

Characteristics of NiO_x as Hole Transport layer using Atomic Layer Deposition

by

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Abstract

This research evaluates the fabrication of inorganic nickel oxide NiO_x as a hole transport layer in inverted perovskite solar cells using Atomic Layer Deposition (ALD). Inorganic hole transport layers are desired for their long term stability and degradation resistance. Systematic optimization established a self-limiting growth rate of 0.0457 nm per cycle using a 3.0 s nickel precursor pulse and a 0.2 s H_2O co-reactant pulse for the ALD system. The resulting NiO_x films exhibited highly conformal growth on bare silicon and indium tin oxide substrates with less than a nanometer of roughness and sample-to-sample uniformity, maintaining over 90% visible transparency and a stable optical band gap of approximately 3.84 eV.

Post-deposition annealing in ambient air and nitrogen at 300 °C for 15 minutes increased the relative fraction of Ni^{3+} surface states and lowered the absolute work function to an operative range of 4.35 to 4.55 eV, whereas ozone treatments proved detrimental by forming surface hydroxides. When integrated into photovoltaic devices, a 7.5 nm air-annealed NiO_x layer emerged as the optimum configuration compared to thinner 5 nm and thicker 10 nm samples, yielding a peak power conversion efficiency 3.90%, alongside a V_{oc} of 0.874 V and a J_{sc} of 12.33 mA cm^{-2} . Ultimately, this performance lagged behind the efficiency of organic PTAA which by comparison achieved a power conversion efficiency of 8.99%, a V_{oc} of 0.992 V, a J_{sc} of 16.84 mA cm^{-2} , and a fill factor of 53.82% reference cells. This is due to significant interfacial charge extraction barriers that caused S-shaped current-voltage deformations. This study shows that further research is needed to better characterize the interactions/reactions between the NiO_x and the perovskite layer.

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Introduction

The growing demand for clean, reliable, and sustainable energy has become one of the defining scientific and technological challenges of the 21st century. The development of efficient renewable energy technologies has become essential as global energy consumption continues to increase alongside concerns over climate change and its potential catastrophic consequences [1], [2]. Meeting these challenges requires not only a reduction in fossil fuel consumption, but also a large-scale deployment of existing renewable energy systems and continuous innovation in materials and device engineering to improve performance, reduce manufacturing costs, and enable widespread adoption [3], [4]. Among the various renewable energy technologies under active development, solar energy has emerged as one of the most promising solutions due to its abundance, accessibility, and clean nature [5].

The transition toward sustainable energy systems has become a central global priority in response to the environmental and economic challenges associated with fossil fuel consumption. Among various renewable energy technologies, photovoltaics have gained widespread attention due to their ability to directly convert sunlight into electricity with no moving parts and minimal operational emissions. Conventional solar cells based on silicon currently dominate the photovoltaic market because of their high efficiencies and long-term reliability. Over several decades of development, continuous improvements in material quality, device design, and fabrication techniques have enabled silicon solar cells to achieve power conversion efficiencies that exceed 28%, as seen in Figure 1.1.

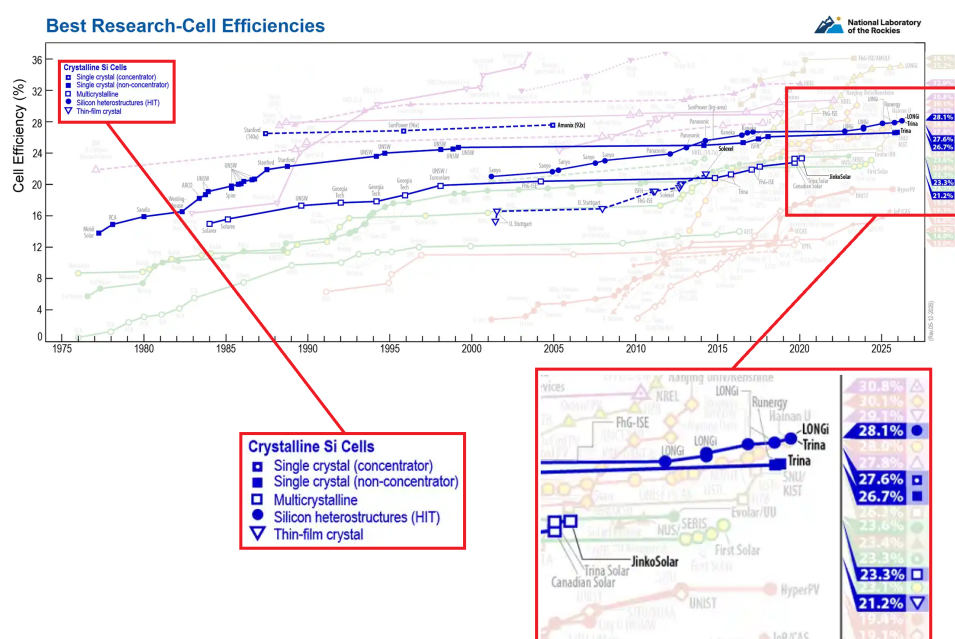


Figure 1.1: Silicon PV technology record efficiency [6].

Despite this progress, further efficiency improvements in single-junction silicon solar cells have become increasingly difficult due to fundamental physical limitations. The maximum theoretical efficiency of a single-junction photovoltaic device under standard solar illumination is described by the Shockley-Queisser limit, which predicts an upper efficiency of approximately 33% [7], shown in Figure 1.2. This limit arises from intrinsic loss mechanisms, including the inability of photons with energies below the semiconductor band gap to generate charge carriers and the thermalization of excess energy from high-energy photons. As state-of-the-art silicon devices continue to approach this theoretical ceiling, further gains through conventional device optimization alone become increasingly marginal.

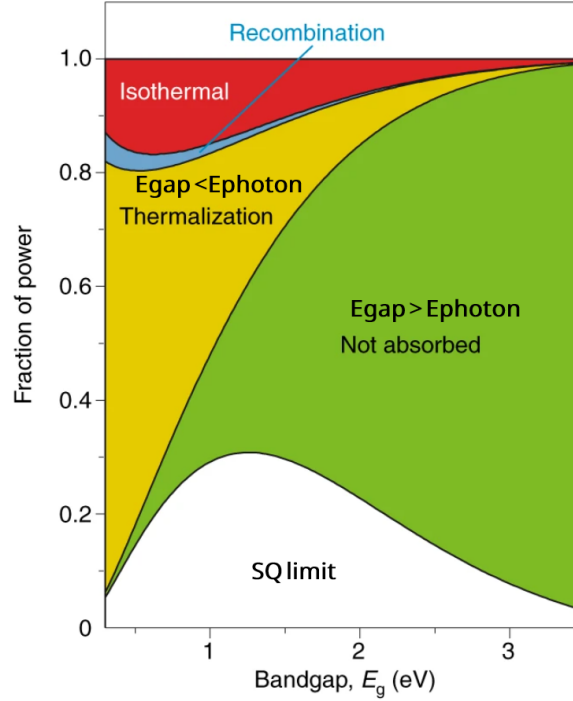


Figure 1.2: The Shockley-Queisser theoretical efficiency limit as function of the band gap of a solar cell [8].

These limitations have led to extensive research into alternative photovoltaic materials and device architectures capable of surpassing the efficiency limits of single-junction silicon. Among the most promising candidates are perovskite solar cells, whose exceptional optoelectronic properties and low-temperature fabrication processes have driven unprecedented advances in photovoltaic performance. Furthermore, the tunable band gap of perovskite materials makes them ideally suited for tandem solar cells, in which a perovskite absorber is stacked on top of a silicon bottom cell. By allowing different portions of the solar spectrum to be absorbed by materials with complementary band gaps, tandem architectures significantly reduce thermalization and transmission losses, enabling power conversion efficiencies that exceed the single-junction Shockley-Queisser limit. As a result, perovskite-silicon tandem solar cells are widely regarded as one of the most promising pathways towards next-generation high-efficiency photovoltaics [9].

Despite these remarkable advances, achieving long-term operational stability and efficient charge extraction from perovskite cells remains a significant challenge. Addressing these limitations requires careful optimization of the device architecture, particularly through the incorporation of selective charge transport layers that facilitate efficient carrier extraction while minimizing recombination losses.

An essential component in perovskite solar cells is the hole transport layer (HTL), which is responsible for selectively extracting and transporting positive charge carriers (holes) from the perovskite absorber to the electrode, while blocking electrons to minimize recombination losses. An effective HTL must therefore possess suitable energy level alignment, high hole mobility, optical transparency, and good chemical compatibility with adjacent layers. Traditionally, organic materials such as Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) have been widely used. However, their relatively high cost, complex synthesis, and limited long-term

stability have motivated the search for alternative materials.

Inorganic metal oxides have thus emerged as promising candidates for HTL applications, offering improved thermal stability and cell durability. Among these, nickel oxide (NiO_x) stands out as a p-type wide band gap semiconductor with high optical transparency and favourable electronic properties for hole transport. NiO_x can effectively facilitate hole extraction while acting as a barrier to electrons, thereby improving charge selectivity and reducing recombination at interfaces. Moreover, its robustness under thermal and environmental stress makes it particularly attractive for durable device operation, which are needed for commercial photovoltaics.

To fully exploit the potential of NiO_x as an HTL, precise control over film thickness, composition, and morphology is required. Atomic layer deposition (ALD) is a thin-film fabrication technique uniquely suited to meet these requirements. Based on sequential, self-limiting surface reactions, ALD enables conformal coating of substrates with atomic-scale precision. This level of control allows for systematic tuning of NiO_x properties, such as stoichiometry and defect density, which directly influence the electrical performance. Incorporating ALD-deposited NiO_x as a hole transport layer has therefore become an area of growing interest in perovskite solar cell research. By combining the intrinsic advantages of NiO_x with the precision of ALD, researchers aim to enhance device efficiency, reproducibility, and long-term stability, contributing to the broader goal of advancing cost-effective and sustainable photovoltaic technologies.

1.1. Project objective

The goal of this project is to implement NiO_x as a hole transport layer in an inverted (p-i-n) perovskite solar cell. For this to happen, it is necessary first to characterize the newly added ALD machine in the Else Kooi Lab (EKL) and also the deposited NiO_x layer. The recipe for depositing the NiO_x layer with the ALD was in an early stage of optimization therefore, the key research questions addressed are as follows:

- Which process parameters ensure that atomic layer depositions are more consistent and uniform?
- How do ALD parameters affect the deposition of NiO_x ?
- What are the effects of post deposition treatments on the deposited NiO_x layer?
- To what extent can ALD deposited NiO_x serve as a competitive alternative to organic HTLs in perovskite solar cells?
- How do post deposition treatments of the ALD NiO_x layer affect the performance of a complete device?

1.2. Report outline

The research is divided into six main chapters. Chapter 2 introduces the perovskite solar cell and the function of transport layers, and provides an overview of how atomic layer deposition (ALD) functions. Chapter 3 describes the experimental methods used in this research, including how the samples are fabricated and the characterization techniques employed and their underlying principles. Chapter 4 presents the results of the experiments, which are discussed in Chapter 5 in relation to the research question. Finally, Chapter 6 concludes the research by summarizing the main findings.

2

Theory

This section is split up into three main sections, mainly an introduction to perovskite solar cells (PSC) with its strengths and weaknesses, followed by the necessity for transport layers (TL). The chapter concludes with an overview of atomic layer deposition (ALD) as a deposition technique.

2.1. Perovskite solar cells

Perovskite solar cells (PSCs) use an absorber layer composed of a material with a crystal structure ABX_3 , where A and B are cations and X is an anion. The crystal structure is illustrated in Figure 2.1. The elements in the crystal structure consist of caesium (Cs^+) or formamidinium (FA^+) as A-site cations, lead (Pb^{2+}) with now tin (Sn^{2+}) alternative as B-site cations, and bromide (Br^-) or iodide (I^-) as X-site cations. Unlike the rigid covalent crystal structure of silicon, the ionic perovskite lattice is more structurally flexible and can accommodate certain defects without severely degrading its electronic properties. This defect tolerance, together with the relatively low formation energy of the crystal, enables perovskite materials to be processed at relatively low temperatures while still achieving excellent optoelectronic performance. In contrast, conventional silicon solar cells require highly ordered, high-purity crystals that must be grown under carefully controlled conditions [10][11].

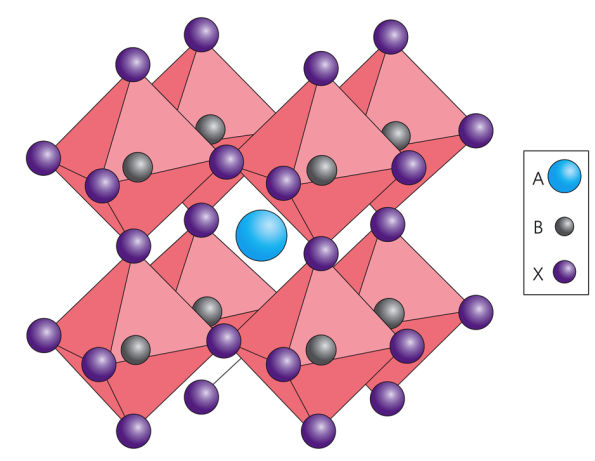


Figure 2.1: Perovskite crystal structure [12].

One of the main benefits of perovskites is that there are various configurations that can be made with different material choices for the ABX_3 structure, which in turn adjust the material properties, such as its band gap [13]. The band gap of perovskite solar cells can be tuned to optimize absorption across different regions of the solar spectrum, maximizing light absorption and increasing power conversion efficiency (PCE) [14]. It also enables tandem solar cells, where perovskite layers are paired with silicon absorber layer to capture the sunlight's wavelength spectrum better and achieve higher efficiencies. Perovskite films also have high carrier mobility

and long diffusion lengths inherent to the crystal structure [15]. This ensures that charges can travel relatively long distances to the electrodes without being trapped by defects, which should yield high efficiency cells [16]. These solar cells started relatively humble with the first recorded efficiencies around 3.8% in 2009, but Figure 2.2 show how the performance of perovskite devices has rapidly grown to a record PCE of 27.3% for single-junction solar cells and 35.2% for 2-terminal perovskite-silicon tandems in 2025.

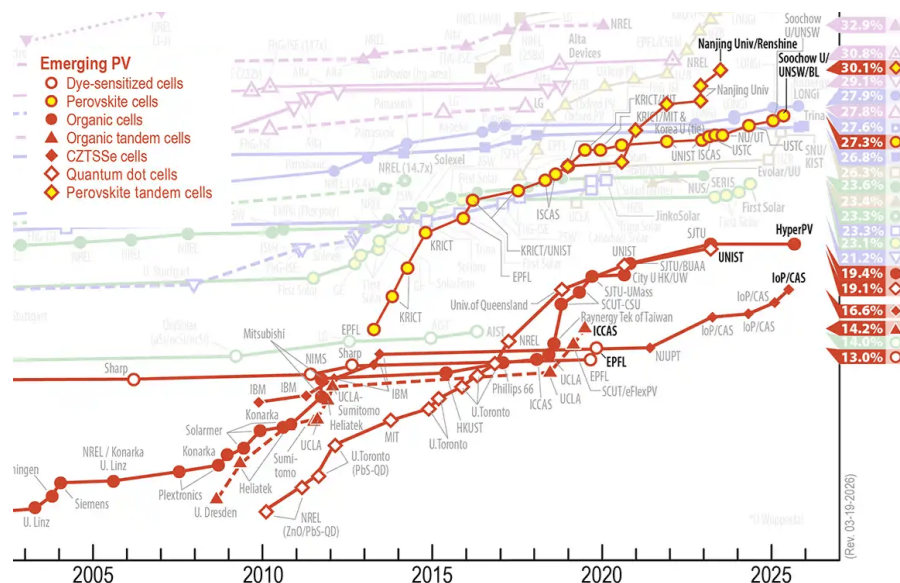


Figure 2.2: Emerging PV technology record efficiency [6].

Although perovskite solar cells have achieved record power conversion efficiencies, these results are typically obtained using solution-processed spin-coated devices fabricated on small laboratory devices (0.076 cm^2). Spin-coating is a commonly used technique in which a small amount of perovskite precursor is dissolved in a solution and dropped onto the center of a rotating substrate. The solution is then accelerated into rotation, where a centrifugal force flies the liquid outward toward the edges of the substrate. The excess liquid is ejected off of it, leaving behind a thin film. This works well for small samples, but increasing the substrate size ruins the uniformity of the layer because of the higher velocity at the edges that causes turbulence, resulting in drastically lower cell efficiencies.

Vacuum deposition offers a promising and alternative approach to bridge this gap between laboratory-scale performance and large-scale manufacturing, such as thermal evaporation. Here, the perovskite precursors are placed in heated crucibles within a vacuum chamber, where the precursors are heated until they begin to sublime. The vaporized molecules travel upward to the cooler substrate, where they condense back into a solid and form a thin film. This thermal evaporation (TE) technique produced cells up to 25 cm^2 with comparable performances to their solution based spin-coated cousin and offers extremely precise control over thickness and composition, leading to highly uniform films across large areas [17]. It is also inherently compatible with industrial fabrication and multilayer device stacks with the added benefit of avoiding solvents. Although TE perovskite solar cells have historically lagged behind spin-coated devices in terms of efficiency, research into TE perovskites is comparatively more recent. Nevertheless, recent advances have significantly narrowed the performance gap, with PCE reaching 26.21%.

Perovskite solar cells operate by converting light energy into electrical energy through a sequence of physical processes occurring within a multilayer semiconductor device. As shown in Figure 2.3, the perovskite absorber layer is sandwiched between an electron transport layer (ETL) and a hole transport layer (HTL), which selectively extract electrons and holes, respectively. The process begins with photoexcitation, when a photon with energy equal to or greater than the material's band gap (E_g) is absorbed by the perovskite layer ($E_{\text{photon}} = h\nu \geq E_g$) promoting an electron from the valence band (VB) to the conduction band (CB). The generated charge carriers are transported through the ETL and HTL to their respective electrodes.

Depending on the order in which the transport layers are deposited relative to the transparent conducting

oxide (TCO) substrate, the device adopts either an n-i-p or a p-i-n architecture. In the regular n-i-p configuration, the n-type electron transport layer is deposited directly onto the transparent electrode, followed by the perovskite absorber and finally the p-type hole transport layer. This configuration is considered regular because it originates from dye-sensitized solar cell architectures, where an n-type metal oxide such as titanium dioxide (TiO_2) serves as the electron-selective scaffold. In contrast, the p-i-n architecture reverses this sequence, with the hole transport layer deposited first, followed by the perovskite absorber and finally the electron transport layer.

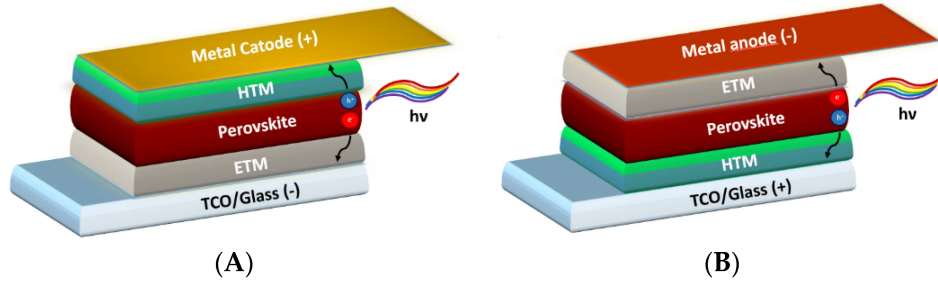


Figure 2.3: Schematic of a perovskite solar cell consisting of (a) n-i-p and (b) p-i-n stack [18].

Excitation creates two charge carriers, mainly a negatively charged electron in the conduction band and a positively charged "hole", which is essentially the absence of an electron, in the VB. To generate an electric current, these carriers must be extracted in opposite directions before they can recombine, a process where the electron falls back into a hole and essentially "wastes" the energy as heat or light. This directional movement is driven by the internal architecture of the cell, which features an electron transport layer (ETL) on one side and a hole transport layer (HTL) on the other. Transport layers act as selective filters that dictate the flow of electricity. The ETL extracts electrons while blocking holes, whereas the HTL extracts holes while blocking electrons. Their operation will be discussed in greater detail in Section 2.2.

Efficient charge extraction requires appropriate energy level alignment between the perovskite and the transport layers. The conduction band of the ETL should lie slightly below that of the perovskite, creating an energetically favourable pathway for electron extraction while preventing hole transport. Similarly, the highest occupied molecular orbital (HOMO), or valence band, of the HTL should align closely with the perovskite VB to selectively extract holes while blocking electrons, as shown in Figure 2.4. This selective carrier transport is driven by the resulting chemical potential gradient.

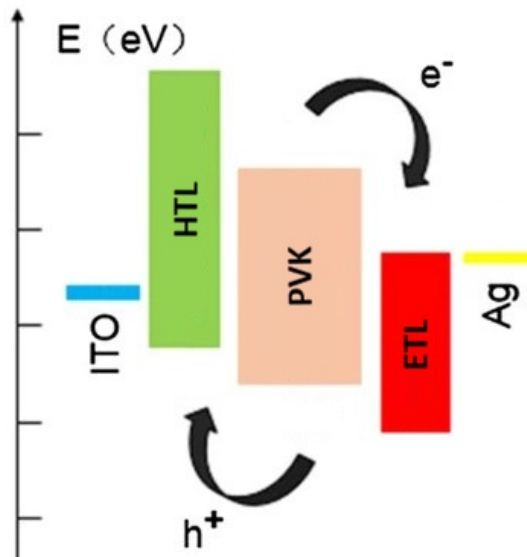


Figure 2.4: Band alignment overview of the perovskite and transport layers while extracting charge carriers [19]

The choice of ETL and HTL materials therefore depends strongly on their energy levels and work functions.

The work function is defined as the minimum energy required to remove an electron from the Fermi level of a material to the vacuum level immediately outside its surface. The Fermi level, E_F , represents the chemical potential of electrons in a material and determines the occupation probability of electronic states according to the Fermi–Dirac distribution. At 0 K, all states below the Fermi level are occupied and those above it are unoccupied, while at finite temperatures, an electronic state at the Fermi level has a 50% probability of being occupied. In semiconductors, the position of the Fermi level depends on the concentrations of electrons and holes, which can be influenced by intentional doping as well as intrinsic defects. An increase in electron concentration shifts the Fermi level closer to the conduction band, whereas an increase in hole concentration shifts it closer to the valence band (Figure 2.5). The position of the Fermi level is therefore an important parameter in determining the electronic properties and dominant charge carriers of a semiconductor, while the work function provides an important measure of its energetic alignment with other materials.

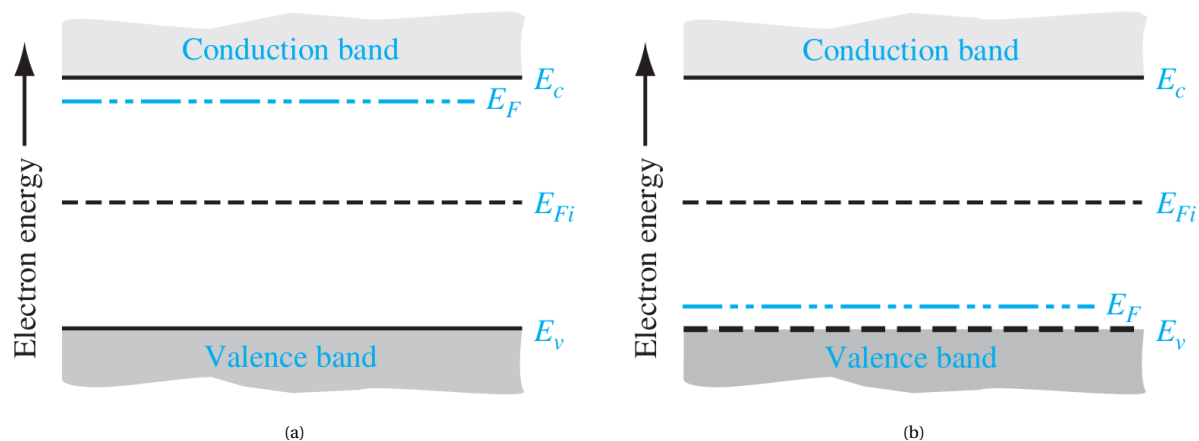


Figure 2.5: Band diagrams illustrating Fermi level shifts in doped semiconductors. (a) In an n-type semiconductor, the Fermi level (E_F) moves toward the conduction band due to increased electron concentration, while (b) in a p-type semiconductor, it shifts toward the valence band due to increased hole concentration [20].

Once the electrons reach the ETL and the holes reach the HTL, they migrate toward their respective electrodes. The difference in quasi-Fermi levels between electrons and holes defines the implied open-circuit voltage (iV_{OC}), which represents the maximum voltage potential of the absorber before losses associated with charge extraction and contacts are considered. In a complete device, the difference in electrochemical potential between the two contacts defines the open-circuit voltage of the cell (V_{OC}). When the device is connected to an external circuit, the electrons flow through the load to reunite with the holes at the back contact, completing the circuit and providing usable electrical power.

2.2. Transport layers

The transport layers serve as selective contacts that facilitate efficient charge extraction while contributing to the overall stability of the perovskite device. In an inverted p-i-n architecture, the HTL is typically deposited onto a transparent conductive oxide (TCO), such as fluorine-doped tin oxide (FTO) or indium tin oxide (ITO), followed by deposition of the perovskite absorber layer. The HTL is a p-type material and is frequently an organic semiconductor, such as poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD), or poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS). An electron transport layer (ETL), such as buckminsterfullerene (C_{60}), is subsequently deposited on top of the perovskite, followed by a metal electrode, such as silver, to complete the device.

The primary function of the HTL is to facilitate the movement of holes from the perovskite active layer to the anode while simultaneously acting as an energetic barrier to electrons. This selectivity is achieved through precise band-gap engineering. For an effective HTL, the energy levels must align appropriately with those of the perovskite absorber. In organic HTLs, this is described in terms of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), whereas inorganic HTLs are characterized by their valence and conduction band edges. In both cases, the HTL HOMO or valence band edge (VB) should closely align with the valence band maximum (VBM) of the perovskite to minimize the interfacial en-

ergy offset and enable efficient hole extraction. Simultaneously, the HTL LUMO or conduction band edge (CB) should lie significantly higher in energy than the perovskite conduction band, thereby blocking electron transfer and suppressing interfacial recombination. This high-energy offset creates a large potential barrier that prevents electrons from reaching the anode. If electrons were allowed to pass through, they would recombine with holes at the electrode surface, leading to massive energy losses and a reduction in the open-circuit voltage (V_{oc}). Similarly for the ETL, but by facilitating electrons and blocking holes.

The HTL also governs the morphology of the subsequent perovskite layer. A well-optimized HTL promotes the growth of large, high-quality perovskite grains with minimal grain boundaries. Fewer grain boundaries mean fewer trap states, which are physical defects in which charge carriers can become stuck and undergo non-radiative recombination. Furthermore, the HTL acts as a physical and chemical buffer. It prevents the diffusion of metal ions from the electrode into the perovskite layer and blocks volatile species from escaping the perovskite when the cell heats up during operation. The conductivity of the HTL is also a critical factor as it must be high enough to transport charges to the electrode without significant series resistance, yet the layer must be thin enough to maintain high transparency such that incoming photons can reach the absorber layer with minimal parasitic absorption.

(In)organic hole transport layer

Hole transport materials (HTMs) for perovskite solar cells can be broadly classified into two categories: organic and inorganic. The highest-performing HTLs are typically organic materials deposited using solution-based techniques such as spin coating, making them simple and cost-effective to fabricate. Perovskite solar cells employing organic, solution-processed HTLs have achieved PCE of up to 24%. However, these materials generally suffer from limited thermal and UV stability, raising concerns about their long-term reliability under operating conditions.

Inorganic HTMs, particularly NiO_x , offer a promising alternative due to their excellent thermal and moisture stability. In addition, NiO_x is compatible with vacuum-based deposition techniques commonly used in industrial manufacturing, enabling uniform and conformal thin-film deposition. Various deposition methods have been demonstrated for NiO_x [21]. Early solution-processed devices achieved PCEs of 1.97% [22] and 7.8% [23], while continued optimization has increased efficiencies to over 20% for both single-junction and tandem devices [24][25]. Sputtered NiO_x has similarly achieved PCEs exceeding 20% [26][27], with tandem devices surpassing 30% [28]. Atomic layer deposition (ALD), the focus of this report (Section 2.3), has also been successfully employed to deposit NiO_x , yielding efficiencies ranging from the mid-teens to over 21% [29][30]. Overall, NiO_x combines competitive device efficiencies with excellent long-term stability, making it one of the most promising inorganic HTMs for perovskite solar cells [31].

2.3. Atomic layer deposition

Atomic layer deposition (ALD) is a promising technique for depositing NiO_x as a hole transport layer due to its ability to produce highly uniform and conformal ultra thin films. ALD is a vacuum-based deposition technique consisting of two half-cycles: one involving the precursor and the other the co-reactant (Figure 2.6). The desired film thickness is achieved by repeating these cycles until the required number has been completed. The defining characteristic of ALD is its reliance on self-limiting surface reactions, which build the film in an atomic layer-by-layer fashion. This provides exceptional control over film thickness, composition, and uniformity, making ALD particularly well suited for the fabrication of high-quality NiO_x layers for perovskite solar cells [30].

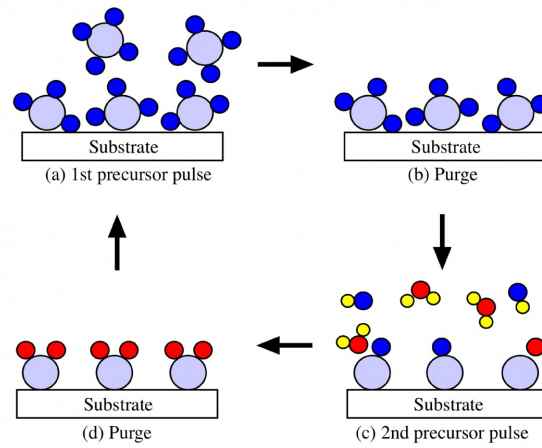


Figure 2.6: Schematic of the two half-cycles and self limiting chemical reactions [32]

Many parameters such as the deposition temperature, pulse and purge times are kept constant, while the number of cycles is steadily increased. This should yield a linear increase in deposited material thickness. Linearity is the mathematical proof that the ALD process is behaving predictably. It describes a proportional relationship between the number of cycles performed and the final thickness achieved. With an ideal recipe, the film thickness increases at a constant rate regardless of cycle count. This relationship is defined by the formal equation:

$$d = \text{GPC} \times N \quad (2.1)$$

In this formula, d is the total film thickness, GPC is the thickness added per cycle, and N is the total number of cycles. GPC is a crucial parameter of the ALD process can be found by taking the slope of this curve, shown in Figure 2.7.

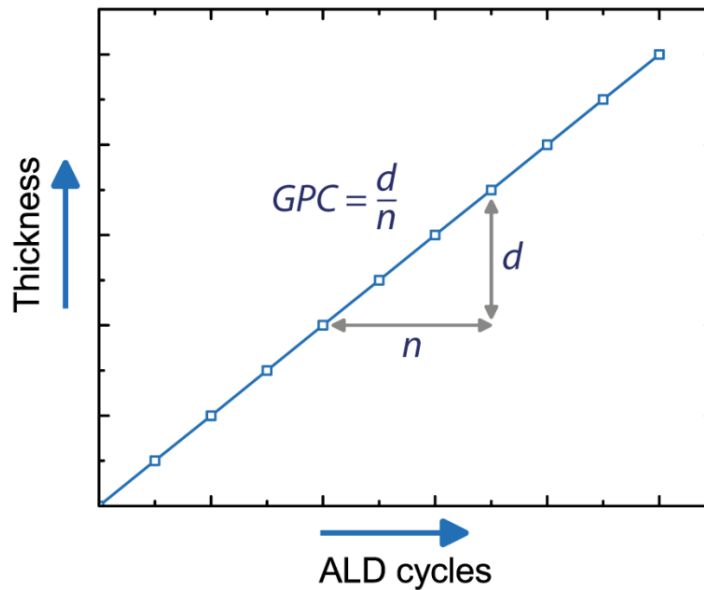


Figure 2.7: Theoretical ALD thickness linearity while increasing amount of cycles

The GPC represents the average thickness of material deposited during one complete four-step cycle (two half cycles): the first precursor pulse, a purge, the second precursor pulse, and a final purge, as shown in Figure 2.6. Because ALD is a self-limiting process, the chemical reactions naturally stop once all available surface sites are occupied. However, one cycle does not equal one full atomic monolayer. In reality, steric hindrance, where bulky precursor molecules physically block neighbouring reactive sites, usually, limits the GPC to a fraction of a monolayer.

A one-variable-at-a-time approach can be used to assess the onset of self-limiting ALD growth to check the validity of the recipe. The precursor pulse, co-reactant pulse, and inert gas pulse durations were systematically varied over a range where first over the amount of cycles to get the GPC and then over the dosing time. This should result in a plot as shown in Figure 2.8. The goal is to determine the minimum dosing time required to achieve the self-limiting surface reactions characteristic of ALD. Dosing beyond this point unnecessarily increases material consumption and may promote undesirable reactions that increase film roughness or otherwise degrade film quality.

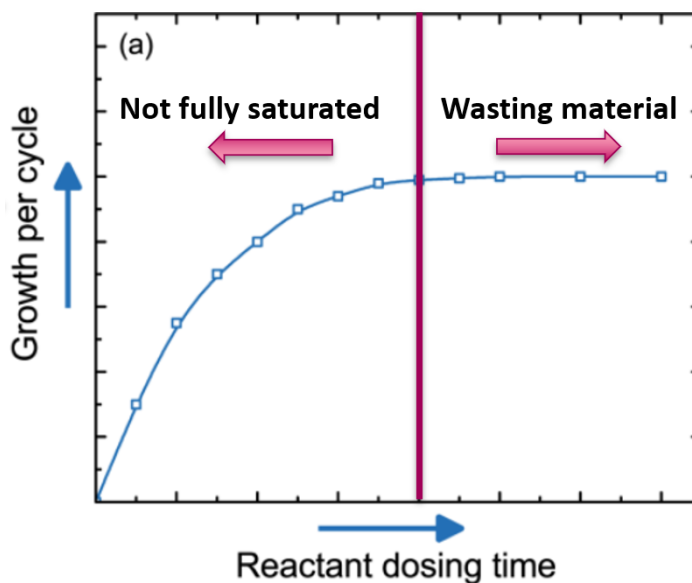


Figure 2.8: Theoretical ALD self limiting GPC characteristic after reaching optimal dosing time

The hole transport materials (HTMs) deposited by ALD are predominantly inorganic metal oxides, where control over composition, stoichiometry, and defect concentration is important for tailoring their electronic properties. A common example is nickel oxide (NiO_x), where variations in oxygen content influence conductivity, work function, and charge transport characteristics. In an ALD process for NiO_x , a nickel precursor such as nickelocene or bis(cyclopentadienyl) nickel may be used, along with an oxidizing co-reactant such as oxygen (O_2), ozone (O_3), or water (H_2O). During each cycle, the nickel precursor adheres to the substrate surface, where oxidant then converts it to nickel oxide while a subsequent nitrogen purge removes the remaining organic ligands. Thermal ALD relies on thermally activated surface reactions between gaseous precursors, where heat provides the energy required for the reactions to occur. In contrast, plasma-enhanced ALD (PEALD) uses a plasma to generate highly reactive species from the reactant, typically through radio-frequency (RF) or microwave power. The use of these reactive species enables PEALD to operate at lower substrate temperatures than conventional thermal ALD. Thermal ALD typically requires deposition temperatures of around 200°C , while PEALD can operate at temperatures below 150°C . But that does come at the cost of potential surface damage from ion bombardment. The precursor $\text{Ni}(\text{}^t\text{Bu}_2\text{AMD})_2$ ($\text{C}_{20}\text{H}_{42}\text{N}_4\text{Ni}$), shown in Figure 2.9, with water as a co-reactant, is suitable for thermal ALD of NiO_x . The process can be performed at a deposition temperature of 150°C , enabling relatively low-temperature ALD deposition[33].

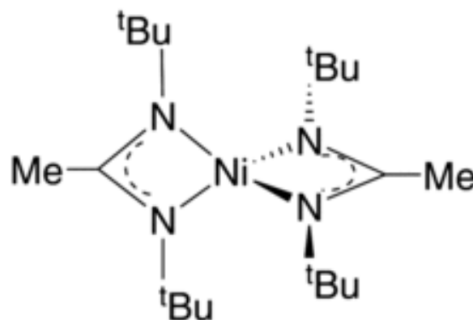


Figure 2.9: Chemical structure of precursor $\text{Ni}(\text{tBu}_2\text{AMD})_2$ used for thermal ALD of NiO_x [34]

A key advantage of ALD is its high conformality, which enables the deposition of uniform films over surfaces with nanoscale roughness[33]. This is particularly relevant for the present device architecture, where the NiO_x layer is deposited directly onto ITO. Although ITO appears smooth on the macroscopic scale, its surface exhibits nanoscale roughness that can become significant when depositing an ultrathin NiO_x layer. The conformal nature of ALD can therefore promote more uniform coverage of the ITO surface and reduce the formation of pinholes, helping to form a continuous NiO_x layer. This is important for the subsequent perovskite deposition, as incomplete coverage of the ITO could result in direct contact between the perovskite and ITO and potentially increase interfacial recombination or introduce shunting pathways.

However, there are also challenges and trade-offs to consider for material integration as device level. One issue is that ALD processes are relatively slow because they rely on sequential exposures and purging steps. This can limit throughput for large-scale manufacturing. Additionally, some ALD precursors or oxidants can chemically interact with the perovskite, causing degradation or altering its composition [35]. Another concern is that very thin HTLs may not provide sufficient conductivity, while thicker layers can introduce series resistance, so optimization of thickness is crucial[36]. To maintain a stable GPC, the reactor must operate within the ALD window, which is the specific temperature range where the precursors are reactive enough to bond, but not hot enough to decompose, as shown in Figure 2.10.

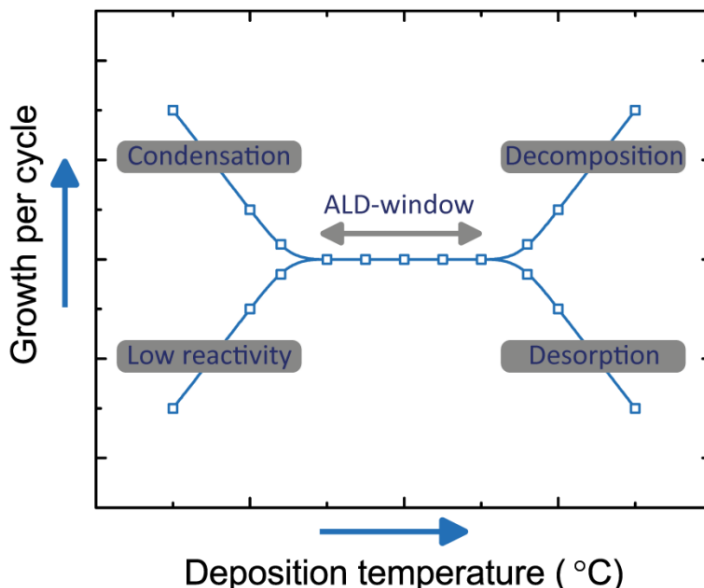


Figure 2.10: Growth per cycle as function of the deposition temperature to highlight the ALD window.

2.4. Post deposition treatment

Post-deposition treatments (PDTs) are commonly employed to modify the structural, chemical, and electronic properties of ALD-deposited NiO_x films after growth. The properties of an as-deposited NiO_x layer are determined not only by the ALD process conditions, but also by the precursor chemistry and the extent to which the deposited film has undergone ligand removal, oxidation, and crystallization. Depending on the deposition temperature and process chemistry, the as-deposited material can contain residual organic ligands, hydroxyl groups, carbon-containing species, structural disorder, and a non-stoichiometric ratio of nickel to oxygen. These characteristics can influence the density of defects and the concentration of charge carriers within the film and, consequently, its conductivity, work function, and energy-level alignment with the perovskite absorber.

A PDT can provide additional energy or chemical species to drive reactions that are kinetically limited during the ALD process, thereby allowing the film to evolve toward a more thermodynamically stable composition and structure. Thermal annealing is one of the most common approaches and can promote the removal of residual ligands and volatile species, densification of the film, structural relaxation, and, depending on the temperature and atmosphere, the formation or improvement of crystalline NiO_x [37]. Increasing the degree of crystallinity can reduce structural disorder and modify the density and nature of defects within the film, although excessive thermal treatment can also be detrimental if it promotes undesirable stoichiometric changes, interdiffusion, or degradation of the underlying substrate.

The oxygen chemical potential during the treatment is particularly important for NiO_x , since nickel oxide is frequently non-stoichiometric and can contain nickel vacancies and other defects that affect its electronic structure. Under suitable oxidizing conditions, the oxygen content and defect chemistry of the film can be modified, potentially increasing the concentration of nickel vacancies and associated Ni^{3+} species. These defects can contribute to p-type conductivity by introducing acceptor states, thereby increasing the hole concentration and shifting the Fermi level. At the same time, changes in the concentration of Ni^{2+} and Ni^{3+} species can alter the electronic structure, work function, and valence-band position of the material.

Consequently, a PDT can be used not only to improve the physical quality of the NiO_x film but also to tune its electronic properties to provide more favorable energetic alignment with the perovskite absorber. This is particularly important for NiO_x used as a hole transport layer, where efficient hole extraction requires suitable alignment between the NiO_x valence-band states and the valence band of the perovskite, while an appropriate conduction-band offset can help suppress electron transfer toward the HTL.

Surface chemistry is also modified during post-deposition treatment. Removal of surface contaminants or residual precursor fragments can change the surface energy, wettability, and density of surface states, which can subsequently influence the nucleation and growth of the perovskite deposited on top of the NiO_x . This is significant because the NiO_x /perovskite interface is a major source of non-radiative recombination in perovskite solar cells. Surface defects and unfavorable chemical species can act as trap states, capturing photo-generated carriers and increasing recombination losses, whereas an appropriately treated NiO_x surface can reduce defect-mediated recombination and facilitate more efficient hole extraction.

Post-deposition treatments can therefore influence device performance through several interconnected mechanisms: modification of the film's composition and crystallinity, removal of residual impurities, control of defect chemistry, alteration of carrier concentration and conductivity, adjustment of the work function and energy-level alignment, and modification of the surface properties governing perovskite growth. However, these effects are strongly dependent on the treatment conditions, including temperature, duration, atmosphere, oxygen partial pressure, and heating rate. There is therefore a trade-off between insufficient treatment, which may leave residual precursor species and defects in the film, and excessive treatment, which may cause undesirable changes to the NiO_x stoichiometry, morphology, or the underlying ITO substrate.

In the context of ALD NiO_x as an HTL, post-deposition treatment can consequently be viewed as an additional process parameter through which the material properties of the as-deposited film are tailored to achieve a favorable combination of conductivity, work function, surface quality, and interfacial compatibility with the perovskite absorber.

3

Experimental method

This chapter describes the experimental setups used for this research. Firstly, an introduction to atomic layer deposition (ALD) and the characteristics of ALD depositions. Secondly, a section for the deposition characterization techniques explaining how they function.

3.1. Sample preparation

The samples are all prepared and made inside a Class 10000 clean room at Else Kooi Laboratory (EKL) at TU Delft. Three main types of substrates were used for different purposes: polished silicon wafers, pre-made ITO-coated glass, and bare quartz. The polished bare silicon wafers were hand-cut into approximately 1.5×1.5 cm pieces from a 20 cm diameter circular wafer and were used to optimize the ALD process and establish the initial deposition recipe. The pre-made ITO-coated glass substrates were supplied in standard 2.5×2.5 cm pieces, while the bare quartz substrates were pre-cut to 2.5×1.0 cm. The ITO-coated glass substrates were used to investigate the performance of the deposited NiO_x films when integrated into a complete perovskite solar cell, while the bare quartz substrates were used to characterize the properties of the NiO_x films independently without interference from other device layers. For p-i-n stacked perovskite devices, the substrates were first cleaned in a sonicator for 15 minutes in acetone, followed by another 15 minutes in isopropyl alcohol (IPA). The samples were then blow-dried using a nitrogen gas gun and subjected to ozone treatment for 20 minutes at 100°C to remove the remaining contaminants and increase the surface oxygen concentration.

The substrates were then transferred into a nitrogen-filled glovebox containing the Picosun R200 ALD reactor, where they were loaded onto a 20-slot substrate holder, shown in Figure 3.1a, where each slot of the substrate holder accommodates a substrate of up to 2.5×2.5 cm. The substrate holder was subsequently inserted into the designated holder slot inside the ALD reactor (Figure 3.1b). The reactor lid was then lowered to seal the deposition chamber prior to the start of the ALD process. The process begins by evacuating the chamber while simultaneously heating the substrate and precursor to 150°C and 100°C , respectively. Once the substrate temperature stabilizes for 90 minutes, the deposition cycle begins. During the first half-cycle, the nickel precursor is transported into the chamber by a carrier gas and chemically binds to the substrate surface. This reaction is ideally self-limiting, occurring only at available reactive surface sites until saturation is reached. Any excess precursors and reaction by-products are removed by purging the chamber with inert nitrogen (N_2).



Figure 3.1: The (a) 20-slot substrate holder used to accommodate up to 20 substrates with dimensions of 2.5 x 2.5 cm and (b) the Picosun R200 ALD reactor with the lid open, with the red rectangle indicating the location where the substrate holder lays.

During the second half-cycle, water (H_2O) is introduced as the co-reactant. It reacts with the adsorbed precursor species to form the desired nickel oxide (NiO_x) while regenerating reactive surface sites for the next cycle. This reaction is also ideally self-limiting and terminates automatically once all available surface species have reacted. A second nitrogen purge removes the remaining reaction products, completing one ALD cycle. Repeating these cycles results in layer-by-layer film growth at a rate of less than one monolayer per cycle. This process is illustrated in Figure 3.2. After the desired number of cycles has been completed, the reactor is cooled to 30 °C before being returned to atmospheric pressure, allowing the chamber to be opened and the completed samples to be removed.

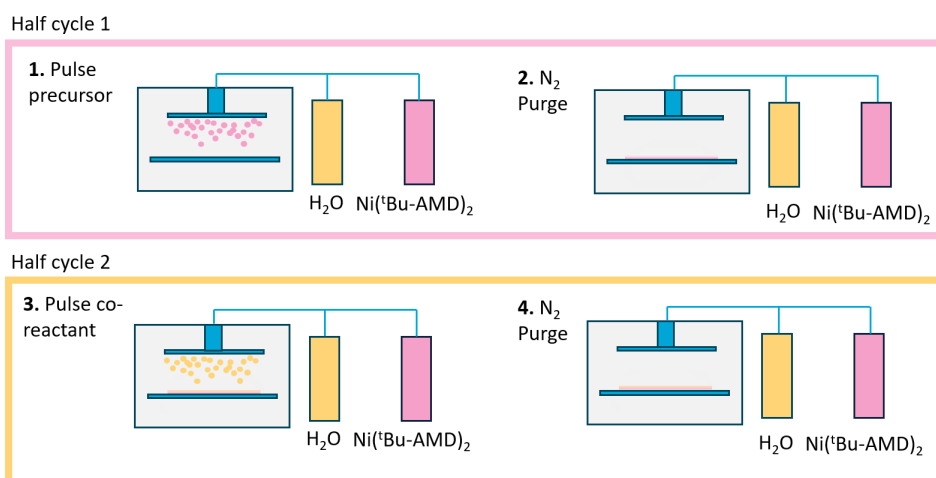


Figure 3.2: Schematic overview on how ALD functions describing the two half cycles. *Courtesy of Mare Dijkstra.*

3.1.1. Post deposition treatment

Four separate post-deposition treatments were performed to investigate their effect on the deposited NiO_x films:

1. Annealing at 300 °C for 15 minutes inside the nitrogen-filled glovebox.
2. Annealing at 300 °C for 15 minutes in air under a fume hood.
3. UV-ozone treatment for 20 minutes at 100 °C.
4. Thermal treatment under vacuum at 300 °C and for 15 minutes.

Annealing in the glovebox and under the fume hood was performed using two separate Cole-Parmer Stuart HP-400 hotplates, which were preheated to 300 °C prior to transferring the samples onto the hotplates. Following annealing, the samples were placed on a metal surface (aluminium block) and allowed to cool for 10 s before being transferred back into their sample boxes. The same procedure was followed for the UV-ozone treatment. The PCE-22 Desktop Ultraviolet (UV) Ozone Cleaner was switched on and allowed to preheat for 10 min at 100 °C prior to loading the samples into the treatment chamber. After the treatment, the samples were transferred back to their boxes. The sample boxes were subsequently returned to the nitrogen-filled glovebox containing the ALD reactor, where the samples were either stored for subsequent cell fabrication or removed for characterization using the various analytical techniques described in Section 3.2.

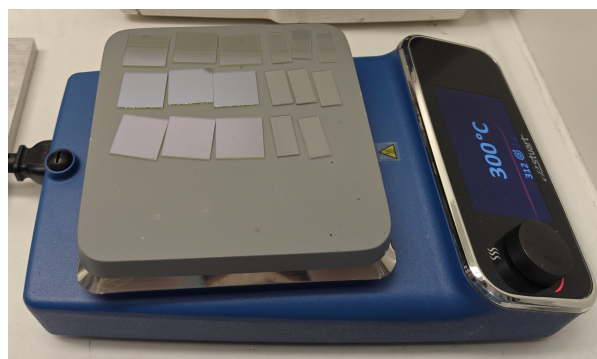


Figure 3.3: Picture of the Cole-Parmer Stuart HP-400 hotplate with NiO_x deposited onto ITO substrates and quartz annealing at 300 °C.

For annealing under vacuum, the Picosun R200 ALD reactor was preheated to approximately 375 °C, with all gas flows set to zero. A preheating temperature higher than the required annealing temperature of 300 °C was selected to compensate for heat loss during the unloading and loading of the substrate holder. The samples were then evacuated to a pressure of approximately 2 hPa, and the reactor temperature was set to 312 °C for the annealing step. This temperature was selected to compensate for the temperature offset observed during previous ALD deposition process optimization, ensuring that the actual sample temperature was closer to the intended annealing temperature of 300 °C. After 15 min of annealing, the reactor was returned to ambient pressure, after which the samples were removed and placed on a metallic surface for 10 s to cool. The samples were subsequently transferred to their respective sample boxes for either characterization or further processing.

3.1.2. Perovskite layer fabrication

The perovskite absorber layer is deposited by co-sequential vacuum evaporation using a PEROVap system (MBRAUN). The deposition process is divided into two sequential steps based on the different evaporation characteristics of the inorganic and organic precursors.

In the first step, PbI_2 and CsBr are co-sublimated, with the deposition of each inorganic precursor independently controlled through its respective source. For the standard deposition conditions, PbI_2 is deposited to a nominal thickness of 8900 Å at 2.2 Å s^{-1} , while CsBr is deposited to 1700 Å at 0.4 Å s^{-1} . The simultaneous deposition of these precursors enables controlled incorporation of the inorganic components into the perovskite layer.

Following the inorganic deposition, FAI is deposited in a separate step. Compared with the inorganic precursors, the deposition of the organic FAI component is less precisely controlled. A typical FAI deposition used in the investigated devices was approximately 9000 Å at a rate of 1.8 Å s^{-1} . The nominal FAI thickness is periodically adjusted as part of the deposition optimization; therefore, this parameter may vary between deposition runs.

This sequential approach allows the inorganic and organic precursor deposition to be controlled separately while enabling the formation of the mixed-cation perovskite absorber layer.

3.2. Characterization

A variation of characterization techniques was utilized to verify if the thermal ALD process successfully created an optimal NiO_x layer. For example, checking if the layer is the correct thickness, or composes of the correct elements, and many more. The fundamental principles underlying these characterization techniques are discussed in the following sections.

3.2.1. Spectroscopic ellipsometry

Spectroscopic ellipsometry (SE) measures the change in the polarization state of light upon reflection from a planar surface to determine the physical properties of thin-film stacks. The fundamental measurement revolves around the complex reflectance ratio ρ , which defines the transformation of the electric field vector.

The incident light is decomposed into two orthogonal components, namely the p -polarized component, which is parallel to the plane of incidence and the s -polarized component, which is perpendicular to the plane of incidence. Upon reflection, the electric field amplitudes E are modified by the complex Fresnel reflection coefficients r_p and r_s . These coefficients account for both the attenuation of amplitude and the shift in phase. The relationship is expressed via the fundamental equation of ellipsometry:

$$\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta} \quad (3.1)$$

Where Ψ represents the angle whose tangent is the ratio of the magnitude of the reflection coefficients, while Δ represents the phase difference between the p and s waves: $\Delta = \delta_p - \delta_s$, visualized in Figure 3.4.

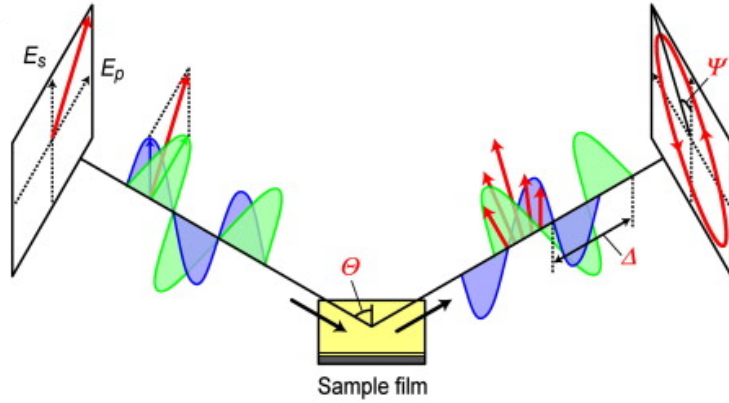


Figure 3.4: Schematic representation of the spectroscopic ellipsometry displaying the change in phase δ and angle ψ [38].

For a single interface between two semi-infinite media (ambient and substrate), the Fresnel coefficients are governed by the angle of incidence θ_i and the complex refractive indices $\tilde{n} = n + ik$, which describes electromagnetic radiation's interaction with materials. The coefficients are calculated as:

$$r_p = \frac{\tilde{n}_1 \cos \theta_i - \tilde{n}_0 \cos \theta_t}{\tilde{n}_1 \cos \theta_i + \tilde{n}_0 \cos \theta_t} \quad (3.2)$$

$$r_s = \frac{\tilde{n}_0 \cos \theta_i - \tilde{n}_1 \cos \theta_t}{\tilde{n}_0 \cos \theta_i + \tilde{n}_1 \cos \theta_t} \quad (3.3)$$

When light hits a thin film, it will bounce back and forth between the top surface and the bottom interface. To account for this, the total reflection coefficients r_p and r_s are used, which combines the contribution of all internal bounces of reflected waves. This requires the phase shift β , which represents the optical phase difference accumulated by the light as it propagates through a film of thickness d :

$$\beta = 2\pi \left(\frac{d}{\lambda} \right) \tilde{n}_1 \cos \theta_t \quad (3.4)$$

Because the thickness d or the material properties (n and k) cannot be measure directly, a "best-fit" strategy using regression analysis is used. First, the experimental Ψ and Δ values are measured across many wavelengths. Then, a dispersion mathematical model that guesses the film's properties is built. The experimental

data is then compared against the model using a Levenberg-Marquardt algorithm to minimize the Mean Squared Error (MSE):

$$MSE = \sqrt{\frac{1}{2N - M} \sum_{i=1}^N \left[(\Psi_i^{exp} - \Psi_i^{mod})^2 + (\Delta_i^{exp} - \Delta_i^{mod})^2 \right]} \quad (3.5)$$

where N is the number of (Ψ, Δ) pairs and M is the number of fit parameters. The sensitivity of Δ to phase makes this technique capable of resolving film thicknesses with a precision of 0.01 nm.

In this sense it is shown that ellipsometry technique is an indirect measuring method that relies on an accurate model to infer desired parameters from. There are also a few restrictions where the surface of the sample can not be too rough which can cause the light to fully experience diffuse scattering and thus lose the phase relationship δ . But also that the film is not too absorbent causing the light to not be able to reach the interface. For this experiment an SE system from J.A. Woollam Co. was utilized to measure film layer properties.

3.2.2. Ultraviolet-Visible spectroscopy

Ultraviolet-Visible (UV-Vis) spectroscopy is a technique used to characterize a material's optical properties, including its absorbance (A), reflectance (R), and transmission (T). This is done by measuring the light absorption of the sample across the ultraviolet and visible ranges of the electromagnetic spectrum. The sample can absorb photons and move electrons from a lower-energy electronic state to a higher-energy one when exposed, where the energy of the photon is described in Equation 3.6.

$$E = \frac{h \cdot c}{\lambda} \quad (3.6)$$

Where h is Planck's constant (6.626×10^{-34} J·s), c is the speed of light (2.998×10^8 m/s), and λ is the wavelength of the light. The quantitative utility of UV-Vis is governed by the Beer-Lambert Law, which establishes a linear relationship between absorbance and the properties of the material.

$$I = I_0 e^{-\alpha b} \quad (3.7)$$

Where (I) is the incident light intensity, (I_0) the amount of light transmitted through the sample, α the material absorption coefficient and b the thickness of the layer. Absorption only occurs when the photon's energy matches the energy difference between the incident light energy and the transmitted light energy. The machine records this as Absorbance (A), which is the base-10 logarithm of the inverse of Transmittance (T):

$$A = \log_{10} \left(\frac{I_0}{I} \right) = -\log_{10}(T) \quad (3.8)$$

The light that falls on the sample can either be absorbed, reflected or transmitted. Based on the assumption that all these components together should be equal to the original intensity of the initial beam. As such this relation is shown in Equation 3.9.

$$A + T + R = 1 \quad (3.9)$$

3.2.3. Atomic force microscopy

Atomic Force Microscopy (AFM) is a high-resolution scanning probe microscopy technique that is used to obtain high-resolution three-dimensional images of a material's surface at nanoscale. AFM measurements provide information about surface features such as topography, roughness, and structural variations by measuring the interaction between a sharp probe and the sample surface. A schematic representation of an AFM system is shown in Figure 3.5. An AFM system operates on the basis that a sharp tip mounted on the end of a flexible cantilever is scanned across the sample surface. As the tip moves over regions with different heights or surface features, interactions between the tip and the sample cause the cantilever to deflect. These changes are detected using a laser beam reflected from the back of the cantilever onto a position-sensitive photodiode. The recorded cantilever movement is converted into surface height information, allowing the reconstruction of a three-dimensional topographical map of the sample[39].

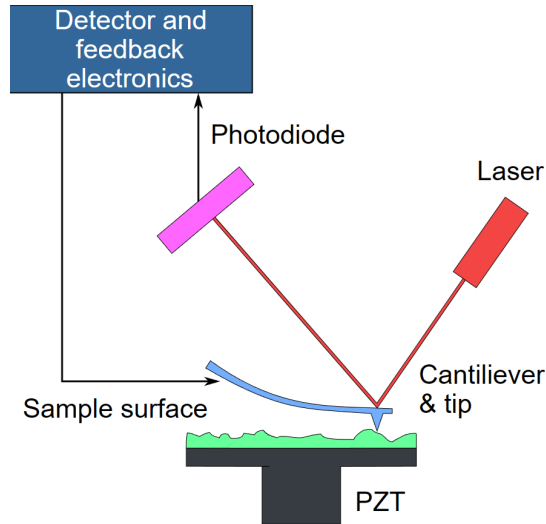


Figure 3.5: Schematic representation of an AFM system [40].

There are various ways to measure using AFM, but for this research tapping mode AFM is utilized. In this mode the cantilever is oscillated near its resonance frequency while the tip intermittently contacts the sample surface. During scanning, variations in the surface structure modify the interaction between the tip and the sample, resulting in changes in the oscillation amplitude of the cantilever[41], shown in Figure 3.6. A feedback system continuously adjusts the vertical position of the scanner to maintain a constant oscillation amplitude. The required adjustments are recorded and used to generate the surface topography image. Tapping-mode AFM enables the characterization of nanoscale surface morphology while reducing the mechanical influence of the probe on the sample[39][41]. In this research an AFM-Raman by Horiba in tap mode with PPP-NCHR cantilevers by NANOSENSORS was utilized to acquire AFM roughness images.

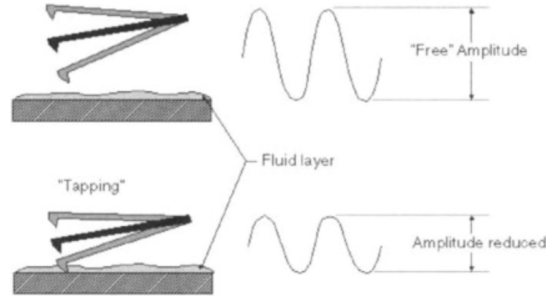


Figure 3.6: Schematic representation of an AFM frequency change when in tapping mode [41].

3.2.4. X-ray photoelectron spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a widely used characterization technique to investigate the elemental composition, oxidation states, and chemical bonding states of materials. XPS is a surface analytical technique based on the photoelectric effect, where a material is irradiated with monochromatic X-rays, causing the emission of photoelectrons from atoms within the sample. The kinetic energy of these emitted electrons is measured, and the corresponding binding energy of the electrons is calculated according to the relationship:

$$E_B = E_{ph} - E_K - \phi \quad (3.10)$$

Where (E_B) is the electron binding energy, (E_{ph}) is the energy of the incident X-ray photon, (E_K) is the measured kinetic energy of the emitted electron, and (ϕ) represents the spectrometer work function. XPS provides information about both elemental identity and chemical state because the binding energy of the core-level electrons is characteristic of each element and is influenced by the chemical environment of the atom.

In a typical XPS measurement, the sample surface is placed under ultra-high vacuum conditions to minimize interference from gas-phase molecules and contaminants, shown in Figure 3.7. An X-ray source, commonly

using Al $K\alpha$ radiation (1486.6 eV) or Mg $K\alpha$ radiation (1253.6 eV), is directed onto the sample surface. The emitted photoelectrons are collected by an electron energy analyzer, which separates electrons according to their kinetic energies. The resulting spectrum consists of photoelectron intensity as a function of binding energy, where characteristic peaks correspond to specific elements present within the analyzed region.

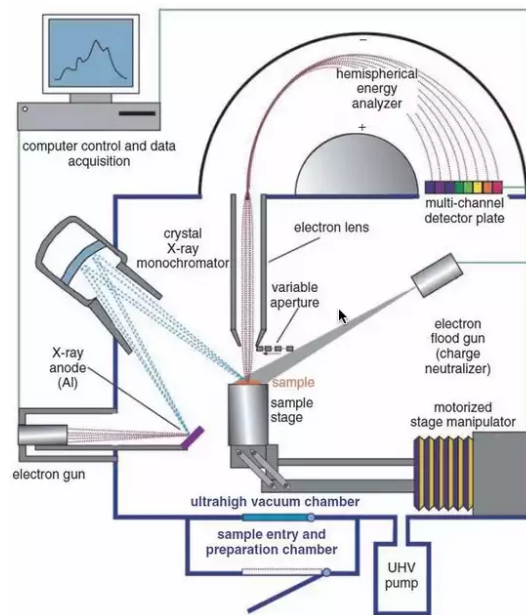


Figure 3.7: Schematic representation of an XPS instrument [42].

3.2.5. Kelvin probe

The Kelvin probe (KP) is a non-contact technique used to determine the work-function difference between a sample and a reference electrode. The technique is based on the vibrating capacitor principle and enables the measurement of the contact potential difference (CPD) without establishing direct electrical contact with the sample. This characteristic makes the Kelvin probe particularly suitable for investigating the electronic properties of conductive materials, semiconductors, thin films, and surfaces under controlled environmental conditions. The work function, Φ , is defined as the minimum energy required to remove an electron from the Fermi level of a material to the vacuum level:

$$\Phi = E_{\text{vac}} - E_F$$

where E_{vac} is the vacuum energy level and E_F is the Fermi energy. When two materials with different work functions are electrically connected, electrons flow from the material with the lower work function toward the material with the higher work function until their Fermi levels become equilibrated. This redistribution of charge produces an electrical potential difference between the two materials, referred to as the contact potential difference.

In a Kelvin probe system, a conducting reference tip is positioned at a small distance from the sample, forming a capacitor with the sample. The capacitance of this arrangement can be approximated as

$$C = \frac{\epsilon A}{d}$$

where ϵ is the permittivity of the medium between the tip and sample, A is the effective electrode area, and d is the tip-to-sample separation. The reference tip is mechanically vibrated relative to the sample. Consequently, the tip-to-sample distance varies periodically, resulting in a time-dependent capacitance. If a contact potential difference exists between the tip and sample, the periodic variation of capacitance generates an alternating electrical signal. The magnitude and phase of this signal depend on the potential difference between the two electrodes.

An external bias voltage can therefore be used to compensate for the contact potential difference. In the conventional null method, the applied bias is adjusted until the alternating component of the measured signal is zero. Under this condition, the applied potential corresponds to the contact potential difference, subject to the sign convention used by the instrument. The relationship between the contact potential difference (CPD) and the work functions of the Kelvin probe tip and sample can generally be expressed as

$$\Phi_{\text{sample}} = \Phi_{\text{tip}} + eV_{\text{CPD}}.$$

where Φ_{sample} is the work function of the sample, Φ_{tip} is the work function of the KP tip, e is the elementary charge, and V_{CPD} is the measured contact potential difference.

Since the Kelvin probe measures a difference in work function rather than an absolute work function, the work function of the probe tip must first be determined through calibration. This can be achieved by measuring a reference material with a well-established work function, such as a clean gold (Au) surface. If the known work function of the gold reference is denoted by Φ_{Au} , and the CPD measured between the Kelvin probe tip and the gold reference is $V_{\text{CPD,Au}}$, the work function of the Kelvin probe tip can be determined from

$$\Phi_{\text{tip}} = \Phi_{\text{Au}} - eV_{\text{CPD,Au}}.$$

Here, the sign follows the CPD convention defined by the measurement system. Once the tip work function has been calibrated, the same tip can be used to determine the work function of the experimental samples. For an experimental sample with a measured CPD of $V_{\text{CPD,sample}}$, its work function can therefore be calculated as

$$\Phi_{\text{sample}} = \Phi_{\text{tip}} + eV_{\text{CPD,sample}}.$$

Thus, the measurement procedure consists of first determining the work function of the Kelvin probe tip using a reference material with a known work function, followed by measurement of the CPD of the experimental samples. The calibrated tip work function can then be used to convert the measured CPD values into the corresponding absolute work functions of the samples. It is important that the calibration and sample measurements are performed under the same experimental conditions, as changes in the tip surface condition, contamination, or measurement environment can alter the effective tip work function. Furthermore, the CPD sign convention used by the specific Kelvin probe system must be maintained consistently throughout the calibration and subsequent sample measurements.

UHV Kelvin probe measurement using KP Technology

The fundamental operating principle described above is also applicable to the ultra-high-vacuum (UHV) Kelvin probe systems manufactured by KP Technology which is used in this research. In these systems, the vibrating reference electrode and sample form a non-contact capacitor, while the measurement is performed under UHV conditions. The UHV environment significantly reduces the influence of atmospheric contaminants, adsorbed water, oxygen, and other surface species that can modify the measured work function.

KP Technology UHV Kelvin probe systems additionally employ an off-null detection approach together with automatic control of the tip-to-sample separation. Rather than relying solely on a conventional zero-signal condition, the electrical response produced by the vibrating probe is analyzed to determine the surface potential while maintaining a controlled probe height. This approach helps reduce the influence of parasitic capacitance and electrical noise and improves the stability and reproducibility of the measurement.

3.2.6. Solar simulator

A solar simulator is a laboratory light source designed to reproduce the spectral distribution, intensity, and spatial uniformity of natural sunlight under controlled conditions. It enables accurate and repeatable testing of solar cells and photovoltaic (PV) devices without relying on changing outdoor weather conditions. Solar simulators are widely used to evaluate the electrical performance, efficiency, and reliability of photovoltaic devices.

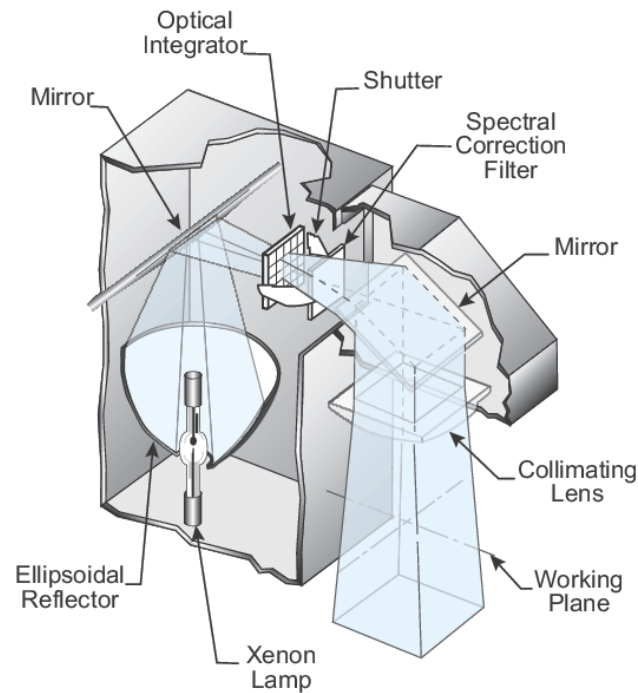


Figure 3.8: Schematic representation of the light path of a solar simulator [43].

The primary purpose of a solar simulator is to provide illumination that closely matches the standard solar spectrum defined by the International Electrotechnical Commission (IEC 60904-9) and ASTM standards. Most photovoltaic measurements are performed under Standard Test Conditions (STC), which specify an irradiance of 1000 W m^{-2} , an air mass of AM1.5G, and a cell temperature of 25°C . By reproducing these conditions, the measured performance can be directly compared with results reported in the literature and by manufacturers.

A typical solar simulator consists of several key components:

- **Light Source:** High-intensity xenon arc lamps, metal-halide lamps, tungsten-halogen lamps, or arrays of high-power LEDs are commonly used. Xenon lamps provide a spectrum that closely resembles natural sunlight, while LED-based simulators offer improved spectral control, longer operating life, and lower maintenance.
- **Optical System:** Mirrors, lenses, diffusers, and optical filters are used to shape the light beam, improve spatial uniformity, and match the desired solar spectrum.
- **Power Supply and Control Unit:** These components maintain stable lamp operation and regulate the irradiance level throughout the measurement.
- **Sample Stage:** The solar cell is positioned on a temperature-controlled platform to ensure accurate testing under specified thermal conditions.
- **Measurement System:** Electronic instruments such as a Source Measure Unit (SMU) or an electronic load record the current-voltage (I-V) characteristics of the solar cell during illumination.

The performance of a solar simulator is evaluated based on three major characteristics:

1. **Spectral Match:** The emitted spectrum should closely resemble the AM1.5G reference solar spectrum.
2. **Spatial Uniformity:** The irradiance should be nearly uniform across the illuminated test area, ensuring that the entire solar cell receives consistent illumination.
3. **Temporal Stability:** The light intensity should remain constant throughout the measurement period to minimize experimental errors.

Based on these parameters, IEC 60904-9 classifies solar simulators into different performance classes, such as AAA, ABA, and BBB. A Class AAA solar simulator provides the highest accuracy in spectral match, spatial uniformity, and temporal stability, making it the preferred choice for high-precision photovoltaic characterization. During photovoltaic characterization, the solar simulator illuminates the device under test while the current–voltage (I–V) characteristics are measured. From the resulting I–V curve, important photovoltaic parameters can be extracted, including the open-circuit voltage (V_{OC}), short-circuit current (I_{SC}), maximum power (P_{max}), fill factor (FF), and power conversion efficiency (PCE). These parameters provide a comprehensive evaluation of the solar cell's performance and facilitate comparisons between different materials, fabrication methods, and device architectures.

4

Results

This chapter presents the experimental results obtained throughout this research. The observed findings are reported and summarized, while their interpretation and discussion are reserved for Chapter 5. First, the optimization of the ALD process with respect to film homogeneity is presented, followed by the effects of post-deposition treatments, and finally, the device performance results.

4.1. ALD process optimization

Atomic layer deposition (ALD) is a cyclic deposition technique in which the precursor and co-reactant are introduced sequentially, enabling controlled and conformal film growth through self-limiting surface reactions. In this work, the ALD process was optimized by systematically varying the precursor and co-reactant pulse times to identify suitable deposition conditions for obtaining uniform NiO_x layers. A more detailed piece of how ALD functions is shown in Section 2.3. Establishing an appropriate ALD recipe is crucial, as insufficient exposure to precursor or co-reactant may prevent the surface reactions from reaching saturation across the entire substrate. Consequently, spatial variations in growth per cycle (GPC) can occur, leading to non-uniform film thickness and, in some cases, variations in film composition. Optimizing the pulse durations is therefore essential to achieve self-limiting ALD growth and ensure homogeneous film deposition.

Thickness and uniformity from recipe optimization

The ALD process was optimized by determining the minimum precursor and co-reactant pulse durations required to achieve saturated film growth. To straightforwardly evaluate the thickness of the film using spectroscopic ellipsometry (SE), NiO_x films were deposited onto approximately 1.5×1.5 cm silicon substrates. Pulse saturation experiments were performed by varying one pulse parameter at a time while keeping all other deposition conditions constant. The resulting GPC values were used to identify the onset of self-limiting surface reactions and to establish the deposition recipe used throughout the remainder of this work.

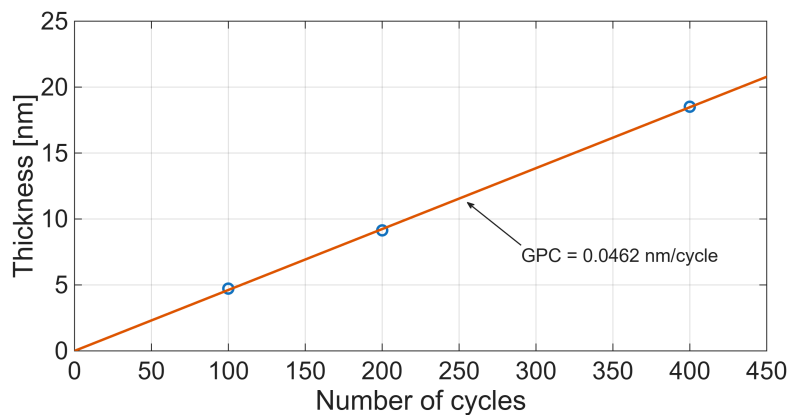


Figure 4.1: Film thickness as a function of the number of ALD cycles for the NiO_x deposition process using a 4.0 s Ni precursor pulse and a 0.1 s H_2O pulse. The thickness at each data point represents an average of approximately 18 samples. The solid red line represents a linear fit to the experimental data (blue markers). The slope of the linear fit corresponds to the growth per cycle (GPC).

To determine the GPC of the NiO_x ALD process, a series of depositions was carried out using different numbers of ALD cycles while maintaining deposition conditions constant. The resulting film thicknesses were measured after deposition and are plotted in Figure 4.1.

A linear relationship between film thickness and the number of ALD cycles was observed over the investigated range, indicating stable and reproducible film growth. A minimal deviation from linearity was detected, suggesting the absence of significant nucleation delays or growth inhibition under the selected deposition conditions.

The GPC was determined from the slope of the linear fit according to

$$GPC = \frac{\Delta \text{Thickness}}{\Delta \text{Cycles}}. \quad (4.1)$$

As for the batch parameters shown in Figure 4.1, the fitted slope corresponds to a GPC of 0.0460 nm/cycle, which was used as the reference growth rate for the subsequent pulse saturation experiments. The strong linear correlation confirms the repeatability and stability of the ALD process under the chosen deposition conditions.

The GPC value of 0.0460 nm/cycle serves as one data point in the pulse saturation study, where the GPC was determined for multiple precursor and co-reactant pulse durations. Under saturated ALD conditions, increasing the pulse duration beyond the saturation threshold should not result in a significant increase in GPC. Consequently, comparing the GPC values obtained for different recipes enables the identification of the minimum pulse durations required to achieve self-limiting growth. Figure 4.2 shows this phenomenon where the GPC curve experiences very minimal gain despite increasing the pulse durations for the Ni precursor or H_2O co-reactant.

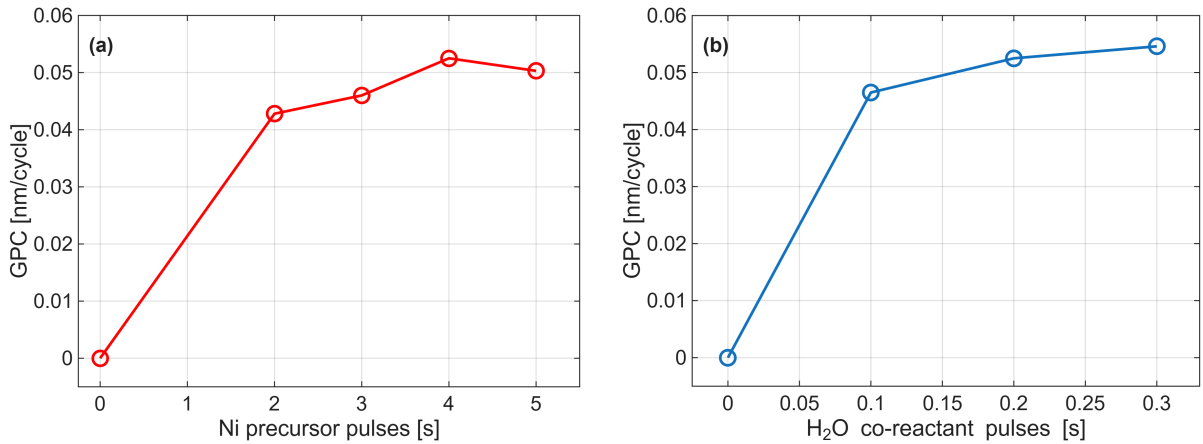


Figure 4.2: GPC as function of (a) Ni and (b) H_2O co-reactant pulses. The value corresponding to for example the H_2O pulse = 0.1 seconds is obtained from Figure 4.1

During the GPC experiments, it was apparent that the deposited NiO_x layer exhibited significant sample-to-sample thickness variation across the substrate holder. For deposition recipes that employ short pulse durations for the Ni precursor or H_2O co-reactant, a systematic thickness gradient was observed, with lower film thicknesses toward the top of the sample holder. This effect can be seen in Figure 4.3a where the Ni precursor pulse duration was reduced to 2.0 seconds. Increasing the pulse duration reduced this variation, resulting in more homogeneous film thicknesses across the samples, as shown in the heat map in Figure 4.3b.

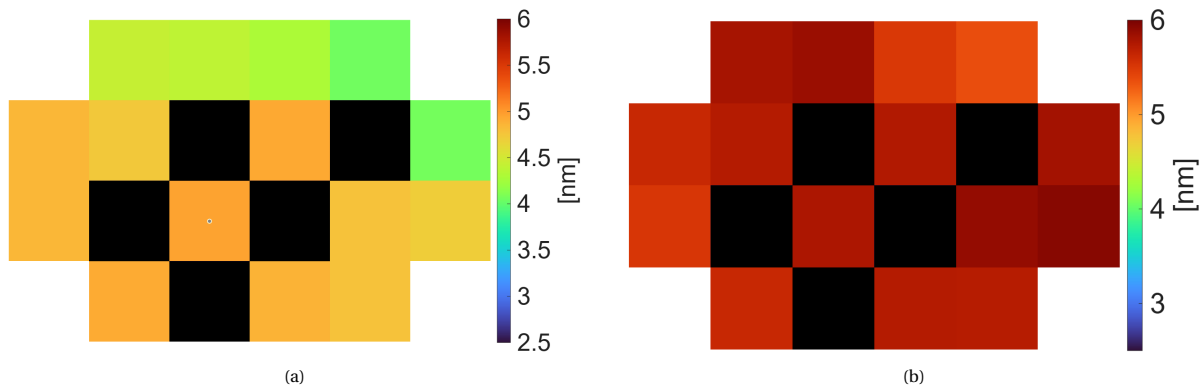


Figure 4.3: A heatmap showing the thickness of 15 samples across the holder area for a process consisting of 100 cycles for a NiO_x co-reactant puls of a) of 2.0 seconds and b) 5.0 seconds (black squares indicate that no sample is placed in that position).

The thickness distributions obtained for the different deposition recipes were compared using box plots. The spread of the measured thickness values provides a direct indication of film uniformity: a narrower distribution corresponds to more consistent thickness across the substrate holder. As shown in Figure 4.4, increasing the duration of the Ni precursor pulse generally reduced the variation in film thickness, indicating improved deposition uniformity. With the pulse combination of 2.0 s Ni precursor, the measured thickness distribution corresponded to a 1σ non-uniformity of 6.63%. In contrast, using 3.0 s or 5.0 s Ni precursor resulted in a substantially more homogeneous thickness distribution, with the 1σ non-uniformity decreasing to 1.72% and 2.77% respectively. An exception was observed for the deposition performed with a Ni pulse duration of 4.0 seconds, which exhibited a larger thickness spread with a 1σ non-uniformity of 16.50%.

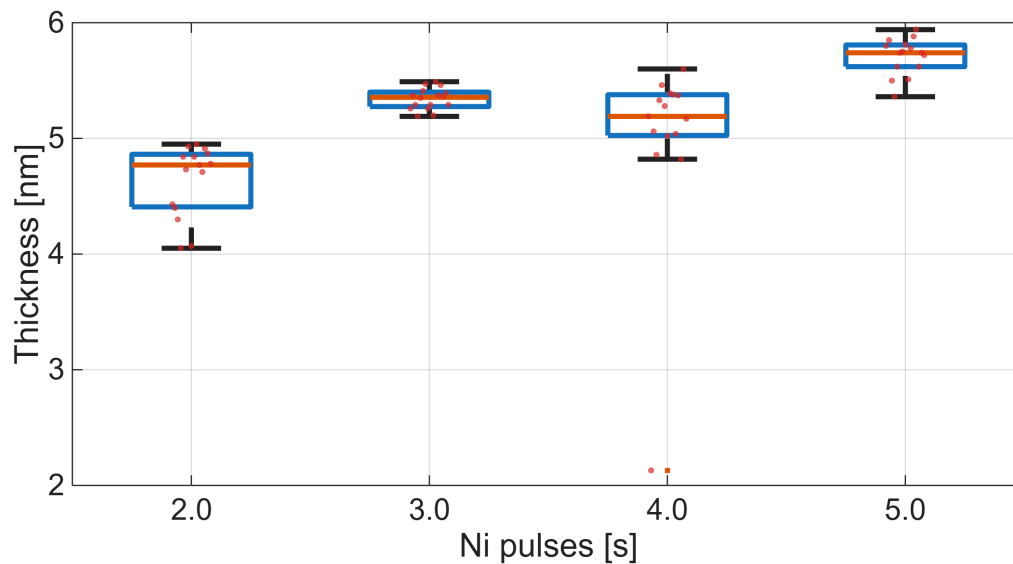


Figure 4.4: Thickness distributions measured by SE for 15 samples prepared using four different Ni pulse times at 100 ALD cycles. Box plots show the spread of the measured film thicknesses for each deposition recipe, with individual measurements overlaid in red.

The same methodology was applied to the co-reactant pulses (H_2O). The result in Figure 4.5 shows that increasing the pulse time can have an effect on the thickness spread across the substrate holder. Just like the Ni precursor pulses, the spread does narrow with increasing pulse time

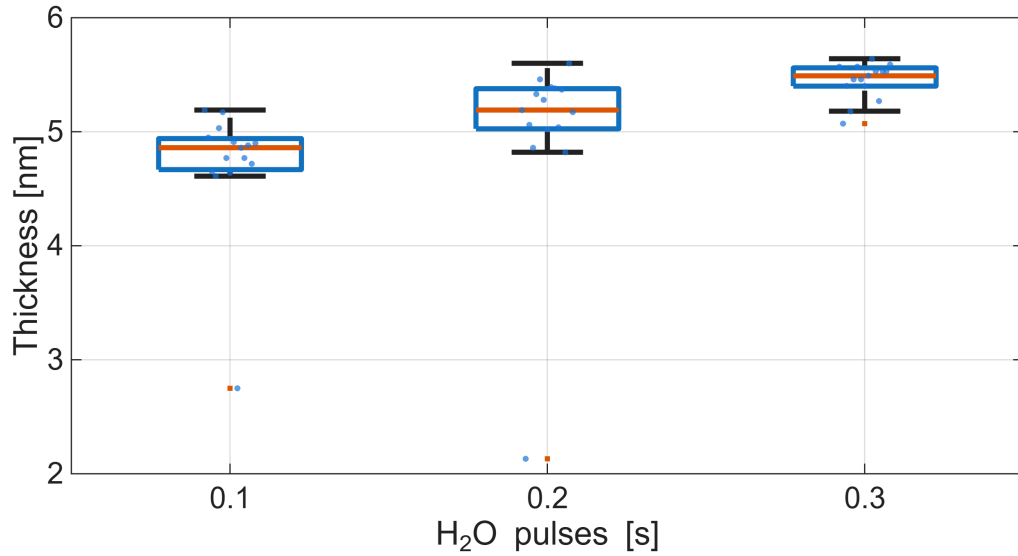


Figure 4.5: Thickness distributions measured by SE for 15 samples prepared using three different H₂O pulse times at 100 ALD cycles. Box plots show the spread of the measured film thicknesses for each deposition recipe, with individual measurements overlaid in blue.

In some batches, a small number of samples exhibited localized surface defects, characterized by a raised, spot-like feature accompanied by slight discoloration of the surrounding area. An example of this is shown in Figure 4.6. These samples were generally associated with lower deposition thicknesses than expected. It is hypothesized that these defects may originate from particles generated during the cutting of the silicon wafer. Small silicon fragments produced during an imperfect or rough cut may become deposited onto the wafer surface and subsequently interfere with the deposition process, resulting in a localized reduction in film thickness.

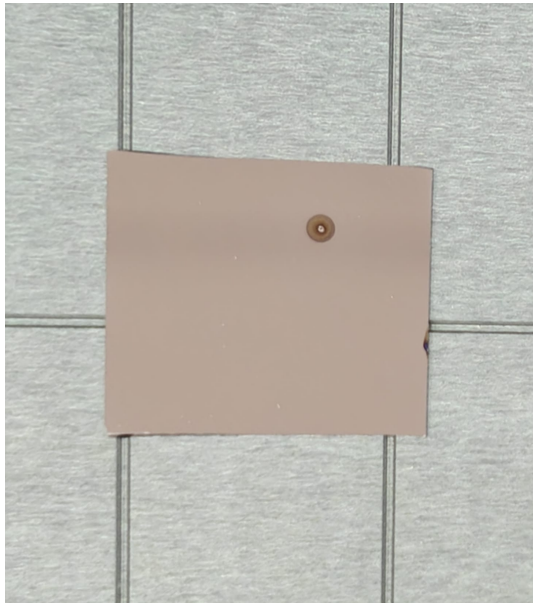


Figure 4.6: Photograph of the silicon wafer showing a visible particle at the measurement location, which is suspected to have caused the lower-than-expected film thickness measured by SE.

Surface morphology and roughness

To further investigate the effect of NiO_x deposition on the surface morphology of the substrate, atomic force microscopy (AFM) measurements were performed. AFM provides information on the surface topography and allows changes in the surface morphology and apparent conformity of the deposited layer to be evaluated as a function of film thickness. Figure 4.7 presents the AFM images for three different samples: bare silicon, a 10

nm NiO_x layer, and a 20 nm NiO_x layer. The comparison allows the evolution of the surface topography and roughness to be evaluated with increasing NiO_x thickness.

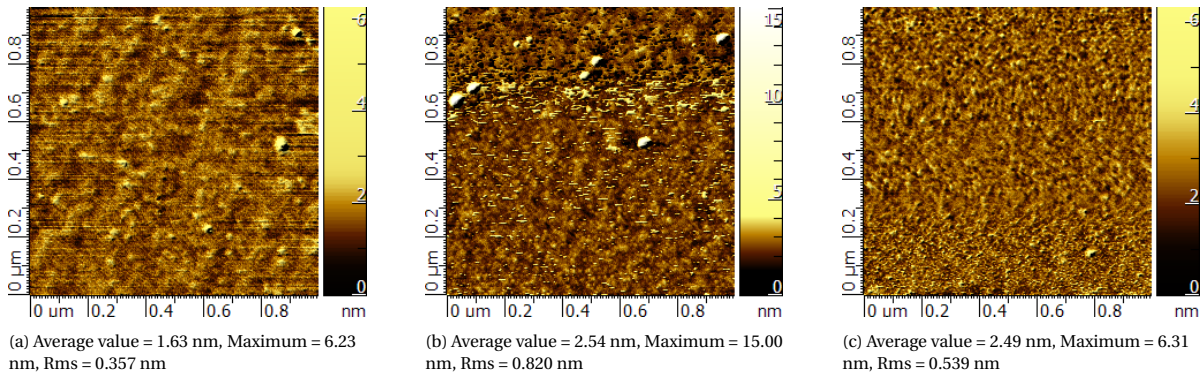


Figure 4.7: AFM topography images showing the surface morphology of (a) bare silicon wafer, (b) silicon wafer with a 10 nm NiO_x layer, and (c) silicon wafer with a 20 nm NiO_x layer.

From Figure 4.7 it can be seen the surface morphology of the bare silicon substrate and silicon substrates coated with 10 nm and 20 nm NiO_x layers. The deposition of the 10 nm NiO_x layer results in an increase in surface roughness, as indicated by the higher root-mean-square (RMS) roughness compared with the bare silicon substrate. Although the 20 nm NiO_x layer also exhibits a higher RMS roughness than the bare silicon substrate, its measured roughness is lower than that of the 10 nm sample. This apparent reduction in roughness may be attributed to the presence of surface particles in the 10 nm sample shown by the white spots, which can influence the AFM measurement and affect the calculated RMS value.

To investigate the NiO_x films in a device-relevant configuration, NiO_x was deposited onto indium tin oxide (ITO) substrates. Figure 4.8 compares the AFM topography of bare ITO with ITO coated with 10 nm and 20 nm of NiO_x . Comparing these surfaces provides insight into how the NiO_x deposition affects the underlying ITO morphology and the resulting surface characteristics.

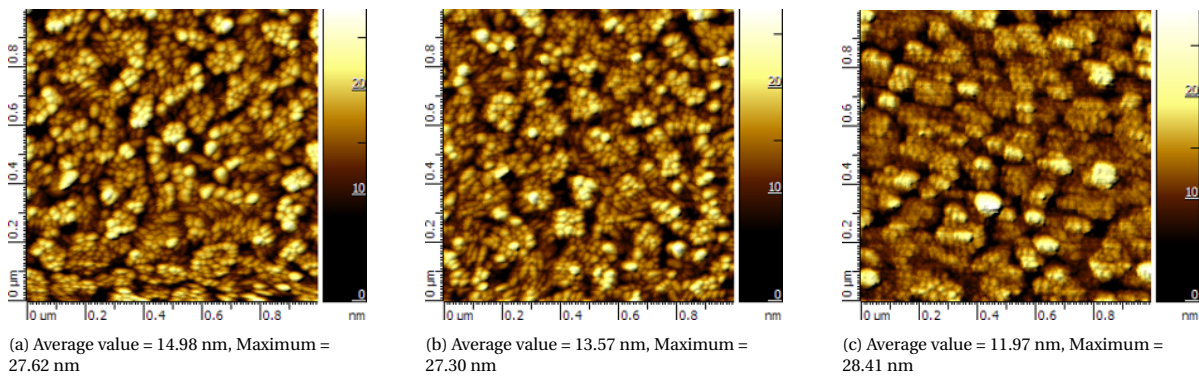


Figure 4.8: AFM topography images showing the surface morphology of (a) bare ITO, (b) ITO with a 10 nm NiO_x layer, and (c) ITO with a 20 nm NiO_x layer.

The AFM images show that the characteristic rough morphology of the underlying ITO substrate remains visible after NiO_x deposition for both film thicknesses, indicating that the deposited layer closely follows the existing surface topography. In particular, the NiO_x appears to conform well to the ITO morphology, including the valleys and depressions between surface features, rather than forming a completely planar overlayer. A slight reduction in the apparent surface roughness can be observed with increasing NiO_x thickness from 10 to 20 nm, suggesting that the thicker layer provides somewhat greater smoothing of the underlying ITO surface. Nevertheless, the conformal NiO_x coating observed on the ITO surface is consistent with the high conformality characteristic of ALD, indicating that the deposition proceeds under conditions consistent with the ALD regime.

4.1.1. Material characterization

To further evaluate the deposited NiO_x layers, complementary material characterization techniques were employed to assess both their chemical composition and optical properties. X-ray photoelectron spectroscopy (XPS) was used to investigate the surface chemical composition, providing insight into the chemical nature and stoichiometry of the deposited film. UV-Vis spectroscopy was used to characterize the optical transmission and absorption behaviour of the layers, which is particularly relevant for NiO_x films used in optoelectronic devices where high optical transparency is desirable. Together, these techniques provide a more comprehensive assessment of the deposited NiO_x layers, complementing the morphological characterization obtained from AFM and helping to determine how the deposition conditions influence the properties of the resulting material.

Chemical composition

The stoichiometry of NiO_x plays an important role in determining its electrical properties, as deviations from the standard nominal 1:1 Ni:O ratio can introduce desirable defects and alter the concentration of charge carriers within the film. In particular, the relative contributions of Ni^{2+} and Ni^{3+} provide an indication of the oxidation state and defect chemistry of the NiO_x layer, with a higher Ni^{3+} contribution generally associated with an increased concentration of nickel vacancies and, consequently, enhanced p-type conductivity. These chemical states can be investigated from the Ni 2p XPS spectrum through the characteristic contributions associated with Ni^{2+} and Ni^{3+} . Complementary information can also be obtained from the O 1s spectrum, where different oxygen environments can be distinguished and related to the stoichiometry and defect structure of the film. Therefore, analysis of both the Ni 2p and O 1s spectra provides insight into how the H_2O deposition conditions influence the stoichiometry, defect chemistry, and expected electrical properties of the NiO_x layers. All XPS spectra are corrected with respect to C-C peak with binding energy at 284.8 eV. The deconvolution of Ni 2p core and O 1s level spectra was fitted by the peaks, as suggested in the existing literature [44] [45]. For NiO, the Ni 2p component at 854 eV was attributed to Ni^{2+} , characteristic of the octahedral Ni-O bonding configuration in cubic NiO. The peak centered at 856 eV was assigned to Ni^{3+} ions associated with Ni vacancies, while the feature at 867 eV and higher corresponds to the Ni 2p shake-up satellites. The O 1s spectrum was similarly fitted where the peak centered at 529 eV, designated as O^{2-} , was attributed to the octahedral Ni-O bonding configuration. The peak at 532 eV, designated as OH, was assigned to bonding between Ni^{3+} and O^{2-} . These spectra for the different H_2O pulse times are shown in Figure 4.9.

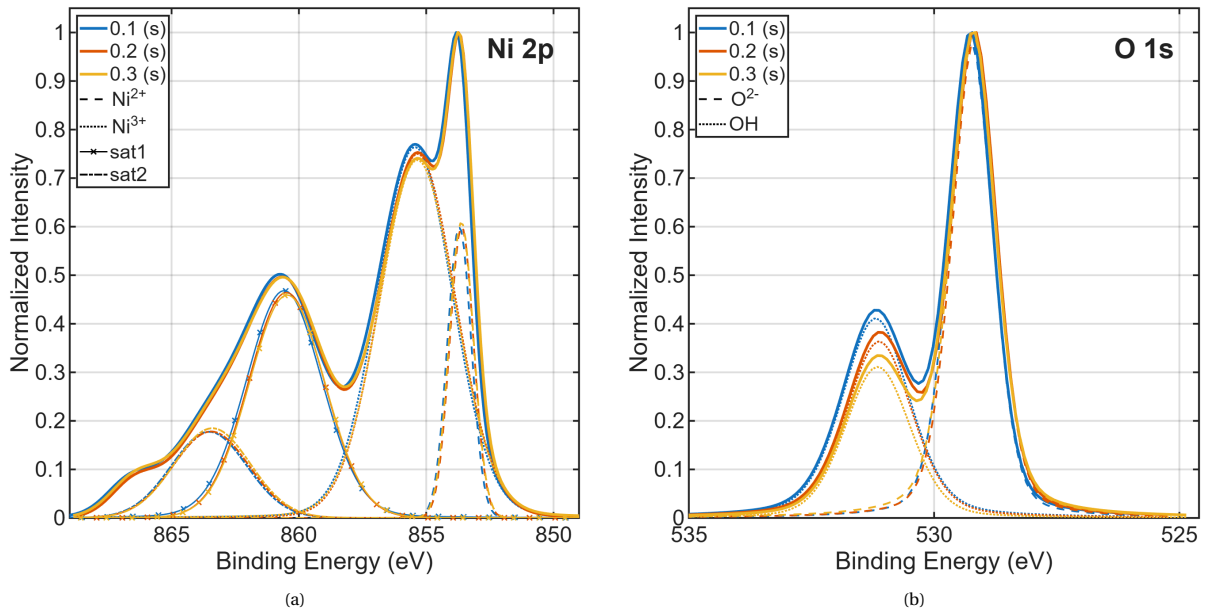


Figure 4.9: XPS spectra of NiO_x deposited silicon wafers using different co-reactant (H_2O) pulse conditions: (a) Ni 2p and (b) O 1s spectra.

In the Ni 2p spectra, the contribution associated with Ni^{3+} , located at approximately 861 eV, decreases in intensity as the H_2O pulse time increases. This trend is more clearly observed in the corresponding O 1s

spectra, where the peak around 532 eV, associated with the higher oxidation-state/defect-related oxygen environment, also decreases with increasing H₂O pulse time. The consistent decrease observed in both spectra suggests that increasing the H₂O pulse time alters the oxidation state and defect chemistry of the NiO_x films, with a reduced relative contribution of Ni³⁺ at higher H₂O exposure. The ratios of the contribution of Ni³⁺ and OH are shown in Table 4.1.

Table 4.1: Fractional contributions of Ni³⁺ and OH species obtained from the Ni 2p and O 1s XPS spectra following H₂O exposure.

H ₂ O (s)	Ni ³⁺	OH
0.1	0.805	0.404
0.2	0.799	0.356
0.3	0.793	0.316

The same procedure is also performed with the precursor pulses for which the results are shown in Figure 4.10.

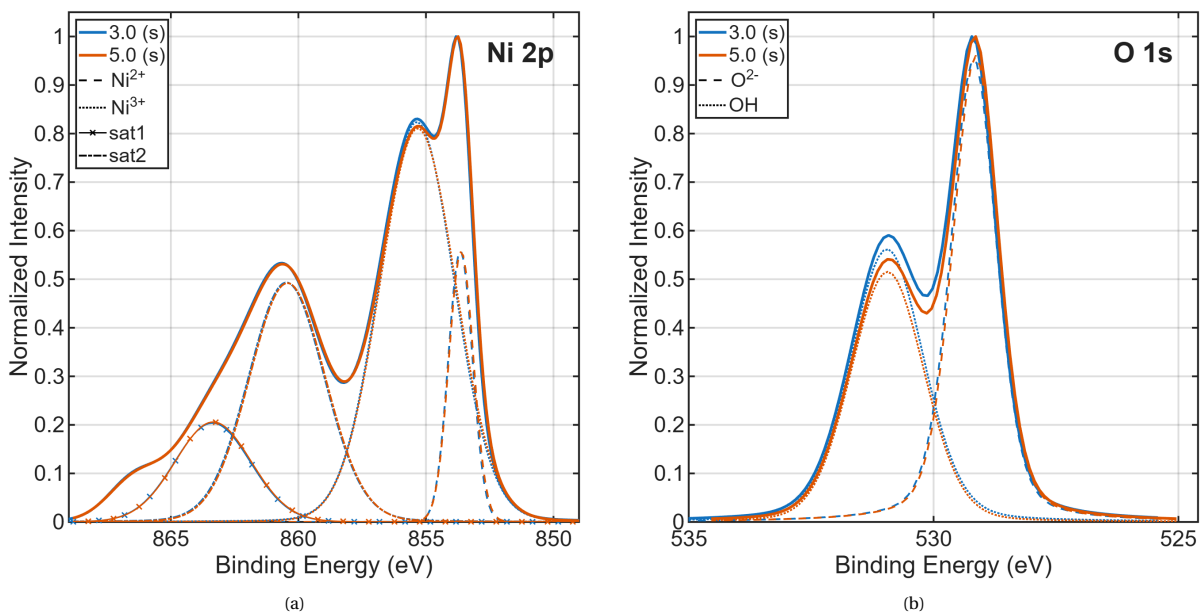


Figure 4.10: XPS spectra of NiO_x deposited on ITO using different precursor (Ni(^tBu₂AMD)₂) pulse times: (a) Ni 2p and (b) O 1s spectra.

Figure 4.10 shows the Ni 2p and O 1s XPS spectra for NiO_x films deposited using Ni(^tBu₂AMD)₂ pulse times of 3.0 and 5.0 s. The same behaviour seems to occur where increasing pulse time reduces relative contribution of Ni³⁺ in the NiO_x films. The ratios of the contribution of Ni³⁺ and OH with different Ni pulse times are shown in Table 4.2.

Table 4.2: Fractional contributions of Ni³⁺ and OH species obtained from the Ni 2p and O 1s XPS spectra following Ni exposure.

Ni (s)	Ni ³⁺	OH
3.0	0.822	0.471
5.0	0.819	0.438

Since increasing the pulse times for both the Ni and H₂O cause a decrease in the Ni³⁺ defect formation, a compromise was taken to the ALD formula. The pulses should be long enough to not cause uniformity issues throughout the substrate holder between the samples, but not too long to greatly affect the defect formation. For this reason a Ni pulse time of 3.0 seconds with a co-reactant H₂O of 0.2 seconds was selected. The GPC for this recipe remained similar at 0.0457 nm/ cycle.

Optical properties

UV-Vis spectroscopy will be used to characterize the optical properties of the deposited films by measuring their transmission and absorption as a function of wavelength. These measurements can be used to inves-

investigate how changes in film thickness influence the optical properties of the material. From the measured absorption data, Tauc plots can be constructed to estimate the optical band gap of the films and determine how layer thickness affects their electronic structure.

As a first step, the effect of film thickness on the optical transmission of NiO_x was investigated. Transmission spectra of NiO_x films with thicknesses of 2.5, 5, 10, and 20 nm deposited on ITO are shown in Figure 4.11.

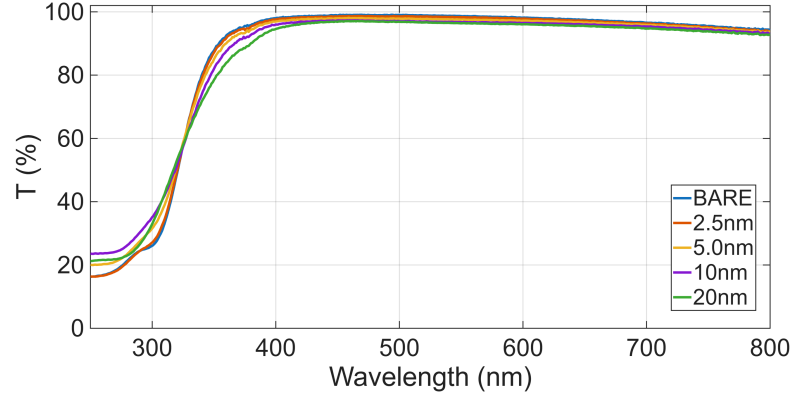


Figure 4.11: Transmission UV-Vis spectra for different NiO_x thickness layers on ITO.

All samples exhibit high optical transparency, with transmission values greater than 90% up to approximately 375 nm. Below this wavelength, the transmission decreases significantly, reaching values of around 20%. A slight decrease in transmission is observed for thicker NiO_x films, indicating that increasing the film thickness leads to greater optical absorption and consequently lower overall transparency.

To further investigate the optical properties of the NiO_x layers independently of the conducting ITO substrate, equivalent NiO_x films were deposited on quartz and characterized using UV-Vis spectroscopy, shown in Figure 4.12. Since quartz has a high optical transparency throughout the measured wavelength range, these measurements provide a more direct assessment of the transmission and absorption behaviour of the NiO_x films.

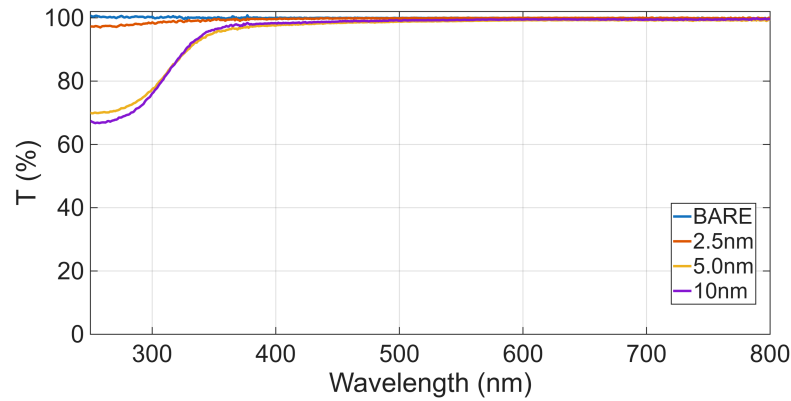


Figure 4.12: Transmission UV-Vis spectra for different NiO_x thickness layers on quartz .

The bare quartz substrate and the 2.5 nm NiO_x film remain highly transparent across the measured wavelength range. In contrast, the 5 and 10 nm NiO_x films exhibit a similar transmission profile, with a distinct absorption edge around 350 nm, after which the transmission decreases rapidly towards shorter wavelengths. At 250 nm, the transmission of both thicker films decreases to approximately 70%. The similar behaviour observed for the 5 and 10 nm films suggests that, within this thickness range, the position of the absorption edge is relatively insensitive to film thickness, while the increased absorption at shorter wavelengths reflects the optical response of the NiO_x layer.

The absorption edge observed in the transmission spectra can be further quantified using Tauc analysis. The

optical band gap can be estimated by extrapolating the linear region of the Tauc plot to the energy axis. Comparing the two thicknesses allows the influence of film thickness on the estimated optical band gap to be evaluated. The similar absorption edges observed in the transmission spectra are also reflected in the Tauc plots, providing an indication of whether the electronic structure of the NiO_x films changes significantly with thickness. Figure 4.13 shows the resulting Tauc plots for the 5 and 10 nm NiO_x films deposited on quartz.

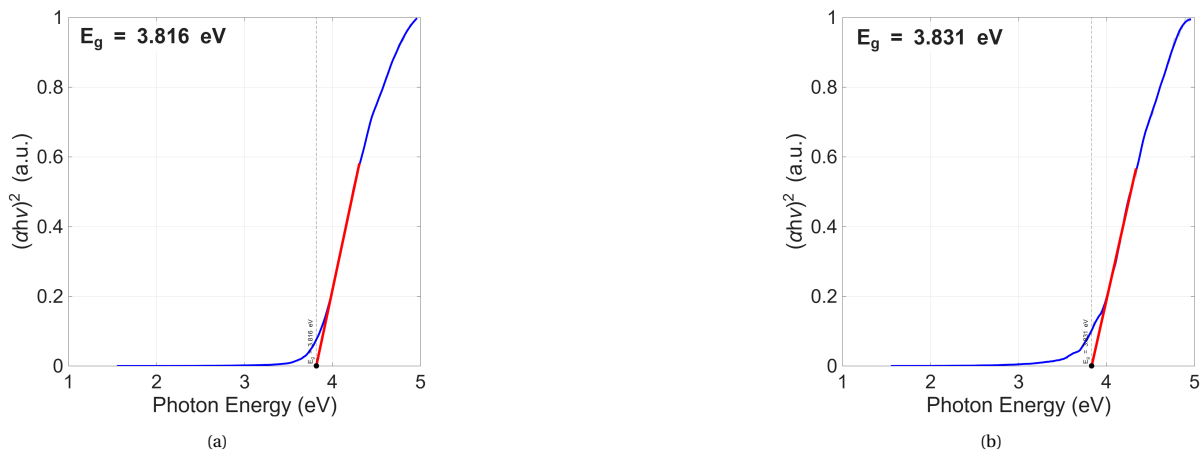


Figure 4.13: Tauc plots of ALD NiO_x deposited on quartz with (a) a 5 nm NiO_x layer and (b) a 10 nm NiO_x layer.

The Tauc plots show very little difference in the estimated optical band gap between the two film thicknesses. The 5 nm NiO_x film exhibits an optical band gap of approximately 3.816 eV, while the 10 nm film gives a slightly higher value of 3.831 eV. This small difference of 0.015 eV suggests that the optical band gap is largely independent of film thickness within the investigated range. This is consistent with similar absorption edges observed in the corresponding UV–Vis transmission spectra.

The optical band gap can also be estimated from spectroscopic ellipsometry (SE) measurements by using the extinction coefficient, k , to determine the absorption coefficient. The resulting absorption data can then be analyzed using a Tauc plot in the same manner as the UV–Vis measurements. Figure 4.14 shows the Tauc plot obtained from the SE data, where the linear extrapolation of the absorption region gives an estimated optical band gap of 3.84 eV. This value is in close agreement with the band gaps obtained from the UV–Vis measurements, supporting the consistency of the optical characterization.

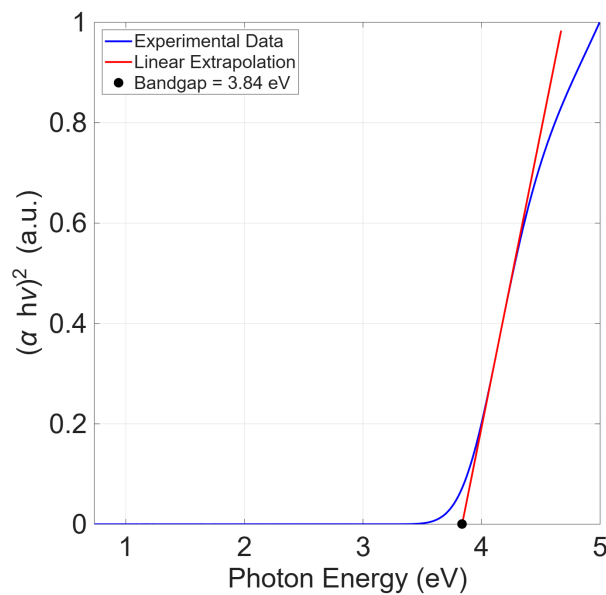


Figure 4.14: Tauc plot estimating the optical band gap of an ALD-deposited NiO_x layer from spectroscopic ellipsometry (SE) measurements.

4.2. Post deposition effects

The initial device results indicated that further optimization of the fabrication process was required. In particular, optimization of the interface between the NiO_x and perovskite layers was considered as a potential route to improve charge extraction and reduce losses at the interface. Post-deposition annealing was therefore introduced to investigate whether thermal treatment could modify the NiO_x surface and increase the relative Ni^{3+} content, which could contribute to improved electrical conductivity and more favorable interfacial properties. To investigate the influence of the annealing environment, thermal treatments were performed under different conditions: in a nitrogen-filled glovebox, in air, under vacuum, and ozone. The effect of these treatments on the material and interfacial properties is discussed in the following section, while their impact on device performance is evaluated subsequently in subsection 4.3.1. Additional XPS spectra for each post deposition treatment are available in Appendix C

Chemical composition

X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical composition of the films and determine how post-deposition annealing affects their surface chemistry. The resulting changes in the chemical environment and relative surface composition are compared in the overlaid XPS spectra of the Ni 2p and O 1s regions shown in Figure 4.15. These spectra provide insight into how the annealing atmosphere influences the nickel and oxygen chemical states, thus the surface chemistry of the films.

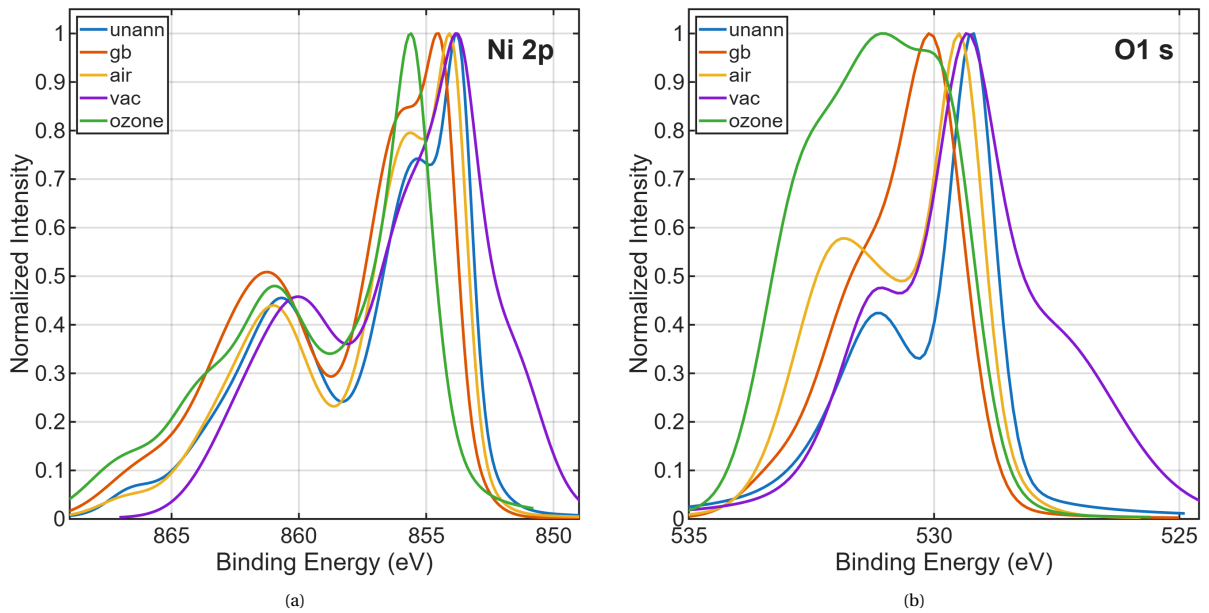


Figure 4.15: XPS spectra of NiO_x deposited on silicon wafer exposed to different post deposition treatments (unannealed (unann), nitrogen filled glovebox (gb), ambient air (air), vacuum (vac) and ozone: (a) Ni 2p and (b) O 1s spectra.

From Figure 4.15a it can be seen that from the Ni 2p spectra of the unannealed sample and samples annealed in a nitrogen-filled glovebox, air, and ozone reveal clear changes in the nickel chemical environment following post deposition treatment. Deconvolution and fitting of the Ni 2p spectra provide a clearer representation of the individual chemical species and their relative concentrations, as shown in Figure 4.16.

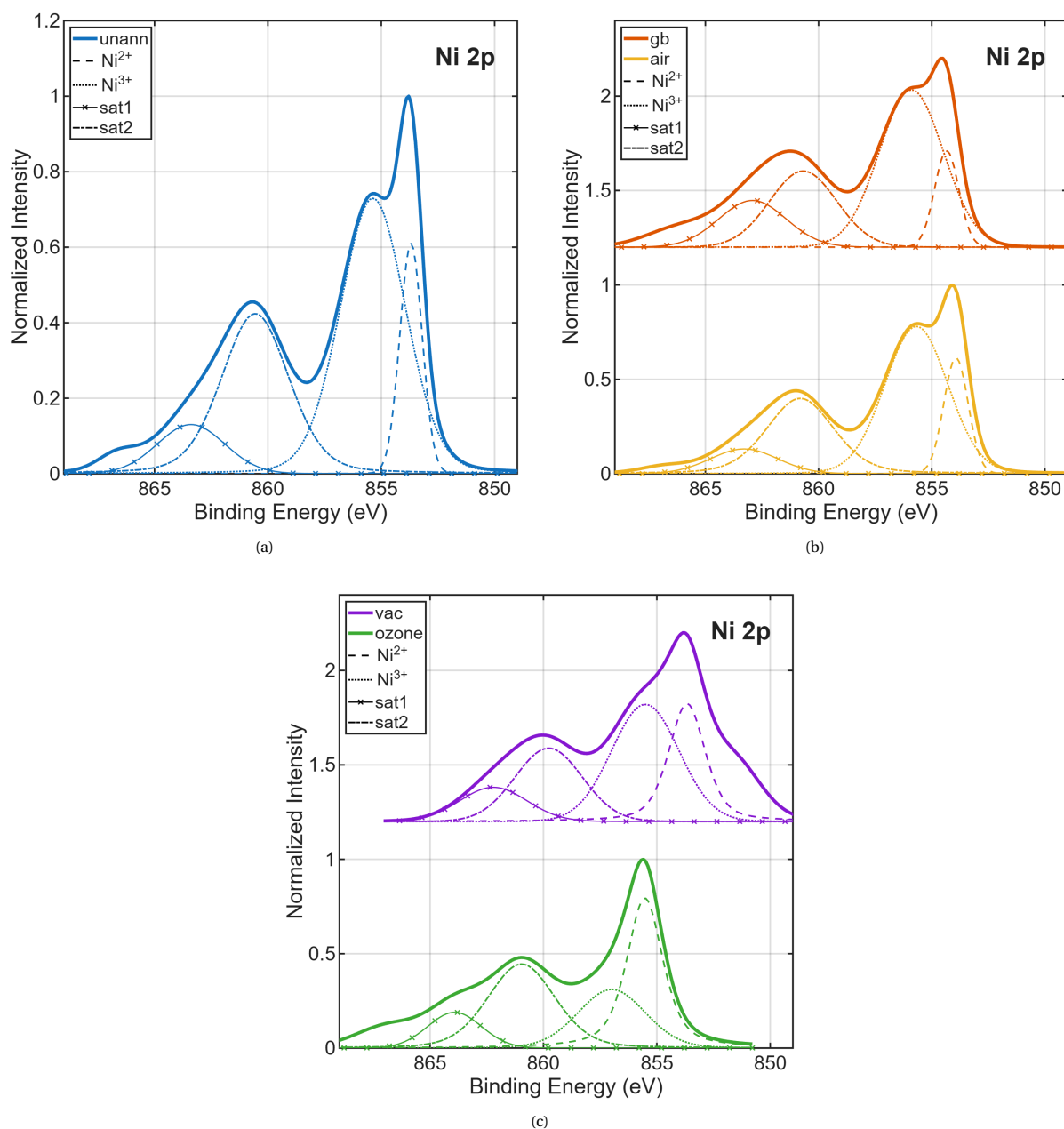


Figure 4.16: XPS Ni 2p spectra of (a) unannealed, (b) nitrogen- and air-annealed NiO_x , (c) vacuum- and ozone-annealed NiO_x , including the corresponding deconvoluted and fitted components.

From the fitted version it can be better observed that in the unannealed sample, the Ni 2p spectrum exhibits distinct contributions from Ni^{2+} and Ni^{3+} , with the Ni^{3+} -associated feature appearing as a hump around 856 eV. Following annealing in both the nitrogen-filled glovebox and air, the intensity of the Ni^{3+} feature increases, suggesting a greater contribution from the Ni^{3+} chemical state. At the same time, the Ni^{2+} peak around 854 eV shows a slight shift toward higher binding energy (a shift to the left in the plotted spectra). In contrast, the vacuum- and ozone-annealed samples show a substantially different spectral profile, with the distinct Ni^{2+} and Ni^{3+} features becoming less resolved and merging into a single dominant peak centered around 856 eV. This indicates that these treatment strongly modifies the nickel-hydroxides chemical composition at least at the surface compared with the other annealing conditions.

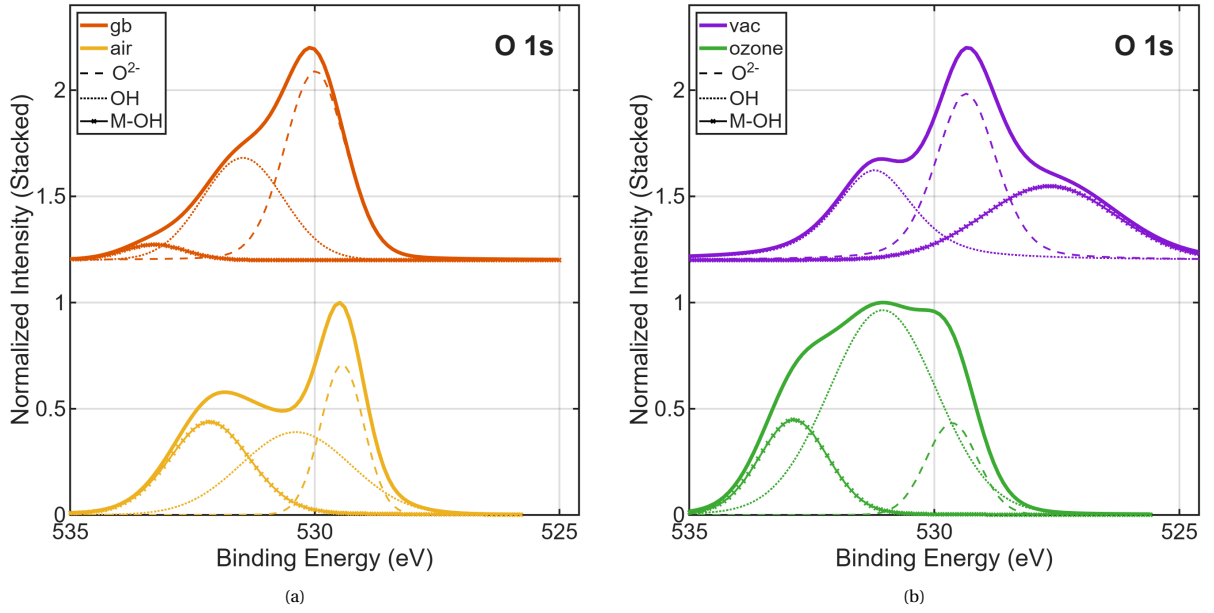


Figure 4.17: XPS O 1s spectra of (a) air- and nitrogen-annealed NiO_x , and (b) vacuum- and ozone-annealed NiO_x , including the corresponding deconvoluted and fitted components.

Similar to the Ni 2p spectra, the O 1s spectra show clear changes in the surface chemical environment following annealing under the different conditions shown in Figure 4.15b. For the sample annealed in air, an increase in intensity is observed around 532 eV, which can be attributed to O^{2-} species associated with Ni^{3+} bonding. Following annealing in the nitrogen-filled glovebox, the O 1s components become less distinct and begin to merge, indicating a change in the relative contributions of the different oxygen species. The most pronounced change is observed after ozone annealing, where the spectrum develops into a broad feature centered around 532 eV. This broadening appears to include an increased contribution from oxygen species associated with metal hydroxides, together with hydroxyl groups adsorbed on the surface at higher binding energies around 533 eV. Overall, the O 1s spectra indicate that the annealing atmosphere strongly influences the surface oxygen chemistry, with ozone treatment producing the greatest broadening and contribution from higher-binding-energy oxygen species.

The ratios corresponding to Ni^{3+} and OH can be found by calculating the area of the species and dividing with each other. The results are shown in Table 4.3.

Table 4.3: Fractional contributions of Ni^{3+} and OH species obtained from the Ni 2p and O 1s XPS spectra for different PDT conditions.

PDT	Ni^{3+}	OH
Unann	0.787	0.549
GB	0.813	0.407
Air	0.770	0.584
Vac	0.604	0.438
Ozone	0.377	0.826

The exact ratios show more clearly the distinct shifts in surface chemistry across the various post-deposition treatment conditions. Compared to the unannealed baseline sample, which shows a Ni^{3+} fraction of 0.787 and an OH fraction of 0.549. Annealing in a nitrogen-filled glovebox maximizes the relative Ni^{3+} content to 0.813 while lowering the hydroxyl component to 0.407. Ambient air annealing produces a comparable Ni^{3+} fraction of 0.770 alongside a slightly higher hydroxyl fraction of 0.584. Vacuum annealing further decreases both parameters, yielding a Ni^{3+} fraction of 0.604 and an OH fraction of 0.438. In stark contrast, ozone treatment drastically alters the surface profile by dropping the Ni^{3+} fraction to its lowest value of 0.377 while causing the hydroxyl fraction to spike to a maximum of 0.826 due to extensive surface oxidation and hydroxide formation.

Optical properties

Following the investigation of the chemical composition and surface chemistry, the effect of post-deposition annealing on the optical properties of the NiO_x layers was investigated using UV-Vis spectroscopy. The NiO_x films were subjected to the same post-deposition treatments where the optical transmission of the resulting films was measured to evaluate how the annealing atmosphere influences their transparency and electronic structure. The transmission spectra as shown in Figure 4.18, together with the corresponding Tauc analyses shown in Figure 4.19, provide insight into changes in the band-gap energy of the NiO_x layers induced by the different annealing conditions.

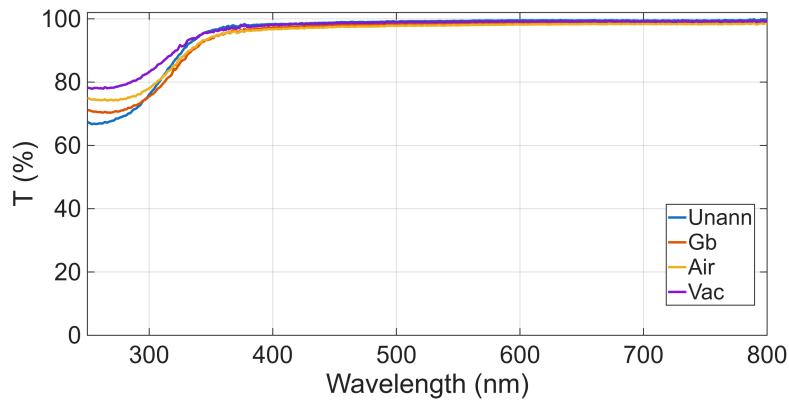


Figure 4.18: Effect of post-deposition annealing conditions on the optical transmission of a 10 nm NiO_x layer on quartz, comparing the as-deposited film with films annealed in air, a nitrogen filled glovebox, and vacuum.

The UV-Vis transmission spectra of NiO_x layers with a fixed thickness, comparing the unannealed sample with samples subjected to post-deposition annealing in air, a nitrogen-filled glovebox, and under vacuum. Overall, the annealed samples exhibit a slight increase in transparency at shorter wavelengths, particularly in the 250–350 nm range, compared with the unannealed layer. Among the different treatments, vacuum annealing results in the highest transmission, reaching nearly 80% at its lowest transmission value within the measured spectral range. These changes indicate that the post-deposition annealing atmosphere influences the optical transparency of the NiO_x layers.

The optical band-gap energies were further evaluated using Tauc analysis of the corresponding transmission data. The resulting Tauc plots for the air-, nitrogen-filled glovebox-, and vacuum-annealed NiO_x layers are presented in Figure 4.19a, Figure 4.19b, Figure 4.19c respectively, allowing the influence of the different post-deposition treatments on the optical band gap to be compared.

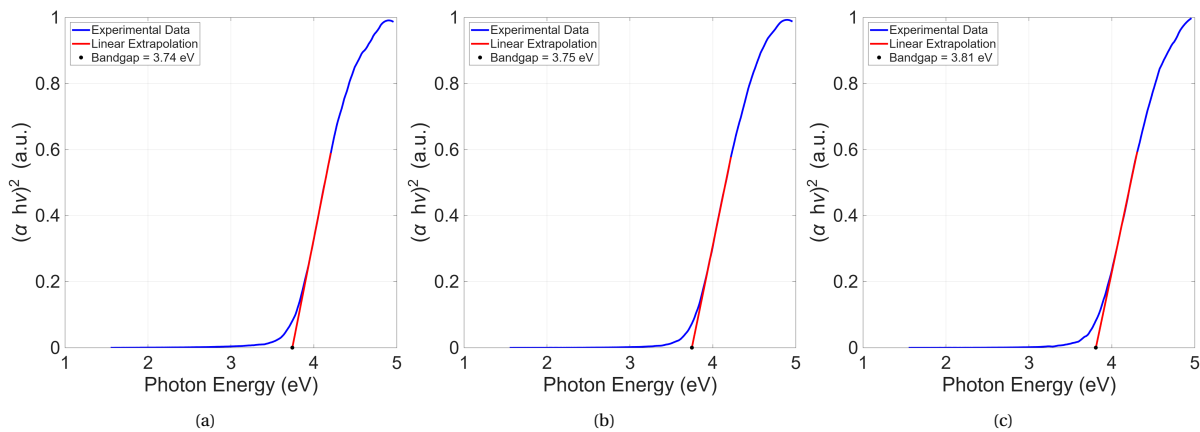


Figure 4.19: Tauc plots of NiO_x layers deposited on quartz and annealed under three different conditions: (a) in air, (b) in a nitrogen-filled glovebox, and (c) under vacuum. The plots are used to determine the optical band gap of the NiO_x layers following each post-deposition annealing treatment.

The extracted optical band-gap energies show a slight decrease compared with the unannealed NiO_x layer, which has a band gap of 3.84 eV. Following annealing, the band gap decreases to 3.74 eV for the air-annealed

sample and 3.75 eV for the glovebox-annealed sample, while the vacuum-annealed sample exhibits a smaller decrease to 3.81 eV. These results indicate that annealing in air and in the nitrogen-filled glovebox produces a more pronounced reduction in the optical band gap, whereas vacuum annealing results in only a minor change.

Electronic properties

To further investigate the electronic properties of the NiO_x layers and the influence of post-deposition annealing, Kelvin probe measurements were performed to determine the work function of the deposited films. The work function is an important parameter for understanding the electronic structure of NiO_x and its suitability as a charge-selective layer in optoelectronic devices. Measurements were carried out on the unannealed films and following the different post-deposition treatments, namely annealing in air, in a nitrogen-filled glovebox, and under vacuum. The results are shown in Table 4.4.

Table 4.4: Work function of NiO_x layer under different PDT conditions.

PDT	7.5 nm (eV)	10 nm (eV)
Unannealed	4.50	4.69
Air	4.45	4.55
Nitrogen	4.35	4.60
Vacuum	4.42	4.56

The measurements presented in Table 4.4 show that the work function of the NiO_x layers remains relatively consistent across the different post-deposition annealing treatments, with only minor changes observed. Compared to the unannealed sample with an absolute work function of approximately 4.50 eV, the annealing treatments result in a slight decrease in the work function magnitude. The largest change is observed for the nitrogen-filled glovebox treatment, where the work function decreases to approximately 4.35 eV. Overall, the small variation between the different treatments suggests that post-deposition annealing has only a limited effect on the work function of the NiO_x layers.

4.3. Perovskite devices with NiO_x as hole transport layer

To evaluate the performance of the NiO_x layers in a device-relevant configuration, the films were incorporated into devices with NiO_x thicknesses. The resulting device performance was evaluated by measuring the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}) and fill factor (FF) for each layer thickness. The measured J_{sc} and V_{oc} values are presented in Figure 4.23a and Figure 4.21, respectively, allowing the influence of NiO_x layer thickness on the device performance to be assessed. Only complete devices with a PCE of at least 1% were initially included. Figure 4.20 compiles the best achieved cell performance for the different NiO_x thicknesses.

However, as shown by the J - V curves in Figure 4.20, none of the devices with NiO_x as HTL achieved a PCE of 1% or higher. The cells with a NiO_x layer exhibited upon visual inspection J_{sc} values that were several times lower than those of the PTAA reference cells and were even lower than those of the cells without an HTL. In contrast, the V_{oc} values were only slightly lower compared with the PTAA cells. The PTAA cells also exhibited non-ideal behaviour, as indicated by the steep slope of the J - V curve near J_{sc} . Therefore, the inclusion criterion was relaxed to require a positive fill factor (FF) instead. The J_{sc} , V_{oc} and FF of this batch comparing it next to PTAA is shown in Figure 4.21.

Figure 4.21 provides a clearer overview of the device performance. The NiO_x cells exhibit comparable average V_{oc} and FF values to the PTAA reference cells, but their performance is severely limited by the substantially lower J_{sc} . The difference in NiO_x layer thickness does not appear to significantly affect J_{sc} . However, the thicker layer results in a more consistent FF, although the values remain relatively low.

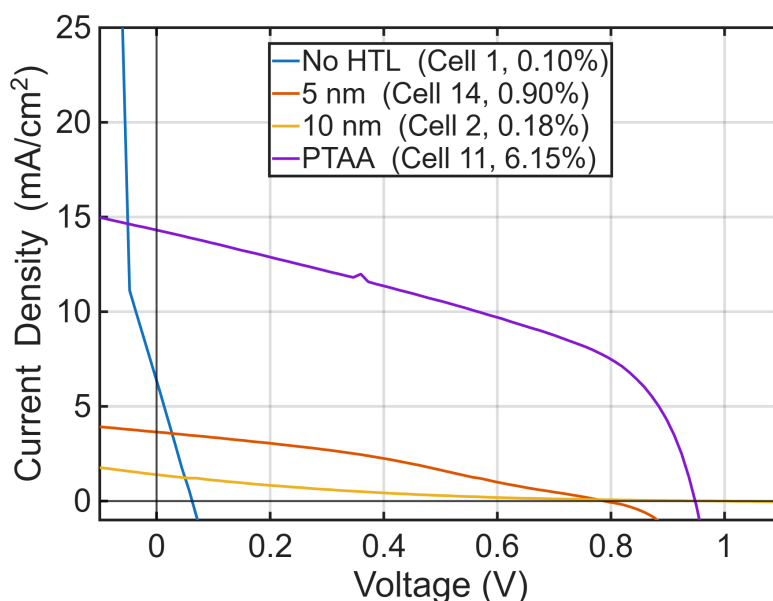


Figure 4.20: J - V curves of best cell performance for different thickness NiO_x layer, 5 nm and 10 nm compared to no HTL and PTAA.

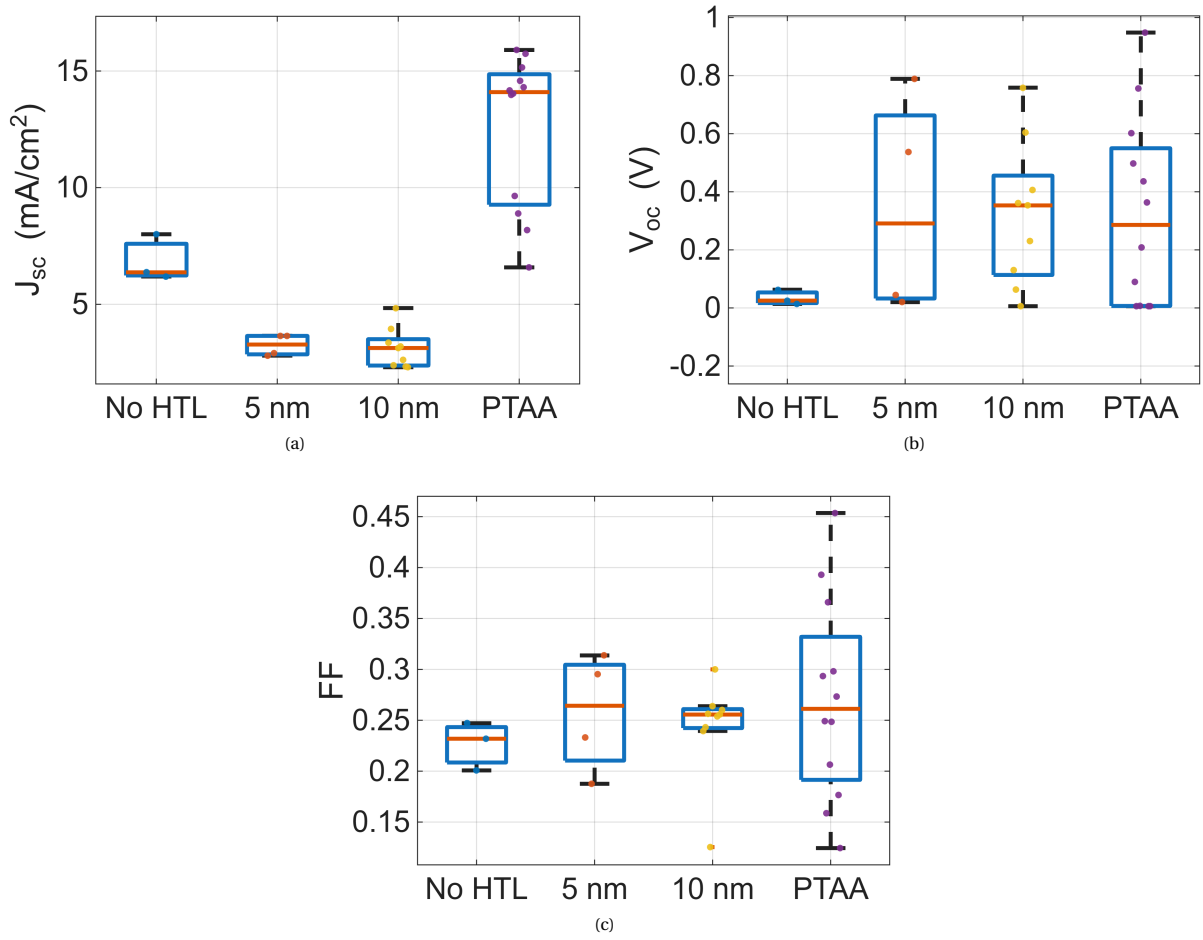


Figure 4.21: Effect of different NiO_x layer thicknesses on the photovoltaic parameters compared to PTAA: (a) short-circuit current density (J_{sc}), (b) open-circuit voltage V_{oc} , shown as box plots, and (c) the fill factor (FF).

These results persisted through subsequent depositions and post-deposition treatments, with the characteristics of not even the reference PTAA cells improving. Therefore, it was decided to tweak the experimental perovskite formulation currently used to a perovskite with a lower band gap. The resulting $J-V$ curves, shown in Figure 4.22, compare the champion cells with different NiO_x layer thicknesses against the PTAA reference cell.

Already from the PTAA curve, it can be seen that the steep decrease in slope near J_{sc} has been reduced. The cells incorporating NiO_x still underperform in terms of J_{sc} , although their values have nearly doubled compared with those obtained using the previous perovskite formulation. The $J-V$ curves of these cells, however, still exhibit an almost linear shape, similar to that observed with the previous perovskite formulation. Despite the limited J_{sc} , the overall efficiency of the cells has approximately doubled, with several cells now comfortably exceeding the 1% efficiency threshold.

Comparing the results between the two batches, it can be seen that, although the preparation and deposition of the NiO_x layer remained unchanged, modifying the perovskite formulation resulted in a noticeable improvement in device performance. The figure also clearly demonstrates that the improved performance is associated with the thinner NiO_x layer, with the thinner 5 nm and 7.5 nm layer outperforming the 10 nm layer.

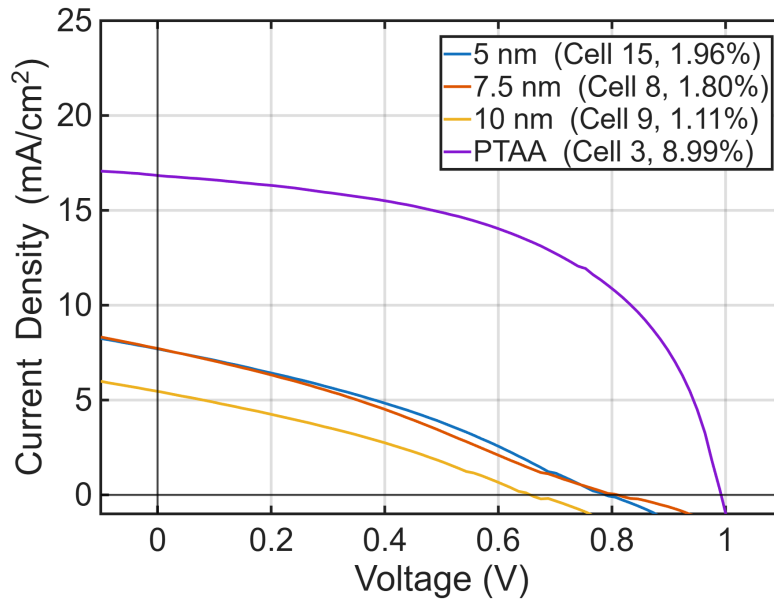


Figure 4.22: J - V curves of best cell performance for different thickness NiO_x layer, 5 nm, 7.5 nm, and 10 nm compared to PTAA.

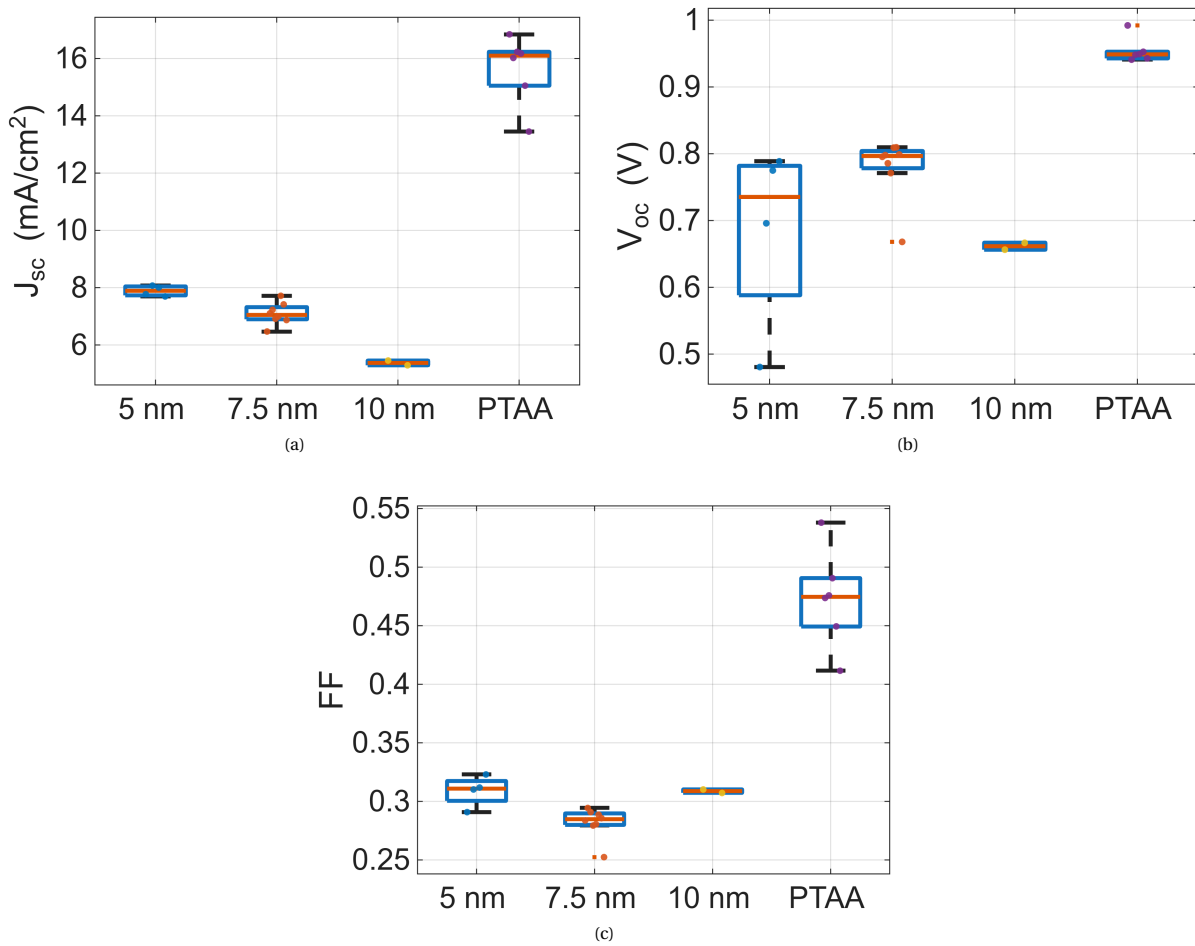


Figure 4.23: Effect of different NiO_x layer thicknesses on the photovoltaic parameters compared to PTAA: (a) short-circuit current density (J_{sc}), (b) open-circuit voltage V_{oc} , shown as box plots, and (c) the fill factor (FF).

Results shown in Figure 4.23, affirms that lowering the NiO_x layer thickness leads to an improvement in the

maximum achievable J_{sc} . Although there seem to be a limit when looking at the V_{oc} . The devices with 5 and 10 nm NiO_x layers exhibit noticeably lower V_{oc} values compared with those containing a 7.5 nm layer, with thinner layer experiencing a large spread and less working devices (noted by the lesser amount of dots). The 7.5 nm devices show the highest V_{oc} , with the average value approaching 0.8 V, indicating that this intermediate NiO_x thickness provides the most favorable conditions for achieving a high open-circuit voltage.

4.3.1. Effects of annealing

To evaluate the impact of the post-deposition treatment (PDT) on the performance of the deposited NiO_x layers, solar-cell devices were fabricated using films with thicknesses ranging from 5 to 10 nm. The devices were subjected to four different conditions: no post-deposition treatment, annealing in air, annealing in nitrogen (GB), annealing in vacuum, and ozone treatment. The resulting device performance was evaluated based on the short-circuit current density (J_{sc}), open-circuit voltage V_{oc} , fill factor (FF), and overall device efficiency. These parameters were used to assess the effect of the different NiO_x thicknesses and post-deposition treatments on device performance. Comparing these parameters across the different NiO_x thicknesses and post-deposition conditions allows the influence of both film thickness and thermal treatment on device performance to be assessed. This provides a direct link between the material properties of the NiO_x layers and their practical performance when incorporated into solar cell devices.

Figure 4.24 show the J_{sc} and V_{oc} distributions for devices with a 7.5 nm NiO_x layer subjected to the two different post-deposition treatments, in nitrogen (Gb) and (Air). Unfortunately vacuum- and ozone-annealing were not able to produce working cells with their respective batch. For J_{sc} , an increase is observed from the unannealed to the GB-annealed treatment, with a further increase following air annealing. This indicates that the post-deposition treatment has a positive effect on photocurrent generation, with air annealing resulting in the highest J_{sc} . In contrast, V_{oc} decreases when moving from the unannealed to the GB-annealed treatment, while air annealing results in an overall similar V_{oc} compared with the unannealed devices. However, the air-annealed devices show a noticeably narrower spread in V_{oc} compared with the unannealed and GB-annealed devices, indicating greater consistency in the measured V_{oc} .

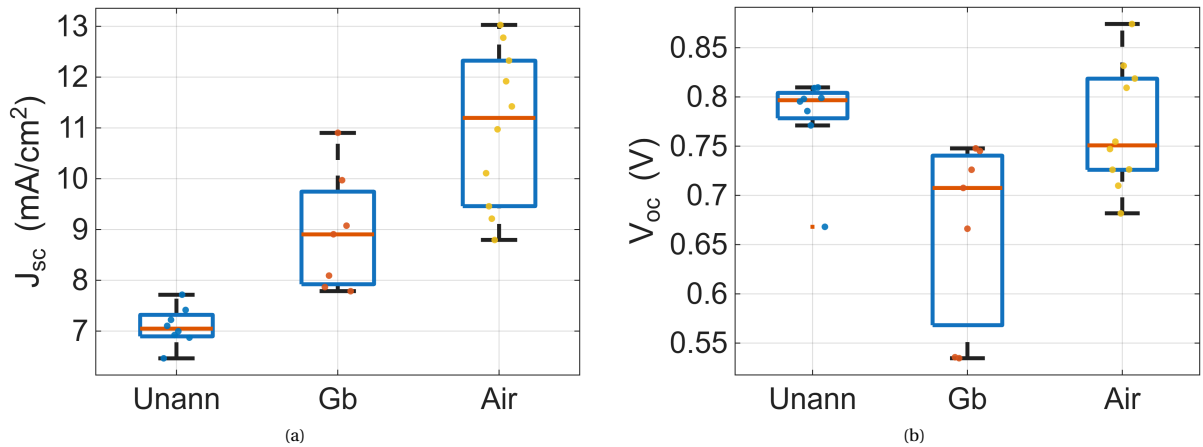


Figure 4.24: Effect of post-deposition annealing on the photovoltaic parameters: (a) short-circuit current density (J_{sc}) and (b) open-circuit voltage V_{oc} , shown as box plots for the different deposition treatments for a NiO_x layer thickness of 7.5 nm.

Figure 4.25 presents the J–V characteristics of the best-performing perovskite solar cells fabricated with NiO_x layers subjected to different post-deposition annealing conditions. The effect of the NiO_x layer thickness was also evaluated by comparing devices containing 5 nm and 7.5 nm thick NiO_x layers. Additional curves for the other cells in the batch are provided in Appendix D.

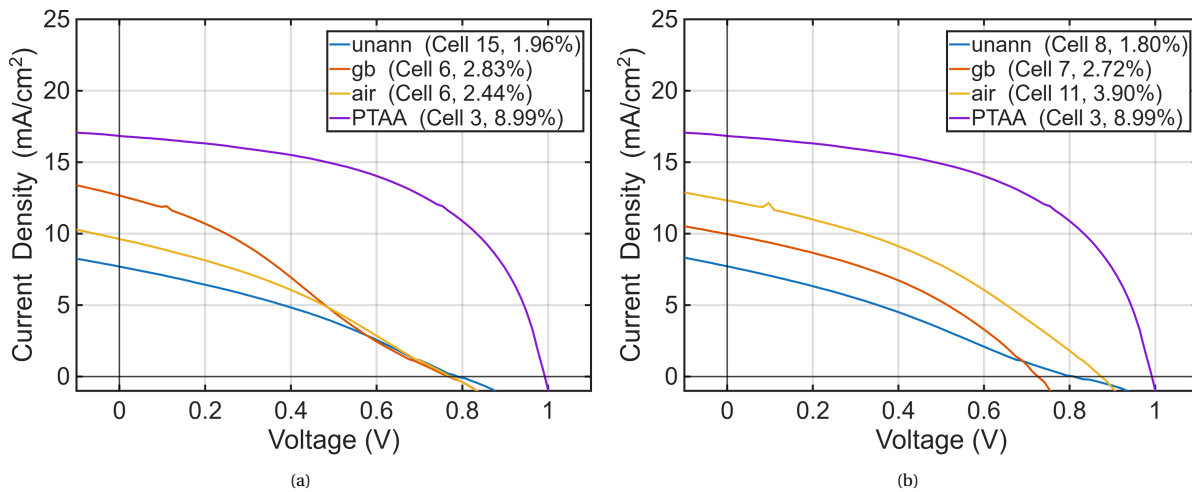


Figure 4.25: J - V curves of best cell performance for each post-deposition annealing for NiO_x layer (a) 5 nm and (b) 7.5 nm.

Comparing the results obtained for the 5 nm and 7.5 nm NiO_x layers, it can be observed that both annealing conditions improve the overall device efficiency, primarily through an increase in the short-circuit current density (J_{sc}). The highest-performing device was obtained for the 7.5 nm NiO_x layer annealed in air, achieving an efficiency of 3.90%, followed by the 5 nm NiO_x layer annealed in the nitrogen-filled glovebox, which reached an efficiency of 2.83%. However, none of the measured J - V characteristics exhibit clear diode-like behaviour. Instead, most of the curves suggest the presence of an interfacial or transport barrier within the device, as indicated by the distorted J - V characteristics. In particular, the 5 nm NiO_x device annealed in the glovebox exhibits a pronounced S-shaped J - V curve, which is characteristic of a significant transport barrier or interfacial limitation.

Comparing the J - V results across the different conditions, it can be seen that annealing generally improves the device efficiency. Among the investigated conditions, annealing the 7.5 nm NiO_x layer at 300 °C in air resulted in the best overall performance, exhibiting higher J_{sc} and V_{oc} values compared with the unannealed samples and the other layer thicknesses. The champion device achieved a PCE of 3.90%, with a V_{oc} of 0.874 V, a J_{sc} of 12.33 mA cm^{-2} , and an FF of 36.17%. Unfortunately even this fall short compared to its organic counterpart PTAA. Champion PTAA cell achieved a PCE of 8.99%, with a V_{oc} of 0.992 V, a J_{sc} of 16.84 mA cm^{-2} , and an FF of 53.82%.

5

Discussion

The results shown in Chapter 4 are discussed in this chapter.

5.1. Thickness and pulse time variation of layers

The strong dependence of the deposition uniformity on the reactant pulse times indicates that reactant exposure and transport play an important role in the investigated NiO_x ALD process. Interestingly, the improved uniformity was obtained by reducing the Ni precursor pulse rather than increasing it, shown in Figure 4.4. The shorter precursor exposure resulted in a more homogeneous deposition, suggesting that the longer precursor pulse did not provide a benefit in terms of spatial uniformity and may have resulted in an unnecessarily high precursor dose. The selected Ni precursor pulse was therefore chosen close to the onset of saturation. Operating near this saturation boundary provides sufficient precursor exposure for the surface reaction while avoiding unnecessarily long pulses. This reduces both process time and precursor consumption without compromising the deposition. In contrast, the H_2O pulse was increased to ensure that the co-reactant exposure was beyond the saturation threshold since lower pulse time could not be input in the machine.

Although the GPC of the recipe can be found with a linear approximation, the GPC compared with the literature is of higher value[46]. Literature state a GPC of 0.039 nm/ cycle compared to 0.046 nm/ cycle found in Figure 4.1. This may result from differences in precursor and co-reactant exposure, purge conditions, reactor geometry, substrate surface condition. The longer H_2O exposure used here may promote a more complete surface reaction and could therefore contribute to the higher growth rate. Consequently, the selected chamber temperature is lower than that from literature, 150 °C versus 200 °C, which may help with minimizing desorption of the layers. Although there are other studies with these temperature achieving a slightly higher GPC 0.043 nm/ cycle[47][48].

The surface morphology was additionally evaluated by AFM on both Si wafers and ITO substrates to assess the effect of the deposition on surface roughness and conformality. The deposited layers showed highly conformal growth, with the underlying surface morphology of the ITO remaining clearly visible after deposition. This indicates that the NiO_x film followed the topography of the underlying substrate rather than significantly smoothing or modifying it, consistent with the characteristic conformal growth behavior of ALD[29] [30]. For most samples, the increase in RMS roughness was below 1 nm, demonstrating that the deposition introduced only a minor change in surface morphology[49]. The larger roughness increase observed for some measurements was attributed most likely to small particles introduced during sample handling, cutting, or mounting onto the small AFM chuck. These particles can locally increase the measured RMS roughness and are therefore not necessarily representative of the intrinsic roughness of the deposited NiO_x layer.

XPS measurements used to evaluate the chemical composition and oxidation state of the deposited NiO_x films show that although the overall spectral shapes remained similar across the investigated recipes, a slight decrease in the relative contribution of the Ni^{3+} component was observed with increasing pulse times. The greater sensitivity of the O 1s signal can be attributed to its contribution from different oxygen environments, including lattice oxygen, hydroxyl species, and other surface-related oxygen species. Changes in reactant exposure can therefore modify the relative abundance of these species and consequently affect the shape of O

1s line more strongly. The relatively small changes observed across the different recipes indicate that varying the pulse times primarily affected the growth rate and spatial uniformity rather than fundamentally changing the chemical nature of the deposited film[36]. The similar overall XPS spectra therefore suggest that the investigated process conditions produced chemically comparable NiO_x layers, while the subtle changes in the O 1s region may reflect differences in surface termination or the relative concentration of oxygen-containing species.

The optical properties of the deposited NiO_x layers were evaluated using UV-Vis spectroscopy. The films remained highly transparent in the visible wavelength range, with transmittance above 90% between approximately 400 and 800 nm. At shorter wavelengths, the transmittance decreased more strongly, indicating increased absorption in the near-UV region. Importantly, the transmission spectra of the different NiO_x thicknesses closely followed that of the bare ITO substrate throughout the visible range. This indicates that the NiO_x layer introduces only minor additional optical losses, even as the film thickness is increased. The high visible transparency is therefore maintained across the investigated thickness range, demonstrating that the deposited NiO_x layers are well suited for applications where optical transparency of the underlying ITO electrode must be preserved. Many other experiments achieve slightly lower transmission spectra which is can be caused by depositing on glass instead of quartz[46].

The optical band gap of the deposited NiO_x layers was evaluated using Tauc plots from UV-Vis measurements on quartz substrates. For the measurable film thicknesses, the extracted band gap was approximately 3.82 eV, in good agreement with reported values for NiO_x [49][31]. This indicates that the deposited layers exhibit the expected optical properties and that the selected process conditions do not substantially alter the optical band structure. For the thinnest layer, with a nominal thickness of 2.5 nm, a reliable Tauc analysis could not be performed because the film remained highly transparent over the measured wavelength range. Consequently, no clear absorption edge could be identified. This may indicate that the film was too thin for its absorption to be resolved reliably by the measurement, although incomplete or non-uniform deposition cannot be excluded. Therefore, the absence of a measurable band gap for this sample should not be interpreted directly as a change in the intrinsic optical properties of NiO_x .

When making devices, increasing the thickness to the intermediate range resulted in more consistently high device performance. This suggests that a sufficiently thick NiO_x layer is required to provide an effective HTL while maintaining efficient charge transport. In contrast, the 10 nm layers showed less consistent performance and generally lower J_{SC} and V_{OC} . The reduced performance at greater thickness may result from increased transport resistance through the HTL, making further increases in thickness detrimental once sufficient coverage has been achieved[49][36]. The observed thickness dependence is in agreement with the general trend reported in the literature, where high-performing devices are commonly obtained with NiO_x HTL thicknesses in the range of approximately 5-10 nm[50][49]. The results therefore indicate that an intermediate NiO_x thickness provides the most suitable balance between sufficient surface coverage and efficient charge transport, with the investigated 5 and 7.5 nm layers giving the most favorable and similar device performance.

Although the resulting PCEs were lower than anticipated, the thickness dependence of the device performance remains clear. The J-V characteristics generally exhibited a relatively low fill factor, with the curves appearing compressed, together with a lower J_{SC} compared with the organic PTAA reference devices used in the laboratory. The reduced J_{SC} may indicate less efficient charge generation or extraction, while the low fill factor could be associated with increased series resistance, non-ideal charge transport, or recombination losses within the device. These effects may partly originate from the NiO_x layer or from the interfaces formed during device fabrication. Previous studies have reported that surface hydroxyl and Ni^{3+} species in NiO_x can participate in interfacial redox reactions with the initial perovskite layers. These reactions can modify the oxidation state of the NiO_x surface and generate interfacial defects or non-radiative recombination centers, thereby hindering efficient hole extraction and reducing device performance.

Such interfacial reactions could therefore contribute to the relatively low J_{SC} and FF observed in the present devices, particularly if the NiO_x surface contains a significant concentration of hydroxyl or other reactive species[35]. The XPS results showed small changes in the relative Ni^{3+} contribution with the deposition conditions, which could potentially influence the reactivity of the NiO_x surface. However, the present measurements do not directly demonstrate that an interfacial redox reaction occurred in the fabricated devices, and

this would require dedicated analysis of the NiO_x /perovskite interface. Nevertheless, the reported sensitivity of this interface provides a possible explanation for part of the performance gap relative to the PTAA reference devices.

5.2. Annealing effects

In contrast to the relatively small changes observed when varying the ALD pulse times, post-deposition annealing had a much stronger effect on the surface chemistry observed by XPS. The Ni 2p spectra showed a shift towards higher binding energy with increasing annealing treatment, accompanied by an increasing contribution from Ni-OH-related species. Under ozone annealing, the hydroxyl-related contribution became dominant, indicating that the surface chemistry was substantially modified by the strongly oxidizing treatment. Similar changes in NiO_x surfaces have been associated with the formation of hydroxyl and oxyhydroxyl species, particularly at the surface, where these species can strongly influence the measured XPS signal.

Interestingly, the nitrogen-annealed sample showed the largest deviation from the unannealed spectrum after the ozone treatment, rather than the air-annealed sample. This may result from the different balance between surface oxidation and hydroxyl removal in the respective atmospheres. Air provides oxygen during annealing and can promote oxidation and restructuring of the NiO_x surface, whereas an inert N_2 atmosphere can favor the removal or redistribution of weakly bound surface species without continuously supplying oxygen. Thermal treatment can therefore alter the defect structure and local chemical environment of the NiO_x surface even in the absence of an oxidizing atmosphere. In particular, changes in nickel vacancies and oxygen-related defects can modify the $\text{Ni}^{2+}/\text{Ni}^{3+}$ balance and produce noticeable changes in the Ni 2p spectrum. The pronounced change after N_2 annealing should therefore not necessarily be interpreted as evidence for a more strongly oxidized surface. Instead, it may indicate that the thermal treatment caused significant restructuring of the surface chemistry, including changes in hydroxyl coverage, defect concentration, and nickel oxidation states. This interpretation is consistent with the complex nature of Ni 2p spectra, where changes in peak position and relative intensity can arise from several overlapping chemical and electronic contributions. The O 1s spectrum is consequently important for distinguishing changes associated with lattice oxygen from those related to hydroxyl and other surface oxygen species.

The effect of post-deposition treatment on the optical properties was further investigated by UV-Vis spectroscopy of NiO_x films deposited on quartz. The annealed samples showed an increase in transmittance in the 250-400 nm region compared with the unannealed film, while the transmission at longer wavelengths remained largely unchanged. Since this wavelength range is close to the absorption edge of NiO_x , the observed change is likely related to modifications of the electronic states and defect structure near the band edge rather than a substantial change in the overall optical properties of the film. Thermal treatment can alter the defect structure and local chemical environment of NiO_x , potentially reducing defect-related absorption and resulting in increased near-UV transmission. This is consistent with the slightly reduced apparent optical band gap observed from the Tauc plots after air and nitrogen annealing, which may result from changes in defect-related states near the band edges.

5.3. Process and characterization limitations

Throughout the project, various issues and challenges were encountered during the ALD deposition and annealing processes. Some of these are described in the following section.

5.3.1. ALD

Throughout the project the ALD exhibited inconsistencies not necessarily limited to the recipe of the deposition. Back to back deposition thickness consistency could vary substantially while practically performing everything identically. The machine was already previously identified to have a sealing issue, where the lid did not fully align with the gas distribution hole to the shower head leading to a potential pressure gradient affecting the deposition flow. This was somewhat mitigated by performing trial and error depositions while slightly rotating the lid when lowering it and marking its location. In the end a single orientation was found to perform the best and was marked at the top of the lid such that to perform a "reliable" deposition, the lid must be manually nudged to the marker while it is being lowered. Processes that rely on manual execution are inherently more susceptible to human error and inaccuracies, which can introduce slight variations in positioning. These variations may prevent the lid from fully aligning with the gas delivery lines, potentially

resulting in non-uniform gas flow and variations in deposition. Although higher pulse rates for the precursor and co-reactant can help mitigate this effect, they cannot fully eliminate it. Instead, the increased pulse rates may mask the underlying issue by compensating for variations in gas delivery, making the problem less apparent while the root cause remains unresolved.

Another issue occurred when the rack holding the sample holder hit the side wall of the ALD chamber. Upon further inspection it was revealed that the screws that hold the rack loosened over time causing it to tilt and hit the edge of the chamber, shown in Figure 5.1. The screws were tightened and adjusted based on a visual estimate to quickly restore the machine to operational condition.



Figure 5.1: Tilted sample holder rack due to the screws loosening over time marked in the red circle.

The eventual collision of the holder with the machine wall suggests that the holder may have been gradually tilting before the malfunction occurred. This progressive misalignment of the sample holder over multiple batches can be another possible explanation for the sample uniformity issues experienced in the earlier batches. Since the holder was subsequently realigned based on visual estimation, any remaining alignment error may also have contributed to the observed variability. As the holder is not perfectly level, the precursor and co-reactant flows may not be distributed uniformly across the substrate, potentially resulting in non-uniform deposition thickness, particularly toward the top of the substrate.

In subsequent depositions, it was observed that the deposited NiO_x layer thickness had decreased drastically, accompanied by issues with film uniformity. The deposition recipe and precursor flows were carefully checked, as well as the bracket holding the sample holder beneath the chamber lid, to determine whether it had become loose and caused the sample holder to shift or become misaligned. However, no issues were identified during these checks.

It was subsequently suggested that the precursor bottle may have been depleted. After replacing the precursor bottle and performing several dummy depositions to flush the system, the ALD system appeared to return to normal operation, with the deposited NiO_x thickness and uniformity recovering.

5.3.2. Hot plates and ALD chamber for annealing

For annealing the samples either inside the glovebox or under ambient air, laboratory-grade Stuart hot plates were used. These hot plates are capable of reaching temperatures up to 325°C , which exceeds the required annealing temperature of 300°C . However, the hot plates exhibit significant temperature inaccuracies and

fluctuations. When set to 300 °C, the temperature typically overshoots the setpoint initially before decreasing again, followed by a substantial undershoot. This oscillatory behaviour can persist for approximately 30 minutes before the temperature eventually stabilizes.

The temperature fluctuations become more pronounced when relatively cold samples at room temperature are placed on the hot plate. The hot plate temperature rapidly decreases to approximately 270 °C, after which it slowly undergoes another cycle of overshooting and undershooting before returning to the desired temperature. This behaviour is undesirable because it results in a different thermal treatment from the intended annealing profile. Furthermore, prolonged heating is particularly undesirable inside the glovebox, where it may unnecessarily heat the surrounding environment and potentially affect other temperature-sensitive materials or processes.

To minimize these temperature fluctuations and obtain a more reproducible annealing procedure, an alternative approach was adopted. The hot plate was first set to its maximum temperature of 325 °C and allowed to stabilize before placing the samples on the surface. Upon placing the room-temperature samples on the hot plate, the temperature rapidly decreased to approximately 300 °C. The temperature was then manually regulated using the hot plate control knob to prevent substantial overshooting or undershooting. Although this approach does not provide an ideal or precisely controlled annealing profile, it was found to be more consistent and considerably faster than setting the hot plate directly to 300 °C and waiting for the full temperature oscillation to subside.

The observed behaviour is likely related to the limited temperature-control range when operating close to the maximum temperature of the hot plate. At 300 °C, the available heating capacity may be insufficient to compensate rapidly for the temperature drop caused by placing the relatively cold samples on the surface, resulting in prolonged temperature fluctuations.

Annealing under vacuum in the ALD chamber presents a different set of challenges and limitations. Unlike the hot plates, where temperature control is limited by operation close to the maximum heating capacity, the ALD system is capable of reaching the required high temperatures. However, because the chamber can currently only be heated under vacuum and has a relatively large internal volume, it takes approximately 30 minutes to reach the desired temperature. Furthermore, the actual temperature of the sample holder is somewhat uncertain. Temperature stickers were previously used to assess the temperature at lower setpoints and indicated a small discrepancy between the displayed temperature and the actual temperature of the sample holder. As temperature stickers suitable for the higher annealing temperature were not available, this measured temperature difference was assumed to remain constant and was added to the target temperature of 300 °C when setting the ALD chamber.

An additional complication arises from the chamber evacuation procedure. Depressurizing the chamber takes approximately 5 minutes, during which the heating is switched off. Opening the chamber then causes further cooling. The 20-slot sample holder must subsequently be carefully removed, the samples transferred onto it, and the holder reinserted into the ALD chamber, which takes approximately another 5 minutes. The chamber must then be evacuated and reheated before the intended annealing conditions are restored.

This ultimately means that the samples are subjected to a temperature profile that deviates from the intended annealing conditions, with the exact thermal exposure varying between batches. This introduces uncertainty in both the effective annealing temperature and duration, resulting in somewhat inconsistent annealing conditions between samples.

5.3.3. Kelvin probe

Throughout most of the project, the Kelvin probe (KP) was either unavailable due to high demand or undergoing repairs. As the KP is a UHV system, it relies on a vacuum pump to achieve the required pressure. The pump exhibited intermittent issues, occasionally failing to pump down the chamber properly. In such cases, restarting the pump several times was often necessary before it would operate normally. When the KP eventually became available for use, the pump failed completely and was no longer able to achieve the required vacuum. It took some time before a replacement pump could be sourced and installed. Consequently, not all of the samples that were intended to be characterized could be measured.

Initially, the intention was to characterize the samples using Kelvin probe force microscopy (KPFM). However,

the KPFM system experienced issues with the supplied measurement tips, resulting in inconsistent measurements. The cause of these inconsistencies could not be identified despite repeated attempts. After several unsuccessful measurements, the decision was therefore made to switch to the conventional KP as an alternative method for determining the work function.

6

Conclusion

6.1. Conclusions

The main objective of this thesis was to characterize and evaluate the atomic layer deposited NiO_x films and create a perovskite solar cell with this inorganic layer. Inorganic transport layers are beneficial due to generally exhibiting greater long-term stability and are less susceptible to degradation over time. The study shows that precise control over precursor and co-reactant exposure time is critical for optimizing hole transport layers in perovskite solar cells. For this, the film thickness, surface morphology and stoichiometry, optical properties, work function and device performance were investigated.

Systematic pulse saturation experiments established a reproducible, self-limiting growth rate of 0.0457 nm per cycle. By balancing spatial uniformity constraints with the defect chemistry required for effective p-type conductivity, an optimal deposition recipe utilizing a 3.0 s nickel precursor pulse and a 0.2 s H_2O co-reactant pulse was identified. Topographical analyses confirmed that these films are exceptionally conformal, seamlessly propagating the underlying roughness of both bare silicon and indium tin oxide (ITO) substrates. Furthermore, the optical integrity of the NiO_x layers remained robust, exhibiting high intrinsic transparency exceeding 90% in the visible spectrum and maintaining a stable fundamental band gap of approximately 3.84 eV across all investigated film thicknesses.

Post-deposition thermal treatments were investigated as a way to change and tune the stoichiometry of the NiO_x layer and proved instrumental in tuning the stoichiometric and electronic properties of the transport layers. X-ray photoelectron spectroscopy (XPS) revealed that annealing the films in ambient air and nitrogen atmospheres successfully enhanced the relative fraction of Ni^{3+} surface states. Whereas ozone treatments resulted in detrimental surface hydroxide formation. Correspondingly, these favorable thermal treatments induced a subtle narrowing of the optical band gap and systematically lowered the absolute work function to an operative range of 4.35 to 4.55 eV. This confirms that targeted post-deposition environments can effectively dictate the surface chemistry and electronic band alignment prior to integration with the perovskite absorber.

The subsequent integration of these optimized NiO_x films into full photovoltaic architectures underscored the sensitivity of device performance to hole transport layer thickness. Utilizing a modified low-band gap perovskite formulation, an intermediate NiO_x thickness of 7.5 nm emerged as the structural optimum. This specific configuration maximized short-circuit current density while mitigating the severe open-circuit voltage degradation observed in both the ultra-thin 5 nm and thicker 10 nm regimes. Consequently, the champion device utilizing a 7.5 nm NiO_x layer annealed in ambient air achieved a peak power conversion efficiency of 3.90%, alongside a V_{oc} of 0.874 V and a J_{sc} of 12.33 mA cm^{-2} . Nevertheless, despite the successful synthesis of highly conformal and chemically tunable NiO_x films, the persistent S-shaped deformations dominating the optimal current density and voltage characteristics highlight a fundamental charge extraction barrier. Resolving this non-ideal interfacial alignment and mitigating transport resistance between the charge-selective layer and the perovskite absorber remains the primary challenge to be addressed.

Overall, this research demonstrates that the current implementation of ALD NiO_x remains highly experimental. The J – V characteristics and overall device efficiency lag significantly behind the organic reference

counterpart, PTAA, which by comparison achieved a power conversion efficiency of 8.99%, a V_{oc} of 0.992 V, a J_{sc} of 16.84 mA cm^{-2} , and a fill factor of 53.82%.

6.2. Recommendation

Equipment Calibration and Deposition Consistency

To eliminate unintended deposition variations, the mechanical alignment of the ALD system must be refined. Specifically, the reaction chamber lid requires a more consistent or permanent alignment mechanism, and the internal bracket supporting the sample holder must be carefully calibrated. Addressing these hardware inconsistencies is essential to remove a significant, unaccounted source of experimental uncertainty from the current deposition process.

Interfacial Dynamics and Intrinsic Conductivity

Future work should prioritize an in-depth investigation of the interfacial dynamics between the NiO_x hole transport layer and the perovskite absorber to identify the physical origin of the observed charge transport barriers. Additionally, the intrinsic charge carrier dynamics and conductivity of the bare NiO_x films should be evaluated independently of a full device architecture. Time-Resolved Microwave Conductivity (TRMC) is highly recommended for this purpose; as a contactless technique, TRMC measures the mobility and lifetime of photo-generated charge carriers. This will offer direct insight into the intrinsic electronic quality and recombination kinetics of the film without interference from adjacent layers or metal contacts.

Thermal Treatment Optimization

The post-deposition annealing procedures require both hardware and methodological improvements. Upgrading to a more robust and precisely calibrated hotplate will minimize temperature fluctuations and ensure greater batch-to-batch reproducibility. Furthermore, future thermal treatment protocols should investigate the effects of a controlled temperature ramp rather than subjecting the samples to immediate thermal shock. Gradually annealing the films may facilitate a more controlled structural relaxation and defect formation process, potentially yielding a more favorable stoichiometric and energetic state for the NiO_x layers.

References

- [1] I. P. on Climate Change (IPCC), *Climate Change 2022 – Impacts, Adaptation and Vulnerability: Working Group II Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, 2023.
- [2] S. K. Ghosh, “Fossil fuel consumption trend and global warming scenario: Energy overview,” *Global Journal of Engineering Sciences*, 2020. [Online]. Available: <https://api.semanticscholar.org/CorpusID:234941656>.
- [3] C. McGlade and P. Ekins, “The geographical distribution of fossil fuels unused when limiting global warming to 2 °c,” *Nature*, vol. 517, no. 7533, pp. 187–190, 2015, ISSN: 1476-4687. DOI: 10.1038/nature14016. [Online]. Available: <https://doi.org/10.1038/nature14016>.
- [4] Z. Bi, R. Guo, and R. Khan, “Renewable adoption, energy reliance, and co₂ emissions: A comparison of developed and developing economies,” *Energies*, vol. 17, no. 13, p. 3111, 2024, ISSN: 1996-1073. DOI: 10.3390/en17133111. [Online]. Available: <https://doi.org/10.3390/en17133111>.
- [5] F. J. M. M. Nijse et al., “The momentum of the solar energy transition,” *Nature Communications*, vol. 14, no. 1, p. 6542, 2023, ISSN: 2041-1723. DOI: 10.1038/s41467-023-41971-7. [Online]. Available: <https://doi.org/10.1038/s41467-023-41971-7>.
- [6] National Renewable Energy Laboratory, *Best research-cell efficiency chart*, Accessed: 2026-04-30, 2026. [Online]. Available: <https://www.nrel.gov/pv/cell-efficiency>.
- [7] A. Richter, M. Hermle, and S. W. Glunz, “Reassessment of the limiting efficiency for crystalline silicon solar cells,” *IEEE Journal of Photovoltaics*, vol. 3, no. 4, pp. 1184–1191, 2013. DOI: 10.1109/JPHOTOV.2013.2270351.
- [8] J.-F. Guillemoles, T. Kirchartz, D. Cahen, and U. Rau, “Guide for the perplexed to the shockley–queisser model for solar cells,” *Nature Photonics*, vol. 13, no. 8, pp. 501–505, Aug. 2019. DOI: 10.1038/s41566-019-0479-2. [Online]. Available: <https://doi.org/10.1038/s41566-019-0479-2>.
- [9] VDMA. “International technology roadmap for photovoltaics (itrpv),” VDMA, Accessed: Aug. 31, 2026. [Online]. Available: <https://www.vdma.eu/en-GB/international-technology-roadmap-photovoltaic>.
- [10] B. Das, Z. Liu, I. Aguilera, U. Rau, and T. Kirchartz, “Defect tolerant device geometries for lead-halide perovskites,” *Materials Advances*, vol. 2, no. 11, pp. 3655–3670, Jun. 2021, ISSN: 2633-5409. DOI: 10.1039/d0ma00902d. eprint: <https://pubs.rsc.org/ma/article-pdf/2/11/3655/7289176/d0ma00902d.pdf>. [Online]. Available: <https://doi.org/10.1039/d0ma00902d>.
- [11] I. Mosquera-Lois, Y.-T. Huang, H. Lohan, J. Ye, A. Walsh, and R. L. Z. Hoye, “Multifaceted nature of defect tolerance in halide perovskites and emerging semiconductors,” *Nature Reviews Chemistry*, vol. 9, no. 5, pp. 287–304, Apr. 2025. DOI: 10.1038/s41570-025-00702-w.
- [12] M. A. Green, A. Ho-Baillie, and H. J. Snaith, “The emergence of perovskite solar cells,” *Nature Photonics*, vol. 8, no. 7, pp. 506–514, 2014, ISSN: 1749-4893. DOI: 10.1038/nphoton.2014.134. [Online]. Available: <https://doi.org/10.1038/nphoton.2014.134>.
- [13] N. J. Jeon et al., “Compositional engineering of perovskite materials for high-performance solar cells,” *Nature*, vol. 517, no. 7535, pp. 476–480, 2015. DOI: 10.1038/nature14133. [Online]. Available: <https://doi.org/10.1038/nature14133>.
- [14] J. Sala et al., “Compositional investigation for bandgap engineering of wide bandgap triple cation perovskite,” *ACS Applied Energy Materials*, vol. 4, no. 7, pp. 6377–6384, Jul. 2021, ISSN: 2574-0962. DOI: 10.1021/acsaem.1c00810. eprint: <https://pubs.acs.org/aaemcq/article-pdf/4/7/6377/4435883/ae1c00810.pdf>. [Online]. Available: <https://doi.org/10.1021/acsaem.1c00810>.
- [15] S. D. Stranks et al., “Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber,” *Science*, vol. 342, no. 6156, pp. 341–344, Oct. 2013. DOI: 10.1126/science.1243982.

- [16] A. Al-Ashouri et al., "Monolithic perovskite/silicon tandem solar cell with >29% efficiency by enhanced hole extraction," *Science*, vol. 370, no. 6522, pp. 1300–1309, 2020. DOI: 10.1126/science.abd4016. eprint: <https://www.science.org/doi/pdf/10.1126/science.abd4016>. [Online]. Available: <https://www.science.org/doi/abs/10.1126/science.abd4016>.
- [17] S.-R. Bae, D. Heo, and S. Kim, "Recent progress of perovskite devices fabricated using thermal evaporation method: Perspective and outlook," *Materials Today Advances*, vol. 14, p. 100232, 2022, ISSN: 2590-0498. DOI: <https://doi.org/10.1016/j.mtadv.2022.100232>. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S2590049822000285>.
- [18] M. Stefanelli, L. Vesce, and A. Di Carlo, "Upscaling of carbon-based perovskite solar module," *Nanomaterials*, vol. 13, Jan. 2023. DOI: 10.3390/nano13020313.
- [19] T. Ma, S. Wang, Y. Zhang, K. Zhang, and L. Yi, "The development of all-inorganic cspb_x3 perovskite solar cells," *Journal of Materials Science*, vol. 55, no. 2, pp. 464–479, Jan. 2020. DOI: 10.1007/s10853-019-03974-y.
- [20] D. A. Neamen, *Semiconductor Physics and Devices: Basic Principles*, 4th ed. McGraw-Hill, 2011, ISBN: 978-0-07-352958-5.
- [21] S.-K. Kim et al., "Comparison of niox thin film deposited by spin-coating or thermal evaporation for application as a hole transport layer of perovskite solar cells," *RSC Advances*, vol. 10, no. 71, pp. 43847–43852, Dec. 2020, ISSN: 2046-2069. DOI: 10.1039/d0ra08776a. eprint: <https://pubs.rsc.org/ra/article-pdf/10/71/43847/7510864/d0ra08776a.pdf>. [Online]. Available: <https://doi.org/10.1039/d0ra08776a>.
- [22] J. Jung, D. L. Kim, S. H. Oh, and H. J. Kim, "Stability enhancement of organic solar cells with solution-processed nickel oxide thin films as hole transport layers," *Solar Energy Materials and Solar Cells*, vol. 102, pp. 103–108, 2012. [Online]. Available: <https://api.semanticscholar.org/CorpusID:95959685>.
- [23] J. R. Manders et al., "Solution-processed nickel oxide hole transport layers in high efficiency polymer photovoltaic cells," *Advanced Functional Materials*, vol. 23, no. 23, pp. 2993–3001, 2013. DOI: <https://doi-org.tudelft.idm.oclc.org/10.1002/adfm.201202269>. eprint: <https://advanced-onlinelibrary-wiley-com.tudelft.idm.oclc.org/doi/pdf/10.1002/adfm.201202269>. [Online]. Available: <https://advanced-onlinelibrary-wiley-com.tudelft.idm.oclc.org/doi/abs/10.1002/adfm.201202269>.
- [24] D.-W. Kuo et al., "Inverted mapbi3 perovskite solar cells based on optimized niox hole-transporting material and an interlayer of photovoltaic polymers exhibit a power conversion efficiency over 21% with an extended stability," *ACS Applied Electronic Materials*, vol. 5, no. 12, pp. 6897–6907, 2023. DOI: 10.1021/acsaelm.3c01318. eprint: <https://doi.org/10.1021/acsaelm.3c01318>. [Online]. Available: <https://doi.org/10.1021/acsaelm.3c01318>.
- [25] B. Tyagi et al., "Compact-porous hole-transport-layer for highly efficient near-infrared region transparent perovskite solar cells for tandem applications," *Journal of Alloys and Compounds*, vol. 960, p. 170970, 2023, ISSN: 0925-8388. DOI: <https://doi.org/10.1016/j.jallcom.2023.170970>. [Online]. Available: <https://www.sciencedirect.com/science/article/pii/S0925838823022739>.
- [26] J. W. Kim et al., "Enhancing efficiency of inverted perovskite solar cells by sputtered nickel oxide hole-transport layers," *Solar RRL*, vol. 8, 2023. [Online]. Available: <https://api.semanticscholar.org/CorpusID:266243797>.
- [27] Y. Luo et al., "Dc reactive-sputtered niox hole transport layers with tailored nickel vacancies for perovskite single-junction and textured perovskite/silicon tandem solar cells," *Small*, e06247, 2025. [Online]. Available: <https://api.semanticscholar.org/CorpusID:280684020>.
- [28] Y. Jin et al., "Recrystallizing sputtered niox for improved hole extraction in perovskite/silicon tandem solar cells," *Advanced Energy Materials*, vol. 15, 2024. [Online]. Available: <https://api.semanticscholar.org/CorpusID:273551881>.

- [29] H. Park, P. Nandi, Y. In, and H. Shin, "Practical and thermal atomic layer deposition of nio as hole-transporting layers for inverted perovskite solar cells," *Solar RRL*, vol. 8, no. 4, p. 2300858, 2024. DOI: <https://doi-org.tudelft.idm.oclc.org/10.1002/solr.202300858>. eprint: <https://onlinelibrary-wiley-com.tudelft.idm.oclc.org/doi/pdf/10.1002/solr.202300858>. [Online]. Available: <https://onlinelibrary-wiley-com.tudelft.idm.oclc.org/doi/abs/10.1002/solr.202300858>.
- [30] F. Guo et al., "Ald-deposited hydroxyl-rich niox to enhance sam anchoring for stable and efficient perovskite solar cells," *Molecules*, vol. 30, no. 6, 2025, ISSN: 1420-3049. DOI: 10.3390/molecules30061299. [Online]. Available: <https://www.mdpi.com/1420-3049/30/6/1299>.
- [31] Y. Wei et al., "Enhancing performance of niox-based inverted perovskite solar cells: Advances in buried interface material modification strategy," *Small*, vol. 21, no. 12, p. 2411630, 2025. DOI: <https://doi-org.tudelft.idm.oclc.org/10.1002/smll.202411630>. eprint: <https://onlinelibrary-wiley-com.tudelft.idm.oclc.org/doi/pdf/10.1002/smll.202411630>. [Online]. Available: <https://onlinelibrary-wiley-com.tudelft.idm.oclc.org/doi/abs/10.1002/smll.202411630>.
- [32] CleanEnergyWiki, *Atomic layer deposition ald*, https://cleanenergywiki.org/index.php?title=Atomic_Layer_Deposition_ALD, Accessed: 2026-07-13, 2009.
- [33] K. Mukherjee, C. A. A. van Helvoirt, C. H. L. Weijtens, M. A. Verheijen, and M. Creatore, "On the impact of atomic layer deposition processing on the chemical and opto-electrical properties of NiO thin films," *Journal of Vacuum Science and Technology A*, vol. 43, no. 6, p. 062404, 2025. DOI: 10.1116/6.0004826.
- [34] Ereztech, *Nickel bis(n,n'-ditertialbutylacetamidinate)*, CAS No. 940895-79-4, accessed 2026-05-27, 2026. [Online]. Available: <https://ereztech.com/product/nickel-bisnn-ditertialbutylacetamidinate-940895-79-4/>.
- [35] X. Yu et al., "Controlled niox defect engineering to harnessing redox reactions in perovskite photo-voltaic cells via atomic layer deposition," *ACS Applied Materials & Interfaces*, vol. 16, no. 24, pp. 31114–31125, Jun. 2024, ISSN: 1944-8244. DOI: 10.1021/acsami.4c03761. eprint: <https://pubs.acs.org/aamick/article-pdf/16/24/31114/880736/am4c03761.pdf>. [Online]. Available: <https://doi.org/10.1021/acsami.4c03761>.
- [36] X. Kuang, Z. Liu, Y. Hong, Y. Chen, Y. Xiao, and Z. Liang, "Effects of adjusting nickel pulse count on niox films prepared by atomic layer deposition," *Physical Chemistry Chemical Physics*, vol. 26, no. 42, pp. 26886–26894, Nov. 2024, ISSN: 1463-9076. DOI: 10.1039/d4cp03553d. eprint: <https://pubs.rsc.org/cp/article-pdf/26/42/26886/9636811/d4cp03553d.pdf>. [Online]. Available: <https://doi.org/10.1039/d4cp03553d>.
- [37] M. Imran, H. Coskun, N. A. Khan, and J. Ouyang, "Role of annealing temperature of nickel oxide (NiOx) as hole transport layer in work function alignment with perovskite," *Applied Physics A*, vol. 127, no. 2, Jan. 2021. DOI: 10.1007/s00339-021-04283-5.
- [38] S. Jena and N. K. Sahoo, "Evolutionary design, deposition and characterization techniques for interference optical thin-film multilayer coatings and devices," in *Recent Advances in Thin Films*, S. Kumar and D. K. Aswal, Eds. Singapore: Springer Singapore, 2020, pp. 281–343, ISBN: 978-981-15-6116-0. DOI: 10.1007/978-981-15-6116-0_10. [Online]. Available: https://doi.org/10.1007/978-981-15-6116-0_10.
- [39] N. Ishida, "Atomic force microscopy," in *Non-Destructive Material Characterization Methods*, A. Otsuki, S. Jose, M. Mohan, and S. Thomas, Eds., Elsevier, 2024, pp. 89–125, ISBN: 9780323911504. DOI: 10.1016/B978-0-323-91150-4.00011-2.
- [40] OverlordQ, *Atomic force microscope block diagram*, <https://commons.wikimedia.org/w/index.php?curid=3592868>, Public domain. Accessed: 2026-07-20.
- [41] S. Magonov, "Visualization of polymers at surfaces and interfaces with atomic force microscopy," in *Handbook of Surfaces and Interfaces of Materials*, H. S. Nalwa, Ed., Academic Press, 2001, pp. 393–430. DOI: 10.1016/B978-012513910-6/50029-3.
- [42] Science Education Resource Center (SERC), Carleton College, *Schematic diagram of the components of an xps instrument*, Diagram from Malgorzata Kot, PhD dissertation. Accessed: 2026-07-20, 2021. [Online]. Available: https://serc.carleton.edu/download/images/256274/schematic_diagram_xps_instrument.jpeg.webp.

- [43] Newport Corporation, *Figure 4: Light path of a solar simulator*, Online image, Figure retrieved from the Newport Solar Simulation webpage. Accessed: 2026-07-20. [Online]. Available: <https://www.newport.com.cn/n/solar-simulation>.
- [44] A. R. Blume, W. Calvet, A. Ghafari, T. Mayer, A. Knop-Gericke, and R. Schlögl, "Structural and chemical properties of niox thin films: The role of oxygen vacancies in niooh formation in a h2o atmosphere," *Physical Chemistry Chemical Physics*, vol. 25, pp. 25 552–25 565, 2023. DOI: 10.1039/D3CP02047A.
- [45] N. Phung et al., "Enhanced self-assembled monolayer surface coverage by ald nio in p-i-n perovskite solar cells," *ACS Applied Materials & Interfaces*, vol. 14, no. 1, pp. 2166–2176, Dec. 2021, ISSN: 1944-8244. DOI: 10.1021/acsami.1c15860. eprint: <https://pubs.acs.org/aamick/article-pdf/14/1/2166/3532003/am1c15860.pdf>. [Online]. Available: <https://doi.org/10.1021/acsami.1c15860>.
- [46] C.-C. Hsu, H.-W. Su, C.-H. Hou, J.-J. Shyue, and F.-Y. Tsai, "Atomic layer deposition of NiO hole-transporting layers for polymer solar cells," *Nanotechnology*, vol. 26, no. 38, p. 385 201, 2015. DOI: 10.1088/0957-4484/26/38/385201.
- [47] R. Zhao, S. Xiao, S. Yang, and X. Wang, "Surface thermolytic behavior of nickel amidinate and its implication on the atomic layer deposition of nickel compounds," *Chemistry of Materials*, vol. 31, no. 14, pp. 5172–5180, 2019. DOI: 10.1021/acs.chemmater.9b01267.
- [48] N. Phung et al., "Atomic layer deposition of nio applied in a monolithic perovskite/perc tandem cell," *Solar Energy Materials and Solar Cells*, vol. 261, p. 112 498, 2023. DOI: 10.1016/j.solmat.2023.112498.
- [49] S. Seo et al., "An ultra-thin, un-doped NiO hole transporting layer of highly efficient (16.4%) organic–inorganic hybrid perovskite solar cells," *Nanoscale*, vol. 8, no. 22, pp. 11 403–11 412, 2016, ISSN: 2040-3364, 2040-3372. DOI: 10.1039/C6NR01601D. Accessed: Nov. 24, 2025. [Online]. Available: <https://xlink.rsc.org/?DOI=C6NR01601D>.
- [50] K. Mukherjee, D. Kreugel, N. Phung, C. Van Helvoirt, V. Zardetto, and M. Creatore, "On the V_{OC} loss in NiO-based inverted metal halide perovskite solar cells," *Materials Advances*, vol. 5, no. 21, pp. 8652–8664, 2024, ISSN: 2633-5409. DOI: 10.1039/D4MA00873A. Accessed: Nov. 24, 2025. [Online]. Available: <https://xlink.rsc.org/?DOI=D4MA00873A>.

A

GPC

This section shows all the acquired GPC for the different ALD recipes.

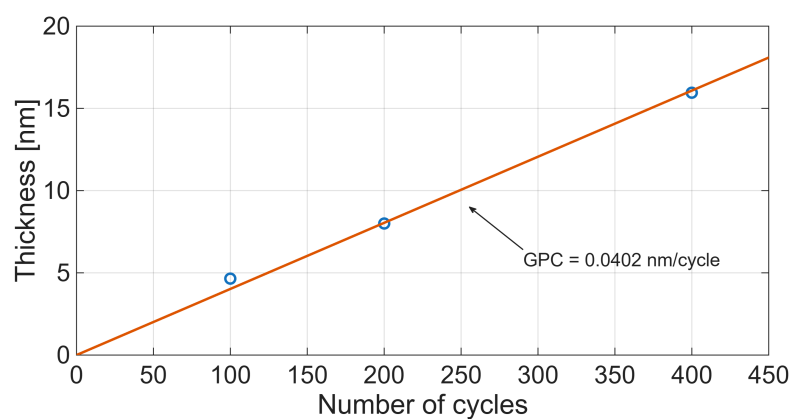


Figure A.1: GPC linear fit for the ALD recipe with Ni precursor pulse set to 2.0 seconds and H₂O co-reactant pulse set to 0.2 seconds.

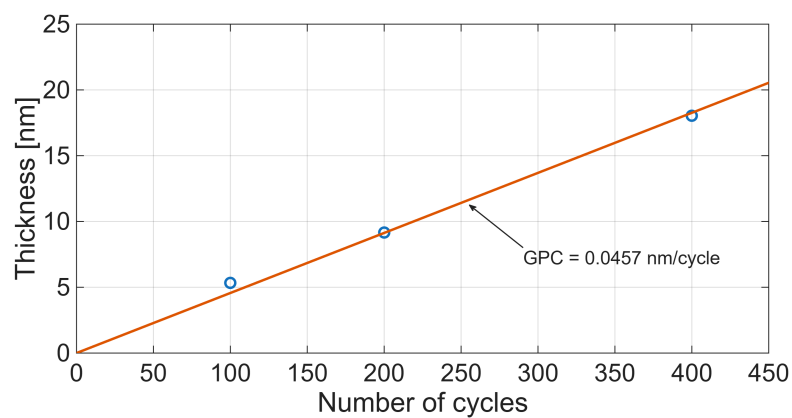


Figure A.2: GPC linear fit for the ALD recipe with Ni precursor pulse set to 3.0 seconds and H₂O co-reactant pulse set to 0.2 seconds.

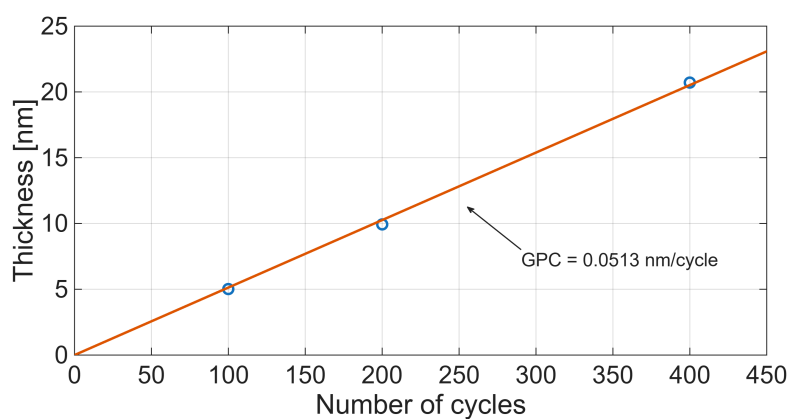


Figure A.3: GPC linear fit for the ALD recipe with Ni precursor pulse set to 4.0 seconds and H₂O co-reactant pulse set to 0.2 seconds.

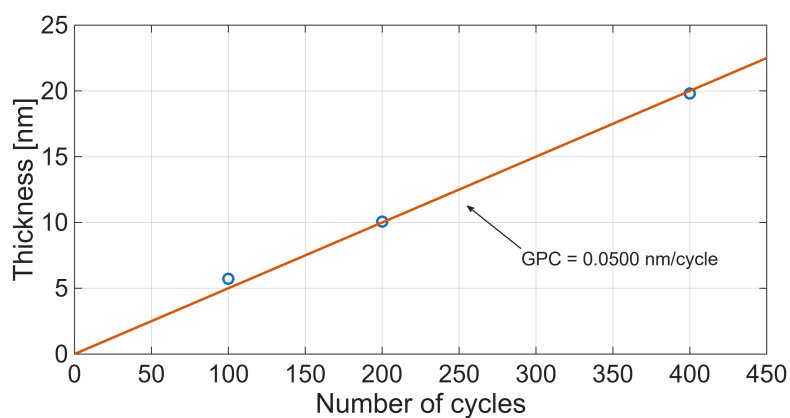


Figure A.4: GPC linear fit for the ALD recipe with Ni precursor pulse set to 5.0 seconds and H₂O co-reactant pulse set to 0.2 seconds.

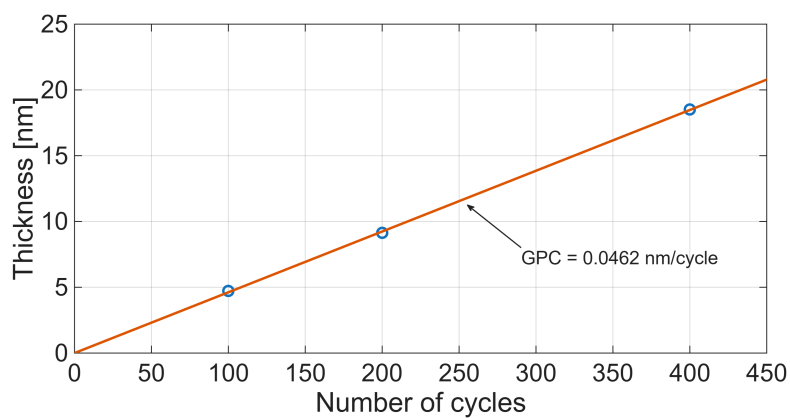


Figure A.5: GPC linear fit for the ALD recipe with Ni precursor pulse set to 4.0 seconds and H₂O co-reactant pulse set to 0.1 seconds.

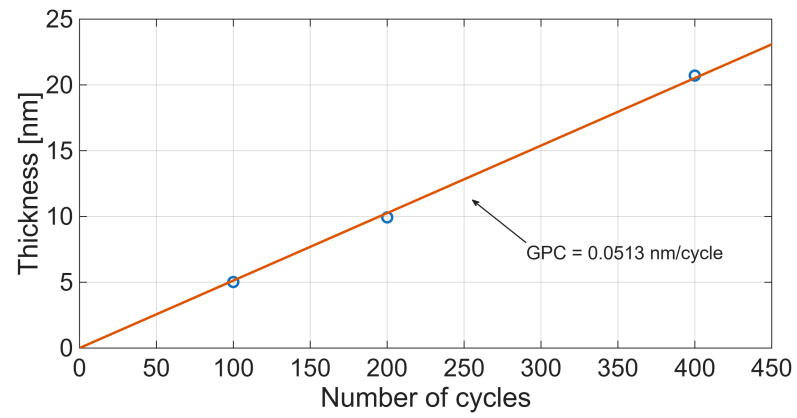


Figure A.6: GPC linear fit for the ALD recipe with Ni precursor pulse set to 4.0 seconds and H₂O co-reactant pulse set to 0.2 seconds.

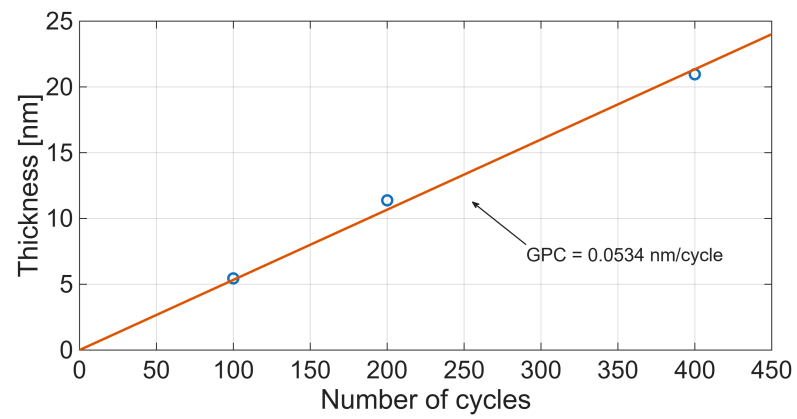


Figure A.7: GPC linear fit for the ALD recipe with Ni precursor pulse set to 4.0 seconds and H₂O co-reactant pulse set to 0.3 seconds.

B

Uniformity heatmaps

This section shows the heatmaps regarding the sample-to-sample thickness variation measured by the SE for different recipes.

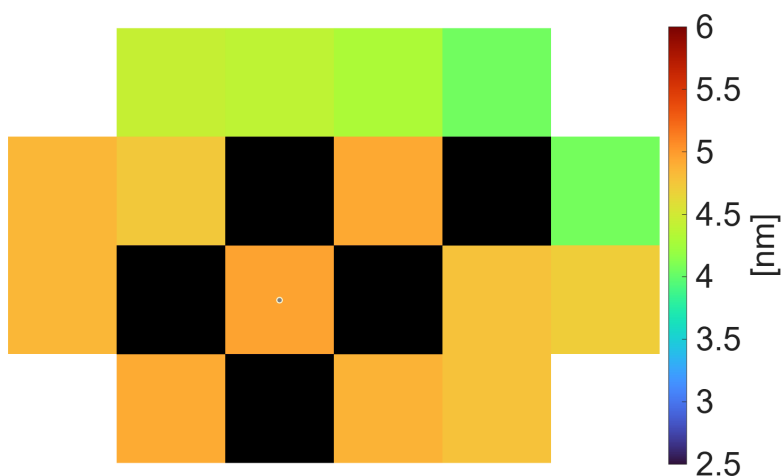


Figure B.1: Sample-to-sample thickness heatmap for ALD recipe with a Ni precursor pulse of 2.0 s and an H₂O co-reactant pulse of 0.2 s.



Figure B.2: Sample-to-sample thickness heatmap for ALD recipe with a Ni precursor pulse of 3.0 s and an H₂O co-reactant pulse of 0.2 s.



Figure B.3: Sample-to-sample thickness heatmap for ALD recipe with a Ni precursor pulse of 4.0 s and an H₂O co-reactant pulse of 0.2 s.

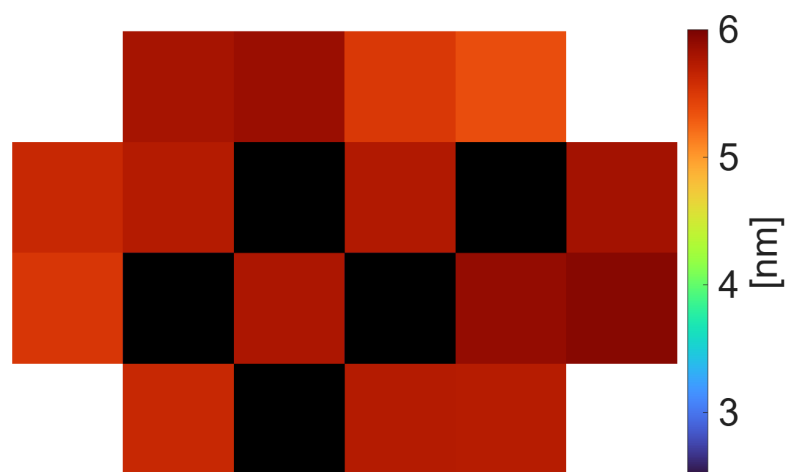


Figure B.4: Sample-to-sample thickness heatmap for ALD recipe with a Ni precursor pulse of 5.0 s and an H₂O co-reactant pulse of 0.2 s.

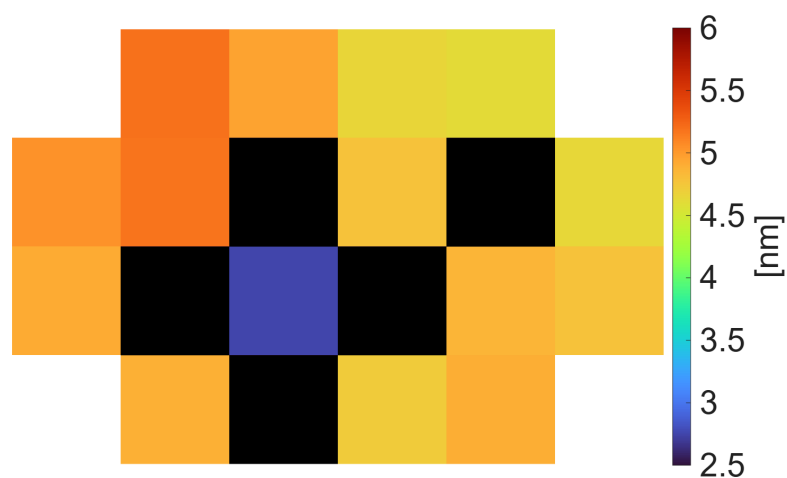


Figure B.5: Sample-to-sample thickness heatmap for ALD recipe with a Ni precursor pulse of 4.0 s and an H₂O co-reactant pulse of 0.1 s.



Figure B.6: Sample-to-sample thickness heatmap for ALD recipe with a Ni precursor pulse of 4.0 s and an H₂O co-reactant pulse of 0.2 s.



Figure B.7: Sample-to-sample thickness heatmap for ALD recipe with a Ni precursor pulse of 4.0 s and an H₂O co-reactant pulse of 0.3 s.

C

XPS results

This section has the results for the XPS measurements for the different post deposition treatments overlapping each other.

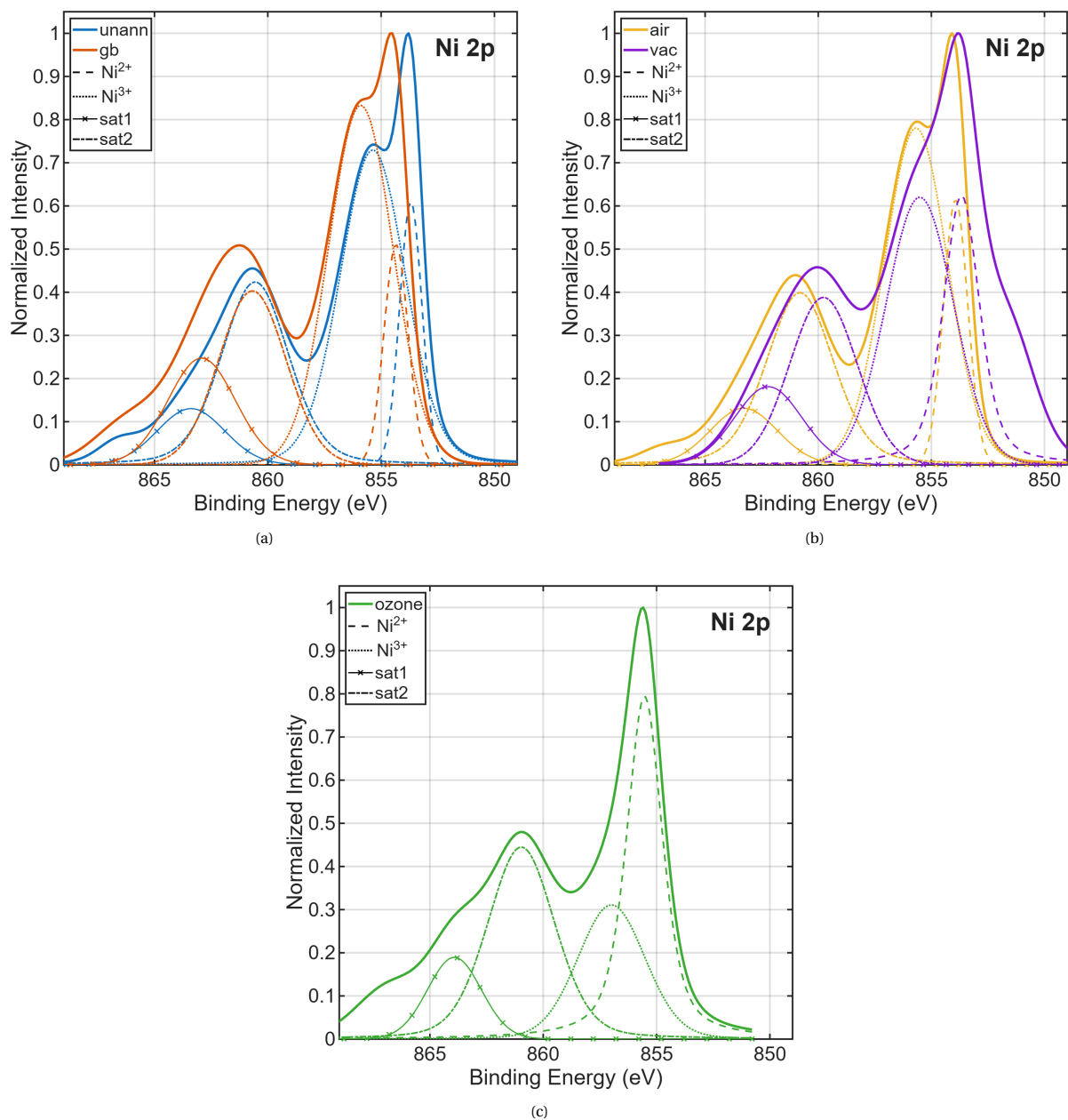


Figure C.1: XPS Ni 2p spectra of (a) unannealed and nitrogen-annealed NiO_x, (b) air- and vacuum-annealed NiO_x, and (c) ozone-annealed NiO_x, including the corresponding deconvoluted and fitted components.

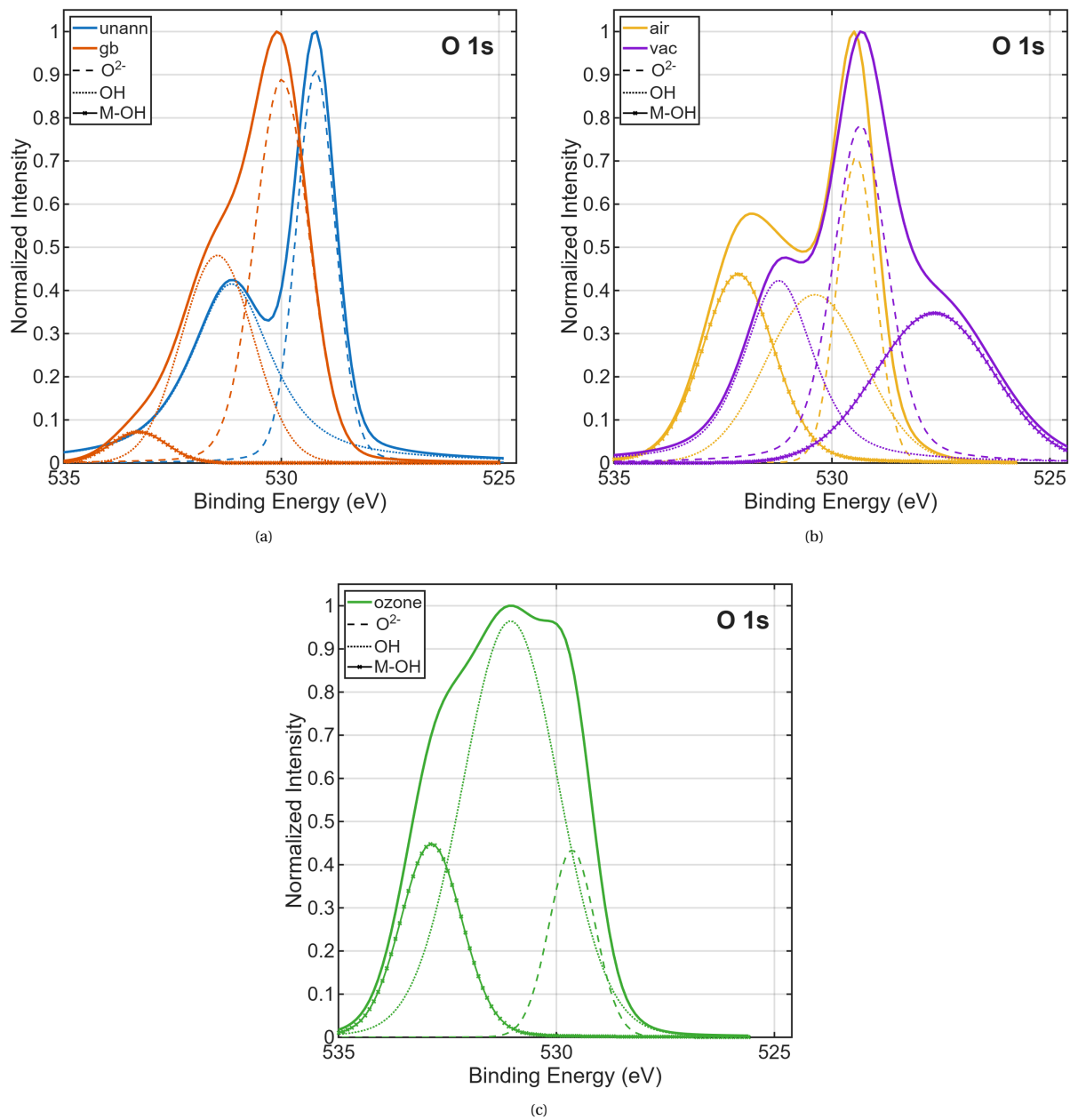


Figure C.2: XPS O 1s spectra of (a) unannealed and nitrogen-annealed NiO_x , (b) air- and vacuum-annealed NiO_x , and (c) ozone-annealed NiO_x , including the corresponding deconvoluted and fitted components.

D

Cell performance results

This section presents the $J - V$ curves for the rest of the cells.

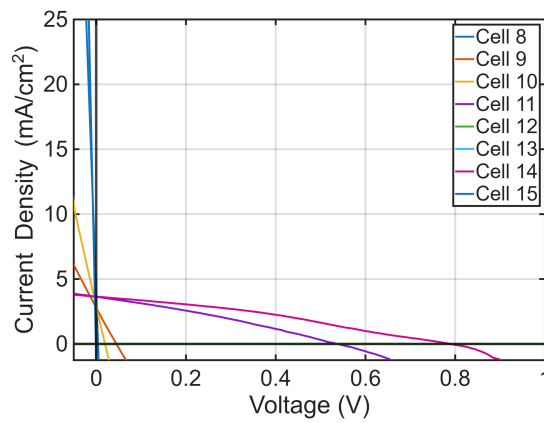


Figure D.1: J-V curves of the devices utilizing the old perovskite formulation with a 5 nm thick NiO_x hole transport layer.

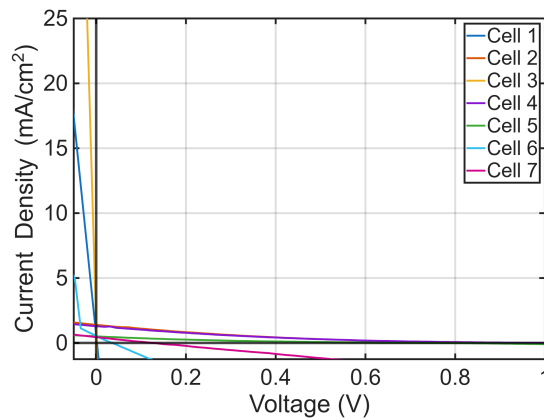


Figure D.2: J-V curves of the devices utilizing the old perovskite formulation with a 10 nm thick NiO_x hole transport layer.

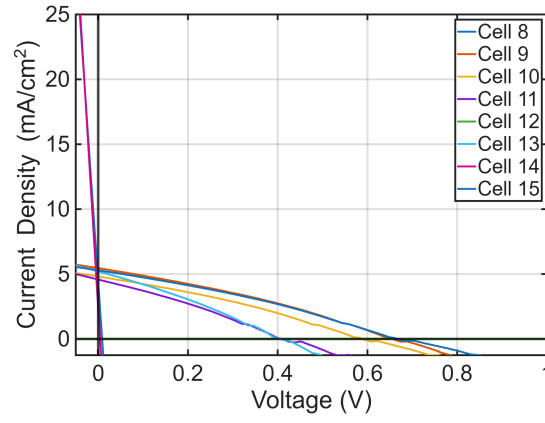


Figure D.3: J-V curves of the devices utilizing the new perovskite formulation with an unannealed 10 nm thick NiO_x hole transport layer.

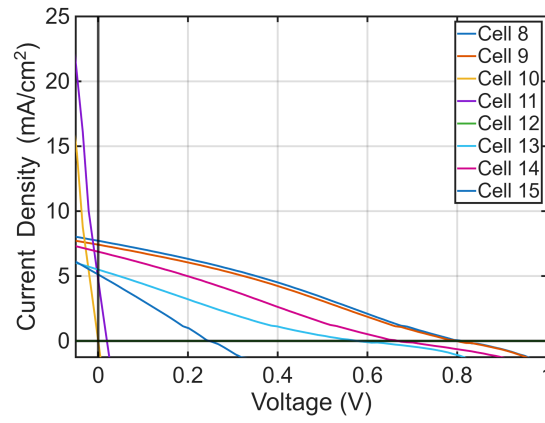


Figure D.4: J-V curves of the devices utilizing the new perovskite formulation with an unannealed 7.5 nm thick NiO_x hole transport layer.

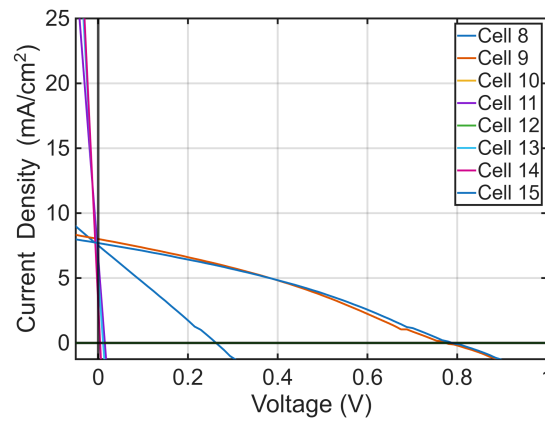


Figure D.5: J-V curves of the devices utilizing the new perovskite formulation with an unannealed 5 nm thick NiO_x hole transport layer.

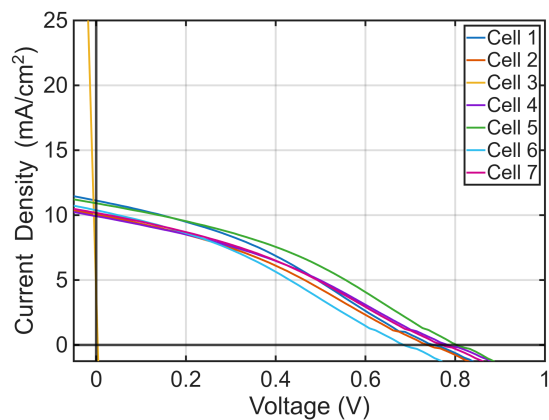


Figure D.6: J-V curves of the devices utilizing the new perovskite formulation with a 10 nm thick NiO_x hole transport layer annealed in a nitrogen-filled glovebox.

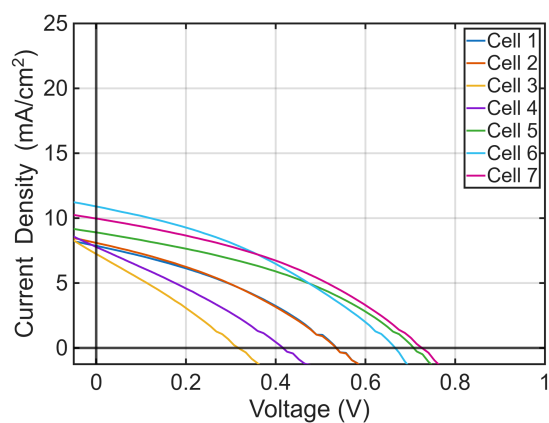


Figure D.7: J-V curves of the devices utilizing the new perovskite formulation with a 7.5 nm thick NiO_x hole transport layer annealed in a nitrogen-filled glovebox.

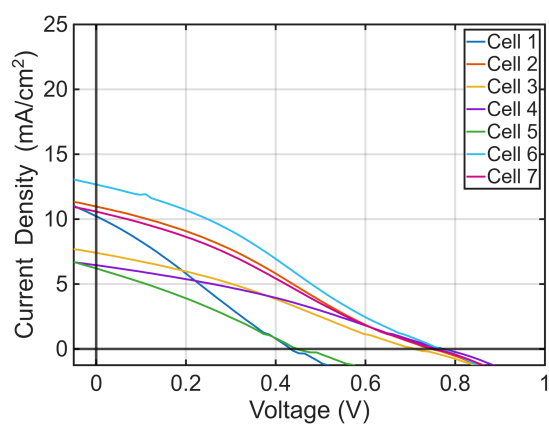


Figure D.8: J-V curves of the devices utilizing the new perovskite formulation with a 5 nm thick NiO_x hole transport layer annealed in a nitrogen-filled glovebox.

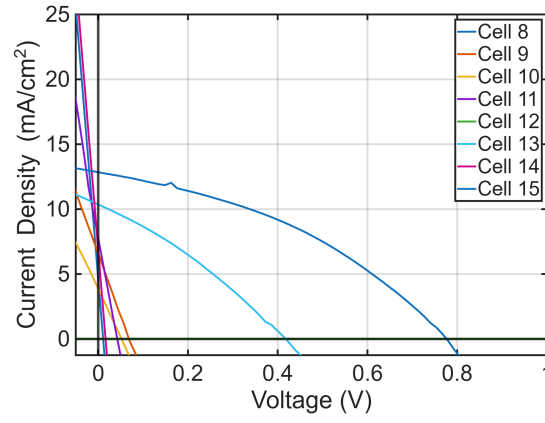


Figure D.9: J-V curves of the devices utilizing the new perovskite formulation with a 10 nm thick NiO_x hole transport layer annealed in ambient air.

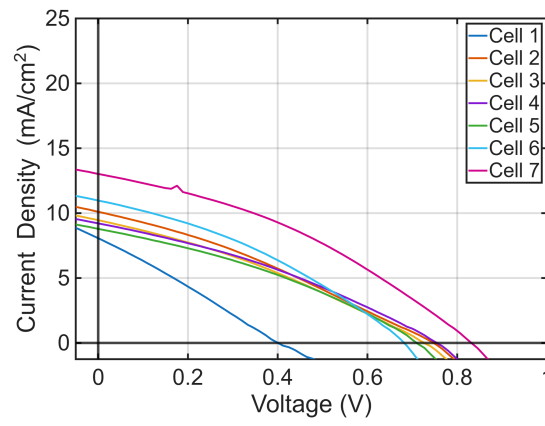


Figure D.10: J-V curves of the devices utilizing the new perovskite formulation with a 7.5 nm thick NiO_x hole transport layer annealed in ambient air.

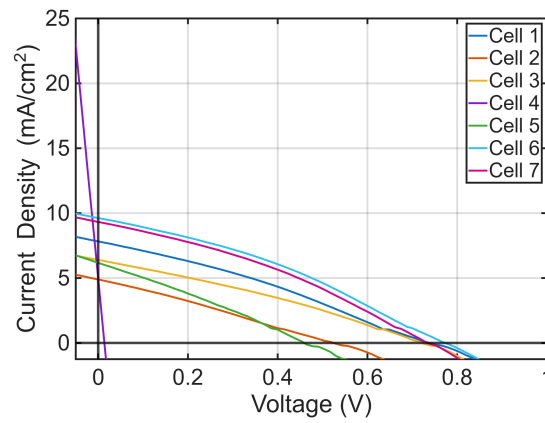


Figure D.11: J-V curves of the devices utilizing the new perovskite formulation with a 5 nm thick NiO_x hole transport layer annealed in ambient air.