

Journal of Materials Chemistry A

Materials for energy and sustainability

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: V. Kannampalli, M. Schmickler, B. Fabre, L. Largeau, A. Seyeux, A. Jose, S. D. Elliott, A. Devi and L. Santinacci, *J. Mater. Chem. A*, 2025, DOI: 10.1039/D5TA04555J.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Cite this: DOI: 00.0000/xxxxxxxxxx

Atomic Layer Deposition of NiO_x: Harnessing the Potential of New Precursor Combinations for Photoelectrochemical Water Oxidation[†]

Vyshnav Kannampalli,^a Marcel Schmickler,^{b,c} Bruno Fabre,^d Ludovic Largeau,^e Antoine Seyeux,^f José Alvarez,^{g,h} Simon Elliott,ⁱ Anjana Devi,^{b,c,j} and Lionel Santinacci^{a,*}

Received Date
Accepted Date

DOI: 00.0000/xxxxxxxxxx

Atomic layer deposition enables the fabrication of uniform, conformal, and pinhole-free thin films with precise sub-nanometer thickness control. This work presents the first report of thermal ALD of NiO_x using two nickel precursors –AlanisTM and [Ni(ⁱpki)₂]– in combination with two different oxygen source (H₂O and O₃), over a temperature range of 75–250°C. The Alanis/O₃ composition exhibited one of the highest growth per cycle (1.2 Å) and a broad ALD window between 100–175°C. In contrast, the Alanis/H₂O and [Ni(ⁱpki)₂]/O₃ combinations yielded lower growth rates of 0.74 Å at 150°C and 0.40 Å at 250°C, respectively. Comprehensive structural, morphological, optical, and chemical characterisations revealed that the choice of precursor combination and the reaction temperature significantly impact the film composition, strongly influencing its suitability for various applications. Notably, those parameters closely determined the photoelectrochemical performance and the stability of the Si/NiO_x-based photoanode towards oxygen evolution reaction. Photoelectrodes fabricated with Alanis/O₃ at 200°C demonstrate stability exceeding 24 h and exhibit a remarkable OER onset potential of 1.15 V vs RHE for a photocurrent density of 1 mA·cm⁻².

1 Introduction

Over the past decade, semiconductor oxides have gained significant advancements, leading to their widespread application in

various fields, including electronic devices such as photovoltaics, sensors, thin-film transistors, LEDs, and nonvolatile memory devices, as well as in catalysis, solar-fuels and other emerging technologies.^{1–6} Their stable electronic properties, combined with the ability to fabricate high-quality films at low temperatures,^{1,6–8} make them highly attractive for diverse applications.

The studies of oxide electronics has largely focused on *n*-type semiconductors for both flexible and rigid devices,^{2,5} but *p*-type oxides are gaining more and more attention due to their crucial role in next-generation technologies. These include protective and catalytic layers in photoelectrochemical (PEC) systems, transparent complementary metal-oxide semiconductors (CMOS) for integrated circuits, hole transport layers (HTLs) in photovoltaics, and flexible *p*-*n* junctions.^{9–12} Among *p*-type oxides, tin monoxide (SnO), cuprous oxide (Cu₂O), and nickel oxide (NiO) are currently the most extensively studied.¹³ However, SnO and Cu₂O are metastable at room temperature and they tend to undergo phase transformation into *n*-type tin dioxide (SnO₂) or lower-bandgap cupric oxide (CuO), respectively.⁵ In contrast, NiO exhibits excellent stability under ambient conditions, making it as a promising candidate for various applications. For instance, in addition to its chemical and thermal stability, NiO's wide direct

^a Aix Marseille Univ, CNRS, CINaM, Marseille, France. E-mail: lionel.santinacci@univ-amu.fr

^b Inorganic Materials Chemistry, Faculty of Chemistry and Biochemistry, Ruhr-University Bochum, 44801 Bochum, Germany.

^c Leibniz-Institute for Solid State and Materials Research Dresden, Helmholtzstrasse 20, 01069 Dresden, Germany.

^d CNRS, ISCR (Institut des Sciences Chimiques de Rennes)-UMR6226, Univ Rennes, Rennes F-35000, France

^e Centre de Nanosciences et de Nanotechnologies, CNRS, Université Paris-Saclay, 91120 Palaiseau, France.

^f Institut de Recherche de Chimie Paris, Research Group Physical Chemistry of Surfaces, Chimie ParisTech-CNRS, PSL Research University, Paris 75005, France.

^g CNRS, Laboratoire de Génie Electrique et Electronique de Paris, Sorbonne Université, 75252 Paris, France.

^h CentraleSupélec, CNRS, Laboratoire de Génie Electrique et Electronique de Paris, Université Paris-Saclay, 91192 Gif-sur-Yvette, France.

ⁱ Schrödinger GmbH, Glücksteinallee 25, 68163 Mannheim, Germany.

^j Leibniz-Institute for Solid State and Materials Research Dresden, Helmholtzstrasse 20, 01069 Dresden, Germany.

^k Chair of Materials Chemistry, Faculty of Chemistry and Food Chemistry, TU Dresden, 01066, Germany.

[†] Supplementary Information available. See DOI: 00.0000/00000000.



band gap (E_g), excellent optical transparency, and deep valence band edge (E_v) make it highly advantageous for electrocatalytic applications.

Defects are generally detrimental to many systems, particularly electronic devices. However, they can be beneficial in other fields, such as sensors or electrochemical systems for oxygen evolution reaction (OER).^{14,15} In the case of NiO, it is generally accepted that charge compensation of nickel vacancies ($V_{Ni}^{\bullet}$) is the main driving mechanism leading to *p*-type conductivity, since it is very easy to form as compared with oxygen vacancies.^{16–19} Considering that flaws play an essential role in the properties of NiO and that it is often produced in non-stoichiometric compositions, it is referred to as NiO_x in the following. Rädinger et al.²⁰ investigated the role of defects by comparing the electrochemical activity of highly defective amorphous material with that of single-crystal. Their findings revealed that lattice defects promote the formation of Ni(OH)₂, facilitating its oxidation to active Ni(oxy)hydroxides (NiOOH), which significantly enhances electrocatalytic performance.

Surface defects also have a strong influence. Weilder et al.²¹ demonstrated that an increased surface concentration of hydroxide moieties lowers the overpotential (η) for the OER process by accelerating the Ni(OH)₂/NiOOH phase transition at the surface. This demonstrates the critical influence of the NiO_x surface on the expected functional properties. Moreover, it exhibits distinct surface conditions in aqueous and aprotic electrolytes, which also have a significant impact on the OER response of the system.²²

Since the electronic and electrochemical properties of NiO_x can be tuned by adjusting bulk and/or surface defects, it has been successfully used for water photosplitting. Recent works have reported efficient and highly stable photoanodes by growing catalytic NiO_x layers onto silicon.^{23–25} Previously, TiO₂ was deposited prior to Ni islands to protect the *n*-Si²⁶ but NiO_x is highly valuable since it acts as both protection and catalyst.

NiO_x layers can be synthesised using a wide range of techniques that potentially lead to different properties. Physical and chemical methods include pulsed laser deposition,²⁷ sputtering,²⁸ thermal evaporation,²⁹ sol-gel processing,^{30,31} chemical bath deposition,³² spray pyrolysis,³³ and atomic layer deposition (ALD).^{34–36} The latter, in particular, offers exceptional control on a sub-nanometric scale, resulting in uniform, high-quality thin films with excellent surface coverage.³⁷ As a chemical method, ALD operates through a sequence of self-limited reactions, enabling the deposition of pinhole-free conformal coatings over micro- or nanostructured surfaces that can exhibit enhanced optical absorption. Such approach has been demonstrated, for OER, by deposition of TiO₂ on porous Si resulting in an longer electrode's lifetime and a better electrochemical response.³⁸ The precise control and reproducibility of ALD allow for fine-tuning of the chemical, optical, and electronic properties, ensuring consistent stoichiometry, material density, and controlled doping.^{39,40} The synthesis parameters play, however, a crucial role. In previous studies, we have shown that both precursor chemistry and deposition temperature (T_{ALD}) have a critical influence on the physico-chemical and electrochemical properties on TiO₂ thin films.^{41,42} In the case of NiO_x, it has recently been demonstrated a signifi-

cant variation in lateral resistivity and electrochemical activity in layers grown according to two different ALD processes.⁴³ A three-fold increase in activation is reported for NiO_x grown by plasma-assisted compared to thermal ALD.

Despite the numerous benefits offered by ALD, growing NiO_x via this technique remains challenging. Over the past two decades, various ALD processes have been pursued to synthesize NiO_x films using different nickel and oxygen precursor combinations. These include Ni(Cp)₂,^{44–46} Ni(MeCp)₂,^{34,36} Ni(EtCp)₂,⁴⁷ Ni(dmamp)₂,⁴⁸ Ni(dmamb)₂,^{49,50} Ni(acac)₂,⁵¹ Ni(apo)₂,⁵² Ni(dmng)₂,⁵² Ni(thd)₂,⁵² and Ni(amd)₂,⁵³ frequently paired with O₃, H₂O, H₂O₂, or O₂ plasma. However, like most metal-based ALD processes, these approaches generally result in low growth per cycle (GPC), often less than 1.0 Å.^{54–58} Recently, Holden et al.⁵⁹ reported ALD of NiO with a GPC of 1.2 Å using Ni(ⁱBu₂DAD)₂ with O₃ as co-reactant. However, the requirement of the large amount of metallic precursor with narrow ALD window further limits the usage of this precursor for wide applications.

In recent years, there has been a growing interest in the development and evaluation of heteroleptic precursors for ALD. Such compounds are characterized by a metal atom bonded to two or more distinct ligands. The appeal of this approach lies in the potential to engineer a precursor that combines advantageous properties, such as enhanced vapor pressure (V_p), optimised reactivity, and improved thermal stability by integrating the desirable characteristics of the individual homoleptic parent compounds. For ALD of NiO, the heteroleptic complex [Ni(acac)₂(TMEDA)] is the only reported precursor, exhibiting an impressive GPC of 2 Å, along with superior volatility and thermal stability compared to Ni(acac)₂.⁵⁴ However, its bulky ligands necessitate a higher Ni precursor dose to reach saturation, potentially limiting reaction kinetics. Despite promising material properties, the NiO with a large T_{ALD} range starting at a relatively low temperature ($T_{ALD} < 150^\circ\text{C}$) is still challenging due to various factors such as lower GPC, poor reaction kinetics or even the poor reactivity of the co-reactant.^{49,60,61}

In this work, we report for the first time the use of two precursors in thermal ALD processes —Alanis™ (Fig. 1a), a nickel heteroleptic amidinate, and bis(4-(isopropylamino)-pent-3-en-2-onato)nickel(II), [Ni(ⁱpki)₂], a β -ketoiminate complex (Fig. 1b). This precursor has previously been employed in both chemical vapour deposition (CVD)⁶² and spatial-ALD.⁶³ In Alanis, R and R₁ represent CH groups restricted to alkyl chains, while R₂ refers to a substituent consisting solely of C and H atoms. Such com-

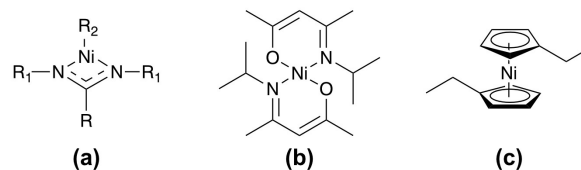


Fig. 1 Chemical formula of the Ni precursors: (a) Alanis™ (with R, R₁ and R₂ standing for C, H only hydrocarbon ligands), (b) [Ni(ⁱpki)₂] and (c) [Ni(EtCp)₂].



pounds form relatively weak Ni–C bonds that are O₃ and H₂O sensitive. Alanis shows a significantly higher vapor pressure with lower temperature stability (see the thermogravimetric analysis in Fig. S1a) with a tunable reactivity due to its heteroleptic ligand moieties, which further helps to optimise the ALD process carried out at lower temperatures. On the other hand, β -ketonates are the interesting complexes having two different types of atoms (N and O) bonded on the central metal atom with a tunable reactivity and stability⁶⁴ (Fig. S2).

In addition, to investigate the effect of the Ni precursors on the NiO_x deposition, the influence of two co-reactants, O₃ and H₂O, are studied because they can induce different properties in the grown layers. Water proceeds via deprotonation but its reactivity is limited by steric effects of the Ni precursor and is less favourable at lower reactor temperature (T_{ALD}), resulting in slower or incomplete reactions. Using higher T_{ALD} might cause precursor desorption (limiting the growth) or thermal decomposition (resulting in CVD and poor film quality). Water adsorbs strongly, elongating the purge step, and might induce incorporation of hydroxyl into the layer, exhibiting low quality. Water is an easy-to-handle, harmless compound that exhibits high vapour pressure. Conversely, O₃ is toxic but much more reactive. It may even damage the surface, introduce defects, and result in a rough deposit. A stable O₃ concentration is required, and high T_{ALD} can lower the O₃/O₂ ratio. It reacts with the amidinate backbone and decomposes the organic via a radical mechanism. In many examples, C incorporation occurs due to the formation of metal-carbonates from the reaction between O₃ and the ligands. Although O₃ might lead to higher GPC at lower T_{ALD} , both reaction pathways exhibit detrimental effects such as ligand fragment incorporation, stoichiometric defects, and rough layers. It is therefore difficult to predict the best oxygen source. Consequently, it is relevant to study the process using both oxygen sources to assess their effects on the final properties of the layers and to choose according to the intended application.

ALD reactions are initially optimised with Alanis/O₃, Alanis/H₂O and [Ni(ⁱpki)₂]/O₃ precursor combinations while [Ni(EtCp)₂]/O₃ (Fig. 1c), studied previously,⁶⁵ is used as reference. A comprehensive comparative study is subsequently conducted on the morphological, structural, and chemical characteristics of the NiO_x layers, alongside their optical and photoelectrochemical properties. It is shown that the nature of the precursors and the deposition temperature drive the physicochemical and functional properties of the films.

2 Experimental

2.1 Materials

2.1.1 sample preparation

The NiO_x deposition was performed on various substrates such as *n*-type silicon (Siltronix, 1–10 Ω -cm, 525 $\pm$ 25 μ m, single side polished), *p*⁺-Si (Siltronix, 0.0011–0.017 Ω -cm, 255–295 μ m, single-side polished) and, fluorine-doped tin oxide (FTO, TEC10, from Solems), fused-silica (FS, 150 μ m, double-side polished from Neyco).

All the silicon substrates were cleaned according to the RCA

cleaning protocol, consisting of initial 10 min sonications in acetone, isopropanol, and methanol, successively. The samples were then dipped in the SC-1 solution for another 5 min (SC-1 is prepared by mixing H₂O, NH₃(28%) and H₂O₂(30%) in a volume ratio of 5:1:1, heated at 75°C) after rinsing thoroughly with deionized water (resistivity of 18.2 M Ω -cm). After, they were immersed, for 10 min, in SC-2 (H₂O, HCl (37%) and H₂O₂ (30%) in a volume ratio of 6:1:1, heated at 75°C) followed by a HF (10%) dipping for another 30 s to etched the SiO₂ layer. The Si wafers were rinsed with deionized water and immersed a second time in SC-1 solution. This process is repeated three times. The samples were finally rinsed with deionized water and dried under a N₂ stream. This preparation leads to a uniform SiO₂ layer with a thickness of 1–2 nm on the Si surfaces. The fused silica was cleaned by the same procedure by skipping the HF etching step. The cleaning process was done just before the deposition process. The FTO substrates were cleaned initially by sonication in deionized water followed by organic solvents such as acetone, ethanol, and isopropanol, and the substrate is keeping in the isopropanol solution, and taken just before the ALD reaction.

2.2 ALD of NiO_x

NiO_x films were grown by thermal ALD in a shower-head hot-wall reactor Fiji 200 (Veeco/Cambridge Nanotech) equipped with a 10 g·h^{−1} solid state O₃ generator (Plasma Technology Inc., USA) and an in situ M2000V spectroscopic ellipsometer (J. A. Woollam Inc) for monitoring the growth in real time. Tauc-Lorentz oscillator model, reported earlier,^{65,66} was used in CompleteEASE software (v4.72) for extracting both layer thickness (t_{NiO}) and refractive index (n).

As mentioned above, the deposition was performed using three different Ni precursors: [Ni(EtCp)₂] (98% from Strem Chemicals), Alanis™ (98.4% from Air Liquide Advanced Materials⁶⁷) and [Ni(ⁱpki)₂] synthesised according to a previously reported study.⁶² Two O-sources were used with Alanis: O₃ and H₂O. The first one was produced from O₂ (99.999%, Linde Electronics) leading to an O₃ concentration around 150 mg·L^{−1}. Freshly produced deionized water was stored in a canister at room temperature in the second case. Ar (99.999%, Linde Electronics) served as vector gas.

During the processes, T_{ALD} was varied from 75 to 250°C. Its influence on the deposition is described below in section 3. The temperature of the canister (T_c) containing the Ni precursors was adjusted to optimise the V_p . Fig. S3 shows the evolution of the chamber's pressure against time. The pressure increase (ΔP) corresponding to the precursor pulse is assessed while T_c is stepped for Alanis and [Ni(ⁱpki)₂] and compared to [Ni(EtCp)₂]. T_c was set accordingly to 80, 150 and 90°C for Alanis and [Ni(ⁱpki)₂] and [Ni(EtCp)₂], respectively, to deliver a sufficient amount of molecules into the reactor (i. e. ΔP in the range of 0.01 Torr).

The ALD cycle consisted of sequential pulse, exposure and purge of Ni precursor and O-source, successively. The exposure step was implemented to achieve uniform deposits and to be compatible with three-dimensional substrates. The reaction recipe of the [Ni(EtCp)₂] and O₃ combinations are reported earlier.^{65,68}



The ALD sequences for the new precursor combinations have been optimised within the present work and are reported thereafter in section 3. The thickness of the films were then tuned by adjusting the number of cycles (N_{ALD}).

2.3 Characterisation methods

2.3.1 Morphology and thickness of the films

The morphology of the NiO_x layers was studied by transmission electron microscopies (TEM) using a Titan Themis 200 (ThermoFisher Scientific), respectively. TEM lamella were fabricated by focussed ion beam (FIB) micro-machining using a SCIOS FIB-SEM dual beam (ThermoFisher Scientific). Chemical imaging was performed by energy dispersive spectroscopy (EDS) using a SuperX 4-quadrant (Bruker) mounted on TEM.

In addition to ellipsometry, the thickness was confirmed by X-ray reflectivity (XRR) using a X'Pert Pro MPD diffractometer (Malvern PANalytical Inc.). The incident radiation was $\text{Cu K}\alpha$ ($\lambda = 0.15418 \text{ nm}$) and the operating power was 45 kV and 35 mA. For the incident beam, $(1/32^\circ)$ and $(1/16^\circ)$ slits were used as divergence and cleaning slits, a 5 mm mask was used for the lateral size of the beam. For the detection beam a PPC (parallel plate collimator) with a 0.18° slit was used. A Cu, 0.1 mm, attenuator was used to measure the data until 1° in 2θ , in order to avoid the saturation of the detector. Data were fitted using GenX software (v3.7) to extract the film thickness, density and roughness.

Non-contact atomic force microscopy (AFM) was also used to measure the film roughness using a XE-100 microscope (PSIA). Root mean square roughness (R_{rms}) was extracted from Gwyddion software (v2.63).

2.3.2 Crystalline structure

The crystalline structure of the NiO_x layers was determined by X-ray diffraction (XRD) using a high brilliancy rotating anode (Rigaku, RU-200BH) equipped with a Fox3D Cu 12_INF mirror (Xenocs) and an image plate detector (Rayonix, Mar345). The radiation used was $\text{Cu K}\alpha$, and the beam size was $0.5 \times 0.5 \text{ mm}^2$. The experimental resolution was about 0.3° in 2θ . In addition, selected area diffraction (SAED) was carried out within the TEM to confirm the crystalline nature of the material.

2.3.3 Chemical composition

As mentioned in section 2.3.1, EDS was used to carry out cross sectional chemical mapping during TEM observations. X-ray photoelectron spectroscopy (XPS) using a NEXSA G2 (ThermoFisher Scientific) equipped with a monochromatic $\text{Al K}\alpha$ source (1486.6 eV) was also performed at various incident angles. Take-off-angle (TOA) was varied from 30° to 90° to probe either the top surface or deeper within the film, respectively. The binding energy (BE) was corrected using the C 1s peak at 284.8 eV as an internal standard. Data processing was performed with CasaXPS analysis software (v2.3.26) using a Shirley-type background subtraction. The component peaks are defined by E_{BE} , full width at half maximum (FWHM) and Gaussian-Lorentzian envelop ratio.

The composition of the films was determined by Rutherford backscattering spectrometry (RBS) in combination with nuclear reaction analysis (NRA) experiments performed at the 4 MV ac-

celerator facility of RUBION/Ruhr-University Bochum. RBS measurements were performed with a 4He^+ ion beam of 2.0 MeV. With a high sensitivity to O as well as to C and N elements, NRA was performed by using an ion beam of 1.0 MeV deuterons. The SIMNRA program was employed for RBS and NRA raw data processing and analysis.

Depth profiling was performed by time-of-flight secondary ion mass spectrometry (ToF-SIMS) using a ToF-SIMS 5 spectrometer (IonToF GmbH, Germany) operating at a pressure of 10^{-9} mbar. Analyses were achieved by applying a 2 keV Cs^+ sputter beam over a $500 \times 500 \mu\text{m}^2$ area with 100 nA target current. It was interlaced with analyses performed using a pulsed 25 keV Bi^+ primary ion source, delivering 1.1 pA of current over a $100 \times 100 \mu\text{m}^2$ area. Negative ion depth profiles were acquired.

In addition to in vacuo chemical analyses, surface chemistry was also assessed via static contact angle (SCA) measurements using an OCA 20 instrument (DataPhysics). The experiments were conducted with $9 \mu\text{L}$ of deionised water, and the contact angles were determined using SCA20 software by averaging the left and right SCAs from multiple trials.

2.4 Optical investigations

In addition to the ellipsometric investigations, the optical properties of the thin films were measured using a Cary 5000 UV-Vis-NIR spectrophotometer (Agilent) connected with an external diffuse reflectance accessory (DRA) system consisting of a $\varnothing 150 \text{ mm}$ integrating sphere. In order to probe the bulk absorption of the material, 50 nm-thick films were grown on the fused silica substrates which were used as baseline for the measurements.

2.5 Electronic properties

The work function (W_f) of the NiO_x layers was measured by Kelvin probe using a KP020 system (KP Technology) equipped with a $\varnothing 2 \text{ mm}$ tungsten probe and a freshly exfoliated graphite sample as reference. The experiments were achieved in a controlled humidity atmosphere (40%).

2.6 Electrochemical investigations

Electrochemical and photoelectrochemical investigations were carried out in a three-electrode configuration. The sample was used as a working electrode. Contact was established at the rear by placing it on a copper plate. Ohmic contact was achieved by smearing InGa eutectic in the back side of Silicon. A Pt wire and a mercury/mercuric oxide electrode (Hg/HgO , 1 M KOH, $E^\circ = 0.098 \text{ V}$ vs SHE) respectively served as counter and reference electrodes. All potentials in the following are referred to reversible hydrogen electrode (RHE) to take into account the pH effect. The samples were pressed against the o-ring of the electrochemical cell leaving an area of 0.28 cm^2 exposed to the de-oxygenated electrolyte (N_2 bubbling), which consisted of 1 M KOH (Sigma-Aldrich, analytical grade). The electrochemical cell was connected to a SP-200 potentiostat (Biologic SAS) and the setup was placed in a dark room to avoid any uncontrolled photoelectrochemical effects. Photoelectrochemical investigations were performed using HAL-320 solar simulator (Asahi Spectra).



AM1.5G illumination was shined onto the sample through a transparent quartz window.

The Mott-Schottky (MS) experiments are carried out in the dark, in a three-electrode configuration with a Pt wire as a counter electrode and a silver/silver chloride reference electrode (Ag/AgCl, 3M KCl, $E^\circ = 0.212\text{ V vs SHE}$). Capacitance was measured as a function applied voltage in the depletion region. A 10 mV-amplitude sinusoidal potential perturbation at a frequency (f) in the range of 12 kHz was overlaid to the DC bias. All the analysis were carried out in a monobasic phosphate buffer made by an aqueous solution of 1 M Na_2SO_4 with a 0.1 M (NaH_2PO_4). The pH of this buffer was adjusted to 11.96 via the dropwise addition of 1 M NaOH solution.

3 Results and discussion

3.1 Optimisation of the ALD processes

As mentioned above, Alanis exhibits interesting properties since it allows for depositing at relatively low temperature. Optimisation of ALD processes using this heteroleptic precursor in combination with O_3 and H_2O is compared to $[\text{Ni}(\text{pki})_2]$, a stable β -ketoiminate. $[\text{Ni}(\text{CpEt})_2]$ -based process has been studied previously^{65,68}, it is taken as reference (optimised recipe and GPC are indicated in Table 1).

3.1.1 Alanis/ O_3

The ALD sequence for the Alanis/ O_3 combination is based on the process using the $\text{Ni}(\text{EtCp})_2/\text{O}_3$ which was optimised previously.^{65,68} The study started, therefore, with pulse, exposure, and purge durations of 2:15:30 s and 0.4:12:33 s for Alanis and O_3 , respectively. The purging steps were left long while optimising the Alanis and O_3 pulse times in order to suppress their effect. As seen on GPC vs pulse time curves at $T_{\text{ALD}} = 150^\circ\text{C}$ (Figs. S4a and S4b), saturation is reached after 1.5 and 0.3 s for Alanis and O_3 , respectively. For shorter injections, deposition does not achieve the highest GPC while longer pulses lead to a constant value and therefore a waste of precursors.

The purge times were then assessed using these pulse times. GPCs decrease rapidly with purge time (Figs. S4c and S4d), reaching plateaus near $1.2\text{ \AA}$ after 20 s. This suggests a CVD contribution for short purge times, whereas the process is self-limited after 20 s. The optimised ALD recipe is achieved with pulse, exposure, and purge sequences of 1.5:15:20 s and 0.3:12:20 s for Alanis and O_3 , respectively, resulting in a GPC of $1.2\text{ \AA}$ (see Table 1).

After such optimisation at $T_{\text{ALD}} = 150^\circ\text{C}$, saturation of the Ni precursor's pulse was assessed on the whole temperature range while keeping other parameters at maximum (see Fig. S5a). The GPC vs T_{ALD} evolution could therefore be plotted with optimised sequences on Fig. 2a. It exhibits a nearly constant growth rate over a broad temperature range (100 to 175°C) with a GPC of 1.1 to $1.2\text{ \AA}$. This corresponds to the so-called ALD window where self-limited deposition occurs and therefore conformality is achieved.

At $T_{\text{ALD}} = 75^\circ\text{C}$, GPC is significantly higher ($\approx 1.4\text{ \AA}$). It continuously increases with Alanis pulse time and no saturation could be observed for purge duration as long as 60 s. This behaviour can be attributed to the condensation of the Ni precursor onto

the substrate. It leads to a non-self-limiting process and the composition of the film is no longer controlled (Fig. S6).

At $T_{\text{ALD}} = 200^\circ\text{C}$, GPC is also higher than the ALD window ($\approx 1.4\text{ \AA}$). Such GPC improvement is usually ascribed to either precursor decomposition associated with a CVD contribution or reaction enhancement due to the greater amount of energy transferred to the system. Since GPC exhibits the expected saturation trend when increasing Alanis's pulse time (Fig. S6), precursor decomposition does not seem to occur (note that Alanis's purge time was adjusted accordingly for the longest pulse time to ensure removal of physisorbed molecules). To validate this further, the ALD reaction was conducted without injecting an oxygen source. The evolution of the GPC against Alanis's pulse time (Fig. S7) indicates that no deposition occurs up to $T_{\text{ALD}} = 200^\circ\text{C}$. A weak growth is measured at higher temperatures but it becomes significant only above 250°C . This indicates that the precursor is decomposing, which induces a CVD contribution to the deposition process. The later high temperature has therefore not been considered for the Alanis/ O_3 combination to avoid uncontrolled growth process. In addition, the XRD trend indicate that the crystallinity of the as deposited layer enhances with reaction temperature (see after in Fig. 4b), which further rules out the possibility of the decomposition below $T_{\text{ALD}} = 200^\circ\text{C}$.

3.1.2 Alanis/ H_2O

H_2O is an user-friendly O-source for metal oxide synthesis via ALD. However, due to its lower reactivity, the metal precursor chemistry plays a crucial role in the reaction. Regarding Alanis, the high reactivity of the amidinate moiety^{53,69} enables the investigation of its reaction with H_2O . Similar to the previous precursor combination, the ALD process is optimised at 150°C by analyzing the GPC vs pulse and purge time curves. According to the saturation curves (Fig. S8), the optimised sequence is then set to 1.5:15:30 s and 1:12:60 s for Alanis and H_2O , respectively, achieving a GPC of $0.74\text{ \AA}$. The process is then optimised within the Alanis stability temperature range, as shown in Fig. 2a. A lower GPC is measured until $T_{\text{ALD}} = 175^\circ\text{C}$, where it becomes close to Alanis/ O_3 . This lower deposition rate is in line with the lower reactivity of water in comparison to ozone. The H_2O -based process requires a longer purge step as water usually sticks more onto the surfaces. However, the deposition proceed according to a self-limited reaction up to $T_{\text{ALD}} = 200^\circ\text{C}$ (Fig. S5b). No clear ALD window can though be defined since GPC is continuously increasing up to 225°C where thermal decomposition of the Ni precursor leads to stabilisation.

In addition to the lower GPC, a significant difference is observed between the O_3 - and H_2O -based recipes. Fig. 2b compares t_{NiO} vs N_{ALD} curves when using H_2O and O_3 at $T_{\text{ALD}} = 150^\circ\text{C}$. In the case of O_3 , a linear increase crossing the x -axis in 0 is observed. Conversely, for H_2O , the growth rate is initially very low ($N_{\text{ALD}} \leq 40$ cycles) and it follows the expected linear evolution only for higher numbers of cycles ($N_{\text{ALD}} \geq 40$ cycles). This retarded deposition is called nucleation delay ($N_{\text{ALD}}^* = 40$ cycles). The GPC is deduced from the slope of the linear part of the curve (i. e. for $N_{\text{ALD}} \geq N_{\text{ALD}}^*$). It is slightly lower than for O_3 . This comparison clearly demonstrates the critical effect of the O-source on



Table 1 The optimised ALD sequences for NiO_x using different precursor combinations.

	Alanis/O ₃	Alanis/H ₂ O	[Ni(ⁱ pki) ₂]/O ₃	[Ni(EtCp) ₂]/O ₃
ALD sequence for Ni-precursor (s)	1.5:15:20	1.5:15:30	1.0:18:35	2.0:15:30
ALD sequence for O-source (s)	0.3:12:20	1.0:12:60	0.4:12:35	0.3:12:33
GPC (Å)	1.2	0.74	0.40	0.15
Deposition duration for 50 nm (hrs)	10	23	38	98

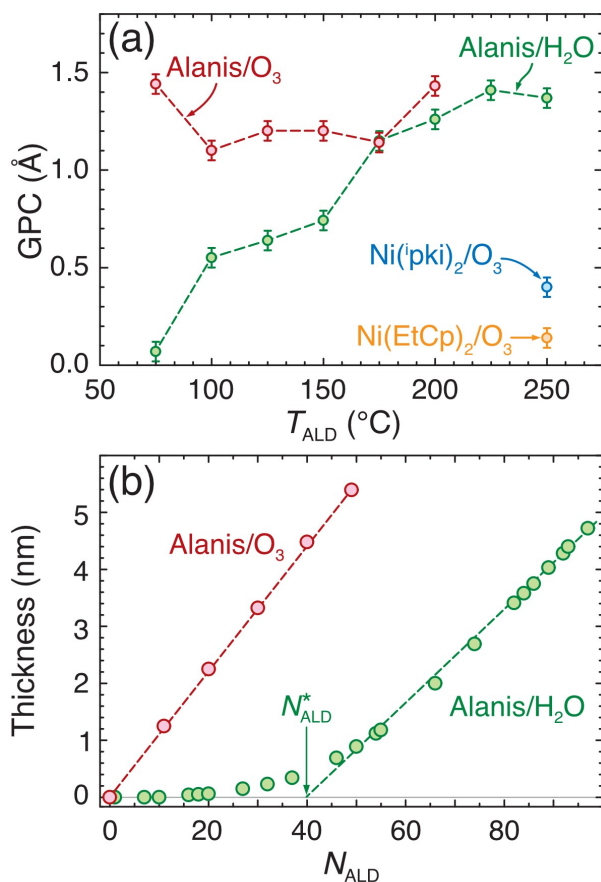


Fig. 2 The optimised ALD window of the NiO_x using different precursor combinations: Alanis/O₃, Alanis/H₂O, [Ni(ⁱpki)₂]/O₃, and [Ni(EtCp)₂]/O₃, (b) The evolution of the film thickness with number of ALD cycles for Alanis/O₃ and Alanis/H₂O combinations. N_{ALD}^* is referred in the text.

the ALD of NiO. Since the difference between the two processes is the O-source, the nucleation delay observed with water could be explained by its lower reactivity. Retarded nucleation can result from a different surface termination of the substrate and/or by the preferential adsorption of the liberated ligands on the substrate.⁷⁰

Contact-angle measurements were performed to probe the surface state before ALD and after O₃ or H₂O exposures (Fig. S9). In the case of the as-prepared surfaces (RCA cleaned), an angle of 62° is measured. This low wettability reflects a low density of surface hydroxyl groups. After 30 pulses of O₃, the contact angle drops down to 32° while it remains at 63° after being exposed to 30 pulses of H₂O. This shows that the SiO_x surfaces achieved af-

ter preparation are covered with a large number of hydroxyl functions during the Alanis/O₃ process whereas their concentration is lower for Alanis/H₂O. This might cause the nucleation delay in the latter combination.

The precursor's chemical nature also contributes. In both processes, the hydrocarbon ligand of Alanis is likely to react readily with protons on the SiO_x-OH surface and eliminate, thereby anchoring the remaining precursor fragment to the surface, with the amidinate ligand still bound to Ni. According to literature reports,^{71–73} the amidinate ligand does not detach from the Ni atom at these temperatures in the absence of a co-reactant, and thus is not expected to transfer intact to the silica surface. Consequently, the observed nucleation delay is unlikely to result from substrate poisoning due to ligand release, as previously proposed by Goldstein et al.⁷⁰ The amidinate ligand might decompose so as to transfer N or NH to the silica surface, producing some form of silicon nitride (Si–N–H) that could be inert towards further adsorption, while at the same time allowing the Ni cation to get O from Si. However the chemical analyses of section 3.2.2 below rule out the formation of silicon nitride, since the CN[−] profile (ToF-SIMS) are similar for both precursor combinations. Nitride formation is therefore also an unlikely reason for the nucleation delay. Decomposition of the amidinate into a carbonaceous residue (involatile C or CH_x) is another possibility for the nucleation delay. H₂O might not be able to remove such a residue and it could accumulate as a H-rich carbide of silicon or of nickel (or both), resisting precursor adsorption and causing the nucleation delay. By contrast, O₃ can be expected to efficiently burn off any CH_x residue and restore the SiO_x-OH surface, ready for the next Ni pulse. The ToF-SIMS analyses of section 3.2.2 confirm the presence of carbonaceous residue when using Alanis in combination with O₃ and H₂O (RBS). The carbon content is, however, larger with water. ToF-SIMS profiles (Fig. 8a and 8b) also indicate a larger amount of C with water with a slight accumulation at the interface. These data support the hypothesis that, while the hydrocarbon ligand of Alanis is eliminated efficiently, the amidinate ligand decomposes and coats SiO_x with an involatile carbonaceous residue that is incompletely removed by H₂O until the surface is fully covered by NiO_x (i. e. for $t_{\text{NiO}} \geq 4 \text{ Å}$).

3.1.3 [Ni(ⁱpki)₂]/O₃

The excellent thermal stability of the [Ni(ⁱpki)₂] prompted to investigate the ALD reaction at higher temperature ($T_{\text{ALD}} = 250^\circ\text{C}$). The reaction is initiated with O₃ as a co-reactant and the saturation curve is shown in the Fig. S10. Since the regeneration of the vapour inside the canister is challenging for this precursor, the duration of the ALD cycle was increased to 100 s by slightly ad-



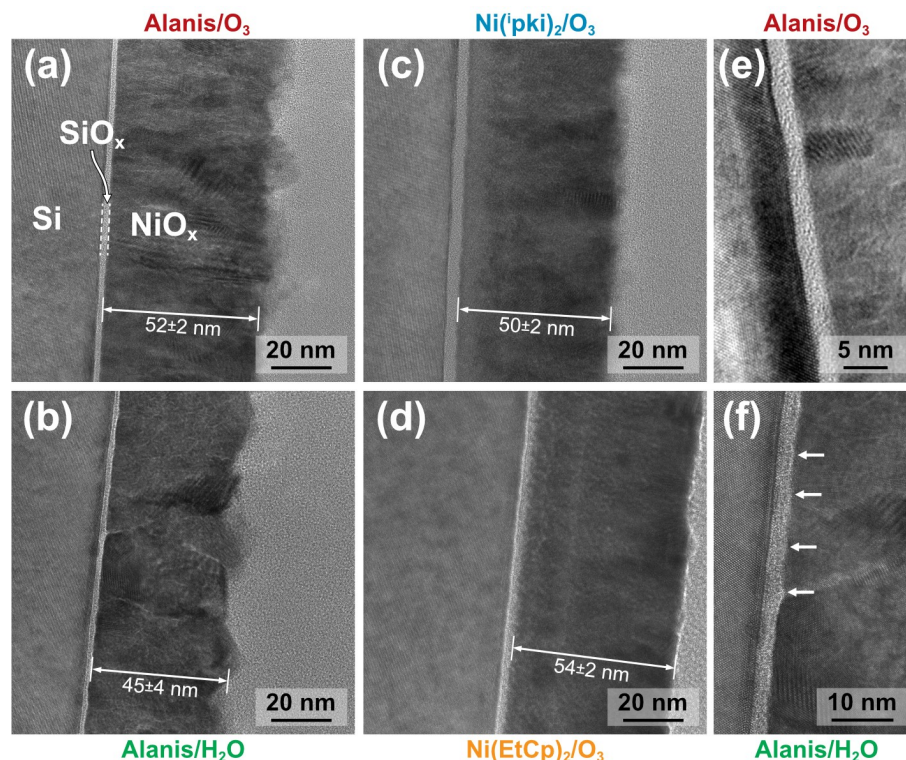


Fig. 3 TEM cross sections of NiO_x films grown using the different precursor combinations: (a) Alanis/ O_3 , (b) Alanis/ H_2O , (c) $[\text{Ni}(\text{i'pki})_2]/\text{O}_3$, and (d) $[\text{Ni}(\text{EtCp})_2]/\text{O}_3$. (e) and (f) are higher magnifications of the interface for Alanis/ O_3 and Alanis/ H_2O , respectively (arrows are referred on the text). $N_{\text{ALD}} = 450, 650, 1250$, and 3600 cycles in (a), (b), (c), and (d), respectively.

justing the exposure and purge times of the recipe. The optimised ALD recipe consists of pulse, exposure, and purge durations of 1:18:35 s and 0.4:12:35 s for $[\text{Ni}(\text{i'pki})_2]/\text{O}_3$, respectively, resulting in a GPC of $0.4 \text{ \AA}$ at $T_{\text{ALD}} = 250^\circ\text{C}$ (Fig. 2a). In addition to the O_3 -based reactions, the process was also attempted using H_2O as the co-reactant. However, no deposition was observed under these conditions, which could be attributed to the lower reactivity of the oxygen source.

3.2 Characterization of the films

3.2.1 Morphology and crystalline structure

Fig. 3 shows TEM cross section observations of NiO_x layers grown using the four precursor combinations. EDS mappings (Fig. S11) confirm the chemical nature of the three areas observed on the micrographs. In all cases, NiO_x covers uniformly the Si substrate and, due to the surface preparation method, an ultra-thin SiO_x film is always present at the interface. The NiO_x thicknesses indicated on Fig. 3 are in agreement with the ellipsometric measurements and validate, therefore, the Tauc-Lorentz model.

A close observation of the NiO_x films reveals their polycrystalline structure. This is confirmed by SAED, presented in Fig. S12, where the indexed rings correspond to the main interreticular distances (d) of the polycrystalline NiO_x while the spots are ascribed to the single-crystalline Si substrate.

X-ray diffraction pattern presented in Fig. 4a are in agreement with SAED. The expected cubic rock salt structure of NiO_x (Fm $\bar{3}$ m space group) is indeed identified. The main reflections corre-

sponding to (111), (200) and (220) planes are, respectively, located near the expected angle values 37.279° , 43.311° , and 62.934° listed in the reference PDF card #00-047-1049. Their relative intensity is consistent with the simulated powder XRD pattern, indicating no film texturing. Lattice parameter (a), crystalline size (D), strain (ϵ) and dislocation density (δ) for all the films were determined from the position and full width at half maximum (FWHM) of the (200) plane are reported in Table S1 using equations given in SI.

All NiO_x exhibit a lattice parameter close to the expected $4.1771 \text{ \AA}$ reported in the PDF card #00-047-1049. It confirms the bunsenite-like structure of the deposited films. $[\text{Ni}(\text{i'pki})_2]/\text{O}_3$ yields the best-crystallised film, as it exhibits the largest D and the lowest δ and ϵ . A slightly lower film quality is obtained with $[\text{Ni}(\text{EtCp})_2]/\text{O}_3$. The Alanis-based processes exhibit smaller crystallite size and higher defect concentration, as well as more strain. This could be ascribed to the high GPC observed for these precursor combinations that induces a numerous nucleation site and small crystallites. However, the nucleation delay, occurring when H_2O is used, gives rise to larger crystalline domains ($D = 11.1 \text{ nm}$) as compared to deposition carried out with O_3 ($D = 9.5 \text{ nm}$).

Table S1 also indicates that T_{ALD} plays a significant role in the crystalline quality of the films. The largest D and lowest δ and ϵ are indeed measured for $[\text{Ni}(\text{i'pki})_2]/\text{O}_3$ and $[\text{Ni}(\text{EtCp})_2]/\text{O}_3$ used at 250°C . Fig. 4b presents therefore the evolution of the X-ray diffraction pattern for Alanis/ O_3 for T_{ALD} ranging from 75 to



200°C. At low temperature ($T_{\text{ALD}} < 125^\circ\text{C}$), the layers are amorphous while they crystallise above. As shown in the inset in Fig. 4b, the intensity of the reflection corresponding to the (200) planes increases linearly with T_{ALD} , while the FWHM simultaneously narrows. This reflects a progressive enlargement of D from 12.5 to 38.8 nm, accompanied by reductions in δ and ϵ from 0.6 to $0.1 \times 10^{12} \text{ cm}^{-2}$ and from 7.5 to 2.4×10^{-3} , respectively (for seek of clarity ϵ is plotted in Fig. S13a). It demonstrates the critical effect of T_{ALD} on the crystalline structure of the films. The effect of T_{ALD} is similar with Alanis/ H_2O . Fig. S13b shows a XRD pattern of a well-crystallised film grown at $T_{\text{ALD}} = 200^\circ\text{C}$. However, if the temperature is increased to 250°C , the degradation of the Ni precursor, described above, leads to poorer crystallisation because a larger amount of impurities are embedded.

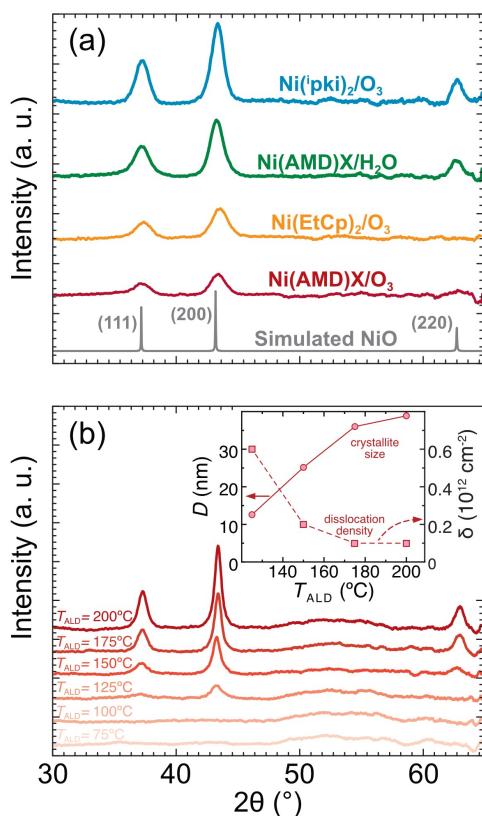


Fig. 4 (a) XRD patterns of NiO_x thin films depending on the precursor combinations (indicated on the plot). For better comparison, $t_{\text{NiO}} = 18 \text{ nm}$ is all cases. (b) Evolution of the XRD pattern with T_{ALD} for Alanis/O_3 (N_{ALD} has been adjusted according to each GPC to achieve $t_{\text{NiO}} = 18$ and 30 nm for (a) and (b), respectively).

Aside from marked grain boundaries in the case of $\text{Alanis}/\text{H}_2\text{O}$, Fig. 3 shows mainly that the deposited films are compact and uniform. XRR was used to assess the density of the layers (ρ) and t_{NiO} . Similarly to TEM observations, XRR data validate the ellipsometric measurements of the t_{NiO} and verify, therefore, the Tauc-Lorentz model. Fig. 5 reports ρ depending on precursor recipes (raw XRR data and fittings are shown in Fig. S14). $[\text{Ni}(\text{pki})_2]/\text{O}_3$ exhibits the highest density ($\rho = 6.46 \text{ g cm}^{-3}$), which is close to the theoretical value of 6.62 g cm^{-3} for NiO . This little discrepancy is expected for polycrystalline deposits since they are dis-

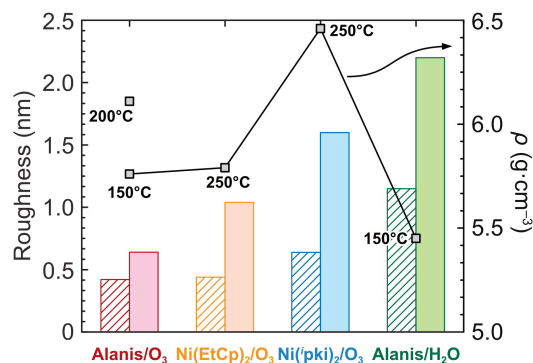


Fig. 5 Roughness of the NiO_x films measured by AFM (hatched bars) and XRR (light bars) depending on the precursor combinations: Alanis/O_3 , $\text{Alanis}/\text{H}_2\text{O}$, $[\text{Ni}(\text{pki})_2]/\text{O}_3$, and $[\text{Ni}(\text{EtCp})_2]/\text{O}_3$. Grey squares correspond to the film densities depending on the precursor combinations (T_{ALD} is indicated on the plot for each value). N_{ALD} has been adjusted according to each GPC to achieve $t_{\text{NiO}} = 18 \text{ nm}$.

ordered and usually less dense.⁷⁴ Using Alanis , the layers show a lower density. This appears to be primarily due to the reduced T_{ALD} . When NiO_x is deposited at a higher temperature ($T_{\text{ALD}} = 200^\circ\text{C}$), ρ increases, indeed, from 5.76 to 6.11 g cm^{-3} (Fig. 5).

In addition to ρ , XRR fittings give also access to the roughness of the layers. These values are also plotted in Fig. 5 where they are compared to root mean square roughness (R_{rms}) extracted from AFM imaging. Such surface topography was carried out on 18 nm -thick NiO_x films grown on Si (AFM images are presented in Fig. S15).

AFM studies revealed the formation of smooth films, with roughness comparable to values reported in previously.^{59,75} Among the various precursor combinations, O_3 -based reactions produced notably smooth films, with R_{rms} ranging from 0.42 to 0.64 nm , regardless of the precursor type or T_{ALD} , as shown in Fig. 5. Rougher surfaces are observed in the H_2O -based processes. It may result from the initial nucleation delay pointed above that led to the larger crystallites observed in Fig. 3b. This is also why we obtain smoother films with O_3 , whereas we would normally expect to see the opposite. The roughness trends are consistent with the values obtained from XRR measurements. However, the roughness values measured by AFM are lower than those derived from XRR. The root mean square roughness is generally higher than the average roughness, R_a (see SI for definitions), and thus the discrepancy between AFM and XRR is not due to differences in roughness calculation.

Rather, it may stem from the inclusion of an additional parameter—the interface roughness between the film and the substrate. While AFM is only sensitive to the outermost surface of the film, XRR provides comprehensive information about the entire $\text{Si}/\text{SiO}_x/\text{NiO}_x$ system. Fig. 3e and 3f compare the interlayer for Alanis/O_3 and $\text{Alanis}/\text{H}_2\text{O}$ that looks rougher in the latter case (see white arrows on Fig. 3f) than for the Alanis/O_3 combination (Fig. 3e) that is the smoothest. This can again be ascribed to the nucleation delay leading to a columnar morphology when using water (Fig. 3b).



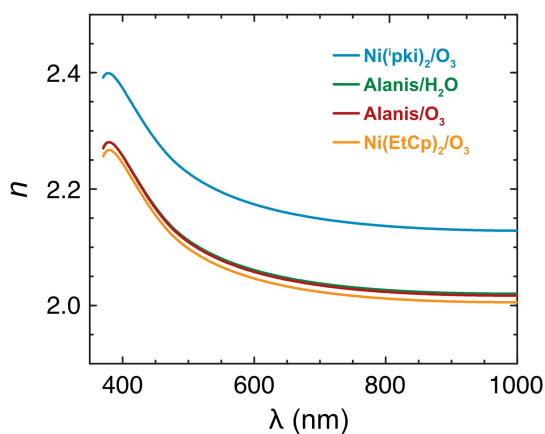


Fig. 6 Refractive index of the NiO_x depending on the precursor combinations: Alanis/ O_3 , Alanis/ H_2O , $[\text{Ni}(\text{'pki})_2]/\text{O}_3$, and $[\text{Ni}(\text{EtCp})_2]/\text{O}_3$. N_{ALD} has been adjusted according to each GPC to achieve $t_{\text{NiO}} = 18 \text{ nm}$.

In addition to t_{NiO} , ellipsometric investigations have also given access to the refractive index of the layers depending on the precursor combinations. Fig. 6 presents the evolution on n against λ in the visible range. In this region, n is in the range of 2 to almost 2.3 for all combinations except for $[\text{Ni}(\text{'pki})_2]/\text{O}_3$ that displays higher values (2.1 to 2.4). The current n are lower than those reported for single-crystalline NiO .⁷⁶ This is expected since polycrystalline films are disordered and their density is lower.⁷⁴ The discrepancy between the Ni β -ketoiminate and the other compounds could, therefore, arise from the higher crystallinity observed for this precursor combination by XRD (Fig. 4a) as well as the higher density deduced from XRR. Note that the roughness does not have significant influence on n . Refractive indices are not as high as other polycrystalline films,^{74,77} because it is known that n increases with the thickness of the films⁷⁴ or, more specifically, with the size of the crystalline domains making up the layer.⁷⁸ In the present work, the explored deposits are thin ($t_{\text{NiO}} \leq 20 \text{ nm}$). This may therefore explain these lower values. It could also be due to impurities. This aspect is studied below.

3.2.2 Chemical composition

The chemical composition of the films was investigated by XPS, RBS/NRA and, ToF-SIMS. XPS, in particular, is a valuable tool for understanding the chemical state of the materials. The survey spectra (Fig. 7a) indicate the presence of C, Ni, and O. When the precursor contains nitrogen (Alanis and $[\text{Ni}(\text{'pki})_2]$), a low-intensity N 1s peak is detected, indicating slight inclusion of ligands in the deposit. The substrate is not detected since there is no Si peak on the spectra. It indicates uniform surface coverage for samples analysed by XPS.

The C 1s peak is studied because it serves as a calibration and carbonaceous compounds from the precursors can be included into the films. In our system, its signal is deconvoluted into three distinct components (Fig. 7b). The primary peak at 284.8 eV corresponds to C–C bonds (Band I), while another peak at 286.4 eV is attributed to C–O species, which result from adventitious carbon contamination due to air exposure (Band II).⁷⁹ Additionally, a peak at 288.3 eV is associated with adsorbed carbonates and

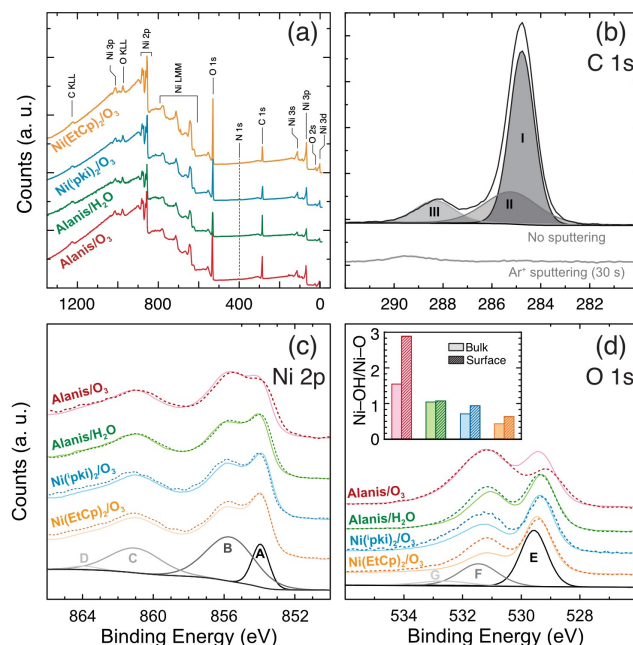


Fig. 7 XPS analysis of the NiO_x layers grown on Si depending on the precursor combinations: Alanis/ O_3 , Alanis/ H_2O , $[\text{Ni}(\text{'pki})_2]/\text{O}_3$, and $[\text{Ni}(\text{EtCp})_2]/\text{O}_3$. (a) Survey spectrum, (b) C 1s, (c) Ni 2p_{3/2} and (d) O 1s. Full and dashed lines correspond to a TOA of 90° and 30°, respectively. Inset in (d) shows the Ni–OH/Ni–O ratios. (The Roman numbers and letters in (b, c, d) identify photoemission contributions referred in the text.) N_{ALD} has been adjusted according to each GPC to achieve $t_{\text{NiO}} = 18 \text{ nm}$.

carbonyl groups from the ligand moieties of the precursor (Band III) as shown in Fig. 7b.⁷⁹ Notably, the C 1s peak diminished to the noise level after 30 s of Ar^+ sputtering, indicating that carbon is mainly confined to the surface and underscoring the purity of the target samples. ToF-SIMS profiling also indicates high C^- and CN^- ion concentrations at the surface that decrease quickly with sputtering time Fig. 8. In the case of $[\text{Ni}(\text{EtCp})_2]$, the carbon content remains low throughout the film, with a slight increase observed at the top surface. The CN^- ion signal is even at the level of the background, further supporting that the detected nitrogen in both analyses likely originates from the ligands of the nitrogen-containing precursors.

In the case of Ni, interpreting and quantifying the chemical states of Ni from the 2p doublet peak is challenging, owing to the presence of complex and extended multiplet structures, shake-up satellites, plasmon loss features, and overlapping chemical states, all of which introduce significant uncertainty.^{80,81}

The main XPS peak for Ni is the 2p_{1/2} and 2p_{3/2} doublet with a spin-orbit splitting (SOS) of 17.4 eV for Ni^0 and slightly larger for Ni^{2+} .⁸² Curve fitting is typically performed on the Ni 2p_{3/2} region in which the Ni^0 peak is expected at 853.2 eV. When the metal is oxidised, the complex line shape in the XPS spectrum primarily arises from the overlap between Ni 3d and O 2p orbitals. The primary peak, centred at 853.8 eV (Band A), is assigned to the Ni^{+2} corresponding to Ni–O bond. A broad satellite peak at 860.9 eV (Band C) comes from the oxygen band bending effect and a small peak at 866 eV (Band D) is attributed to the intersite charge trans-

fer screening.⁸³ In addition to these peaks, there is another important shoulder peak at 855.8 eV (Band B). The origin of this peak is still debated. However, most of the literature reports that it arises from a chemical shift of Ni^{3+} species due to $\text{V}_{\text{Ni}}^{\bullet}$ and is attributed to nickel hydroxides ($\text{Ni}(\text{OH})_2$) or nickel oxyhydroxides (NiOOH) present on NiO_x surfaces.^{43,80,84–86} Some reports suggest this peak could also be related to nickel trioxide (Ni_2O_3) or result from non local screening effects as well as surface effects.

In the present case, the SOS slightly exceeds 17.4 eV, and the characteristic Ni^0 peak at 852.3 eV is absent, indicating the expected oxidised form of Ni. Fig. 7 presents $\text{Ni } 2p_{3/2}$ depending on the precursor combinations. The low energy peak located at 854 eV corresponds to Band A, i. e. it originates from Ni–O bonds in NiO_x . The two peaks centered at 861.1 and 864 eV are allocated to Bands C and D, respectively. As described above, the shoulder at 855.8 eV is ascribed to Band B arising from Ni^{3+} related to Ni_2O_3 , $\text{Ni}(\text{OH})_2$ and NiOOH . Ni_2O_3 can be excluded because its signature on the O 1s peak is different from $\text{Ni}(\text{OH})_2$. It is normally expected at 528.9 eV⁸⁷ whereas the hydroxide comes out at 530.6 eV.⁸⁸ Fig. 7d shows no contribution corresponding to nickel trioxide. Furthermore, no signal of its hexagonal crystal structure is detected in XRD. This is expected because the formation of Ni_2O_3 through dehydration or dehydroxylation necessitates temperatures exceeding 250°C.⁸⁹ Consequently, it is difficult to clearly assign Band B to a single contribution since it could come from $\text{Ni}(\text{OH})_2$, NiOOH , nonlocal screening effects or surface effects without any possible distinction. It is therefore necessary to analyse the O 1s region because it provides information that can be used to discriminate between the various possibilities mentioned above.

Fig. 7d presents the XPS region corresponding to O 1s for the different NiO_x films. The peak centered at 529.3 eV (Band E) confirms the octahedral bonding of Ni–O while peaks at 531.0 eV (Band F) and 532.3 eV (Band G) are ascribed to the presence of the hydroxyl group either due to $\text{Ni}(\text{OH})_2$, or NiOOH and H_2O .⁸⁹

In previous studies, surface Ni–OH groups are shown to strongly influence the OER activity.²¹ To study this, the evolution of Bands A and B were compared as a function of TOA that shows whether some species are more exhibited at the top surface. Although Fig. 7c indicates a slight enhancement of Band B at the top surface ($\text{TOA} = 30^\circ$), dashed lines across all precursor combinations, it is challenging to draw definitive conclusions from these data, as the peak at 855.8 eV arises from multiple overlapping contributions. The Ni–OH/Ni–O ratio is therefore calculated from O 1s region (Fig. 7d) as it decomposes in three peaks: Ni–O main peak, Ni–OH owing to the presence of $\text{Ni}(\text{OH})_2$ and NiOOH , and the high energy component due to the adsorbed water. In all cases, the intensity of the peak at 531.2 eV is enhanced when analyses are performed at grazing incidence compared with perpendicular incidence. The Ni–OH/Ni–O ratio is thus calculated by dividing the areas of Bands E and F, respectively. It is reported in the inset of Fig. 7d for two TOA and the four precursor combinations. It shows a higher value of the Ni–OH/Ni–O ratio at $\text{TOA} = 30^\circ$ indicating, therefore, that the surface of the layers have a higher hydroxyl concentration than the bulk. Among the four samples, Alanis/ O_3 has significantly greater hydroxyl con-

Table 2 O/Ni ratios of the NiO_x layers for the different precursor combinations calculated from AR-XPS at two TOA ($\text{TOA} = 30^\circ$ and 90° correspond to grazing (top surface) and normal (bulk) incidence)

TOA	Alanis/ O_3	Alanis/ H_2O	$[\text{Ni}(\text{pki})_2]/\text{O}_3$	$[\text{Ni}(\text{EtCp})_2]/\text{O}_3$
30°	2.04	1.17	1.07	1.04
90°	1.54	1.06	1.06	0.99

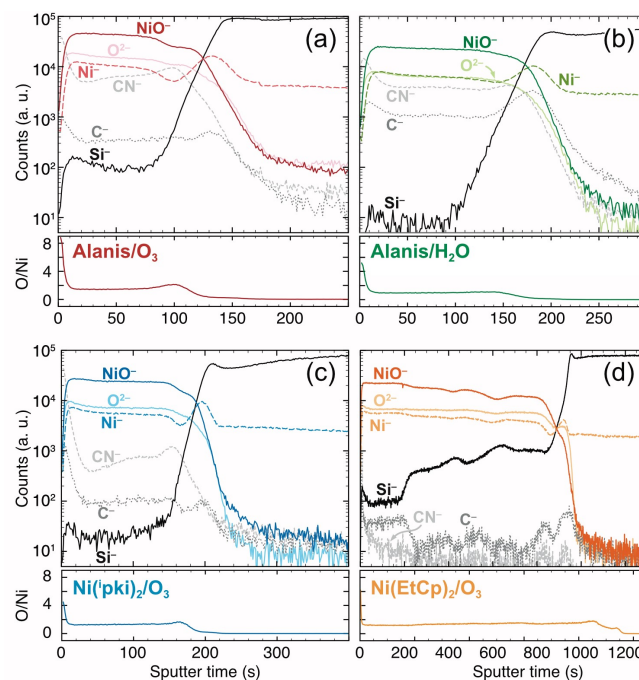


Fig. 8 ToF-SIMS profiling of NiO_x layers grown on Si depending on the precursor combinations: (a) Alanis/ O_3 , (b) Alanis/ H_2O , (c) $[\text{Ni}(\text{pki})_2]/\text{O}_3$, and (d) $[\text{Ni}(\text{EtCp})_2]/\text{O}_3$. The O/Ni signal ratio is plotted below each profiling. $N_{\text{ALD}} = 150, 350, 500$ and 4500 cycles in (a), (b), (c), and (d), respectively.

centration and its value remarkably increases on the surface (inset in Fig. 7d).

The O/Ni ratio was also investigated. It is reported in Table 2 for $\text{TOA} = 30^\circ$ and 90° . At normal incidence, with the exception of Alanis/ O_3 for which it is close to 1.5, this ratio is very closed to 1 for $[\text{Ni}(\text{EtCp})_2]/\text{O}_3$ or slightly greater for the other combinations. This could be ascribed to $\text{V}_{\text{Ni}}^{\bullet}$. The O content is larger when the analysis is carried out using grazing incidence. This higher O/Ni ratio can be ascribed to the elevated Ni–OH contribution at the surface that might be advantageous for OER activity.

Since XPS is a surface-sensitive technique, it tends to overestimate the O/Ni ratio because the surface of NiO_x becomes more oxidised when exposed to air.⁴³ To gain a deeper understanding of the bulk composition of the material, XPS depth profiling was initially performed by in situ Ar^+ sputtering. However, in the case of NiO_x , Ar^+ source has the ability to reduce the Ni^{2+} to Ni^0 ,^{90,91} which limits the study of the bulk composition of the film. RBS/NRA and ToF-SIMS analyses give a better view of the composition and distribution of the elements in the films.

The RBS/NRA study revealed that films based on $[\text{Ni}(\text{EtCp})_2]/\text{O}_3$ and $[\text{Ni}(\text{pki})_2]/\text{O}_3$ display an O/Ni ratio



close to unity. In contrast, films derived from Alanis/O₃ or H₂O exhibit a ratio around 1.1 (Table 3). This is in line with the XPS quantification. It indicates the NiO_x layers grown using [Ni(EtCp)₂]/O₃ and [Ni(ⁱpki)₂]/O₃ contain less defects than with Alanis. As an excess of oxygen is observed in the latter, the flaws are most likely V_{Ni}^{••}. When T_{ALD} is increased to 200°C for Alanis/O₃, a stoichiometric oxide is observed, indicating a lower defect concentration. This is in line with the increase in density ($\rho = 6.1 \text{ g}\cdot\text{cm}^{-3}$) observed by XRR when the Alanis/O₃ process is carried out at 200°C (section 3.2.1).

As mentioned above, when the nickel precursor contains a nitrogen function, the film has a very low nitrogen content. Except in the case of [Ni(EtCp)₂]/O₃, which appears relatively pure, the other films contain a small amount of carbon. This contamination is slightly higher in the case of Alanis/H₂O. As mentioned above, it is likely due to the weaker water reactivity compared to ozone, resulting in less efficient ligand elimination during the process. For Alanis/O₃, increasing T_{ALD} appears to reduce contamination. Note that the zero carbon concentration observed at $T_{\text{ALD}} = 175^\circ\text{C}$ is attributed to the very low thickness of the analysed film, which placed the carbon content below the detection limit.

The concentration profiles achieved by ToF-SIMS are in agreement with the results obtained by XPS and RBS/NRA. Fig. 8 presents the composition profiles for the different precursor combinations. As revealed by XPS, the high C content at the surface is ascribed to adventitious contamination. Impurity levels (C and N) in the bulk films are also in agreement with the RBS/NRA. No N is detected for [Ni(EtCp)₂] as it does not contain a nitrogen atom. Similarly, C level is qualitatively higher for Alanis/H₂O than for the others because H₂O is not sufficient reactive to get rid the residues. The nitrogen detected for Alanis- and [Ni(ⁱpki)₂]-based processes is evenly spread over the whole NiO_x layer. The surface oxygen enrichment spotted by XPS is not easily discernible from the Ni²⁺ and O²⁻ signals. Thus O/Ni ratio is plotted below each analysis. It confirms the higher oxygen concentration at the top surface while remaining constant across the rest of film. In the case of [Ni(EtCp)₂]/O₃, the Si⁻ signal increases in steps as the analysis progresses in depth. This can be attributed to non-uniform deposition, which allows the substrate signal to appear earlier in some locations. Deposits made with Cp-based precursors are, indeed, less reproducible than others.

3.2.3 Optical properties

Since NiO_x is a *p*-type semiconductor, it absorbs light with energy greater than E_g . Therefore, measuring its optical properties is essential to understanding the photoconversion mechanisms at the *n*-Si/NiO_x/electrolyte interface. This is particularly important given that the precursor combination appears to significantly influence the film's properties, as demonstrated above. Fig. 9 presents transmittance (T), reflectance (R) and absorbance (A) depending on the wavelength of the incident beam. Note that A is calculated by subtracting R and T to 100%.

In all cases, T is greater than 60% for $\lambda \geq 375 \text{ nm}$ (Fig. 9a). When comparing T with R and A (Figs. 9b and c), it appears that the main optical loss arises from the reflectance since absorbance is very low. This is expected as the bandgap of the material is in

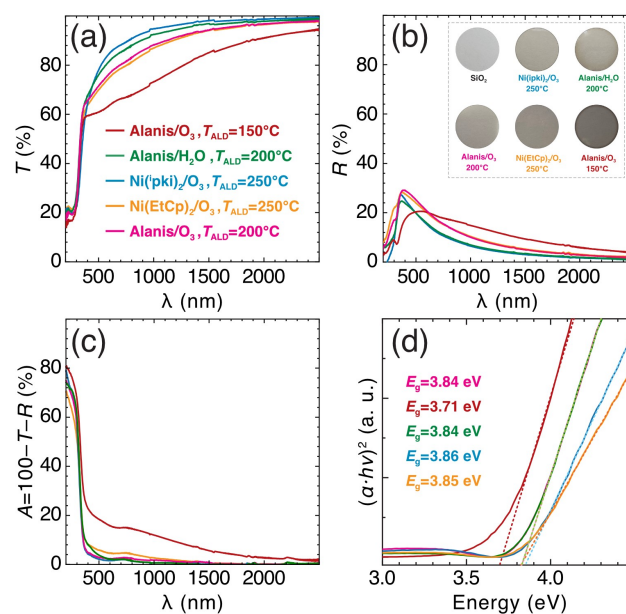


Fig. 9 UV-Vis NIR spectra: (a) transmission, (b) reflectance, and (c) absorbance, and (d) Tauc plot. All the measurements are performed by using air as baseline. The linear extrapolations (dashed lines) in (d) give the E_g values indicated on the plot. N_{ALD} has been adjusted according to each GPC to achieve $t_{\text{NiO}} = 50 \text{ nm}$.

the UV range. While films formed using most precursor combinations at different temperatures are highly transparent, the Alanis/O₃ combination behaves differently. In this case, an absorbance tail in the visible range is measured. This can be attributed to energy states located in the bandgap. It is further confirmed by the Tauc plot presented in Fig. 9d where E_g is calculated according the Tauc relation (Eq. 1) by considering a direct optical transition in NiO_x (i. e., $\gamma = \frac{1}{2}$).

$$(\alpha \cdot h\nu)^{1/\gamma} = A(h\nu - E_g) \quad (1)$$

Except for Alanis/O₃ for which $E_g = 3.71 \text{ eV}$, it is around 3.85 eV for the other precursor combinations. This is in line with literature where values ranging from 3.1 to 4.3 eV are found^{92,93} with 3.7 to 3.8 eV being the commonly accepted range.^{76,94}

[Ni(ⁱpki)₂]/O₃-based films exhibit the highest transparency with lower absorption (Figs. 9a and 9c). This can be attributed to their well-crystallised structure, which reduces the grain boundary surface area, its near-unity O/Ni ratio and low contamination level (Tables 2 and 3).

Temperature can also play a critical role in transparency. Annealing above 200°C shows higher transparency by reducing defect concentration.⁹⁵ In the present work, lower T_{ALD} , which results in a higher concentration of NiOOH surface states and defects, likely contributes to the lower transmittance observed in the Alanis/O₃-based layers when they are grown at 150°C while they become transparent at 200°C. The absorption tail observed for Alanis/O₃ at $T_{\text{ALD}} = 150^\circ\text{C}$ can, thus, be ascribed to energy states located within the bandgap. Such behaviour is commonly observed for transition-metal oxides because achieving precise stoichiometry, is inherently challenging. For NiO_x, this difficulty is

Table 3 RBS/NRA analysis of the NiO_x films for the different precursor combinations and T_{ALD} .

Prec. combinations	T_{ALD} (°C)	Ni (at. %)	O (at. %)	C (at. %)	N (at. %)	O/Ni
Alanis/O ₃	150	44.99	49.85	3.56	1.60	1.11
	175	45.94	52.44	0.00	1.62	1.14
	200	48.50	48.89	1.53	1.07	1.01
Alanis/H ₂ O	150	42.47	48.57	7.59	1.38	1.14
[Ni(ⁱ pki) ₂]/O ₃	250	47.64	49.70	2.50	0.16	1.04
[Ni(EtCp) ₂]/O ₃	250	49.96	49.53	0.51	0.00	0.99

primarily due to the prevalence of defects, particularly $V_{\text{Ni}}^{\bullet}$, which cause E_g to vary.^{94,96,97} Temperature appears to be a critical factor influencing the optical properties, as increasing T_{ALD} leads to better-crystallised films with fewer defects and impurities, and an O/Ni ratio approaching unity.

3.2.4 Mott-Schottky analysis

Chemical analyses have shown that the film composition varies according to the precursor combination or the temperature used for deposition. Among the defects mentioned, $V_{\text{Ni}}^{\bullet}$ can have a significant effect on the doping of NiO_x layers. Mott-Schottky analyses have thus been performed in monobasic phosphate buffer with a $p\text{H} = 11.96$ on layers grown on FTO (Fig. 10). According to Eq. 2, it is possible to determine the doping and the flat band potential (U_{fb}) of the layers.

$$\frac{1}{C^2} = \frac{2}{A^2 \epsilon \epsilon_0 e N_a} \left(U - U_{\text{fb}} - \frac{kT}{e} \right) \quad (2)$$

where ϵ is the relative dielectric constant of the semiconductor ($\epsilon_{\text{NiO}} = 12^{98}$), ϵ_0 is the permittivity of free space, N_a is the carrier concentration (positive for holes), A is the area of the electrode, U is the applied potential, k is the Boltzmann constant, T is temperature, and e is the unit charge.

In all cases, a linear evolution is observed in the depletion region. The negative slopes confirm the p -type behaviour of the material. NiO_x films deposited using Alanis exhibit high doping levels on the order of 10^{20} cm^{-3} , whereas those grown from the β -ketoiminate precursor are significantly less doped, with concentrations around 10^{18} cm^{-3} . This is consistent with the stoichiometric composition of the film (O/Ni = 1) when the Cp-based precursor is used. In contrast, Mott-Schottky analyses confirm that, in the other cases, the doping originates from Ni deficiency in the NiO_x matrix. A slight decrease in N_a was observed with increasing T_{ALD} for the Alanis/O₃ combination (Fig. 10d). Here again, the reduced doping is attributed to a more balanced O/Ni ratio.

As indicated by Eq. 2, the x -intercept of the linear fit gives U_{fb} that ranges from 0.70 to 1.03 V vs RHE depending on the ALD processes. Although these values span approximately 300 mV, they remain within the range generally reported for this material at $p\text{H} = 11.96$ (0.65 to 1.15 V vs RHE).^{36,53,99,100} Variations in U_{fb} can arise from many factors, but as previously reported in the case of NiO_x ALD, the precursors⁵³ and T_{ALD} ¹⁰¹ appear to be critical. Fig. 10 shows that the Alanis/O₃ combination at 150°C has the lowest U_{fb} (0.70 V vs RHE). XPS analyses have indicated

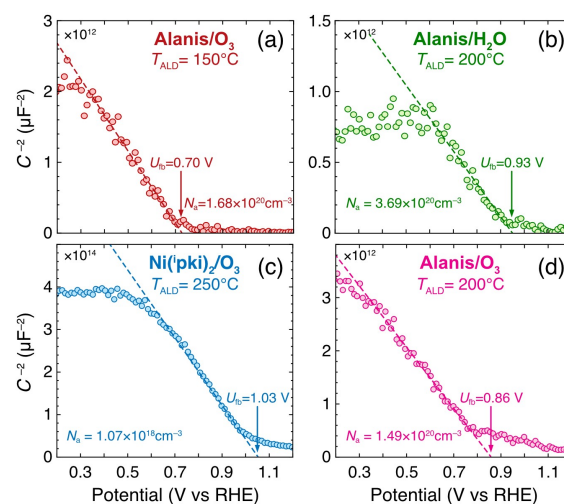


Fig. 10 Mott-Schottky plots of NiO_x layers deposited from (a) Alanis/O₃ at 150°C (b) Alanis/H₂O at 200°C (c) [Ni(ⁱpki)₂]/O₃ at 250°C and (d) Alanis/O₃ at 200°C. U_{fb} and N_a are indicated on the plots. Capacitance measurements are performed with an AC-voltage of 10 mV in 1 M Na₂SO₄ + 0.1 M NaH₂PO₄ at $f = 12 \text{ kHz}$. N_{ALD} has been adjusted according to each GPC to achieve $t_{\text{NiO}} = 50 \text{ nm}$.

that this precursor combination leads to a high concentration of surface hydroxyls. According to literature,¹⁰¹ this causes a negative U_{fb} shift for the NiO_x/electrolyte interface and this is often considered to contribute to a higher OER activity. The other precursor combinations show more positive results U_{fb} (0.93 and 1.03 V for Alanis/H₂O and [Ni(ⁱpki)₂]/O₃, respectively) because they have lower surface hydroxyl concentrations. In addition, NiO_x grown from Alanis/O₃ at $T_{\text{ALD}} = 200^\circ\text{C}$ leads to a more positive U_{fb} (0.86 V). This is probably due to a lower concentration of $-\text{OH}$ on the surface.

3.3 Electrochemical activity toward OER

As mentioned in the introduction, NiO_x layers have been proposed as protective and catalyst for Si-based photoanodes.²³ Section 3.2 has shown the significant influence of the precursor combination and deposition temperature on the physicochemical properties. In the following, the photoelectrochemical response of the anodes is investigated depending on their synthesis parameters. The Si therefore drives the electrode/electrolyte interface.

The influence of t_{NiO} on the OER response was first studied using the Alanis/O₃ combination. Although the interface consists of a double junction, $n\text{-Si}/p\text{-NiO}_x/\text{electrolyte}$, potentiometry per-



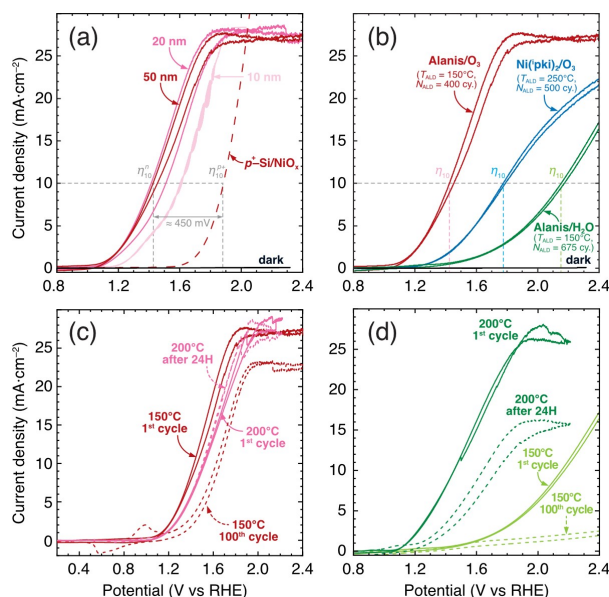


Fig. 11 CVs of NiO_x films deposited on Si performed in 1 M KOH in the dark and under illumination (AM1.5G). (a) NiO_x grown using Alanis/ O_3 at 150°C on n -Si exhibiting increasing thicknesses ($t_{\text{NiO}} = 10, 20$ and 50 nm) and on p^+ -Si ($t_{\text{NiO}} = 50$ nm). (b) Initial CVs of the NiO_x grown using three precursor combinations (indicated on the plot). (c) Comparison of initial (full lines) CVs performed on NiO_x deposited using Alanis/ O_3 at 150 and 200°C with CVs (dashed lines) after 100 cycles and after CA experiment for 24 h, respectively ($t_{\text{NiO}} = 50$ nm). (d) Comparison of initial CVs (full lines) performed on NiO_x deposited using Alanis/ H_2O at 150 and 200°C with CVs (dashed lines) after 100 cycles and after CA experiment for 24 h, respectively ($t_{\text{NiO}} = 50$ nm).

formed in the dark and under illumination (Fig. S16a) reveals a negative photopotential ($U_{\text{ph}} \approx -450$ mV). This indicates that the interface behaves like an n -type semiconductor/electrolyte junction. It is confirmed by the MS plot (Fig. S16b) which shows a linear trend with a positive slope between 1.5 and 3.0 V and indicates that Si drives the electrode/electrolyte interface. This is expected, since holes (h^+) have to be photogenerated in the Si to feed the OER while NiO_x has to act as a catalyst and protection against corrosion.

Fig. 11a shows cyclic voltammograms (CVs) performed on layers with t_{NiO} ranging from 10 to 50 nm. As expected for such n -type Schottky junction, the CV performed in the dark exhibits a negligible anodic current. In contrast, under illumination, the curves display significant photocurrent (j_{ph}) with a steep increase starting around 1.05 V—corresponding to water oxidation—and a plateau ($j_{\text{ph}} \approx 27 \text{ mA cm}^{-2}$) starting near 1.8 V. It is consistent with the U_{fb} of 0.7 V (Fig. S16b) which is expected at a slightly more cathodic potential than the j_{ph} initiation. Whereas t_{NiO} does not affect the level of the current plateau, it influences the onset potential. By comparing the overpotential (η_{10}) at $j_{\text{ph}} = 10 \text{ mA cm}^{-2}$, a 450 mV negative shift is measured for NiO_x layers grown on n -Si with respect to those deposited on p^+ -Si (i.e. a degenerated semiconductor that is not light-sensitive). Additionally, η_{10} shifts negatively, from 1.61 to 1.41 V, as t_{NiO} increases from 10 to 20 nm, respectively, but it remains almost constant from 20 to 50 nm ($\eta_{10} = 1.42$ V). This confirms that NiO_x

acts as a hole-trapping co-catalyst, facilitating water oxidation.

The thickness-dependent performance underscores the balance between catalytic activity and charge-carrier mobility in the NiO_x . For layers thicker than 20 nm, one can consider that bulk properties are observed.

As predicted by the previous characterisations, the photoelectrochemical responses of NiO_x layers should vary depending on the precursor combinations. Fig. 11b compares the initial CVs measured under AM1.5G illumination for Alanis/ O_3 , Alanis/ H_2O and $[\text{Ni}(\text{pki})_2]/\text{O}_3$. The three CVs exhibit, indeed, different behaviours. The comparison of the curves indicates that the highest photoresponse is observed for films deposited from Alanis/ O_3 , followed by $[\text{Ni}(\text{pki})_2]/\text{O}_3$, and finally Alanis/ H_2O . The expected constant photocurrent ($j_{\text{ph}} \approx 27 \text{ mA cm}^{-2}$), starting at 1.9 V, is proportional to the illumination flux. Conversely, lower currents and no plateau are observed for the other precursor combinations. The j_{ph} fluctuations that can appear on the plateau are attributed to O_2 bubbles formed during the OER. This effect is even stronger on Fig. 11d. Similarly, the values of η_{10} are 2.15 , 1.78 , and 1.42 V for films prepared using Alanis/ H_2O , $[\text{Ni}(\text{pki})_2]/\text{O}_3$, and Alanis/ O_3 , respectively. W_f are listed Table 4 with the E_g measured above. The combinations of precursors lead to values of W_f and E_g that are very close to each other. It is therefore difficult to explain the differences observed in Fig. 11b by a different band structure of the electrode/electrolyte junction.

This can be attributed to the higher surface hydroxyl concentration observed when using Alanis/ O_3 . Hydroxylation of the NiO_x surface indeed plays a critical role on the catalytic activity.²¹ During cyclic polarisations, phase transformations between different hydroxides (α - and β - $\text{Ni}(\text{OH})_2$) and oxyhydroxides (β - and γ - NiOOH) occur, which drive the OER kinetics.^{20,43} The chemical analyses presented above show high O/Ni (Table 2) and a high Ni-OH/Ni-O (Fig. 7d) ratios for this precursor combination. These values are lower and close for both $[\text{Ni}(\text{pki})_2]/\text{O}_3$ and Alanis/ H_2O but the latter drives to a much more contaminated layer (Table 3) that could hamper the electrochemical reaction. The surface hydroxyl concentration can also be monitored by MS analysis, as a high $-\text{OH}$ termination density typically induces a negative shift of U_{fb} .¹⁰² U_{fb} for Alanis/ O_3 is accordingly the lowest (0.7 V) compared to the others ($U_{\text{fb}} = 1.03$ V and 0.93 V) and confirms also the effect of hydroxyls on the photoelectrochemical responses observed in Fig. 11b.

The photoelectrode stability was investigated for the three precursor combinations. Figs. 11c and 11d present the CV evolution for Alanis associated with O_3 and H_2O , respectively. Similar CVs for $[\text{Ni}(\text{pki})_2]/\text{O}_3$ are shown in Fig. S17a, though no significant electrochemical changes were detected in this latter system. In the case of Alanis/ O_3 (Fig. 11c), minor j_{ph} decrease and η posi-

Table 4 W_f and E_g of the NiO_x layers depending on the precursor combination

	Alanis/ O_3	Alanis/ H_2O	$[\text{Ni}(\text{pki})_2]/\text{O}_3$
W_f (eV)	4.68	4.57	4.86
E_g (eV)	3.71	3.84	3.85

tive shift are observed when comparing the initial and the 100th CVs. The anodic and cathodic waves associated with oxidation ($\text{Ni}^{2+} \rightarrow \text{Ni}^{3+} + e^-$) and reduction ($\text{Ni}^{3+} + e^- \rightarrow \text{Ni}^{2+}$) reactions, centred at 1 and 0.6 V, respectively, are considerably enhanced after 100 cycles. These electrochemical peaks usually reflect the $\text{Ni}(\text{OH})_2$ and NiOOH phase transformations mentioned above. This is clearly visible on Fig. S17b where the progressive decrease of the current plateau correlates with the gradual enhancement of the peaks while cycling. This phenomenon is not observed when the films are grown with Alanis/ O_3 at 200°C. This might be ascribed to the lower V_{Ni} concentration (Table 3) that also leads to a better stability.

In contrast, the Alanis/ H_2O sample (Fig. 11d) exhibits a lower initial j_{ph} that further decreases significantly after 100 CV cycles. This reduced performance likely stems from elevated organic impurities in the film, which cause a tiny permeability and enable direct contact between the silicon substrate and electrolyte. The j_{ph} degradation may also be attributed to layer contamination, leading to subsequent delamination or dissolution of the films. Similar phenomenon has been reported for NiO_x grown by pulsed laser deposition.²⁴

When depositions are carried out at $T_{\text{ALD}} = 200^\circ\text{C}$, the first CV for Alanis/ O_3 remains almost unchanged while it exhibits a significant enhancement of j_{ph} for Alanis/ H_2O . The current plateau is then at the same level for both oxygen sources. After polarisation at $U = 2\text{ V}$ under illumination for 24 H, no change was measured for O_3 , whereas the response for H_2O decreased by half. The consistent behaviour observed for O_3 is probably due to the negligible change in its properties, as suggested by the MS plot (Fig. 10d) and the better stability can arise from a higher density of the film shown by XRR measurements (Fig. 5). The j_{ph} enhancement of the film formed at $T_{\text{ALD}} = 200^\circ\text{C}$ with H_2O probably comes from a higher density and lower impurity concentration.

The corresponding chronoamperograms (CAs) at $U = 2\text{ V}$ under illumination are shown in Fig. 12a (the full timescale plot is shown in Fig. S18 for seek of clarity). After an initial drop, the photocurrent remains stable for all three precursor combinations. Although the initial j_{ph} is lower for $[\text{Ni}(\text{pki})_2]/\text{O}_3$, it shows a long lasting stability (48 H). In the case of Alanis/ O_3 , a stable j_{ph} is measured up to approximately 24 H with almost no loss. As expected from the CVs, Alanis/ H_2O , j_{ph} is reduced by half after 17 H of polarisation. The stability is, however, significantly better at 200°C (Fig. 11d). This can be attributed to their higher density and an O/Ni ratio that is closer to stoichiometry when the layers are produced at elevated temperatures. The degradation of the NiO_x is further confirmed by XPS analysis performed after the electrochemical investigations. The delamination is indicated by the intense Si and SiO_x signals observed in the Si 2p XPS peak region (Fig. S19).

Given the different photoelectrochemical responses of those NiO_x layer, it is essential to investigate the possible chemical and crystalline modifications. Comparison of the XRD patterns collected before and after the electrochemical studies (Fig. 12b) shows the emergence of two new reflections at 33° and 59.4° , corresponding to the (101) and (300) planes of $\alpha\text{-Ni}(\text{OH})_2$, respectively (highlighted by * in the Figure).^{103,104} This confirms

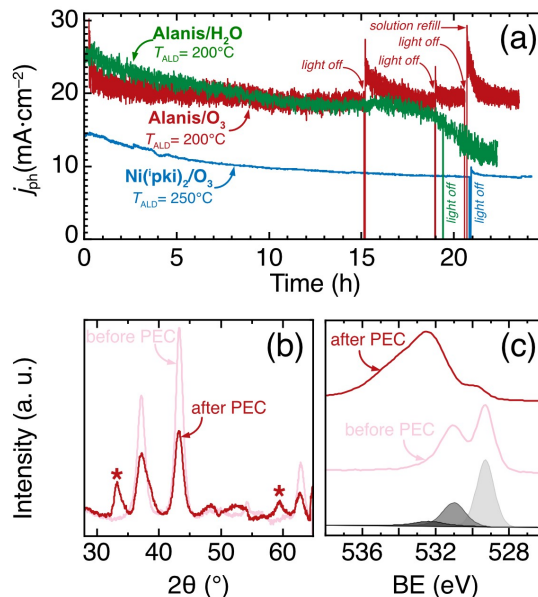


Fig. 12 (a) CAs at $U = 2\text{ V}$, of NiO_x layers grown on $n\text{-Si}$ under AM1.5G illumination for Alanis/ O_3 , Alanis/ H_2O and $[\text{Ni}(\text{pki})_2]/\text{O}_3$ combinations. T_{ALD} are indicated on the plot. (b) XRD analysis of NiO_x before and after photoelectrochemical testing (Alanis/ O_3 at 150°C). The * signs are referred in the text. (c) O 1s XPS peak of the NiO_x before and after photoelectrochemical testing (Alanis/ O_3 at 150°C).

the phase transformations that occur during CVs. It should be noted that the $\alpha\text{-Ni}(\text{OH})_2$ is detected a posteriori because it is the most stable. The $\beta\text{-Ni}(\text{OH})_2$ can be generated in solution but is unstable in air. In situ studies (XRD or XPS) are necessary to identify it accurately and clarify which compound induces the excellent catalytic activity. XPS analyses conducted before and after the PEC studies are consistent with CVs and XRD. As shown in Fig. 12c, the O 1s peak shifts toward higher binding energies, corresponding to hydroxyl and water signatures. This indicates that the surface of the photoanode becomes hydroxylated, providing further evidence for the formation of $\text{Ni}(\text{OH})_2$ or NiOOH .

Conclusion

In this study, NiO_x thin films were successfully deposited via thermal ALD using two novel precursors across three different precursor combinations. It demonstrates that combining the precursors with different co-reactants significantly influenced the film properties, including density, crystallinity, composition, surface roughness, and growth rate. Among them, the Alanis/ O_3 combination exhibited the highest growth rate and a broad temperature window at relatively low deposition temperatures. It is one of the highest GPC ever reported at $T_{\text{ALD}} \leq 200^\circ\text{C}$. Comprehensive structural, crystallographic, and morphological characterisations confirmed the formation of uniform, high-quality films with well-controlled growth behaviour. Optical and photoelectrochemical analyses further revealed that these films possess favorable properties for efficient water oxidation, demonstrating their potential in photoelectrochemical applications. These findings emphasise not only the viability of the new precursors for ALD but also the critical influence of precursor selection on the functional



performance of NiO_x thin films. The present results are highly promising, as the onset potential for Alanis/O₃ is significantly low ($U = 1.15$ V vs RHE for $j_{ph} = 1$ mA·cm⁻²), ranking among the best reported in the literature (see benchmark in Fig. S20). Moreover, optimisation of the ALD process has resulted in 50 nm-thick films exhibiting long-lasting stability when other methods such as PLD require almost twice the thickness to be comparable.²⁴ These electrochemical performances seem to be correlated with the high O concentration and, more particularly, of -OH at the surface of the film. Future work will focus on further optimising deposition parameters (e. g. post deposition thermal treatments) and applying such processes onto micro- or nano-structured Si to further improve the OER and assess their practical applicability of *n*-Si/NiO_x in solar-driven water splitting technologies.

Author contributions

V. Kannampalli: Writing - original draft, Validation, Methodology, Investigation (Fabrication and characterisations of the photoelectrodes), Formal analysis, Data curation, Conceptualisation. **M. Schmickler:** Writing - review & editing, Validation, Investigation (Synthesis and characterisations) Formal analysis. **B. Fabre:** Writing review & editing, Validation, Investigation (Characterisation). **L. Largeau:** Writing review & editing, Validation, Investigation (Characterisation). **A. Seyeux:** Writing review & editing, Validation, Investigation (Characterisation). **J. Alvarez:** Writing review & editing, Validation, Investigation (Characterisation). **S. Elliott:** Writing - Original draft, Validation, Investigation (Mechanisms). **A. Devi:** Writing - review & editing, Validation, Methodology, Investigation (Synthesis and characterisations), Supervision, Resources, Formal analysis. **L. Santinacci:** Writing - original draft, Validation, Investigation, Supervision, Resources, Project administration, Formal analysis, Data curation, Conceptualisation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Vasile Heresanu (CINaM-CNRS) is acknowledged for his precious help in XRD analyses. Dr. Corinne Lagrost from ASPHERYX platform (CNRS – University of Rennes) is also acknowledged for XPS measurements. Nicolas Blasco and Jamie Greer from (Air Liquide Advanced Materials) for providing Ni precursor. This collaborative work was supported by the French Agence Nationale de la Recherche (ANR) under grant ANR-23-CE50-0024-01 (EffiCaWat project) and by the France 2030 PEPR H₂ program managed by the ANR under the grant ANR-22-PEHY-0013 (Nautilus project). V. K. acknowledges Council of Région Sud for funding (DEB #DEP 21-387, 23/07/2021). A. D. and M. S. acknowledge the DFG for supporting this work (REACTIVE project, No. 490773082) This work was partly supported by the French Renatech network (FIB preparation, TEM observations).

References

- 1 K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano and H. Hosono, *Nature*, 2004, **432**, 488–492.

- 2 J. W. Park, B. H. Kang and H. J. Kim, *Adv. Funct. Mater.*, 2020, **30**, 1904632.
- 3 M. Coll, J. Fontcuberta, M. Althammer, M. Bibes, H. Boschker and A. Calleja, *App. Surf. Sci.*, 2019, **482**, 1–93.
- 4 R. L. Z. Hoye, K. P. Musselman and J. L. MacManus-Driscoll, *APL Materials*, 2013, **1**, 060701.
- 5 L. Petti, N. Münzenrieder, C. Vogt, H. Faber, L. Büthe, G. Cantarella, F. Bottacchi, T. D. Anthopoulos and G. Tröster, *App. Phys. Rev.*, 2016, **3**, 021303.
- 6 M. Napari, T. N. Huq, R. L. Z. Hoye and J. L. MacManus-Driscoll, *InfoMat*, 2021, **3**, 536–576.
- 7 E. M. C. Fortunato, P. M. C. Barquinha, A. C. M. B. G. Pimentel, A. M. F. Gonçalves, A. J. S. Marques, L. M. N. Pereira and R. F. P. Martins, *Adv. Mater.*, 2005, **17**, 590–594.
- 8 S. K. Garlapati, J. S. Gebauer, S. Dehm, M. Bruns, M. Winterer, H. Hahn and S. Dasgupta, *Adv. Elect Mater.*, 2017, **3**, 1600476.
- 9 M. D. Irwin, J. D. Servaites, D. B. Buchholz, B. J. Leever, J. Liu, J. D. Emery, M. Zhang, J.-H. Song, M. F. Durstock, A. J. Freeman, M. J. Bedzyk, M. C. Hersam, R. P. H. Chang, M. A. Ratner and T. J. Marks, *Chem. Mater.*, 2011, **23**, 2218–2226.
- 10 H.-J. Kim and J.-H. Lee, *Sens. Actuators, B*, 2014, **192**, 607–627.
- 11 K. Nomura, T. Kamiya and H. Hosono, *Adv. Mater.*, 2011, **23**, 3431–3434.
- 12 Z. Wang, P. K. Nayak, J. A. Caraveo-Frescas and H. N. Alshaareef, *Adv. Mater.*, 2016, **28**, 3831–3892.
- 13 T. S. Tripathi and M. Karppinen, *Adv. Mater. Interface*, 2017, **4**, 1700300.
- 14 J. Zhang, D. Zeng, Q. Zhu, J. Wu, Q. Huang and C. Xie, *The Journal of Physical Chemistry C*, 2016, **120**, 3936–3945.
- 15 J. Wang, K. Liu, W. Liao, Y. Kang, H. Xiao, Y. Chen, Q. Wang, T. Luo, J. Chen, H. Li and others, *Nat. Catal.*, 2025, 1–10.
- 16 F. Jiang, W. C. Choy, X. Li, D. Zhang and J. Cheng, *Adv. Mater.*, 2015, **27**, 2930–2937.
- 17 S. Lany, J. Osorio-Guillén and A. Zunger, *Phys. Rev. B*, 2007, **75**, 241203.
- 18 J. Zhang, D. Zeng, Q. Zhu, J. Wu, K. Xu, T. Liao, G. Zhang and C. Xie, *J. Phys. Chem. C*, 2015, **119**, 17930–17939.
- 19 D.-Y. Cho, S. J. Song, U. K. Kim, K. M. Kim, H.-K. Lee and C. S. Hwang, *J. Mater. Chem. C*, 2013, **1**, 4334.
- 20 H. Radinger, P. Connor, S. Tengeler, R. W. Stark, W. Jaegermann and B. Kaiser, *Chem. Mater.*, 2021, **33**, 8259–8266.
- 21 N. Weidler, J. Schuch, F. Knaus, P. Stenner, S. Hoch, A. Maljusch, R. Schäfer, B. Kaiser and W. Jaegermann, *J. Phys. Chem. C*, 2017, **121**, 6455–6463.
- 22 G. Boschloo and A. Hagfeldt, *J. Phys. Chem. B*, 2001, **105**, 3039–3044.
- 23 K. Sun, F. H. Saadi, M. F. Lichterman, W. G. Hale, H.-P. Wang, X. Zhou, N. T. Plymale, S. T. Omelchenko, J.-H. He,



- K. M. Papadantonakis, B. S. Bruntschwig and N. S. Lewis, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 3612–3617.
- 24 L. He, W. Zhou, D. Cai, S. S. Mao, K. Sun and S. Shen, *Catal. Sci. Technol.*, 2017, **7**, 2632–2638.
- 25 S. Tengeler, M. Fingerle, W. Calvet, C. Steinert, B. Kaiser, T. Mayer and W. Jaegermann, *J. Electrochem. Soc.*, 2018, **165**, H3122.
- 26 S. Hu, M. R. Shaner, J. A. Beardslee, M. Lichterman and N. S. Bruntschwig, Bruce S. and Lewis, *Science*, 2014, **344**, 1005–1009.
- 27 P. Misra, V. K. Sahu, R. S. Ajimsha, A. K. Das and B. Singh, *J. Phys. D: Appl. Phys.*, 2017, **50**, 415106.
- 28 P. Salunkhe, M. A. A.V and D. Kekuda, *Appl. Phys. A*, 2021, **127**, 390.
- 29 S. Pereira, A. Gonçalves, N. Correia, J. Pinto, L. Pereira, R. Martins and E. Fortunato, *Solar Energy Materials and Solar Cells*, 2014, **120**, 109–115.
- 30 D. Mateos, B. Valdez, J. Castillo, N. Nedev, M. Curiel, O. Perez, A. Arias and H. Tiznado, *Ceram. Int.*, 2019, **45**, 11403–11407.
- 31 T. Ivanova, A. Harizanova, M. Shipochka and P. Vitanov, *Materials*, 2022, **15**, 1742.
- 32 T. M. Roffi, S. Nozaki and K. Uchida, *J. Cryst. Growth*, 2016, **451**, 57–64.
- 33 M. Aftab, M. Butt, D. Ali, F. Bashir and T. M. Khan, *Optical Materials*, 2021, **119**, 111369.
- 34 H. Kumagai, M. Matsumoto, K. Toyoda and M. Obara, *J. Mater. Sci. Lett.*, 1996, **15**, 1081–1083.
- 35 H. L. Lu, G. Scarel, C. Wiemer, M. Perego, S. Spiga, M. Fanciulli and G. Pavia, *J. Electrochem. Soc.*, 2008, **155**, H807.
- 36 D. Koushik, M. Jošt, A. Dučinskis, C. Burgess, V. Zardetto, C. Weijtens, M. A. Verheijen, W. M. M. Kessels, S. Albrecht and M. Creatore, *J. Mater. Chem. C*, 2019, **7**, 12532–12543.
- 37 V. Zardetto, B. L. Williams, A. Perrotta, F. Di Giacomo, M. A. Verheijen, R. Andriessen, W. M. M. Kessels and M. Creatore, *Sustainable Energy Fuels*, 2017, **1**, 30–55.
- 38 L. Santinacci, M. W. Diouf, M. K. S. Barr, B. Fabre, L. Joanny, F. Gouttefangeas and G. Loget, *ACS Appl. Mater. Interfaces*, 2016, **8**, 24810–24818.
- 39 H. B. Profijt, S. E. Potts, M. C. M. Van De Sanden and W. M. M. Kessels, *J. Vac. Sci. Technol., A*, 2011, **29**, 050801.
- 40 D. Garcia-Alonso, S. E. Potts, C. A. A. Van Helvoirt, M. A. Verheijen and W. M. M. Kessels, *J. Mater. Chem. C*, 2015, **3**, 3095–3107.
- 41 M. E. Dufond, M. W. Diouf, C. Badie, C. Laffon, P. Parent, D. Ferry, D. Grosso, J. C. S. Kools, S. D. Elliott and L. Santinacci, *Chem. Mater.*, 2020, **32**, 1393–1407.
- 42 M. E. Dufond, J.-N. Chazalviel and L. Santinacci, *J. Electrochem. Soc.*, 2021, **168**, 031509.
- 43 S. Haghverdi Khamene, C. Van Helvoirt, M. N. Tsampas and M. Creatore, *J. Phys. Chem. C*, 2023, **127**, 22570–22582.
- 44 J. Chae, H.-S. Park and S.-w. Kang, *Electrochem. Solid-State Lett.*, 2002, **5**, C64.
- 45 J. Bachmann, A. Zolotaryov, O. Albrecht, S. Goetze, A. Berger, D. Hesse, D. Novikov and K. Nielsch, *Chem. Vap. Dep.*, 2011, **17**, 177–180.
- 46 L. Assaud, E. Monyoncho, K. Pitzschel, A. Allagui, M. Petit, M. Hanbücken, E. A. Baranova and L. Santinacci, *Beilstein J. Nanotechnol.*, 2014, **5**, 162–172.
- 47 H. Lu, G. Scarel, X. Li and M. Fanciulli, *J. Cryst. Growth*, 2008, **310**, 5464–5468.
- 48 T. S. Yang, W. Cho, M. Kim, K.-S. An, T.-M. Chung, C. G. Kim and Y. Kim, *J. Vac. Sci. Technol., A*, 2005, **23**, 1238–1243.
- 49 P. Antony Premkumar, M. Toeller, C. Adelman, J. Meersschaut, A. Franquet, O. Richard, H. Tielens, B. Brijs, A. Moussa, T. Conard, H. Bender, M. Schaeckers, J. A. Kittl, M. Jurczak and S. Van Elshocht, *Chem. Vap. Dep.*, 2012, **18**, 61–69.
- 50 U. Farva and J. Kim, *Vacuum*, 2023, **207**, 111674.
- 51 R. Attri, D. P. Panda, J. Ghatak and C. N. R. Rao, *APL Materials*, 2023, **11**, 091105.
- 52 M. Utriainen, M. Kröger-Laukkanen and L. Niinistö, *Mater. Sci. Eng., B*, 1998, **54**, 98–103.
- 53 E. Thimsen, A. B. F. Martinson, J. W. Elam and M. J. Pellin, *J. Phys. Chem. C*, 2012, **116**, 16830–16840.
- 54 Y. Zhang, L. Du, X. Liu and Y. Ding, *App. Surf. Sci.*, 2019, **481**, 138–143.
- 55 M. Ritala and M. Leskelä, *Handbook of Thin Films*, Elsevier, 2002, pp. 103–159.
- 56 M. Leskelä and M. Ritala, *Angew. Chem. Int. Ed.*, 2003, **42**, 5548–5554.
- 57 T. Blanquart, J. Niinistö, M. Ritala and M. Leskelä, *Chem. Vap. Dep.*, 2014, **20**, 189–208.
- 58 J. P. Klesko, M. M. Kerrigan and C. H. Winter, *Chem. Mater.*, 2016, **28**, 700–703.
- 59 K. E. K. Holden, C. L. Dezelah and J. F. Conley, *ACS Appl. Mater. Interfaces*, 2019, **11**, 30437–30445.
- 60 M.-H. Ko, B. Shong and J.-H. Hwang, *Ceram. Int.*, 2018, **44**, 16342–16351.
- 61 V. Pore, E. Tois, R. Matero, S. Haukka, M. Tuominen, J. Woodruff, B. Milligan, F. Tang and M. Givens, 2015 IEEE International Interconnect Technology Conference and 2015 IEEE Materials for Advanced Metallization Conference (IITC/MAM), Grenoble, 2015, pp. 191–194.
- 62 D. Zywitzki, D. H. Taffa, L. Lamkowski, M. Winter, D. Rogalla, M. Wark and A. Devi, *Inorg. Chem.*, 2020, **59**, 10059–10070.
- 63 S. Porcar, M. Schmickler, H. Okcu, J. Obenlünenschloß, S. d'Ercole, L. Cervera-Gabalda, I. Galarreta-Rodriguez, J. Rubio-Zuazo, J. G. Cuadra, A. Lahlahi, D. Fraga, C. Sanchez-Velasquez, D. Bellet, T. Fix, J. B. Carda, A. Devi and D. Muñoz-Rojas, *Appl. Surf. Sci. Adv.*, 2025, **29**, 100836.
- 64 D. Peeters, A. Sadlo, K. Lowjaga, O. Mendoza Reyes, L. Wang, L. Mai, M. Gebhard, D. Rogalla, H. Becker, I. Giner, G. Grundmeier, D. Mitoraj, M. Grafen, A. Ostendorf, R. Beranek and A. Devi, *Adv. Mater. Interface*, 2017, **4**, 1700155.
- 65 M. K. Barr, L. Assaud, Y. Wu, C. Laffon, P. Parent, J. Bachmann and L. Santinacci, *Electrochim. Acta*, 2015, **179**, 504–



- 511.
- 66 T. Peng, X. Xiao, X. Han, X. Zhou, W. Wu, F. Ren and C. Jiang, *App. Surf. Sci.*, 2011, **257**, 5908–5912.
- 67 Available on request from Air Liquide Advanced Materials, 3040 US-22, Branchburg, NJ 08876, USA, gregory.muhr@airliquide.com, usalam-orders@airliquide.com.
- 68 C. Badie, A. Mirzaei, J. Lee, S. Sayegh, M. Bechelany, L. Santinacci, H. W. Kim and S. S. Kim, *Adv. Mater. Technologies*, 2024, **9**, 2302081.
- 69 C.-C. Hsu, H.-W. Su, C.-H. Hou, J.-J. Shyue and F.-Y. Tsai, *Nanotechnol.*, 2015, **26**, 385201.
- 70 D. N. Goldstein and S. M. George, *Thin Solid Films*, 2011, **519**, 5339–5347.
- 71 R. Zhao, S. Xiao, S. Yang and X. Wang, *Chem. Mater.*, 2019, **31**, 5172–5180.
- 72 C. Ehinger, X. Zhou, M. Candrian, S. R. Docherty, S. Pollitt and C. Copéret, *JACS Au*, 2023, **3**, 2314–2322.
- 73 X. Zhang, Z. Zhou, R. Xu, J. Guo, L. Xu, Y. Ding, H. Xiao, X. Li, A. Li and G. Fang, *Phys. Chem. Chem. Phys.*, 2023, **25**, 13465–13473.
- 74 D. Franta, B. Negulescu, L. Thomas, P. R. Dahoo, M. Guyot, I. Ohlídal, J. Mistrík and T. Yamaguchi, *App. Surf. Sci.*, 2005, **244**, 426–430.
- 75 J. W. F. Innocent, M. Napari, A. L. Johnson, T. R. Harris-Lee, M. Regue, T. Sajavaara, J. L. MacManus-Driscoll, F. Marken and F. Alkhalil, *Mater. Adv.*, 2021, **2**, 273–279.
- 76 R. J. Powell and W. E. Spicer, *Phys. Rev. B*, 1970, **2**, 2182–2193.
- 77 H. L. Lu, G. Scarel, M. Alia, M. Fanciulli, S.-J. Ding and D. W. Zhang, *App. Phys. Lett.*, 2008, **92**, 222907.
- 78 A. López-Beltrán and A. Mendoza-Galván, *Thin Solid Films*, 2006, **503**, 40–44.
- 79 L. Santinacci, M. Bouttemy, M. Petit, A.-M. Gonçalves, N. Simon, J. Vigneron and A. Etcheberry, *J. Electrochem. Soc.*, 2018, **165**, H3131.
- 80 A. P. Grosvenor, M. C. Biesinger, R. S. Smart and N. S. McIntyre, *Surf. Sci.*, 2006, **600**, 1771–1779.
- 81 M. A. Peck and M. A. Langell, *Chem. Mater.*, 2012, **24**, 4483–4490.
- 82 D. Wanger, W. M. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corp., Physical Electronics Division, Eden Prairie, Minnesota, USA, 1979.
- 83 M. A. Van Veenendaal and G. A. Sawatzky, *Phys. Rev. Lett.*, 1993, **70**, 2459–2462.
- 84 S. Chakrabarti, D. Carolan, B. Alessi, P. Maguire, V. Svrcek and D. Mariotti, *Nanoscale Adv.*, 2019, **1**, 4915–4925.
- 85 S. Timoshnev, A. Kazakin, K. Shubina, V. Andreeva, E. Fedorenko, A. Koroleva, E. Zhizhin, O. Koval, A. Kurinnaya, A. Shalin, V. Bobrovs and Y. Enns, *Adv. Mater. Interface*, 2024, **11**, 2300815.
- 86 K. S. Usha, R. Sivakumar, C. Sanjeeviraja, V. Sathe, V. Ganesan and T. Y. Wang, *RSC Adv.*, 2016, **6**, 79668–79680.
- 87 A. N. Mansour and C. A. Melendres, *Surf. Sci. Spectra*, 1994, **3**, 263–270.
- 88 A. N. Mansour, *Surf. Sci. Spectra*, 1994, **3**, 239–246.
- 89 P. Nandi, H. Park, S. Shin, J. Lee, J. Y. Kim, M. J. Ko, H. S. Jung, N. Park and H. Shin, *Adv. Mater. Interface*, 2024, **11**, 2300751.
- 90 Y. S. Chen, J. F. Kang, B. Chen, B. Gao, L. F. Liu, X. Y. Liu, Y. Y. Wang, L. Wu, H. Y. Yu, J. Y. Wang, Q. Chen and E. G. Wang, *J. Phys. D: Appl. Phys.*, 2012, **45**, 065303.
- 91 H. Park, P. Nandi, Y. In and H. Shin, *Solar RRL*, 2024, **8**, 2300858.
- 92 B. Zhao, L. C. Lee, L. Yang, A. J. Pearson, H. Lu, X.-J. She, L. Cui, K. H. Zhang, R. L. Hoye, A. Karani and others, *ACS Appl. Mater. Interfaces*, 2018, **10**, 41849–41854.
- 93 G. A. Sawatzky and J. W. Allen, *Phys. Rev. Lett.*, 1984, **53**, 2339–2342.
- 94 S. Battiatto, M. M. Giangregorio, M. R. Catalano, R. Lo Nigro, M. Losurdo and G. Malandrino, *RSC Adv.*, 2016, **6**, 30813–30823.
- 95 R. Poulain, G. Lumbeeck, J. Hunka, J. Proost, H. Savolainen, H. Idrissi, D. Schryvers, N. Gauquelin and A. Klein, *ACS Appl. Electron. Mater.*, 2022, **4**, 2718–2728.
- 96 J. Keraudy, B. Delfour-Peyrethon, A. Ferrec, J. Garcia Molleja, M. Richard-Plouet, C. Payen, J. Hamon, B. Corraze, A. Goulet and P.-Y. Jouan, *J. Appl. Phys.*, 2017, **121**, 171916.
- 97 S.-H. Lee, H. M. Cheong, N.-G. Park, C. Tracy, A. Mascarenhas, D. K. Benson and S. K. Deb, *Solid State Ionics*, 2001, **140**, 135–139.
- 98 R. Newman and R. M. Chrenko, *Phys. Rev.*, 1959, **114**, 1507–1513.
- 99 S. Seo, I. J. Park, M. Kim, S. Lee, C. Bae, H. S. Jung, N.-G. Park, J. Y. Kim and H. Shin, *Nanoscale*, 2016, **8**, 11403–11412.
- 100 H. L. S. Santos, P. G. Corradini, M. A. S. Andrade and L. H. Mascaro, *J. Solid State Electrochem.*, 2020, **24**, 1899–1908.
- 101 Q. Liu, L. Wei, S. Yuan, X. Ren, Y. Zhao, Z. Wang, M. Zhang, L. Shi, D. Li and A. Li, *RSC Adv.*, 2015, **5**, 71778–71784.
- 102 Y. Yu, K. A. Click, S.-C. Chien, J. Sun, A. Curtze, L.-C. Lin and Y. Wu, *J. Phys. Chem. C*, 2019, **123**, 8681–8687.
- 103 S. Zhou, W. Wei, Y. Zhang, S. Cui, W. Chen and L. Mi, *Sci. Rep.*, 2019, **9**, 12727.
- 104 J. Deng, M. R. Nellist, M. B. Stevens, C. Dette, Y. Wang and S. W. Boettcher, *Nano Lett.*, 2017, **17**, 6922–6926.



The data supporting this article have been included as part of the Supplementary Information.

[View Article Online](#)
DOI: 10.1039/D5TA04555J

