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# On the epitaxial growth in ALD $\text{Co}_3\text{O}_4$ - and NiO-based bilayers†

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NiO and  $\text{Co}_3\text{O}_4$  are versatile materials studied for a plethora of applications, yet their performance for a specific application relies on the control of their crystallographic texture and corresponding surface facets. Achieving such control can be challenging, often requiring hetero-epitaxial growth on single-crystalline substrates, which are frequently incompatible with the requirements of the application. The combination of NiO and  $\text{Co}_3\text{O}_4$  in heterostructures provides potential to control texture due to their similar crystal structures, whilst retaining the possibility to work with more versatile substrates. In this study, atomic layer deposited (ALD) thin films based on cyclopentadienyl precursors and an oxygen plasma are adopted to tailor the crystallographic texture of NiO from  $\langle 100 \rangle$  to  $\langle 111 \rangle$  using an ALD  $\text{Co}_3\text{O}_4$  template layer, and similarly, to modify the  $\text{Co}_3\text{O}_4$  texture from  $\langle 111 \rangle$  to  $\langle 100 \rangle$  on a NiO template. The films are shown to conform to the crystal orientation of the template material, whilst crystallizing directly in their own stable crystal structure with corresponding metal atom coordination. Further investigation includes ALD process parameters for NiO growth: the film texture is found to depend on the choice of co-reactant and the above-highlighted hetero-epitaxial relationship is stronger for plasma-based processes. In conclusion, these results demonstrate an original approach for application-oriented crystallographic engineering in thin films.

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The chemistries of nickel oxide (NiO) and cobalt oxide ( $\text{Co}_3\text{O}_4$ ) are versatile and widely studied for their implementation in various applications such as solar cells,<sup>1–3</sup> supercapacitors,<sup>4–10</sup> gas sensors,<sup>11–14</sup> batteries,<sup>15–22</sup> and (electro-)catalysis.<sup>23–29</sup> A key property influencing the performance of these materials for a specific application is the orientation of the crystals within the film and the type of surface facet correlated to it.<sup>30–37</sup> The NiO (111) facet is, for example, preferred for gas sensors,<sup>38</sup> whilst NiO (110) is more efficient for ethane activation.<sup>39</sup> Similarly,  $\text{Co}_3\text{O}_4$  (111) is preferred for Li–O<sub>2</sub> batteries,<sup>31,40</sup> whilst the (110) surface is preferred for photo-thermal methanol oxidation.<sup>41</sup> In the context of oxygen evolution reaction (OER) electrocatalysts in water electrolysis, the optimal facets are  $\text{Co}_3\text{O}_4$  (100) and NiO (110).  $\text{Co}_3\text{O}_4$  (100) exhibits higher activity due to the formation of a thicker active (oxy)hydroxide skin layer as compared to  $\text{Co}_3\text{O}_4$  (111), possibly

due to differences in metal coordination and/or defects.<sup>42–44</sup> Likewise, NiO (110) facets show superior activity by stabilizing the  $\beta\text{-Ni}(\text{OH})_2$  form, as opposed to the less active  $\alpha\text{-Ni}(\text{OH})_2$  form.<sup>45</sup>

Controlling the crystallographic texture of a NiO or  $\text{Co}_3\text{O}_4$  film is challenging. Films often lack a preferred growth orientation when deposited on amorphous substrates,<sup>46–60</sup> necessitating hetero-epitaxial growth on crystalline substrates such as  $c\text{-Al}_2\text{O}_3$  (0001)<sup>61–66</sup> or MgO (100)<sup>57,63,64,67</sup> to achieve oriented growth.<sup>55,64,68–70</sup> However, these substrates are often not compatible with the targeted applications.

The cubic crystal structures of NiO and  $\text{Co}_3\text{O}_4$  differ in the coordination number of their metal atoms. Interestingly, the interplanar distances in several directions of the two crystal lattices are quite compatible; the  $\text{Co}_3\text{O}_4$  lattice has ~4% smaller interplanar distances compared to equivalent spacings in NiO with similar atomic positions of metal atoms.<sup>71,72</sup> This close alignment enables hetero-epitaxy,<sup>73</sup> providing an opportunity to obtain preferred growth orientations for  $\text{Co}_3\text{O}_4$  and NiO that cannot be obtained by growing single layers, but may be realized by continuing the texture from the underlying layer.

By combining NiO and  $\text{Co}_3\text{O}_4$  in heterostructures, composites and core-shell structures have already been shown to synergistically modulate their chemical and electronic band structures, benefiting applications such as gas sensors, bat-

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teries, and electrocatalysis, among others.<sup>73–80</sup> Zhang *et al.*<sup>73</sup> demonstrated that the NiO–Co<sub>3</sub>O<sub>4</sub> interface is metallic, significantly enhancing conductivity and charge transfer during the OER as compared to NiO and Co<sub>3</sub>O<sub>4</sub>. This heterointerface was therefore identified as the primary driver for improved performance as an OER catalyst. These results suggest that NiO and Co<sub>3</sub>O<sub>4</sub> film stacks could also possibly improve performance in various applications. In the context of electrocatalysis, Co<sub>3</sub>O<sub>4</sub> could act as an active, stable, and protective base layer, while a NiO coating could be utilized to increase the active surface area.<sup>26,73,81–84</sup>

Successful implementation of hetero-stacks requires a discrete, well-defined interface between the oxide layers. In this work, atomic layer deposition (ALD) is adopted; it can be expected to provide such an interface because it is based on sequential self-limiting surface reactions. This self-limiting nature originates from strong adsorption between the selected precursor and anchoring groups (*e.g.* hydroxyl) on the underlying surface. Furthermore, ALD provides an opportunity to work with complex, large surface area substrates that are, for example, required for catalysis. The deposition of NiO using ALD has been successfully demonstrated with various precursors and co-reactants for a range of applications. For example, Koushik *et al.*<sup>1</sup> deposited NiO using Ni(<sup>Me</sup>Cp)<sub>2</sub> and O<sub>2</sub> plasma for application in solar cells, while Chung *et al.*<sup>85</sup> adopted Ni(dmamp)<sub>2</sub> and H<sub>2</sub>O for non-volatile memory devices and Haghverdi Khamene *et al.*<sup>27</sup> employed Ni(<sup>t</sup>Bu-MeAMD)<sub>2</sub> and H<sub>2</sub>O for NiO serving as an oxygen evolution reaction electrocatalyst. Similarly, Co<sub>3</sub>O<sub>4</sub> has been successfully deposited using CoCp<sub>2</sub> and O<sub>2</sub> plasma to fabricate anodes for batteries as reported by Donders *et al.*,<sup>86</sup> while Nandi *et al.*<sup>87</sup> employed Co<sub>2</sub>(CO)<sub>8</sub> and O<sub>3</sub> to synthesize Co<sub>3</sub>O<sub>4</sub> as a catalyst in NaBH<sub>4</sub> hydrolysis.

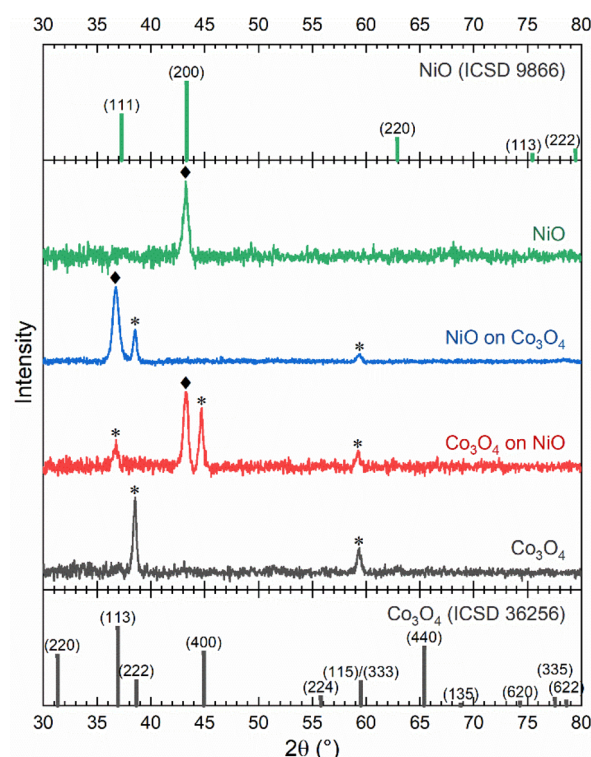
For templating purposes, a textured film is desired. Donders *et al.*<sup>88</sup> have demonstrated a preferential (111) orientation for Co<sub>3</sub>O<sub>4</sub> films based on CoCp<sub>2</sub> and O<sub>2</sub> plasma, whilst the combination of Ni(<sup>Me</sup>Cp)<sub>2</sub> and O<sub>2</sub> plasma has been shown<sup>1,27</sup> to yield a preferential (200) orientation. These processes will therefore be employed to investigate whether the texture of Co<sub>3</sub>O<sub>4</sub> and NiO can be tuned by synthesizing thin-film stacks. However, the crystallinity of ALD films and the texture, *i.e.*, the preferred crystallographic growth direction, are influenced by several factors, including the choice of reactant/co-reactant, deposition temperature, impurity level in the film, film thickness, and the choice of substrate.<sup>89</sup> Following the demonstration of the hetero-epitaxial relationship between NiO and Co<sub>3</sub>O<sub>4</sub>, we will investigate the influence of key process parameters – including the temperature, reactant, and co-reactant – on the growth of NiO on Co<sub>3</sub>O<sub>4</sub>. This will help identify the optimal ALD process conditions required for achieving hetero-epitaxial growth.

## Results and discussion

As an initial step, thin films of the individual oxides on *c*-Si have been characterised. These films were deposited on *c*-Si (100) with 2.5 nm native oxide at a substrate temperature

of 300 °C using previously developed plasma-enhanced ALD processes based on Ni(<sup>Me</sup>Cp)<sub>2</sub> as a precursor for NiO and CoCp<sub>2</sub> as a precursor for Co<sub>3</sub>O<sub>4</sub> and an O<sub>2</sub> plasma co-reactant for both processes.<sup>1,88,90</sup>

The crystal structures of the films were investigated using X-ray diffraction (XRD) (Fig. 1). Note that the ALD films are typically of polycrystalline nature. The 23 nm NiO film shows a prominent feature at  $43.24 \pm 0.04^\circ$ , which is identified as the (200) reflection of the cubic *Fm3m* (225) rock-salt structure.<sup>71</sup> No other diffraction peaks are observed, implying a strong  $\langle 100 \rangle$  texture. The derived lattice constant of  $4.18 \pm 0.01 \text{ \AA}$  is in close agreement with the theoretical value for NiO of  $4.17 \text{ \AA}$  (ICSD 9866). The XRD pattern of the 51 nm Co<sub>3</sub>O<sub>4</sub> film displays two distinct features at  $38.52 \pm 0.04^\circ$  and  $59.36 \pm 0.04^\circ$ , which are identified as the (222) and (333) peaks of the cubic *Fd3m* (227) spinel structure.<sup>72</sup> No other peaks are present, indicating a strong  $\langle 111 \rangle$  texture for spinel Co<sub>3</sub>O<sub>4</sub>. It is important to note that this texture led to the assignment of the (333) reflection instead of the (115) reflection for the  $59^\circ$  feature. The extracted lattice constant for Co<sub>3</sub>O<sub>4</sub>,  $8.09 \pm 0.01 \text{ \AA}$ , again closely matches the literature value of  $8.07 \text{ \AA}$  (ICSD 36256). Therefore, it can be concluded that both ALD films are polycrystalline under the investigated growth conditions, and have a strong texture.



**Fig. 1** Goniometric X-ray diffractograms of the *c*-Si/NiO, *c*-Si/Co<sub>3</sub>O<sub>4</sub>, *c*-Si/NiO/Co<sub>3</sub>O<sub>4</sub> and *c*-Si/Co<sub>3</sub>O<sub>4</sub>/NiO stacks. Peaks associated with the NiO rock-salt structure are indicated by ♦ and peaks associated with the spinel phase of Co<sub>3</sub>O<sub>4</sub> are indicated by \*. ICSD reference measurements of both NiO and Co<sub>3</sub>O<sub>4</sub> are provided.



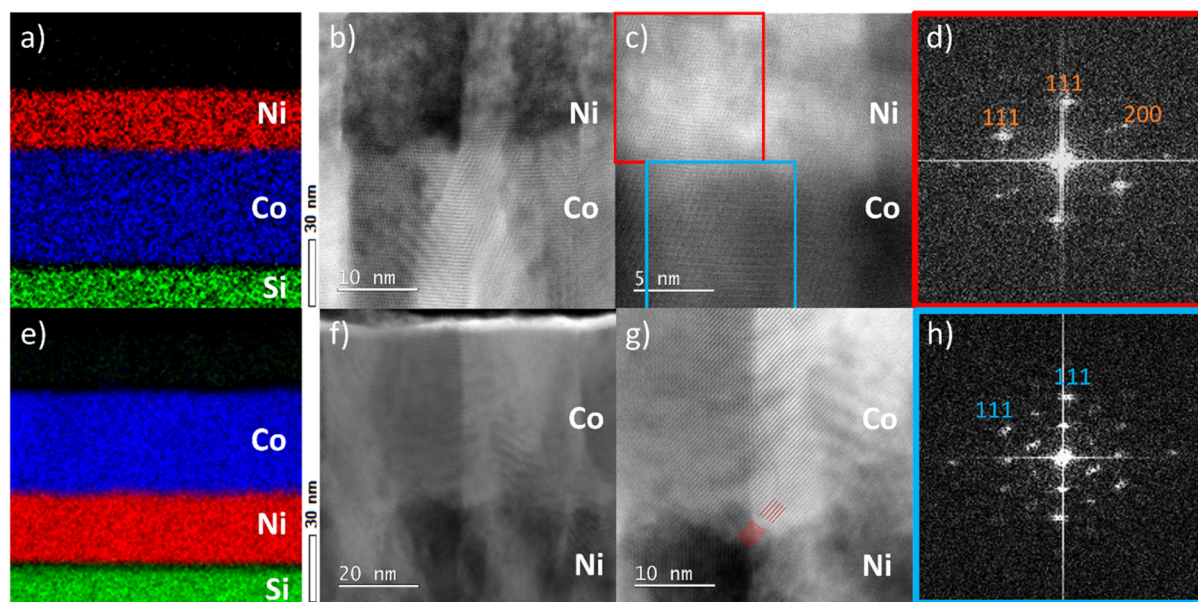
Next, hetero-stacks of the oxides were deposited. The *c*-Si/53 nm Co<sub>3</sub>O<sub>4</sub>/27 nm NiO stack displays three distinct features in the diffractogram. The peaks at  $38.54 \pm 0.04^\circ$  and  $59.36 \pm 0.04^\circ$  correspond to those identified in the  $\langle 111 \rangle$ -textured Co<sub>3</sub>O<sub>4</sub> template. The third peak at  $36.74 \pm 0.04^\circ$  is attributed to the (111) peak of the NiO rock-salt structure. The sole presence of the NiO (111) peak indicates that the NiO layer adapts its preferred growth direction to follow the  $\langle 111 \rangle$  texture of the underlying Co<sub>3</sub>O<sub>4</sub> template. Rocking curve XRD analysis of the angular distribution of the Co<sub>3</sub>O<sub>4</sub> (111) reflection yields an FWHM of the texture orientation of  $\sim 6^\circ$ . The texture of the NiO overlayer closely matches the distribution of the underlying Co<sub>3</sub>O<sub>4</sub> (see the ESI†). The NiO (111) peak position corresponds to a lattice constant of  $4.23 \pm 0.01 \text{ \AA}$ , which is significantly larger than the lattice constant observed for NiO directly deposited on *c*-Si. This out-of-plane elongation of the unit cell is suggested as being attributable to compensation for the compressive strain within the horizontal plane, which facilitates lattice matching between the NiO and Co<sub>3</sub>O<sub>4</sub> layers, as the lattice parameter of Co<sub>3</sub>O<sub>4</sub> is 1.94 times larger than that of NiO, and equivalent interatomic distances of Co<sub>3</sub>O<sub>4</sub> are 0.97 times those of NiO (Table S1†).

Conversely, four features are observed in the diffractogram of the *c*-Si/29 nm NiO/42 nm Co<sub>3</sub>O<sub>4</sub> stack. The feature at  $43.28 \pm 0.04^\circ$  is attributed to the (200) reflection of the NiO template. The dominant Co<sub>3</sub>O<sub>4</sub> feature at  $44.72 \pm 0.04^\circ$  corresponds to the (400) peak of the spinel phase, indicating that Co<sub>3</sub>O<sub>4</sub> adjusts its preferred growth direction to align with the underlying  $\langle 100 \rangle$ -textured NiO template. However, additional features at  $36.76 \pm 0.04^\circ$  and  $59.28 \pm 0.04^\circ$ , attributed to the (113) and (115) reflections of the spinel structure, show the presence of secondary texture components. Furthermore, the lattice con-

stant of  $8.10 \pm 0.01 \text{ \AA}$ , associated with the Co<sub>3</sub>O<sub>4</sub> features, shows that the Co<sub>3</sub>O<sub>4</sub> unit cell is not strained to match with that of NiO.

The crystal growth of the films was further investigated using cross-sectional scanning transmission electron microscopy (STEM) (Fig. 2). The STEM images have been acquired from selected grains that could be imaged along the  $\langle 110 \rangle$  zone axis. These images are assumed representative of the whole film. Cross-sectional energy-dispersive X-ray spectroscopy (EDX) elemental mappings of both stacks confirm the deposition of well-defined, compositionally separated homogeneous films. Bright-field STEM images reveal that both Co<sub>3</sub>O<sub>4</sub> and NiO grow in a columnar morphology, confirming the polycrystalline nature of the films. Co<sub>3</sub>O<sub>4</sub> furthermore displays a larger lateral larger grain size compared to NiO. Based on the bright-field TEM contrast, a larger disorder is observed in the NiO crystals as compared to Co<sub>3</sub>O<sub>4</sub> (see also Fig. S1 and S2†).

In both stacks, crystals are observed to continue their growth across the interface. The hetero-epitaxial relationship between the Co<sub>3</sub>O<sub>4</sub> template and the NiO film is demonstrated in Fig. 2c and the corresponding fast Fourier transforms (FFT) from selected areas are shown in Fig. 2d and h. Both the FFT patterns are characteristic of  $\langle 011 \rangle$  zone-axis patterns. Their identical orientation proves the identical crystallographic orientation of the domains at both sides of the interface. The denser pattern in Fig. 2h reflects the doubled unit cell dimensions of Co<sub>3</sub>O<sub>4</sub> compared to NiO. In the atomic resolution image of Fig. 2c, the hetero-epitaxy relationship can also be recognized; horizontal  $\{111\}$  planes of both crystal structures are aligned parallel to the interface, while an additional set of  $\{111\}$  planes at an inclination of  $71^\circ$  continue across the inter-



**Fig. 2** (a and e) EDX elemental mappings of the stacks. Complementary cross-sectional BF-STEM images of the (b and c) *c*-Si/Co<sub>3</sub>O<sub>4</sub>/NiO stack and the (f and g) *c*-Si/NiO/Co<sub>3</sub>O<sub>4</sub> stack. (d and h) The corresponding  $\langle 011 \rangle$  zone-axis patterns of (c). The  $\{111\}$  planes of both oxides are indicated in (g).





face. Similarly, detailed images of the *c*-Si/NiO/Co<sub>3</sub>O<sub>4</sub> stack also reveal the hetero-epitaxial relationship between NiO and Co<sub>3</sub>O<sub>4</sub> grains. This is highlighted in Fig. 2g, where the diagonally oriented {111} planes of NiO and Co<sub>3</sub>O<sub>4</sub> run parallel. Based on the combined XRD and TEM results, we conclude that NiO grows epitaxially on Co<sub>3</sub>O<sub>4</sub> likely in a compressively strained fashion to accommodate lattice mismatch between both layers. Similarly, Co<sub>3</sub>O<sub>4</sub> predominantly grows epitaxially on NiO. However, no strain is observed in the XRD pattern, suggesting that, in this case, the epitaxial relationship is likely facilitated by misfit dislocations at the interface rather than by lattice strain.

As is evident from the TEM results, rock-salt NiO grows on spinel Co<sub>3</sub>O<sub>4</sub> and *vice versa*. From the STEM images, it cannot be concluded whether this phase transition occurs exactly at the interface between the two layers, as the interface between NiO and Co<sub>3</sub>O<sub>4</sub> is not atomically flat in both stacks. Therefore, X-ray photoelectron spectroscopy (XPS) was employed to further investigate the NiO–Co<sub>3</sub>O<sub>4</sub> interface (Fig. 3). Initial measurements of the single oxides on *c*-Si were performed for reference. NiO exhibits the characteristic 854 eV feature with a shoulder at 856 eV in the Ni 2p spectrum, indicative of the octahedrally coordinated Ni<sup>2+</sup> states expected for its rock-salt structure.<sup>26,90–94</sup> Co<sub>3</sub>O<sub>4</sub> shows both the Co 2p<sub>3/2</sub> feature at 779.7 eV and the characteristic spin–orbit splitting of 15.0 eV, which represents the mixed tetrahedral Co<sup>2+</sup> and octahedral Co<sup>3+</sup> states characteristic of the spinel structure.<sup>26,90,93–96</sup>

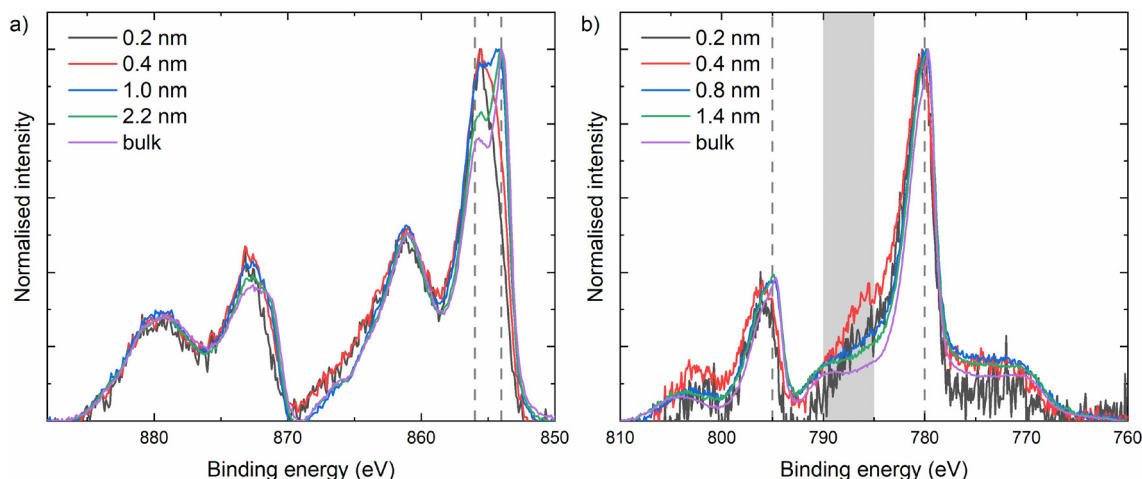
The interface between NiO and Co<sub>3</sub>O<sub>4</sub> has been investigated by depositing layers of NiO from 5, 10, 20, and 40 ALD cycles on a Co<sub>3</sub>O<sub>4</sub> film and *vice versa*. The thickness of the film layers deposited on the template increases with the number of ALD cycles and was calculated using the Thickogram model (see the ESI†). All Ni 2p spectra were corrected for the cobalt oxide Auger features, and all Co 2p spectra were corrected for the nickel oxide Auger features (see the ESI†). NiO growth on

Co<sub>3</sub>O<sub>4</sub> was monitored using the Ni 2p spectrum (Fig. 3a). Initially, the 856 eV shoulder is the dominant feature, which is indicative of the presence of Ni<sup>3+</sup>.<sup>26,90–94</sup> The presence of Ni<sup>3+</sup> is attributed to the NiO adapting to the underlying Co<sub>3</sub>O<sub>4</sub>, which also contains Co<sup>3+</sup>. This observation aligns well with previous work, where we showed that a supercycle ALD process of NiO and Co<sub>3</sub>O<sub>4</sub> can form both NiCoO<sub>2</sub> (rock-salt) and NiCo<sub>2</sub>O<sub>4</sub> (spinel) films depending on the cycle ratio.<sup>90</sup> However, after 20 ALD cycles (~1.0 nm), the 854 eV shoulder becomes dominant again, and after 40 ALD cycles (~2.2 nm), only a small increase in the 856 eV shoulder is observed compared to NiO on *c*-Si. It can therefore be concluded that the NiO film is affected by the underlying spinel only for the first few ALD cycles (~0.5 nm) and returns to its thermodynamically stable valence state of +2 within the first nanometres of deposition.

Similarly, an increased loss feature is observed between 785 and 790 eV in the Co 2p spectrum at 5 and 10 ALD cycles of Co<sub>3</sub>O<sub>4</sub> on NiO (0.2 and 0.4 nm, respectively). This increase in the loss feature is accompanied by an increased spin–orbit splitting of 15.9 and 15.7 eV, respectively, indicating the presence of octahedrally coordinated Co<sup>2+</sup> states. However, after 20 ALD cycles (~0.8 nm), the energy split is reduced to 15.2 eV and the loss feature has decreased in intensity, indicating rapid relaxation of Co<sub>3</sub>O<sub>4</sub> in its spinel structure consisting of Co<sup>2+</sup> and Co<sup>3+</sup>.<sup>26,90,93–96</sup>

Based on these observations, we can conclude that the crystallographic orientation of NiO can be tuned using a Co<sub>3</sub>O<sub>4</sub> template, and *vice versa*, due to a hetero-epitaxial growth relationship between both materials. The two materials adopt the crystal orientation of the template material but crystallize (almost) directly in their own stable crystal structure, with the corresponding metal atom coordination.

As mentioned in the introduction, an ALD process is characterized by a range of parameters that can be tuned to



**Fig. 3** XPS measurements of films following 5, 10, 20 and 40 ALD cycles of (a) nickel oxide on *c*-Si/Co<sub>3</sub>O<sub>4</sub> traced using the Ni 2p spectrum and (b) cobalt oxide deposited on *c*-Si/NiO traced using the Co 2p spectrum. The features at 854 eV and 856 eV are indicated in the Ni 2p spectrum. In the Co 2p spectrum, the 785–790 eV region is highlighted, whilst the dashed lines indicate the 15 eV spin–orbit split.

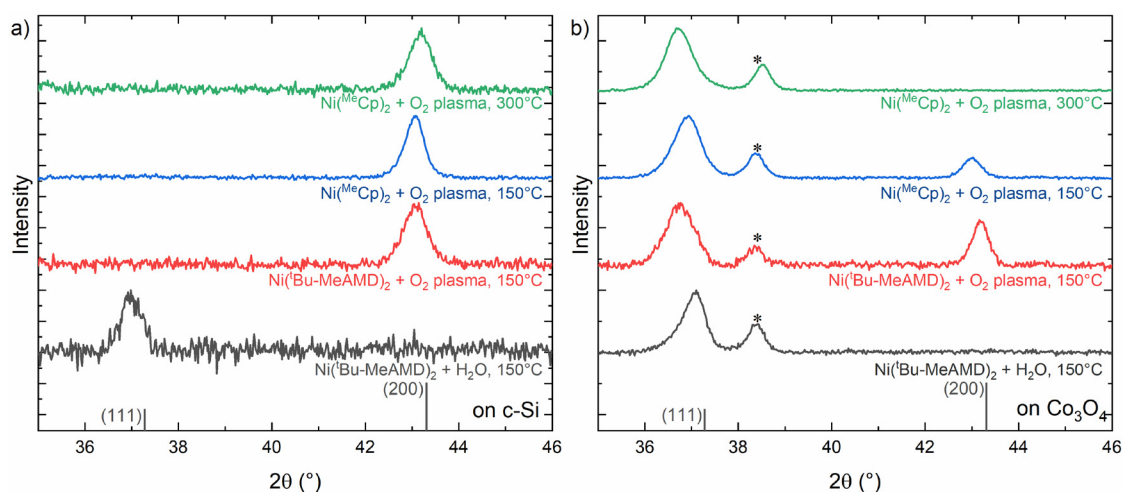


influence the growth behaviour of the oxides. The most common process parameters, *i.e.*, choice of precursor, co-reactant, and temperature, were varied in this study to evaluate their impact on the epitaxial growth of NiO on Co<sub>3</sub>O<sub>4</sub>. The influence of ALD parameters on NiO deposited on *c*-Si/native oxide was investigated initially (Fig. 4a and S7†). First, the substrate table temperature was decreased from 300 °C to 150 °C. This caused a slight shift in the (200) XRD peak to lower  $2\theta$ , such that the lattice constant slightly increased to  $4.20 \pm 0.01$  Å, suggesting the presence of strain. Next, the precursor was changed to Ni(<sup>t</sup>Bu-MeAMD)<sub>2</sub>, while maintaining the 150 °C substrate table temperature. No significant differences were observed between both precursors, as the film also grew in the (100) orientation. The strain observed in both films might be attributed to various factors such as differences in stoichiometry, thermal expansion coefficients, and texture-dependent minimization.<sup>97</sup> At higher substrate temperatures, the strain might be reduced by higher surface mobilities of the adatoms during growth.<sup>89</sup> Finally, the O<sub>2</sub> plasma was replaced with H<sub>2</sub>O as a co-reactant in the Ni(<sup>t</sup>Bu-MeAMD)<sub>2</sub>-based process at a substrate table temperature of 150 °C. This shifted the texture of the film to (111) with a lattice parameter of  $4.21 \pm 0.01$  Å. It is speculated that the change in the preferred growth direction originates from the presence of hydroxyl groups that stabilize the (111) surface.<sup>98</sup> This is consistent with XPS measurements of the O 1s spectrum (Fig. S8†), which show an increase in the hydroxide shoulder only for the H<sub>2</sub>O-based process.

A comparison between the above-mentioned results and those related to NiO deposited on Co<sub>3</sub>O<sub>4</sub> (Fig. 4b and S9†) reveals that the tunability of the NiO texture is influenced by the ALD parameters. At a lower deposition temperature (Ni(<sup>Me</sup>Cp)<sub>2</sub> precursor, 150 °C), both the (111) and (200) peaks are observed, indicating an incomplete epitaxial relationship, although the (111) peak remains dominant. Lattice parameters

of  $4.21 \pm 0.01$  Å and  $4.20 \pm 0.01$  Å are deduced from the (111) and (200) peaks, respectively, suggesting that the film remains strained, albeit to a lesser extent than that at 300 °C. Similarly, for the plasma-enhanced ALD process based on Ni(<sup>t</sup>Bu-MeAMD)<sub>2</sub>, both peaks are present, but the (200) peak is more dominant as compared to that of the Ni(<sup>Me</sup>Cp)<sub>2</sub> film. Interestingly, a distinct difference in the lattice parameters is observed, with  $4.23 \pm 0.01$  Å for the (111) reflection and  $4.20 \pm 0.01$  Å for the (200) reflection. Here, it is important to note that in the goniometric XRD measurements, horizontal lattice planes are probed and the (111) peak originates from a different subset of crystals in the film than the (200) peak. This suggests that the (111)-oriented grains grow epitaxially on the Co<sub>3</sub>O<sub>4</sub> grains in a strained manner to compensate for the difference in lattice parameters between both structures, while the (200)-oriented grains grow independently of the substrate. Additional measurements of a thinner NiO film reveal that the (200) peak is initially not observed (Fig. S10†). It is therefore hypothesized that the epitaxial relationship exists in the initial phase of growth, but the ALD process does not supply enough energy to fully retain the strained epitaxial layer, causing the (100)-oriented growth preferred on *c*-Si to develop also in thicker NiO layers.

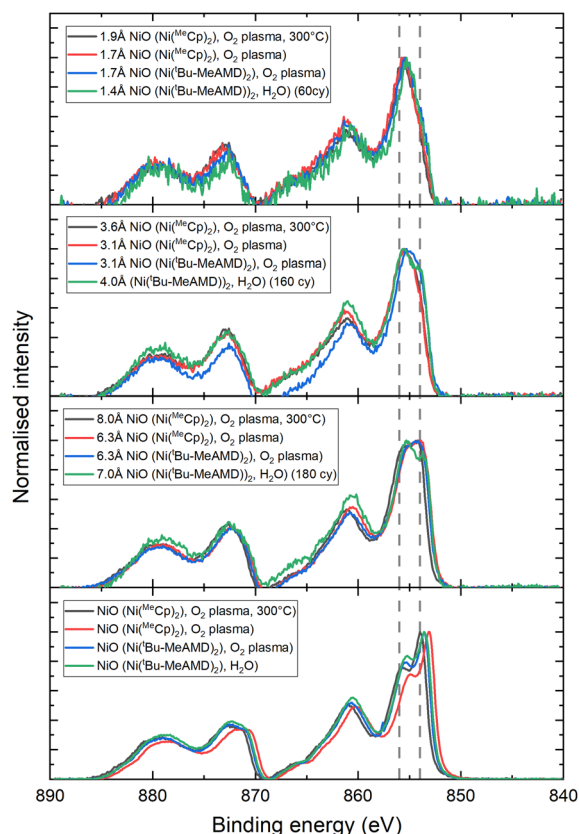
The NiO film based on Ni(<sup>t</sup>Bu-MeAMD)<sub>2</sub> and H<sub>2</sub>O remains fully (111) oriented. However, a shift to higher  $2\theta$  is observed compared to the epitaxial (111) orientations of the plasma-based processes. The lattice parameter of  $4.19 \pm 0.01$  Å shows reduced strain compared to deposition on *c*-Si, suggesting that there is no hetero-epitaxial relationship with the underlying Co<sub>3</sub>O<sub>4</sub> template. Additional cross-sectional TEM measurements (Fig. S11†) confirm that NiO grains do not evolve as continuation of the Co<sub>3</sub>O<sub>4</sub> grains and no epitaxial relationship exists at the interface. This might be related to the absence of the energetic ions generated by the plasma, which potentially stimulate ALD surface reactions. The increased reactivity pro-



**Fig. 4** Goniometric X-ray diffraction patterns of NiO deposited using several ALD processes on (a) *c*-Si and (b) *c*-Si/Co<sub>3</sub>O<sub>4</sub>. The Co<sub>3</sub>O<sub>4</sub> (111) peak is indicated by \* and the ICSD database reference of NiO is provided (ICSD 9866).



vided by plasma species reduces the thermal energy required at the substrate to drive ALD surface chemistries and epitaxy.<sup>99,100</sup>



**Fig. 5** XPS spectra of various thicknesses of ALD NiO films on *c*-Si/ $\text{Co}_3\text{O}_4$ . The features at 854 eV and 856 eV are indicated as a guide to the eye.

**Table 1** Thicknesses of the NiO films as presented in Fig. 4, S4, S6 and S7† as determined by spectroscopic ellipsometry

	On $\text{Co}_3\text{O}_4$	On <i>c</i> -Si
$\text{Ni}(\text{MeCp})_2 + \text{O}_2$ plasma, 300 °C	27 nm	23 nm
$\text{Ni}(\text{MeCp})_2 + \text{O}_2$ plasma, 150 °C	30 nm	40 nm
$\text{Ni}(\text{Bu-MeAMD})_2 + \text{O}_2$ plasma, 150 °C	31 nm	18 nm
$\text{Ni}(\text{Bu-MeAMD})_2 + \text{H}_2\text{O}$ , 150 °C	19 nm	18 nm
$\text{Ni}(\text{Bu-MeAMD})_2 + \text{O}_2$ plasma, 150 °C (thin, see the ESI†)	11 nm	

**Table 2** Elemental concentrations of the films deposited on NiO and  $\text{Co}_3\text{O}_4$  films after 40 ALD cycles as determined by RBS

Template	Template thickness (SE) (nm)	40-cycle film	Film thickness (XPS) (nm)	O (TFU)	Co (TFU)	Ni (TFU)	Density of the template ( $\text{g cm}^{-3}$ )
$\text{Co}_3\text{O}_4$	35	NiO	1.4	$182 \pm 10$	$129 \pm 3$	$8.0 \pm 0.3$	$5.0 \pm 0.3$
NiO	21	$\text{Co}_3\text{O}_4$	2.2	$128 \pm 10$	$8.0 \pm 0.3$	$106 \pm 2.4$	$6.5 \pm 0.6$

1 TFU =  $10^{15}$  atoms per  $\text{cm}^2$ .

Additional XPS studies on the  $\text{Co}_3\text{O}_4$ -NiO interface were conducted for the several ALD NiO processes to investigate whether differences in epitaxial growth are related to the chemical environment. A comparison of the Ni 2p spectra of the NiO films (on *c*-Si) shows that all films exhibit the expected  $\text{Ni}^{2+}$  oxidation state. However, both films deposited using the  $\text{Ni}(\text{Bu-MeAMD})_2$  precursor show small amounts of nitrogen ( $\sim 1.5$  at%  $\text{N}/(\text{N} + \text{O} + \text{Ni})$ ), irrespective of the co-reactant (Fig. S12†). This nitrogen in the  $\text{H}_2\text{O}$  process is assigned to the nickel-bonded N in the surface amidinate moiety in line with the study of Zhao *et al.*,<sup>101</sup> whilst the  $\text{O}_2$  plasma results in nitrate-like bonds.<sup>101,102</sup> The presence of impurities is a known factor preventing crystallization and could therefore partially explain why less epitaxial growth is observed for the plasma process with  $\text{Ni}(\text{Bu-MeAMD})_2$  as compared to  $\text{Ni}(\text{MeCp})_2$ , which has negligible impurity levels.<sup>89,90,103</sup>

Investigation of the nucleation of the NiO layers on  $\text{Co}_3\text{O}_4$  reveals that all plasma-based processes show similar growth behaviour (Fig. 5). Initially, NiO nucleates with  $\text{Ni}^{3+}$  oxidation states, but transitions to the expected  $\text{Ni}^{2+}$ -based film in the early stage of growth within the first 20 cycles. The  $\text{H}_2\text{O}$  process, on the other hand, displays a different nucleation behaviour. Although the sub-monolayer growth is similar, a more defined peak splitting is observed between the main peak and shoulder for thicker films. This could indicate the formation of separate phases, possibly a nickel hydroxide phase, and therefore a more defective growth. Besides the different chemical environments, a major nucleation delay is observed for  $\text{H}_2\text{O}$ -based NiO on  $\text{Co}_3\text{O}_4$ . While a nucleation delay of  $\sim 40$  cycles is common on *c*-Si, a delay of  $\sim 160$  cycles is observed on  $\text{Co}_3\text{O}_4$  (Fig. S13†). This nucleation delay suggests a defect-driven initial growth as opposed to the epitaxial growth for all other NiO processes.

## Conclusions

In this study, we have combined NiO and  $\text{Co}_3\text{O}_4$  in heterostructures using ALD to control their crystallographic texture. ALD films based on cyclopentadienyl precursors and an oxygen plasma exhibit strongly textured  $\langle 100 \rangle$  rock-salt NiO and  $\langle 111 \rangle$  spinel  $\text{Co}_3\text{O}_4$  in a columnar morphology. In the heterostructure,  $\text{Co}_3\text{O}_4$  adapts its growth direction to follow the  $\langle 100 \rangle$  texture of NiO films. Similarly, NiO adapts its crystal orientation to mimic the  $\langle 111 \rangle$ -textured  $\text{Co}_3\text{O}_4$ . While  $\text{Co}_3\text{O}_4$  retains its lattice constant of 8.10 Å when templated on NiO, NiO adapts its out-of-plane lattice constant from 4.18 Å to



4.23 Å to facilitate compressively strained epitaxy with the Co<sub>3</sub>O<sub>4</sub> template. XPS reveals that both materials crystallize in their own stable crystal structure with corresponding metal atom coordination within the first 20 ALD cycles.

Variations in the ALD process parameters of NiO growth reveal that the NiO crystal orientation on *c*-Si is independent of the precursor or temperature but depends on the co-reactant. Switching from O<sub>2</sub> plasma as co-reactant to H<sub>2</sub>O shifts the texture to ⟨111⟩. The epitaxial relationship in the stack, however, is more sensitive to ALD parameters. Lowering the substrate table temperatures from 300 °C to 150 °C leads to a partial loss of the ⟨111⟩ texture, such that ⟨100⟩-oriented grains develop when the film is thick enough. This effect is more pronounced for the Ni(<sup>t</sup>Bu-MeAMD)<sub>2</sub>-based films as compared to the Ni(<sup>Me</sup>Cp)<sub>2</sub>-based films, possibly due to nitrogen impurities in the film. No epitaxial growth is observed for the H<sub>2</sub>O-based process.

In conclusion, we have demonstrated that ALD hetero-stacks offer an effective approach for controlling crystalline texture. Placing our results in perspective, we infer that this method shows strong potential for achieving crystallographic control of thin films on templates relevant for practical applications. This work therefore reveals an additional merit of ALD beyond established benefits such as thickness control, precise composition tuning, and excellent uniformity and conformality. It expands the ALD toolbox to include crystallographic control, opening new opportunities for the design and engineering of thin films.

## Experimental methods

All NiO and Co<sub>3</sub>O<sub>4</sub> films were deposited using a home-built plasma-enhanced ALD reactor described elsewhere.<sup>104</sup> The system features an inductively coupled plasma source powered at 13.56 MHz. The pumping system consists of a turbomolecular pump paired with a rotary vane pump, capable of reaching a base pressure below  $1 \times 10^{-6}$  mbar. The reactors walls were heated to 100 °C, whilst the 4-inch wafer-based substrate holder temperature was varied between 300 °C and 150 °C, as indicated in the manuscript. Cobaltocene (CoCp<sub>2</sub>, 98% purity, ACROS Organics) was placed in a stainless steel cylindrical bubbler and heated to 80 °C and introduced into the chamber using an argon carrier gas through a line at 100 °C. Similarly, 1,1'-dimethylnickelocene (Ni(<sup>Me</sup>Cp)<sub>2</sub>, 97% purity, Sigma-Aldrich) was heated to 55 °C and delivered to the chamber using argon gas through a line at 75 °C. Both precursors reacted with a 100 W O<sub>2</sub> plasma co-reactant. Both precursors were introduced using a 4 s/4 s/5 s precursor dosing/Ar purge/pump sequence with *x* s/1 s/3 s O<sub>2</sub> plasma exposure/O<sub>2</sub> purge/pump sequence, where *x* = 3 s for NiO deposition and *x* = 5 s for Co<sub>3</sub>O<sub>4</sub> deposition.<sup>1,26,88,90</sup> All films were deposited on *c*-Si (100) with 15 minutes of O<sub>2</sub> plasma treatment before deposition. Hetero-stacks were deposited without breaking the vacuum to ensure a clean interface.

Additional NiO deposition processes were based on the bis(*N,N'*-di-*t*-butylacetamidinato)nickel precursor (Ni(<sup>t</sup>Bu-MeAMD)<sub>2</sub>, 99.999% purity, STREM) contained in a stainless steel cylindrical container heated to 90 °C and delivered using Ar through a line heated to 120 °C. In both processes, the precursor is delivered by 2× (3 s precursor dose + 2 s Ar line purge) followed by a 20 s pump. Afterwards, either an O<sub>2</sub> plasma/O<sub>2</sub> purge/purge of 5 s/1 s/10 s or a H<sub>2</sub>O/pump of 1 s/60 s was used. The thicknesses of the various NiO films are presented in Table 1.

The crystallography of the films was investigated using a Bruker Discover D8 (Cu K<sub>α</sub> radiation,  $\lambda$ =1.54060 Å) in goniometric XRD mode at an axis offset of 3° to remove *c*-Si substrate peaks (Fig. S14†). Measurements in the 2θ range from 30.00–80.00° were performed with a step size of 0.04° at an integration time of 1 s, whilst measurements in the 2θ range from 34.00–46.00° were performed with a step size of 0.02° at an integration time of 4 s.

X-ray photoelectron spectroscopy measurements were performed using a Thermo Scientific KA 1066 spectrometer with monochromatic Al K<sub>α</sub> X-rays. The binding axis was calibrated by the 248.8 eV adventitious C 1s peak. Thickness values were determined from the XPS data using a Thickett model based on the Ni 3p (66.6 eV) and Co 3p (59.1 eV) features. The attenuation length was determined using the Tanuma–Powell–Penn-2M method, with a bandgap of 2 eV<sup>105</sup> and a density of 5.0 g cm<sup>−3</sup> for Co<sub>3</sub>O<sub>4</sub>. For NiO, a bandgap of 3.8 eV<sup>1</sup> was used in combination with a density of 6.5 g cm<sup>−3</sup> for plasma NiO and a density of 5.1 g cm<sup>−3</sup> for thermal NiO<sup>2</sup>. Densities of NiO (plasma, Ni(<sup>Me</sup>Cp)<sub>2</sub>, 300 °C) and Co<sub>3</sub>O<sub>4</sub> were determined by Rutherford backscattering spectrometry (RBS) (Table 2). RBS was carried out by Detect99 using a 200 keV He<sup>+</sup> beam at perpendicular incidence and two detectors at scattering angles of 170° and 107°. Channel mode was used to reduce the background under the oxygen peaks. PIXE was used to distinguish Co from Ni. For PIXE, a 2.7 MeV H<sup>+</sup> beam was applied at perpendicular incidence. The X-ray detector was positioned at an angle of 45° between the beam and the specimen normal, and 30 μm Kapton was used as an absorber. The PIXE spectra were analysed with the Gupix<sup>106</sup> PIXE simulation package, and the resulting Co/Ni ratio was entered as a Co<sub>*x*</sub>Ni<sub>*y*</sub> “molecule” in the WinDF<sup>107</sup> RBS simulation package to determine the absolute amounts. Electron microscopy images were acquired using a probe-corrected JEOL ARM 200F transmission electron microscope operated at 200 kV equipped with a 100 mm<sup>2</sup> Centurio SDD EDX detector. Cross-sectional TEM samples were made using a focused ion beam (FIB) following a standard lift-out sample preparation protocol.

## Data availability

The data that support the findings of this study are openly available in Zenodo at <https://doi.org/10.5281/zenodo.14160831>.





## Conflicts of interest

There are no conflicts to declare.

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