with 5 and 8 at% Cu. The thin films of  $\text{NiO}_{1+\delta}$  are characterized and evaluated as a hole-transporting layer (HTL) in perovskite solar cells (PSCs). The  $\text{NiO}_{1+\delta}$  devices are benchmarked against state-of-the-art self-assembled monolayers (SAM) ([2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (also known as MeO-2PACz)-based PSCs. The best-performing  $\text{NiO}_{1+\delta}$  PSC achieves an efficiency ( $\eta$ ) of  $\approx 16\%$  without a passivation layer at the HTL interface and demonstrates better operational stability compared to the SAM device. The findings suggest that further optimization of GFS  $\text{NiO}_{1+\delta}$  devices can lead to higher-performing and more stable PSCs.

silicon solar cells,<sup>[5]</sup> perovskite solar cells (PSCs),<sup>[6]</sup> thin film transistors,<sup>[7]</sup> light-emitting diodes,<sup>[8,9]</sup> photocatalytic water splitting,<sup>[10]</sup> resistive switching memory,<sup>[11]</sup> electrochromic devices,<sup>[12]</sup> supercapacitors,<sup>[13]</sup> batteries,<sup>[14]</sup> and chemical sensors.<sup>[15]</sup> The stoichiometric nickel oxide ( $\text{NiO}$ ) is an excellent insulator (resistivity larger than  $10^{16} \Omega\text{cm}$ , below 100 °C),<sup>[16]</sup> and has the highest Neel temperature ( $T_N$ ) of  $\approx 525 \text{ K}$  (amongst all antiferromagnetic transition metal monoxides), below which it is antiferromagnetic.<sup>[17–19]</sup> The p-type conductivity of the nickel oxide ( $\text{NiO}_{1+\delta}$ ) grown in an oxygen-rich environment originates from the native acceptor defects such as  $\text{Ni}^{2+}$  ion vacancies ( $V_{\text{Ni}}$ ) and/or oxygen interstitials ( $\text{O}_i$ ) which are energetically favorable.<sup>[20–23]</sup> The conductivity of the  $\text{NiO}_{1+\delta}$  further enhances with doping with Li, Ag, Cu, Cr, Co, Mg, and even rare-earth elements.<sup>[24–28]</sup>  $\text{NiO}_{1+\delta}$  has a high optical

bandgap ( $E_g$ ) in the range of 3.6–4 eV, making it transparent in the near ultraviolet and visible range.<sup>[29,30]</sup> The work function (WF) of the  $\text{NiO}_{1+\delta}$  has been reported to be as high as 5.3 eV,<sup>[31]</sup> making them suitable for hole-transporting layer (HTL) in PSCs.<sup>[22]</sup> PSCs employing  $\text{NiO}_{1+\delta}$  have been reported with photo

## 1. Introduction

Nickel oxide is a well-known p-type transparent semiconductor material that has been widely used in electronic, catalytic, and magnetic applications.<sup>[1–4]</sup> Some of the applications include

S. H. B. Vinoth Kumar, R. Muydinov, N. Alktash, B. B. O. Seibertz, B. Szyszka  
Technology for Thin-Film Devices  
Institute of High-Frequency and Semiconductor System Technologies,  
Faculty IV  
Technische Universität Berlin  
Einsteinufer 25, Berlin 10587, Germany  
E-mail: s.vinothkumar@tu-berlin.de;  
ruslan.muydinov@campus.tu-berlin.de

N. Maticiu, I. Lauermann  
Competence Center Photovoltaics (PVcomB)  
Helmholtz-Zentrum Berlin für Materialien und Energie  
Schwarzschildstraße 3, Berlin 12489, Germany

M. Rusu, T. Unold  
Department Structure and Dynamics of Energy Materials  
Helmholtz-Zentrum Berlin für Materialien und Energie  
Lise-Meitner Campus, Hahn-Meitner-Platz 1, Berlin 14109, Germany

H. Köbler, A. Abate  
Department Novel Materials and Interfaces for Photovoltaic Solar Cells  
Helmholtz-Zentrum Berlin für Materialien und Energie  
Kekuléstraße 5, Berlin 12489, Germany

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/aesr.202300201>.

© 2023 The Authors. Advanced Energy and Sustainability Research published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/aesr.202300201

conversion efficiency ( $\eta$ ) exceeding 20%,<sup>[2]</sup> and as high as 22.13%.<sup>[32]</sup>

Numerous techniques are available to produce  $\text{NiO}_{1+\delta}$  films. These include the solution-processing methods such as sol-gel,<sup>[33]</sup> solution-combustion,<sup>[34]</sup> nanoparticle processing,<sup>[35]</sup> and electrochemical deposition,<sup>[36]</sup> and vacuum-based methods such as thermal evaporation,<sup>[37]</sup> electron beam evaporation,<sup>[38]</sup> atomic layer deposition,<sup>[39]</sup> and sputtering.<sup>[40]</sup>

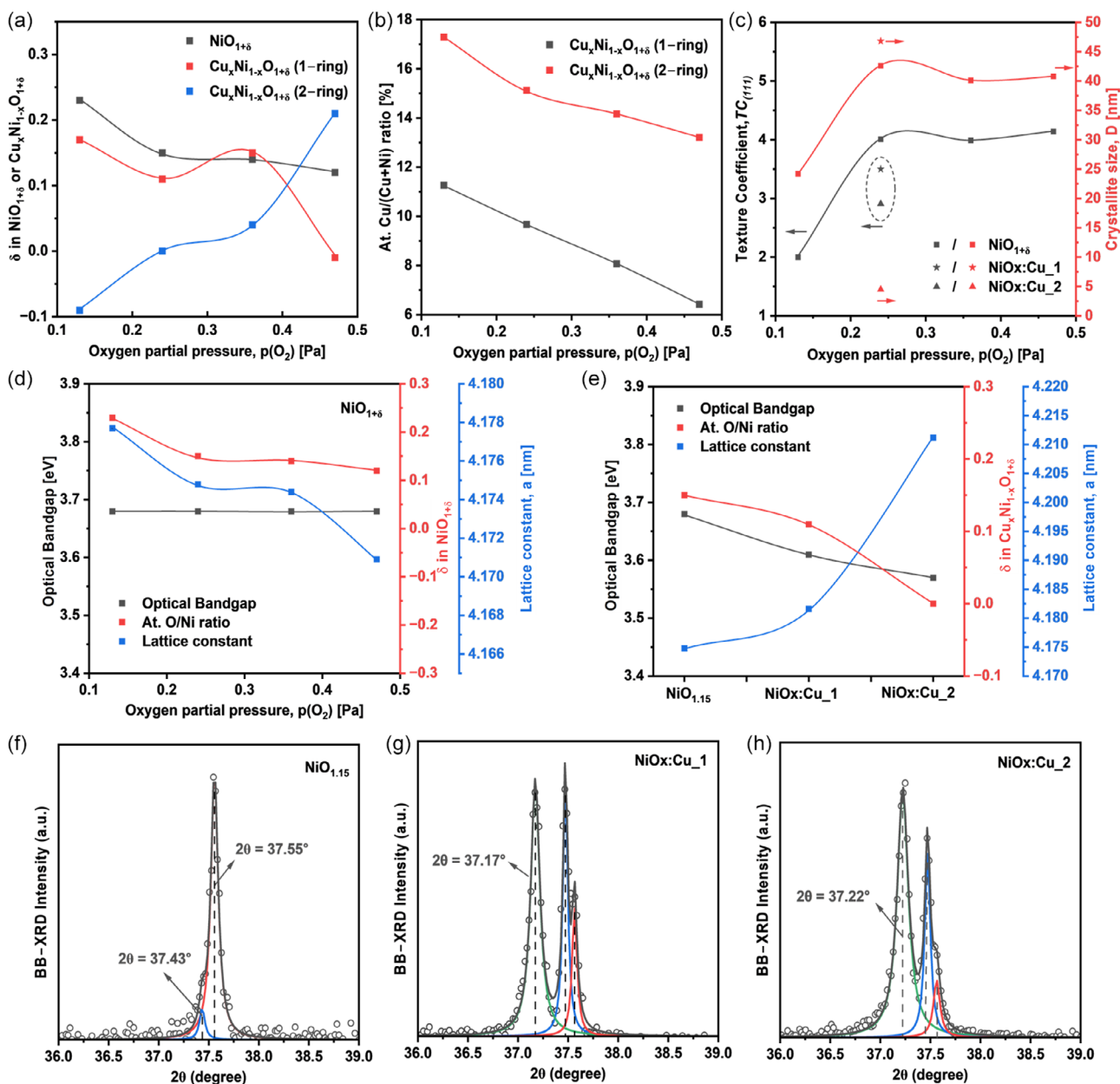
Disadvantages of the solution-processing approach generally are challenges in precise control of composition, batch-to-batch reproducibility, high-sintering temperatures, removal of solvents and ligands, and crystallinity control.<sup>[41]</sup> Among these methods, owing to excellent film growth and property control, high compatibility, low cost, scalability, high throughput, and versatility, the sputtering method is more promising for the industry. Magnetron sputtering is the most widely used sputtering and physical vapor deposition technique.<sup>[41,42]</sup> However, the hollow cathode gas flow sputtering (GFS) has distinctive advantages over the conventional sputtering process. The main advantages of the GFS are as follows: 1) due to source cathode design, GFS does not need a magnetic trap for electrons; 2) operation at a low vacuum level ( $\approx 1$  mbar range) alleviates the costs associated with high-vacuum machinery; 3) high plasma density (up to  $10^{-18} \text{ m}^{-3}$ ) combined with adjustable ion-energies enables surface diffusion for soft growth on sensitive substrates; 4) efficient target utilization due to homogeneous sputtering of the entire surface due to the hollow cathode effect; 5) high deposition rate ( $\approx 3\text{--}6 \text{ nm s}^{-1}$ ) enabling rapid processing; 6) applicability to a wide range of coating materials; 7) precise control of stoichiometry in contrast to the magnetron sputtering, and, the remote plasma operation prevents the target poisoning due to the interaction of reactive gas and target surface; and 8) linear upscaling to 0.5 m target length enables large-area coating.<sup>[43–46]</sup> The material deposition rate in this work was  $\approx 7 \text{ nm s}^{-1}$ , which is between 560 and 1450 times higher than that for comparable films deposited by magnetron sputtering.<sup>[47]</sup>

While numerous studies were published on conventional sputtering,<sup>[48–57]</sup> in this work, we develop for the preparation of  $\text{NiO}_{1+\delta}$  and Cu-doped  $\text{NiO}_{1+\delta}$  ( $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$ ) films by the hollow cathode GFS method. The GFS deposition system used in this work has been described elsewhere.<sup>[58]</sup> The  $\text{NiO}_{1+\delta}$  was deposited at a low temperature of 100 °C which makes the process feasible for temperature-sensitive flexible applications and monolithic perovskite-Cu(In, Ga)(Se, S)<sub>2</sub> (CIGSe) tandem solar cells application.<sup>[6,56,57]</sup> The thin film properties of the various  $\text{NiO}_{1+\delta}$  were systematically investigated for various oxygen partial pressures ( $p(\text{O}_2)$ : 0.1–0.5 Pa) during the sputtering process, and the films were integrated as HTL in PSCs. The fabricated PSCs were based on the “triple-cation” perovskite absorber and [2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACz) self-assembled monolayers (SAMs, as control HTL), which are used in high-performance devices.<sup>[59,60]</sup> The best-performing  $\text{NiO}_{1+\delta}$ -PSC had an  $\eta$  of  $\approx 16\%$ . All  $\text{NiO}_{1+\delta}$ -PSCs had higher operational stabilities ( $\text{N}_2$ , 85 °C, ISOS-L-21)<sup>[61]</sup> than the SAM-based PSC. The  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$ -PSCs were exceptional with  $\approx 90\%$  of  $\eta$  retention over 9 d. With further optimization, the developed GFS method for the preparation of  $\text{NiO}_{1+\delta}$  thin films promises higher-performing and stable PSCs.

## 2. Results and Discussion

In experimental settings where the properties of the thin films were examined, the thickness was varied between 100 and 500 nm (for an overview of various  $\text{NiO}_{1+\delta}$  film thicknesses used in experiments, see Table S1, Supporting Information). For the investigation of the elemental composition of the films, we used the electron probe microanalyzer (EPMA). The results are shown in Figure 1a,b and summarized in Table S2, Supporting Information. Figure 1a,b illustrates the variation of  $\delta$  in  $\text{NiO}_{1+\delta}$  and  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  and the atomic ratio of Cu to the total cation (Ni+Cu). In  $\text{NiO}_{1+\delta}$  and  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  (1-ring) films, as the  $p(\text{O}_2)$  increased, the cation/anion ratio surprisingly increased. This was contrary in the case of  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  (2-ring) films where the anion content in the film increased with increasing  $p(\text{O}_2)$ . In all  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  films, the Cu content decreased with increasing  $p(\text{O}_2)$ . The effect of decreasing anion (oxygen) content in  $\text{NiO}_x$  films with  $p(\text{O}_2)$  has also been previously reported by Sun et al.<sup>[62]</sup> In this work,<sup>[62]</sup> optical emission spectroscopy disclosed that at higher  $p(\text{O}_2)$ , the oxygen concentration in plasma dropped significantly, indicating that more oxygen reacted with the Ni-target surface (“target poisoning”). It was supported by the fact that the deposition rate simultaneously decreased.<sup>[62]</sup> The deposition rate for the GFS  $\text{NiO}_{1+\delta}$  also decreases with increasing  $p(\text{O}_2)$ .<sup>[63]</sup> However, target poisoning in an intensive argon flow is less probable. We suggest a formation of bound Ni–O species in a gas phase and their elimination by the gas flow at higher  $p(\text{O}_2)$ .<sup>[44,64]</sup> As shown in Figure 1b, with an increasing  $p(\text{O}_2)$ , the relative ratio of Cu-to-Ni decreased. This also counters target poisoning since NiO is thermodynamically more stable than  $\text{Cu}_2\text{O}$ . Copper can readily bind to oxygen at a lower O/metal ratio due to its stable oxidation states (+1 and +2), potentially resulting in the binding of more oxygen atoms compared to nickel, which has oxidation states (+2 and +3). This implies that, theoretically, a single oxygen atom could bind to more copper atoms than to nickel atoms. For simplicity, the  $\text{NiO}_{1+\delta}$  films will be denoted as  $\text{NiO}_{1.23}$ ,  $\text{NiO}_{1.15}$ ,  $\text{NiO}_{1.14}$ , and  $\text{NiO}_{1.12}$  (based on at% oxygen/metal ratio from EPMA). While the two  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  films obtained at 0.24 Pa, i.e.,  $\text{Cu}_{0.10}\text{Ni}_{0.90}\text{O}_{1.11}$  and  $\text{Cu}_{0.15}\text{Ni}_{0.85}\text{O}_{1.0}$ , will be denoted as  $\text{NiO}_x\text{:Cu}_{-1}$  and  $\text{NiO}_x\text{:Cu}_{-2}$ , respectively.

To study the crystallinity of the film both the grazing incidence X-Ray diffraction (GI-XRD) and the Bragg–Brentano XRD (BB-XRD) were performed (see Figure S1 and Table S3, Supporting Information). The GFS  $\text{NiO}_{1+\delta}$  thin films exhibited a cubic rock salt structure according to the JCPDS PDF # 47–1049.<sup>[65–68]</sup> GI-XRD detects diffraction from the crystallographic planes with increasing tilting angle to the surface when  $2\theta$  increases. One can therefore estimate if residual stresses exist in the film. The lattice constant determined from each diffraction maximum decreases with  $2\theta$  for all  $\text{NiO}_{1+\delta}$  films considered. This suggests the likelihood of compressive stress in the films. The relative changes of lattice constant are shown in Figure S2, Supporting Information. The BB-XRD indicated a strong preferential orientation along the (111) crystallographic plane which is typical for low-temperature sputtered  $\text{NiO}_{1+\delta}$  films with a columnar growth.<sup>[63,69,70]</sup> According to Song et al.,<sup>[70]</sup> the preferential orientation along the (111) crystallographic plane originates from the growth mechanism according to the Van der Drift competitive model.<sup>[71]</sup> The calculated texture coefficient



**Figure 1.** a)  $\delta$  in  $\text{NiO}_{1+\delta}$  and  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  and b) the at. ratio of Cu/Cu+Ni obtained from EPMA data for  $\text{NiO}_{1+\delta}$  and  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  films. The  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  films were deposited with either one or two 5 mm Cu-ring targets. c) The calculated texture coefficient ( $\text{TC}_{(111)}$ ) from BB-XRD and the estimated crystallite size ( $D$ ) with the Scherrer equation along the (111) crystallographic plane for various 500 nm thick  $\text{NiO}_{1+\delta}$  films (see Supporting Information for more details). Optical bandgap, at. oxygen/metal ratio from EPMA, and lattice constant determined from BB-XRD for d)  $\text{NiO}_{1+\delta}$  and e)  $\text{NiO}_{1+\delta}$  and  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  films deposited at 0.24 Pa  $p(\text{O}_2)$ . The gray, blue, and red lines correspond to the optical bandgap, lattice constant, and  $\delta$  (at. O/metal ratio) in  $\text{NiO}_{1+\delta}$ , respectively. The lines connecting the data points are a guide to the eye. f-h) High-resolution BB-XRD of the various films deposited at 0.24 Pa  $p(\text{O}_2)$ .

(TC) along the (111) crystallographic plane and the average crystallite size from BB-XRD are shown in Figure 1c. All films exhibited a texture along the (111) crystallographic plane, with a  $\text{TC}_{(111)}$  value greater than 1. A maximum  $\text{TC}_{(111)}$  of 4.14 was obtained at the highest  $p(\text{O}_2)$  of 0.47 Pa. According to Ryu et al.,<sup>[72]</sup> when the active species of Ni and O produced by the sputtering process collide separately with the growing film surface, the arrangement of  $\text{O}^{2-}$  ions dictates the crystallographic

orientation in resultant films.  $\text{O}^{2-}$  ions (radius: 1.40 Å), which are larger than  $\text{Ni}^{2+}$  ions (radius: 0.69 Å), are most densely packed along the (111)-plane in the NiO crystal structure. This suggests that the (111) orientation minimizes the surface free energy during the film growth.<sup>[72,73]</sup> Chen et al. demonstrated that when sputtered with <50%  $\text{O}_2/\text{Ar}$  mixture and substrate temperatures up to 673 K, (111)-oriented  $\text{NiO}_{1+\delta}$  are obtained.<sup>[69]</sup>

For  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$ , the BB-XRD peak intensities were relatively weaker when compared to the  $\text{NiO}_{1+\delta}$  and the diffraction angle shifted to lower values (Figure S1 and Table S3, Supporting Information). This is due to the ionic size difference between  $\text{Ni}^{2+}$  (radius: 0.69 Å) and Cu ions ( $\text{Cu}^+$  radius: 0.96 Å;  $\text{Cu}^{2+}$  radius: 0.71 Å).<sup>[74]</sup> Larger Cu ions have been reported to substitute the  $\text{Ni}^{2+}$  ions or occupy the interstitial sites in NiO lattice, and cause crystallinity degradation in  $\text{NiO}_{1+\delta}$  films.<sup>[74–77]</sup> Additionally, XRD patterns did not reveal any Cu-related peaks, suggesting that the addition of Cu did not alter the NiO-type phase structure. For reference, the BB-XRD pattern of a  $\text{Cu}_x\text{O}$  film obtained by sputtering with only a Cu target, as shown in Figure S2, Supporting Information. This is consistent with existing literature that Cu-related diffraction peaks only appear at larger concentrations (>30 at%).<sup>[78–80]</sup> The amount of Cu was found to influence the crystallographic orientation and lattice deformation in the  $\text{NiO}_{1+\delta}$  films as reported in the literature.<sup>[81]</sup> In contrast to the  $\text{NiO}_{1+\delta}$  films without Cu, certain crystal orientations were detected at a specific amount of Cu (see BB-XRD, Figure S1, Supporting Information), and the  $\text{TC}_{(111)}$  progressively decreased with increasing amount of Cu. The secondary electron emission microscopy (SEM) images are shown in Figure S3, Supporting Information. A direct correlation of crystallite sizes from SEM and BB-XRD is not meaningful as the former are obtained from  $\approx 100$  nm films while the latter is from  $\approx 500$  nm films. Moreover, the SEM images represent the surface morphology of the material while the XRD analysis employs a mathematical model to estimate average sizes. This is achieved in the latter by analyzing the broadening of diffraction peaks resulting from the constructive interference of scattered monochromatic X-rays at specific angles from a set of lattice planes.<sup>[82]</sup>

The atomic force microscopy (AFM) images of the indium tin oxide (ITO) substrate and various  $\text{NiO}_{1+\delta}$  coated on ITO are shown in Figure S4, Supporting Information. The average roughness ( $R_a$ ) determined from the AFM images for ITO,  $\text{NiO}_{1.23}$ ,  $\text{NiO}_{1.15}$ ,  $\text{NiO}_{1.14}$ , and  $\text{NiO}_{1.12}$  were 5.5, 10.1, 5.5, and 9.1 nm, respectively. In the case of  $\text{NiO}_x\text{:Cu}_1$  and  $\text{NiO}_x\text{:Cu}_2$ , the  $R_a$  decreased to 5.4 and 6.6 nm, respectively, in comparison to  $\text{NiO}_{1.15}$  with  $R_a$  10.1 nm which were all deposited at a  $p(\text{O}_2)$  of 0.24 Pa.

The optical bandgap determined from the Tauc plot, the lattice constant determined from BB-XRD, and the oxygen/metal ratio (from EPMA) in the films are plotted in Figure 1d,e. Figure S5, Supporting Information, displays the UV-vis spectra and Tauc plots. The determined lattice constant ( $a$ ) for the  $\text{NiO}_{1+\delta}$  films was in the range 4.1777–4.1709 Å when the  $p(\text{O}_2)$  was varied. The decreasing  $a$  with increasing  $p(\text{O}_2)$  is attributed to a reduction in the  $V_{\text{Ni}}$ . When  $V_{\text{Ni}}$  exists in the lattice, the six nearest oxygen atoms move away from the center of the  $V_{\text{Ni}}$ .<sup>[83]</sup> Furthermore, high-resolution XRD in Bragg-Brentano geometry (HR-BB-XRD) was also performed in the  $2\theta$  region of the (111)-plane for  $\text{NiO}_{1+\delta}$  (Figure 1f,h). The XRD peak detected at  $37.17^\circ/37.22^\circ$  (Figure 1g,h) for  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  films is attributed to Cu-substituted  $\text{NiO}_{1+\delta}$  phase ( $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$ , where  $x = 0.05\text{--}0.2$ , according to PDF # 00-025-1049, 01-078-0644, 01-078-0645, and 01-078-0646).

The variation of  $p(\text{O}_2)$  did not have a strong influence on the optical bandgap ( $E_g$ ) of  $\text{NiO}_{1+\delta}$  films, which was  $\approx 3.68$  eV (Figure 1d). In  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  films, the optical bandgap ( $E_g$ )

was marginally lower compared to  $\text{NiO}_{1+\delta}$ , with an increase in Cu content (Figure 1e). The narrowing of optical bandgap in  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  films is consistent with previously reported literature.<sup>[84,85]</sup> The transmittance of  $\text{NiO}_{1+\delta}$  films was found to be influenced by  $p(\text{O}_2)$ , with films deposited at higher  $p(\text{O}_2)$  exhibiting greater transparency compared to those deposited at lower  $p(\text{O}_2)$  levels (Figure S5, Supporting Information). In  $\text{NiO}_{1+\delta}$ , the  $\text{Ni}^{3+}$  ions are known to be the color centers.<sup>[86–88]</sup> Therefore, an increase in the transmittance of  $\text{NiO}_{1+\delta}$  with increasing  $p(\text{O}_2)$  suggests a decrease in the  $\text{Ni}^{3+}$  ion content (in agreement with the X-Ray photoelectron spectroscopy (XPS) analysis presented later). This trend is contrary to the one seen in certain literature where a higher oxygen flow during sputtering results in increased  $\text{Ni}^{3+}$  content in the films.<sup>[47,87,89,90]</sup> In the case of  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  films, the decrease in transmittance correlates with decreasing crystallinity as detected by BB-XRD (weaker diffraction peaks). It is known that good crystallization can improve transparency and vice versa. This is because substituted Cu cations and point defects ( $\text{O}_i$  and  $V_{\text{Ni}}$ ) can absorb or scatter a certain amount of visible light.<sup>[91–93]</sup> For  $\text{NiO}_x\text{:Cu}_1$  and  $\text{NiO}_x\text{:Cu}_2$ , the value of lattice constant increased compared to the  $\text{NiO}_{1.15}$  (Figure 1e). Therefore, along with the  $2\theta$  shift as discussed earlier, this suggests that the larger Cu cations ( $\text{Cu}^+$  and  $\text{Cu}^{2+}$ ) replaced the  $\text{Ni}^{2+}$  cations in the NiO cubic lattice.<sup>[94]</sup>

Raman spectroscopy was performed to investigate the microstructure of the  $\text{NiO}_{1+\delta}$  films. The fitted Raman spectra are shown and tabulated in Figure S6 and Table S4, Supporting Information, respectively. In the bulk NiO with rock salt crystal structure, the one-phonon (1P) transverse optical (TO) and longitudinal optical (LO) modes are forbidden. They are detected between 300 and 600  $\text{cm}^{-1}$  when activated by weak rhombohedral lattice distortion (below Neel temperature, R-3 m structure) or by defects.<sup>[95–98]</sup> Generally, the presence of LO mode is attributed to imperfections within the crystal lattice or point defects such as nickel vacancies or  $\text{Ni}^{3+}$  ions.<sup>[83,99,100]</sup> For the  $\text{NiO}_{1+\delta}$ , the 1P TO and LO modes are resolved into two bands each ( $\text{TO}_1/\text{TO}_2$  and  $\text{LO}_1/\text{LO}_2$ ) which arise from the anisotropy of optical phonons.<sup>[97,98]</sup> The second order (2P) modes ( $\text{TO} + \text{LO}$  and  $2\text{LO}$ ) are detected at 994–1001  $\text{cm}^{-1}$  and 1078–1091  $\text{cm}^{-1}$ , respectively. Additionally, the SO mode (detected at 499–514  $\text{cm}^{-1}$ ) is attributed to the break in the transition symmetry of the surface potential,<sup>[101–103]</sup> and is dependent on the density of surface atoms, surface defects, functional moieties, and dielectric properties of the material and surrounding.<sup>[103–105]</sup> Furthermore, the SO mode is known to be particle size-dependent, it enhances with a decrease in crystallite size.<sup>[106,107]</sup> From the Raman spectra, it was detected that with increasing Cu content in the films, the typical  $\text{NiO}_{1+\delta}$  modes due to defects (LO and TO modes) and surface effects (SO mode) are enhanced without bringing any other fundamental changes to the NiO-type structure in agreement with the GI- and BB-XRD.<sup>[108]</sup>

XPS was used to investigate the surface chemistry of the  $\text{NiO}_{1+\delta}$  films. Before XPS measurements, the surface of the  $\text{NiO}_{1+\delta}$  was sputtered with  $\text{Ar}^+$  ions ( $2.7 \times 10^{-6}$  mbar, 20 W, 20 mins) to remove adsorbed contaminants from the ambient (Figure S7, Supporting Information). With the  $\text{Ar}^+$  sputtering, an obvious partial reduction of  $\text{NiO}_{1+\delta}$  to metallic  $\text{Ni}^0$  was not detected.<sup>[109]</sup> The determination of true oxidation states of Ni from the Ni 2p spectra is complex and controversial.<sup>[109–112]</sup>

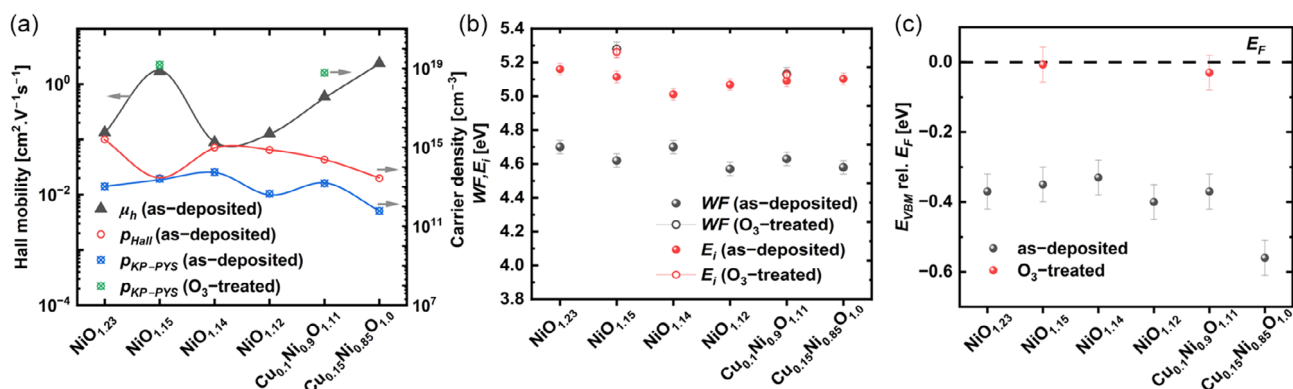


To simplify this approach, we have estimated the ratio of  $\text{Ni}^{3+}/\text{Ni}^{2+}$  states from the O1s spectra, as shown in Figure S8, Supporting Information.<sup>[113,114]</sup> Accurately determining the  $\text{Ni}^{3+}/\text{Ni}^{2+}$  ratio, particularly in the case of  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$ , remains a challenging task with such an approach due to the presence of different valency of Cu bound to oxygen within the material.<sup>[115]</sup> For the sake of simplicity, this contribution is neglected in the determination of the  $\text{Ni}^{3+}/\text{Ni}^{2+}$  ratio from the XPS O1s spectra for  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$ .<sup>[76]</sup> The O1s spectra were deconvoluted into NiO ( $\approx 529.4$  eV), NiOOH ( $\approx 530.6$  eV),  $\text{Ni}_2\text{O}_3$  ( $\approx 531.3$  eV), and NiOOH ( $\approx 532.1$  eV) components (Figure S8, Supporting Information).<sup>[112]</sup> Despite carrying out an  $\text{Ar}^+$ -etching before the XPS measurements, traces of moisture (feature at  $\approx 532.7$  eV) were detected on samples  $\text{NiO}_{1.15}$  and  $\text{NiO}_{1.14}$ . Ratcliff et al. reported such physisorbed  $\text{H}_2\text{O}$  on their  $\text{Ar}^+$  sputter-cleaned  $\text{NiO}_{1+\delta}$  film.<sup>[109]</sup> The  $\text{Ni}^{3+}/\text{Ni}^{2+}$  ratio (Table S5, Supporting Information) decreased as the  $p(\text{O}_2)$  increased and showed a proportionate relationship with the amount of Cu in  $\text{NiO}_{1+\delta}$ . This trend aligns with the variation of transparency with  $p(\text{O}_2)$  (Figure S5a, Supporting Information), i.e., an increase in transparency of the  $\text{NiO}_{1+\delta}$  due to decreasing  $\text{Ni}^{3+}$ . The Cu 2p spectra (Figure S9, Supporting Information) confirm the presence of Cu in the  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$ . The feature detected at 932.6 eV corresponds to the  $\text{Cu}^0$  (metal) or  $\text{Cu}^{+1}$  ( $\text{Cu}_2\text{O}$ ).  $\text{Cu}^0$  and  $\text{Cu}^{+1}$  are indistinguishable by XPS due to the superimposition of their binding energies.<sup>[116,117]</sup> The weak feature at 934.4 eV was detected in both the  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  which is attributed to the  $\text{Cu}^{2+}$  oxidation state.<sup>[118–120]</sup> The Cu atoms were incorporated predominantly as  $\text{Cu}^+$  acceptors with 92.7 and 86.6% on the surface of  $\text{NiO}_x\text{:Cu}_1$  and  $\text{NiO}_x\text{:Cu}_2$ , respectively (Figure S9, Supporting Information). It is to be noted that the XPS-induced reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  could influence the determination of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  from the Cu 2p<sub>3/2</sub> spectra.<sup>[121]</sup> In  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$ , for each  $\text{Cu}^+$  substituted position, the adjacent  $\text{Ni}^{2+}$  will be converted to  $\text{Ni}^{3+}$  to maintain overall charge neutrality in the crystal.<sup>[122]</sup> Also, the excessive  $\text{O}_i$  can trap two electrons to become  $\text{O}_i^{2-}$ , and to balance the  $\text{O}_i^{2-}$  formed, two  $\text{Ni}^{2+}$  must be converted to  $\text{Ni}^{3+}$ .<sup>[122]</sup> The  $\text{Cu}^+$  substitution-induced  $\text{Ni}^{3+}/\text{Ni}^{2+}$  increment is thus noticed in the GFS  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  (Table S5, Supporting Information), i.e., the  $\text{Ni}^{3+}/\text{Ni}^{2+}$  ratio increases from 0.27 in

$\text{NiO}_x\text{:Cu}_1$  to 0.44 in  $\text{NiO}_x\text{:Cu}_2$ . However, the  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  in general had a lower  $\text{Ni}^{3+}/\text{Ni}^{2+}$  ratio compared to the undoped  $\text{NiO}_{1+\delta}$  which could be explained by the filling of Cu ions in  $V_{\text{Ni}}$ .

The conduction mechanism in  $\text{NiO}_{1+\delta}$  films is still under debate; it is explained either by band-like conduction or small polaron hopping (SPH).<sup>[27,123–126]</sup> Small polarons are quasi-particles formed by the strong coupling between charge carriers and phonons in a crystal lattice where the distortion of the lattice due to the charge carrier extends over distances smaller than the lattice constant.<sup>[124]</sup> According to Zhang et al.,<sup>[125]</sup> in  $\text{NiO}_{1+\delta}$ , which exhibits lower mobilities ( $<0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) due to strong electron correlation and localized nature of the valence band (VB), the conduction mechanism is well described by SPH. All undoped  $\text{NiO}_{1+\delta}$  films in this study except  $\text{NiO}_{1.15}$  had a mobility ( $\mu_h$ ) value of  $\approx 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , while the latter had a value of  $3.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (Figure 2a). The antiferromagnetic property of the material, like in the case of  $\text{NiO}_{1+\delta}$ , could add uncertainty to Hall measurements.<sup>[126,127]</sup> For example, the mobility and carrier density values determined by Hall measurements and those derived from electrochemical impedance spectroscopy can vary by a few orders of magnitude.<sup>[127]</sup> The inclusion of Cu in  $\text{NiO}_x\text{:Cu}_1$  resulted in a reduction of  $\mu_h$ , which decreased from  $3.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  measured in  $\text{NiO}_{1.15}$  to  $0.59 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Ideally, with  $\text{Cu}^+$  substitution (at  $\text{Ni}^{2+}$  sites), the hole mobility of the films should increase according to the chemical modulation of valence band theory.<sup>[128,129]</sup> However, the  $\mu_h$  enhancement could be concealed by the increased scattering due to grain boundaries or crystallinity degradation.<sup>[129,130]</sup> With the further addition of Cu, in  $\text{NiO}_x\text{:Cu}_2$ , the  $\mu_h$  increased to  $2.48 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

The kinetic effects in  $\text{NiO}_{1+\delta}$  films were investigated by Hall measurements and the concentration of holes ( $p_{\text{Hall}}$ ), and their mobilities were determined. The concentration of charge carriers was in addition calculated with the data from combined Kelvin probe (KP) and photoelectron yield spectroscopy (PYS) measurements.<sup>[131]</sup> Vacancy defects are prevalent in the densely packed NiO structures, whereas the interstitial defects having high formation energies are difficult to form spontaneously.<sup>[132]</sup>  $V_{\text{Ni}}$  is known to be the common point defect in NiO (promoting p-type conductivity), however, oxygen-deficient growth conditions are known to promote oxygen vacancies ( $V_{\text{O}}$ ) (“hole-killer”), which



**Figure 2.** Thin film electronic properties as a function of composition: a) Hall mobility, charge carrier concentration from Hall measurements, and charge carrier concentration estimated from KP-PYS measurements. The lines connecting the data points are a guide to the eye. b) WF and ionization energy ( $E_i$ ) were determined from KP and PYS measurements, respectively. c) Valence band maximum position ( $E_{\text{VBM}}$ ) with respect to Fermi level ( $E_F$ ). The ozone PDT data are only shown for  $\text{NiO}_{1.15}$  and  $\text{NiO}_x\text{:Cu}_1$  samples.

are stable.<sup>[132,133]</sup> Although the formed  $V_O$  is stable, an n-type conductivity is difficult to form because of deep donor energy levels within the bandgap.<sup>[132–134]</sup> Such  $V_O$  has been identified with photoluminescence investigations in doped NiO nanostructures.<sup>[135]</sup> Thus, the number of vacancy defects ( $V_{Ni}$  and  $V_O$ ) would influence the hole concentration in  $NiO_{1+\delta}$  films.

Charge-carrier density found for as-deposited  $NiO_{1+\delta}$  films from Hall measurements was in the range of  $p_{Hall}$   $10^{13} - 10^{15} \text{ cm}^{-3}$  (Figure 2a). The concentration of holes from KP-PYS investigations ( $p_{KP-PYS}$ ) was calculated by considering for statistical distribution of holes: 1) the valence band maximum energy ( $E_{VBM}$ ) relative to the Fermi level ( $E_F$ ) as calculated with the WF and ionization energy ( $E_i$ ) data (Figure 2b,c); and 2) the effective density of states in the valence band for an effective hole mass ( $m_h^*$ ) of  $0.86 m_o$ ,<sup>[130]</sup> where  $m_o$  is the free electron mass. The hole density  $p_{KP-PYS}$  of as-deposited  $NiO_{1.15}$  films was found as similar to  $p_{Hall}$ . For other film compositions,  $p_{KP-PYS}$  was up to 2 orders of magnitude lower than  $p_{Hall}$ . This is explained by differences between bulk properties as studied by Hall measurements and near-surface properties as investigated by KP-PYS. Note that this concentration of holes, as determined by both Hall and KP-PYS methods, is still too low for the application of the as-deposited films as HTLs in solar cell devices.

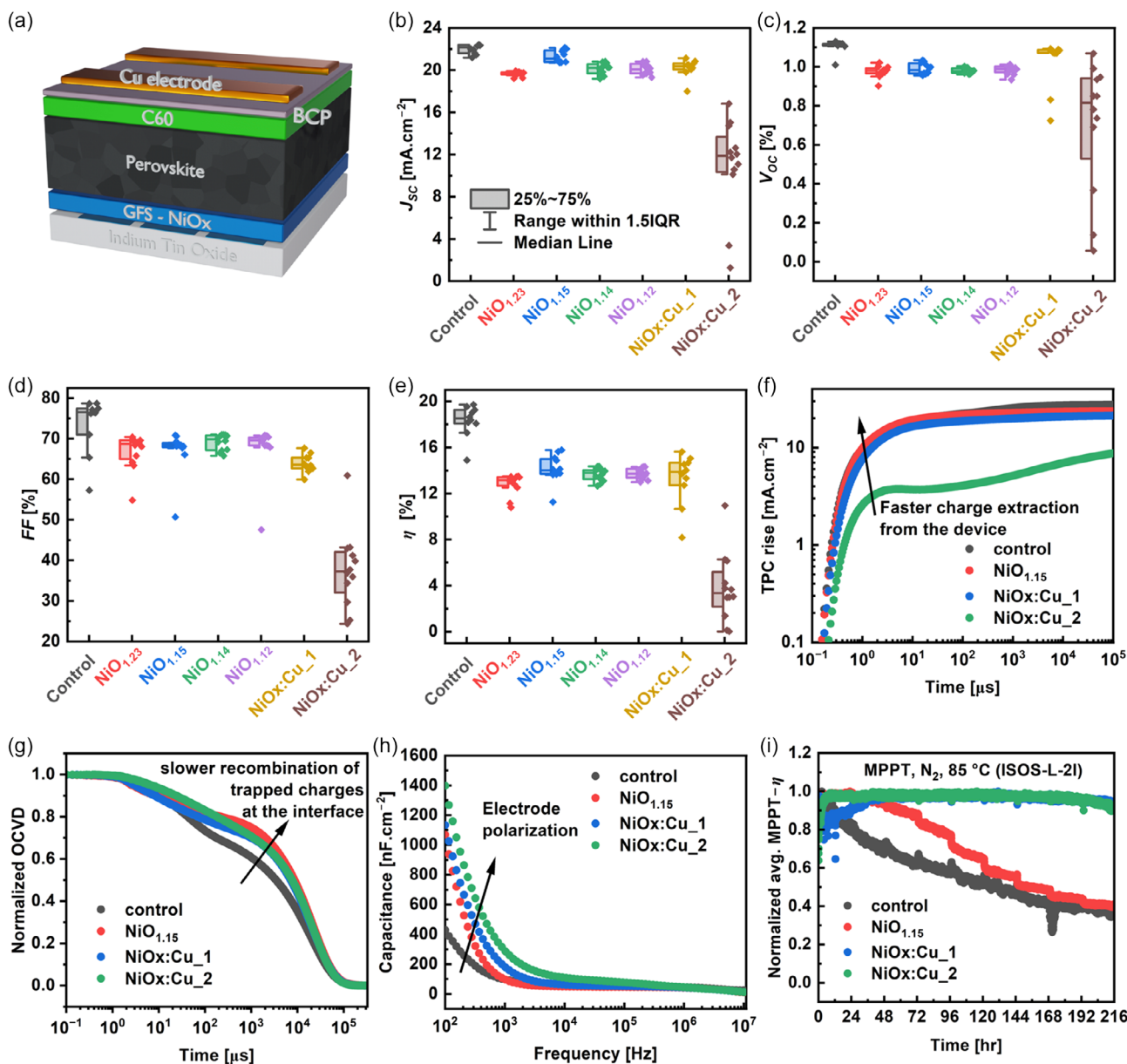
To achieve a higher hole density, we have further conditioned the as-deposited thin films by a postdeposition treatment (PDT) in  $O_3$  ambient for 5 min. It is worth mentioning that such a PDT procedure is usually applied during the PSC fabrication before the spin coating with the perovskite film.<sup>[47]</sup> The measured bulk resistivity ( $\rho$ ) for the 100 nm thick  $NiO_{1.15}$  was  $1.34 \times 10^5 \Omega \text{ cm}$  and  $3.82 \times 10^2 \Omega \text{ cm}$  before and after  $O_3$  PDT treatment, respectively. The electronic properties of the  $NiO_{1.15}$  and  $NiO_x\text{:Cu}_1$  samples were then studied by KP-PYS. The determined  $p_{KP-PYS}$  of the  $O_3$ -PDT conditioned films was found of  $\approx 6$  orders of magnitude higher than that of the as-deposited films. The WF determined by KP and the  $E_i$  measured by PYS for the  $NiO_{1.15}$  and  $Cu_{0.10}Ni_{0.90}O_{1.11}$  PDT samples almost coincided, thus denoting a near degeneration state (Figure 2b). For as-deposited  $NiO_{1+\delta}$  and  $Cu_xNi_{1-x}O_{1+\delta}$  layers, variations of the WF and  $E_i$  with the film composition were found of  $\approx 180$  and  $\approx 100$  meV, respectively, in agreement with Ref.[72] For  $NiO_{1+\delta}$  films, an increase in WF and  $E_i$ , and respectively of  $E_F$  and  $E_{VBM}$  (Figure 2b,c) correlates with the estimated increase of the  $Ni^{3+}$  concentration with  $O_3$  treatment. That has been ascribed to the filling of oxygen vacancies in the film surface by enriched O-species from the ambient,  $NiOOH$ -type dipolar species, and an increase in excess oxygen-related defects.<sup>[136–138]</sup>

The device structure of the inverted PSCs based on  $NiO_{1+\delta}$  is shown in Figure 3a. The control samples were based on SAM, ([2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid) (also known as MeO-2PACz),<sup>[60]</sup> instead of the  $NiO_{1+\delta}$  as HTL. Among all the devices, the SAM-based devices had superior photovoltaic parameters obtained from current–voltage ( $J$ – $V$ ) characteristics (Figure 3b,e and Table S6, Supporting Information). The  $J$ – $V$  characteristics, series resistance ( $R_s$ ), and parallel resistance ( $R_p$ ) of the devices are shown in Figure S10, Supporting Information. Among the  $NiO_{1+\delta}$ -based solar cells, the one with  $NiO_{1.15}$  had superior characteristics in terms of best-performing devices. When considering the best-performing devices, the short-circuit current density ( $J_{sc}$ ) of the  $NiO_{1.15}$  device was

comparable to that of the SAM device. However, the former exhibited decreased open-circuit voltage ( $V_{OC}$ ), fill factor (FF), and  $\eta$  by 132 mV,  $\approx 8\%$ , and 4.5%, respectively, in comparison to the control device. With the addition of  $\approx 5$  at% of Cu into the  $NiO_{1+\delta}$  ( $NiO_x\text{:Cu}_1$  device), a  $\approx 55$  mV improvement in  $V_{OC}$  of the device was found when compared to the  $NiO_{1.15}$  device. However, the aforementioned improvement is compensated by a  $\approx 5\%$  loss in FF leveling the  $\eta$  obtained with  $NiO_{1.15}$ -device. With a higher amount of Cu ( $\approx 8$  at%) in the  $NiO_{1+\delta}$ , all photovoltaic parameters of the device deteriorated (i.e., for the  $NiO_x\text{:Cu}_2$  device) due to degrading optical and interfacial charge transfer properties as known from the literature.<sup>[139,140]</sup> The  $V_{OC}$  and FF losses in the  $NiO_{1+\delta}$  devices are generally attributed to the increased interfacial nonradiative recombination.<sup>[141]</sup> Additionally, a higher  $R_s$  is also known to detrimentally affect the FF.<sup>[142]</sup> The  $R_p$  of  $NiO_{1+\delta}$  devices exhibited a direct correlation with the crystallinity determined by BB–XRD. In other words, higher crystallinity in the sample corresponded to an increase in  $R_p$ .<sup>[140]</sup>

To further evaluate the performance of the devices, transient photocurrent (TPC), open-circuit voltage decay (OCVD), transient photovoltage (TPV), and capacitance–frequency ( $C$ – $f$ ) measurements were performed (Figure 3f,h). It is important to note that a white LED was used for illumination in the aforementioned measurements, unlike the sun-simulator with AM 1.5G spectrum used for  $J$ – $V$  characteristics (see Supporting Information for more details). The TPC rise curve pertains to the devices' charge extraction ability, which is accumulated at its transport layers (in short-circuit conditions).<sup>[143]</sup> The control device, the  $NiO_{1+\delta}$  device, and the  $Cu_{0.10}Ni_{0.90}O_{1.11}$  device portray similar features up to  $10^2 \mu\text{s}$  after which the extracted current density of the control device continues to increase. The maximum extracted current density values for all devices are in correlation to the  $J_{sc}$  values measured. The OCVD decay, as shown in Figure 3g (the device is in open-circuit condition), arises from the relaxation of photoelectrons influenced by perovskite crystal defects and trap states in the bulk and interface, with its transport layers and ion migration within the PSCs.<sup>[143–146]</sup> A relatively faster photovoltage decay is associated with the reduced number of surface defect states and deep-level defect states, thus with the better performance of the device.<sup>[145]</sup> From the OCVD decays, it was found that the control device had a faster decay corresponding to its superior  $V_{OC}$  and FF. It was then followed by the  $Cu_{0.10}Ni_{0.90}O_{1.11}$  device which had the best  $V_{OC}$  among all the  $NiO_{1+\delta}$ -based devices. The TPV decays for the devices are shown in Figure S11, Supporting Information. At a light pulse duration of  $\approx 30 \mu\text{s}$ , an overshoot of the TPV was found for all devices in the increasing order for control,  $NiO_{1.15}$ ,  $NiO_x\text{:Cu}_1$ , and  $NiO_x\text{:Cu}_2$  devices which correspond to the charge trapping at the interfaces with the influence of ion migration.<sup>[147,148]</sup> This observation correlated to the FF, as seen in the devices.

Figure 3h presents the  $C$ – $f$  data for the PSCs measured under illumination. The capacitance response under 10 kHz in the PSCs arises from the electrode polarization due to electronic and ionic accumulation.<sup>[149]</sup> From the  $C$ – $f$  data, it is inferred that the ion migration is higher in the Cu-incorporated  $NiO_{1+\delta}$  devices and the same was least in SAM-passivated control devices. Light-induced degradation and biasing in PSCs are known to increase the  $I^-$  ion concentration at the perovskite and charge–transport layer interface.<sup>[150,151]</sup> The fact that  $I^-$  ions in the



**Figure 3.** a) Schematic of the PSC architecture. Photovoltaic parameters of the GFS NiO<sub>1+x</sub>-based PSCs: b) short-circuit current ( $J_{sc}$ ), c) open-circuit voltage ( $V_{oc}$ ), and d) FF, and e) efficiency ( $\eta$ ) from current–voltage ( $J$ – $V$ ) measurement under AM 1.5G illumination. f) TPC rise, g) normalized OCVD, and h) C–f measurements of the various PSCs. i) Normalized averages of maximum power point tracking- $\eta$  (average of 7 devices of control, 4 for NiO<sub>1.15</sub>, 5 for NiO<sub>x</sub>:Cu<sub>1</sub>, and 6 for NiO<sub>x</sub>:Cu<sub>2</sub>) of the PSCs under the operational stability test. The spikes and step-like  $\eta$  loss noticed are due to the periodical  $J$ – $V$  measurement every 24 h.

perovskite layer interface can chemically react possibly with Cu in the Cu<sub>x</sub>Ni<sub>1-x</sub>O<sub>1+x</sub> films,<sup>[152]</sup> to further increase the recombination sites at the interface and degradation of the performance cannot be ruled out.<sup>[153–155]</sup> To investigate the stability of the solar cells, the devices were tracked at their maximum power point (MPP) under a 1-sun condition in a nitrogen ambient at an elevated temperature of 85 °C, and the data are presented in Figure 3i. The spectrum of the lamp used in the stability test and the absolute  $\eta$  of the PSCs from the tracking are shown in Figure S12 and S13, Supporting Information, respectively. The

NiO<sub>1.15</sub> device retained more of its initial efficiency ( $\eta$ ) compared to the control device, while the Cu<sub>x</sub>Ni<sub>1-x</sub>O<sub>1+x</sub> devices outperformed others in terms of  $\eta$  retention. One of the reasons why the Cu<sub>x</sub>Ni<sub>1-x</sub>O<sub>1+x</sub> devices outperform NiO<sub>1+x</sub> devices in terms of stability is the lower Ni<sup>3+</sup>/Ni<sup>2+</sup> ratio in Cu<sub>x</sub>Ni<sub>1-x</sub>O<sub>1+x</sub>, as determined from the XPS analysis.<sup>[156]</sup> The surface Ni<sup>3+</sup> of NiO<sub>1+x</sub> is known to react with perovskite resulting in the formation of a PbI<sub>2-x</sub>Br<sub>x</sub>-rich, organic cation-deficient perovskite, and, thus, creating energy barriers and recombination centers at the interface.<sup>[50]</sup> The second reason for improved operational stability is

the reduced surface roughness in  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  films compared to  $\text{NiO}_{1.15}$  which is more favorable for coverage of perovskite film on top.<sup>[156]</sup> The current study validates the well-known excellent stability feature of the  $\text{NiO}_{1+\delta}$  transport layers compared to their organic counterparts.<sup>[157–159]</sup>

### 3. Conclusion

In this research, we employed the hollow cathode GFS technique to fabricate  $\text{NiO}_{1+\delta}$  and  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  thin films. The  $\text{NiO}_{1+\delta}$  films displayed a preferred orientation along the (111) crystallographic plane, and an increased  $p(\text{O}_2)$  during the deposition led to a higher degree of this orientation. However, the introduction of Cu for  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  films disrupted this orientation, giving rise to the observation of multiple planes in the BB–XRD pattern. The inclusion of Cu, as indicated by XRD and Raman analyses, demonstrated the preservation of the inherent  $\text{NiO}$ -like structure. XPS unveiled a decrease in the  $\text{Ni}^{3+}/\text{Ni}^{2+}$  ratio in  $\text{NiO}_{1+\delta}$  films with an increase in  $p(\text{O}_2)$  during deposition. Additionally, the predominant Cu valency on the surface of  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  was found to be +1 ( $\text{Cu}^+$ ).

The  $\text{NiO}_{1+\delta}$  and  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  films were successfully demonstrated as HTL in PSCs. Ion-migration effects were found to be higher in the  $\text{NiO}_{1+\delta}$  device, and it was further pronounced in the case of  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  devices when compared to the SAM device. In the operational stability test at 85 °C, the  $\text{NiO}_{1+\delta}$  PSC retained its original efficiency better than the SAM device. Our key finding is that the  $\text{Cu}_x\text{Ni}_{1-x}\text{O}_{1+\delta}$  devices, although exhibited an inferior  $\eta$  compared to the  $\text{NiO}_{1+\delta}$ -device, outperformed other devices in the stability test ( $\approx 90\%$   $\eta$  retained after 9 d). Additional optimization and exploring interface engineering options such as the use of a passivation layer, bilayer HTL, etc. can further enhance the device performance and operation stability of the PSCs reported here. The GFS  $\text{NiO}_{1+\delta}$  is a promising substitute for organic HTL and solution-processed  $\text{NiO}_{1+\delta}$  for mass production of large-area PSCs.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

### Acknowledgements

The authors acknowledge the financial support by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—grant number AOBJ 649257 (for the X-Ray diffractometer used in this work), and by the German Federal Ministry for Economic Affairs and Energy (BMWi) under contract number 0324095H (speedCIGS). The authors are grateful to Jorg Nissen (ZELMI, Technische Universität Berlin) for the EPMA measurements; Christoph Hums and Nisarg Nijanandi (Fraunhofer Institute for Telecommunications (Heinrich-Hertz-Institute), Berlin) for Hall measurements; Emil List-Kratochvil (Humboldt-Universität Berlin) for providing access to the Raman and SEM measurement setup; Steve Albrecht (Helmholtz-Zentrum Berlin für Materialien und Energie) and the Helmholtz Innovation Lab HySPRINT for the PSC fabrication infrastructure.

### Conflict of Interest

The authors declare no conflict of interest.

### Author Contributions

S.H.B.V.K.—original draft; R.M. —manuscript correction; R.M., S.H.B.V.K., N.M., and N.A. —design of experiments; R.M., N.A., and S.H.B.V.K.—GFS  $\text{NiO}_{1+\delta}$  film preparation; N.M. —PSC fabrication and J–V curves; H.K.—PSC aging and operation test, A.A. —supervision; R.M.—SEM and Raman measurements; R.M., B.B.O.S., and S.H.B.V.K. —XRD measurements; M.R., T.U. — KP, PYS measurements, and analysis; N.M., S.H.B.V.K., and I.L.—XPS measurements and analysis, I.L.—supervision; S.H.B.V.K. —UV-vis, AFM, TPC, TPV, OCVD, and C–f measurements; R.M. and B.S. (XRD) and R.M., I.L., and B.S. (speedCIGS) —funding acquisition. All authors agreed to the current version of the manuscript.

### Data Availability Statement

The data that support the findings of this study are available on reasonable request from the corresponding author.

### Keywords

gas flow sputtering, hollow cathode, hybrid perovskite solar cells, nickel oxide, p-type transparent conducting oxides (TCO)

Received: September 20, 2023

Revised: December 15, 2023

Published online: December 28, 2023

- [1] V. Baltz, A. Manchon, M. Tsoi, T. Moriyama, T. Ono, Y. Tserkovnyak, *Rev. Mod. Phys.* **2018**, *90*, 015005.
- [2] D. Di Girolamo, F. Di Giacomo, F. Matteocci, A. G. Marrani, D. Dini, A. Abate, *Chem. Sci.* **2020**, *11*, 7746.
- [3] W. Ahmad, S. Chandra Bhatt, M. Verma, V. Kumar, H. Kim, *Environ. Nanotechnol. Monit. Manag.* **2022**, *18*, 100674.
- [4] A. Krishnan, A. Ajith, A. V. Krishnan, R. E. Saji, S. Syamli, S. M. A. Shibli, *Surf. Interfaces* **2023**, *36*, 102619.
- [5] W. Zhang, H. Shen, M. Yin, L. Lu, B. Xu, D. Li, *ACS Omega* **2022**, *7*, 16494.
- [6] Y. Wang, R. Wenisch, R. Schlattmann, I. Lauermaun, *Adv. Energy Mater.* **2018**, *8*, 1801692.
- [7] Z.-W. Shang, H.-H. Hsu, Z.-W. Zheng, C.-H. Cheng, *Nanotechnol. Rev.* **2019**, *8*, 422.
- [8] H. H. Yen, H. C. Kuo, W. Y. Yeh, *Phys. Status Solidi C* **2008**, *5*, 2152.
- [9] S. Chen, K. Shih, J. Hwang, C.-F. Yu, *J. Mater. Chem. C* **2019**, *7*, 13510.
- [10] S. Fang, Y. H. Hu, *Int. J. Energy Res.* **2019**, *43*, 1082.
- [11] D. Kumar, R. Aluguri, U. Chand, T. Y. Tseng, *Ceram. Int.* **2017**, *43*, S547.
- [12] G. Cai, J. Wang, P. S. Lee, *Acc. Chem. Res.* **2016**, *49*, 1469.
- [13] R. S. Kate, S. A. Khalate, R. J. Deokate, *J. Alloys Compd.* **2018**, *734*, 89.
- [14] G. Zhou, W. Ding, Y. Guan, T. Wang, C. Liu, L. Zhang, J. Yin, Y. Fu, *Chem. Rec.* **2022**, *22*, e202200111.
- [15] T. P. Mokoena, H. C. Swart, D. E. Motaung, *J. Alloys Compd.* **2019**, *805*, 267.
- [16] M. A. Wittenauer, L. L. Van Zandt, *Philos. Mag. B* **1982**, *46*, 659.
- [17] E. N. Abarra, K. Takano, F. Hellman, A. E. Berkowitz, *Phys. Rev. Lett.* **1996**, *77*, 3451.
- [18] X. Y. Lang, W. T. Zheng, Q. Jiang, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, *73*, 012101.



- [19] N. Rinaldi-Montes, P. Gorria, D. Martínez-Blanco, A. B. Fuertes, I. Puente-Orench, L. Olivi, J. A. Blanco, *AIP Adv.* **2016**, 6, 056104.
- [20] S. Lany, J. Osorio-Guillén, A. Zunger, *Phys. Rev. B* **2007**, 75, 241203.
- [21] K. H. L. Zhang, K. Xi, M. G. Blamire, R. G. Egdell, *J. Phys. Condens. Matter* **2016**, 28, 383002.
- [22] X. Yin, Y. Guo, H. Xie, W. Que, L. B. Kong, *Sol. RRL* **2019**, 3, 1900001.
- [23] K. O. Egbo, M. Kong, C. P. Liu, K. M. Yu, *J. Alloys Compd.* **2020**, 835, 155269.
- [24] A. B. Huang, J. T. Zhu, J. Y. Zheng, Y. Yu, Y. Liu, S. W. Yang, S. H. Bao, L. Lei, P. Jin, *J. Mater. Chem. C* **2016**, 4, 10839.
- [25] M. Shkir, V. Ganesh, S. AlFaify, I. S. Yahia, H. Y. Zahran, *J. Mater. Sci. Mater. Electron.* **2018**, 29, 6446.
- [26] X. Chen, L. Xu, C. Chen, Y. Wu, W. Bi, Z. Song, X. Zhuang, S. Yang, S. Zhu, H. Song, *J. Power Sources* **2019**, 444, 227267.
- [27] K. O. Egbo, C. E. Ekuma, C. P. Liu, K. M. Yu, *Phys. Rev. Mater.* **2020**, 4, 104603.
- [28] L. Huang, Y. Wang, X. Zhu, X. Zhao, G. Li, L. Li, W. Sun, *J. Phys. Chem. C* **2021**, 125, 16066.
- [29] D. Adler, J. Feinleib, *Phys. Rev. B* **1970**, 2, 3112.
- [30] R. Merlin, *Phys. Rev. Lett.* **1985**, 54, 2727.
- [31] K. X. Steirer, P. F. Ndione, N. E. Widjonarko, M. T. Lloyd, J. Meyer, E. L. Ratcliff, A. Kahn, N. R. Armstrong, C. J. Curtis, D. S. Ginley, J. J. Berry, D. C. Olson, *Adv. Energy Mater.* **2011**, 1, 813.
- [32] P. Ru, E. Bi, Y. Zhang, Y. Wang, W. Kong, Y. Sha, W. Tang, P. Zhang, Y. Wu, W. Chen, X. Yang, H. Chen, L. Han, *Adv. Energy Mater.* **2020**, 10, 2001610.
- [33] M. Li, X. Xu, Y. Xie, H.-W. Li, Y. Ma, Y. Cheng, S.-W. Tsang, *J. Mater. Chem. A* **2019**, 7, 9578.
- [34] Z. Liu, J. Chang, Z. Lin, L. Zhou, Z. Yang, D. Chen, C. Zhang, *Adv. Energy Mater.* **2018**, 8, 1703432.
- [35] D. Ai, X. Dai, Q. Li, C. Deng, S. Kang, *China Particuol.* **2004**, 2, 157.
- [36] A. Dierstein, H. Natter, F. Meyer, H. O. Stephan, C. Kropf, R. Hempelmann, *Scr. Mater.* **2001**, 44, 2209.
- [37] J.-M. Choi, S. Im, *Appl. Surf. Sci.* **2005**, 244, 435.
- [38] D. Y. Jiang, J. M. Qin, X. Wang, S. Gao, Q. C. Liang, J. X. Zhao, *Vacuum* **2012**, 86, 1083.
- [39] J. Bachmann, A. Zolotaryov, O. Albrecht, S. Goetze, A. Berger, D. Hesse, D. Novikov, K. Nielsch, *Chem. Vap. Depos.* **2011**, 17, 177.
- [40] Y. M. Lu, W. S. Hwang, J. S. Yang, *Surf. Coat. Technol.* **2002**, 155, 231.
- [41] L. Cai, F. Zhu, *Nano Sel.* **2021**, 2, 1417.
- [42] J. Liang, Q. Liu, T. Li, Y. Luo, S. Lu, X. Shi, F. Zhang, A. M. Asiri, X. Sun, *Green Chem.* **2021**, 23, 2834.
- [43] H. Koch, L. J. Friedrich, V. Hinkel, F. Ludwig, B. Politt, T. Schurig, *J. Vac. Sci. Technol., A* **1991**, 9, 2374.
- [44] T. Jung, T. Kälber, V. V. D. Heide, *Surf. Coat. Technol.* **1996**, 86–87, 218.
- [45] B. Szyszka, W. Dewald, S. K. Gurram, A. Pflug, C. Schulz, M. Siemers, V. Sittering, S. Ulrich, *Curr. Appl. Phys.* **2012**, 12, 2.
- [46] R. Bandorf, A. Gröninger, K. Ortner, H. Gerdes, G. Bräuer, *Surf. Coat. Technol.* **2017**, 314, 92.
- [47] H.-J. Seok, J.-H. Park, A. Yi, H. Lee, J. Kang, H. J. Kim, H.-K. Kim, *ACS Appl. Energy Mater.* **2021**, 4, 5452.
- [48] X. Zhao, J. Chen, N. Park, *Sol. RRL* **2019**, 3, 1800339.
- [49] M. Yan, T. Xiang, X. Yu, J. Xiao, W. Li, Z. Ku, F. Huang, J. Zhong, Y. Peng, Y. Cheng, *Mater. Sci. Semicond. Process.* **2020**, 115, 105129.
- [50] C. C. Boyd, R. C. Shallcross, T. Moot, R. Kerner, L. Bertoluzzi, A. Onno, S. Kavadiya, C. Chosy, E. J. Wolf, J. Werner, J. A. Raiford, C. de Paula, A. F. Palmstrom, Z. J. Yu, J. J. Berry, S. F. Bent, Z. C. Holman, J. M. Luther, E. L. Ratcliff, N. R. Armstrong, M. D. McGehee, *Joule* **2020**, 4, 1759.
- [51] S. Zhumagali, F. H. Isikgor, P. Maity, J. Yin, E. Ugur, M. De Bastiani, A. S. Subbiah, A. J. Mirabelli, R. Azmi, G. T. Harrison, J. Troughton, E. Aydin, J. Liu, T. Allen, *Adv. Energy Mater.* **2021**, 11, 2101662.
- [52] J. Sun, C. Shou, J. Sun, X. Wang, Z. Yang, Y. Chen, J. Wu, W. Yang, H. Long, Z. Ying, X. Yang, J. Sheng, B. Yan, J. Ye, *Sol. RRL* **2021**, 5, 2200793.
- [53] W. Zhang, H. Shen, J. Ge, B. Xu, P. Yan, J. Zhang, *J. Mater. Sci.* **2022**, 57, 15889.
- [54] X. Liu, Y. Liu, R. Lang, Y. Liu, W. Lei, R. Cong, S. Jiang, L. Feng, H. Liu, X. Wang, W. Yu, W. Lu, *Energy Technol.* **2023**, 11, 2300355.
- [55] Y. Xu, F. Fei, X. Dong, L. Li, Y. Li, N. Yuan, J. Ding, *Sol. RRL* **2023**, 7, 2300283.
- [56] I. Kafedjiska, G. A. Farias-Basulto, P. Reyes-Figueroa, T. Bertram, A. Al-Ashouri, C. A. Kaufmann, R. Wenisch, S. Albrecht, R. Schlattmann, I. Lauerermann, *Sol. Energy Mater. Sol. Cells* **2023**, 254, 112248.
- [57] I. Kafedjiska, I. Levine, A. Musiienko, N. Maticic, T. Bertram, A. Al-Ashouri, C. A. Kaufmann, S. Albrecht, R. Schlattmann, I. Lauerermann, *Adv. Funct. Mater.* **2023**, 33, 2302924.
- [58] N. Alktash, R. Muydinov, D. Erfurt, M. Hartig, W. Gajewski, B. Szyszka, *Rev. Sci. Instrum.* **2023**, 94, 075104.
- [59] M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt, M. Grätzel, *Energy Environ. Sci.* **2016**, 9, 1989.
- [60] A. Al-Ashouri, A. Magomedov, M. Roß, M. Jošt, M. Talaikis, G. Chistiakova, T. Bertram, J. A. Márquez, E. Köhnen, E. Kasparavičius, S. Levenco, L. Gil-Escrig, C. J. Hages, R. Schlattmann, B. Rech, T. Malinauskas, T. Unold, C. A. Kaufmann, L. Korte, G. Niaura, V. Getautis, S. Albrecht, *Energy Environ. Sci.* **2019**, 12, 3356.
- [61] M. V. Khenkin, E. A. Katz, A. Abate, G. Bardizza, J. J. Berry, C. Brabec, F. Brunetti, V. Bulović, Q. Burlingame, A. Di Carlo, R. Cheacharoen, Y.-B. Cheng, A. Colmann, S. Cros, K. Domanski, M. Duszka, C. J. Fell, S. R. Forrest, Y. Galagan, D. Di Girolamo, M. Grätzel, A. Hagfeldt, E. von Hauff, H. Hoppe, J. Kettle, H. Köbler, M. S. Leite, S. Liu, Y.-L. Loo, J. M. Luther, et al. *Nat. Energy* **2020**, 5, 35.
- [62] H. Sun, S. C. Chen, S. W. Hsu, C. K. Wen, T. H. Chuang, X. Wang, *Ceram. Int.* **2017**, 43, S369.
- [63] B. B. O. Seibert, B. Szyszka, *Thin Solid Films* **2023**, 778, 139887.
- [64] J. Wei Low, N. Nayan, M. Z. Sahdan, M. K. Ahmad, A. Y. Md Shakaff, A. Zakaria, A. F. Mohd Zain, *J. Teknol.* **2015**, 73, 11.
- [65] V. R. Reddy, P. R. S. Reddy, I. N. Reddy, C. J. Choi, *RSC Adv.* **2016**, 6, 105761.
- [66] J. Qiu, Z. Chen, T. Zhao, Z. Chen, W. Chu, N. Yuan, J. Ding, *J. Nanosci. Nanotechnol.* **2018**, 18, 4222.
- [67] M. Kumar, *Mater. Today Proc.* **2020**, 26, 82.
- [68] H. Duan, Z. Chen, N. Xu, S. Qiao, G. Chen, D. Li, W. Deng, F. Jiang, *J. Electroanal. Chem.* **2021**, 885, 114966.
- [69] H. L. Chen, Y. M. Lu, J. Y. Wu, W. S. Hwang, *Mater. Trans.* **2005**, 46, 2530.
- [70] Z. Song, T. Bourgeteau, I. Raifuku, Y. Bonnassieux, E. Johnson, Y. Ishikawa, M. Foldyna, *Thin Solid Films* **2018**, 646, 209.
- [71] A. Van der Drift, *Philips Res. Rep.* **1967**, 22, 267.
- [72] H. W. Ryu, G. P. Choi, W. S. Lee, J. S. Park, *J. Mater. Sci.* **2004**, 39, 4375.
- [73] P. Salunkhe, *Mater. Res. Express* **2020**, 7, 016427.
- [74] S. Mustansar Abbas, S. Tajammul Hussain, S. Ali, N. Ahmad, N. Ali, S. Abbas, Z. Ali, *J. Solid State Chem.* **2013**, 202, 43.
- [75] Y. E. Firat, A. Peksoz, *Electrochim. Acta* **2019**, 295, 645.
- [76] Y. Yu, Y. Liang, J. Yong, T. Li, M. S. Hossain, Y. Liu, Y. Hu, K. Ganesan, E. Skafidas, *Adv. Funct. Mater.* **2022**, 32, 2106387.
- [77] I. Manouchehri, D. Mehrparvar, R. Moradian, K. Gholami, T. Osati, *Optik* **2016**, 127, 8124.
- [78] Z. He, Z. Ji, S. Zhao, C. Wang, K. Liu, Z. Ye, *Sol. Energy* **2006**, 80, 226.
- [79] A. Liu, H. Zhu, Z. Guo, Y. Meng, G. Liu, E. Fortunato, R. Martins, F. Shan, *Adv. Mater.* **2017**, 29, 1701599.
- [80] C. C. Singh, A. N. Roy Choudhury, D. S. Sutar, S. K. Sarkar, *J. Appl. Phys.* **2021**, 129, 095104.

- [81] C. C. Singh, A. N. Roy Choudhury, D. S. Sutar, S. K. Sarkar, *J. Appl. Phys.* **2021**, 129, 095104.
- [82] K. Mongkolsuttirat, J. Buajareern, *J. Phys. Conf. Ser.* **2021**, 1719, 012054.
- [83] M. Feng, M. Wang, H. Zhou, W. Li, X. Xie, S. Wang, Z. Zang, S. Chen, *ACS Appl. Energy Mater.* **2020**, 3, 9732.
- [84] M. Feng, M. Wang, H. Zhou, W. Li, S. Wang, Z. Zang, S. Chen, *ACS Appl. Mater. Interfaces* **2020**, 12, 50684.
- [85] H. Du, L. Ma, X. Wang, Y. Li, M. Xu, X. Liang, D. Chen, Y. Jin, *Chem. – Eur. J.* **2021**, 27, 11298.
- [86] M. Kitao, K. Izawa, K. Urabe, T. Komatsu, S. Kuwano, S. Yamada, *Jpn. J. Appl. Phys.* **1994**, 33, 6656.
- [87] X. Song, G. Dong, F. Gao, Y. Xiao, Q. Liu, X. Diao, *Vacuum* **2015**, 111, 48.
- [88] Y. Zhang, M. Yang, J. Du, L. Yang, L. Fan, X. Liu, J. Yang, F. Wang, *Electrochim. Acta* **2019**, 319, 41.
- [89] M. L. Grilli, F. Menchini, T. Dikonimos, P. Nunziante, L. Pilloni, M. Yilmaz, A. Piegari, A. Mittiga, *Semicond. Sci. Technol.* **2016**, 31, 055016.
- [90] C. Guillén, J. Herrero, *Mater. Res. Express* **2019**, 6, 096410.
- [91] X. Chen, L. Zhao, Q. Niu, *J. Electron. Mater.* **2012**, 41, 3382.
- [92] H. Sun, S.-C. C. Chen, P.-J. J. Chen, S.-L. L. Ou, C.-Y. Y. Liu, Y.-Q. Q. Xin, *Ceram. Int.* **2018**, 44, 3291.
- [93] C.-K. Wen, Y.-Q. Xin, S.-C. Chen, T.-H. Chuang, P.-J. Chen, H. Sun, *Thin Solid Films* **2019**, 677, 103.
- [94] H. Lee, W. Yang, J. Tan, Y. Oh, J. Park, J. Moon, *ACS Energy Lett.* **2019**, 4, 995.
- [95] R. E. Dietz, G. I. Parisot, A. E. Meixner, *J. Appl. Phys.* **1971**, 42, 1484.
- [96] G. George, S. Anandhan, *RSC Adv.* **2014**, 4, 62009.
- [97] E. Aytan, B. Debnath, F. Kargar, Y. Barlas, M. M. Lacerda, J. X. Li, R. K. Lake, J. Shi, A. A. Balandin, *Appl. Phys. Lett.* **2017**, 111, 252402.
- [98] N. Bala, H. K. Singh, S. Verma, S. Rath, *Phys. Rev. B* **2020**, 102, 024423.
- [99] K. S. Usha, R. Sivakumar, C. Sanjeeviraja, V. Sathe, V. Ganesan, T. Y. Wang, *RSC Adv.* **2016**, 6, 79668.
- [100] F. Şenaslan, M. Taşdemir, A. Çelik, *Appl. Phys. A: Mater. Sci. Process.* **2021**, 127, 105337.
- [101] R. Gupta, Q. Xiong, C. K. Adu, U. J. Kim, P. C. Eklund, *Nano Lett.* **2003**, 3, 627.
- [102] Y. Wu, S. Jin, Y. Ye, S. Wang, Z. Feng, C. Li, *J. Phys. Chem. C* **2014**, 118, 30269.
- [103] A. Sunny, K. Balasubramanian, *J. Raman Spectrosc.* **2022**, 53, 1249.
- [104] Q. Xiong, J. Wang, O. Reese, L. C. L. Y. Voon, P. C. Eklund, *Nano Lett.* **2004**, 4, 1991.
- [105] R. N. Juine, B. K. Sahu, S. Amirthapandian, A. Das, *J. Phys. Chem. C* **2020**, 124, 17227.
- [106] Y. N. Hwang, S. H. Park, D. Kim, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, 59, 7285.
- [107] A. Sunny, K. Balasubramanian, *J. Phys. Chem. C* **2020**, 124, 12636.
- [108] K. Varunkumar, R. Hussain, G. Hegde, A. S. Ethiraj, *Mater. Sci. Semicond. Process.* **2017**, 66, 149.
- [109] E. L. Ratcliff, J. Meyer, K. X. Steirer, A. Garcia, J. J. Berry, D. S. Ginley, D. C. Olson, A. Kahn, N. R. Armstrong, *Chem. Mater.* **2011**, 23, 4988.
- [110] A. P. Grosvenor, M. C. Biesinger, R. S. C. Smart, N. S. McIntyre, *Surf. Sci.* **2006**, 600, 1771.
- [111] M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, R. S. C. Smart, *Appl. Surf. Sci.* **2011**, 257, 2717.
- [112] M. Fingerle, S. Tengeler, W. Calvet, T. Mayer, W. Jaegermann, *J. Electrochem. Soc.* **2018**, 165, H3148.
- [113] C. C. Singh, A. N. R. Choudhury, D. S. Sutar, S. K. Sarkar, *J. Mater. Sci.: Mater. Electron.* **2020**, 31, 19836.
- [114] M. D. Dong, J. Y. Shen, C. Y. Hong, P. X. Ran, R.-H. He, H. W. Chen, Q. Y. Lu, J. Wu, *J. Appl. Phys.* **2022**, 132, 220901.
- [115] X. Yang, W. Liu, G. Pan, Y. Sun, *J. Mater. Sci.* **2018**, 53, 11684.
- [116] J. Park, K. Lim, R. D. Ramsier, Y.-C. Kang, *Bull. Korean Chem. Soc.* **2011**, 32, 3395.
- [117] P. Jiang, D. Prendergast, F. Borondics, S. Porsgaard, L. Giovanetti, E. Pach, J. Newberg, H. Bluhm, F. Besenbacher, M. Salmeron, *J. Chem. Phys.* **2013**, 138, 024704.
- [118] J. P. Espinós, J. Morales, A. Barranco, A. Caballero, J. P. Holgado, A. R. González-Elipe, *J. Phys. Chem. B* **2002**, 106, 6921.
- [119] H. L. S. Santos, P. G. Corradini, M. A. S. Andrade, L. H. Mascaro, *J. Solid State Electrochem.* **2020**, 24, 1899.
- [120] B. Wei, Y. Xiong, Z. Zhang, J. Hao, L. Li, W. Shi, *Appl. Catal. B Environ.* **2021**, 283, 119646.
- [121] C. C. Chusuei, M. A. Brookshier, D. W. Goodman, *Langmuir* **1999**, 15, 2806.
- [122] Y. Zhang, J. Zuo, Y. Gao, P. Li, W. He, Z. Zheng, *J. Phys. Chem. Solids* **2019**, 131, 27.
- [123] D. Emin, *Phys. Rev. Lett.* **1970**, 25, 1751.
- [124] A. J. Bosman, H. J. van Daal, *Adv. Phys.* **1970**, 19, 1.
- [125] J. Y. Zhang, W. W. Li, R. L. Z. Hoye, J. L. MacManus-Driscoll, M. Budde, O. Bierwagen, L. Wang, Y. Du, M. J. Wahila, L. F. J. Piper, T.-L. Lee, H. J. Edwards, V. R. Dhanak, K. H. L. Zhang, *J. Mater. Chem. C* **2018**, 6, 2275.
- [126] M. Napari, T. N. Huq, R. L. Z. Hoye, J. L. MacManus-Driscoll, *InfoMat* **2021**, 3, 536.
- [127] M. Napari, T. N. Huq, T. Maity, D. Gomersall, K. M. Niang, A. Barthel, J. E. Thompson, S. Kinnunen, K. Arstila, T. Sajavaara, R. L. Z. Hoye, A. J. Flewitt, J. L. MacManus-Driscoll, *InfoMat* **2020**, 2, 769.
- [128] H. Kawazoe, H. Yanagi, K. Ueda, H. Hosono, *MRS Bull.* **2000**, 25, 28.
- [129] W.-Y. Chen, J.-S. Jeng, K.-L. Huang, J.-S. Chen, *J. Vac. Sci. Technol., A* **2013**, 31, 021501.
- [130] W. Chen, Y. Wu, J. Fan, A. B. Djurišić, F. Liu, H. W. Tam, A. Ng, C. Surya, W. K. Chan, D. Wang, Z.-B. He, *Adv. Energy Mater.* **2018**, 8, 1703519.
- [131] M. Rusu, T. Kodalle, L. Choubrac, N. Barreau, C. A. Kaufmann, R. Schlattmann, T. Unold, *ACS Appl. Mater. Interfaces* **2021**, 13, 7745.
- [132] W. B. Zhang, N. Yu, W. Y. Yu, B. Y. Tang, *Eur. Phys. J. B* **2008**, 64, 153.
- [133] S. Park, H. S. Ahn, C. K. Lee, H. Kim, H. Jin, H. S. Lee, S. Seo, J. Yu, S. Han, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, 77, 134103.
- [134] J. Osorio-Guille'n, S. Lany, A. Zunger, M. Caldas, N. Studart, presented at *AIP Conf. Proc.*, Melville, New York, USA **2010**, <https://doi.org/10.1063/1.3295330>.
- [135] M. N. Siddique, P. Tripathi, *J. Alloys Compd.* **2020**, 825, 154071.
- [136] T. Wang, D. Ding, H. Zheng, X. Wang, J. Wang, H. Liu, W. Shen, *Sol. RRL* **2019**, 3, 1.
- [137] F. Zhang, Z. Zhou, C. Zou, X. Liu, J. Xie, D. Liu, S. Yang, Y. Hou, H. G. Yang, *Chemistry* **2022**, 28, e202200202.
- [138] N. Tiwari, H. Arianita Dewi, E. Erdenebileg, R. Narayan Chauhan, N. Mathews, S. Mhaikar, A. Bruno, *Sol. RRL* **2022**, 6, 2100700.
- [139] S. Yue, K. Liu, R. Xu, M. Li, M. Azam, K. Ren, J. Liu, Y. Sun, Z. Wang, D. Cao, X. Yan, S. Qu, Y. Lei, Z. Wang, *Energy Environ. Sci.* **2017**, 10, 2570.
- [140] F. Khan, B. D. Rezgüi, J. H. Kim, *Sol. Energy* **2020**, 209, 226.
- [141] J. Chen, D. He, N.-G. Park, *Sol. RRL* **2022**, 6, 2100458.
- [142] H. Do Kim, H. Ohkita, *Sol. RRL* **2017**, 1, 1700027.
- [143] Y. Li, J. Shi, B. Yu, B. Duan, J. Wu, H. Li, D. Li, Y. Luo, H. Wu, Q. Meng, *Joule* **2020**, 4, 472.
- [144] N. F. Montcada, M. Méndez, K. T. Cho, M. K. Nazeeruddin, E. Palomares, *Nanoscale* **2018**, 10, 6155.
- [145] R. Hidayat, A. A. Nurunnizar, A. Fariz, Herman, E. S., *Sci. Rep.* **2020**, 10, 19197.
- [146] M. Azzouzi, P. Calado, A. M. Telford, F. Eisner, X. Hou, T. Kirchartz, P. R. F. Barnes, J. Nelson, *Sol. RRL* **2020**, 4, 1900581.

- [147] C. Li, L. Lv, L. Qin, L. Zhu, F. Teng, Z. Lou, Z. Deng, Y. Hu, Q. Cui, Y. Hou, *Materials* **2018**, *11*, 2407.
- [148] V. Raj, S. Ghosh, S. K. Sarkar, *Sol. Energy Mater. Sol. Cells* **2021**, *230*, 111276.
- [149] A. Guerrero, J. Bisquert, G. Garcia-Belmonte, *Chem. Rev.* **2021**, *121*, 14430.
- [150] R. T. Ginting, M.-K. Jeon, K.-J. Lee, W.-Y. Jin, T.-W. Kim, J.-W. Kang, *J. Mater. Chem. A* **2017**, *5*, 4527.
- [151] D. Di Girolamo, N. Phung, F. U. Kosasih, F. Di Giacomo, F. Matteocci, J. A. Smith, M. A. Flatken, H. Köbler, S. H. Turren Cruz, A. Mattoni, L. Cinà, B. Rech, A. Latini, G. Divitini, C. Ducati, A. Di Carlo, D. Dini, A. Abate, *Adv. Energy Mater.* **2020**, *10*, 2000310.
- [152] S. C. Chen, T. Y. Kuo, Y. C. Lin, H. C. Lin, *Thin Solid Films* **2011**, *519*, 4944.
- [153] A. K. Chauhan, P. Kumar, *J. Mater. Sci. Mater. Electron.* **2019**, *30*, 9582.
- [154] G. Jeong, D. Koo, J. Seo, S. Jung, Y. Choi, J. Lee, H. Park, *Nano Lett.* **2020**, *20*, 3718.
- [155] N. N. Udalova, E. M. Nemygina, E. A. Zharenova, A. S. Tutantsev, A. A. Sudakov, A. Y. Grishko, N. A. Belich, E. A. Goodilin, A. B. Tarasov, *J. Phys. Chem. C* **2020**, *124*, 24601.
- [156] Y. Liao, F. Fei, B. Li, Y. Li, Y. Xu, S. Wang, X. Fang, L. Li, N. Yuan, J. Ding, *Sol. RRL* **2023**, *7*, 1.
- [157] J. You, L. Meng, T. Bin Song, T. F. Guo, W. H. Chang, Z. Hong, H. Chen, H. Zhou, Q. Chen, Y. Liu, N. De Marco, Y. Yang, *Nat. Nanotechnol.* **2016**, *11*, 75.
- [158] M. B. Islam, M. Yanagida, Y. Shirai, Y. Nabetani, K. Miyano, *ACS Omega* **2017**, *2*, 2291.
- [159] N. Phung, M. Verheijen, A. Todinova, K. Datta, M. Verhage, A. Al-Ashouri, H. Köbler, X. Li, A. Abate, S. Albrecht, M. Creatore, *ACS Appl. Mater. Interfaces* **2022**, *14*, 2166.