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# Interface Engineering of the Photoelectrochemical Performance of Ni-Oxide-Coated n-Si Photoanodes by Atomic-Layer Deposition of Ultrathin Films of Cobalt Oxide

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**Abstract:**

Introduction of an ultrathin (2 nm) film of cobalt oxide ($CoO_x$) onto n-Si photoanodes prior to sputter-deposition of a thick multifunctional $NiO_x$ coating yields stable photoelectrodes with photocurrent-onset potentials of ~ -240 mV relative to the equilibrium potential for $O_2$(g) evolution and current densities of ~ 28 mA $cm^{-2}$ at the equilibrium potential for water oxidation when in contact with 1.0 M KOH(aq) under 1 sun of simulated solar illumination. The photoelectrochemical performance of these electrodes was very close to the Shockley diode limit for moderately doped n-Si(100) photoelectrodes, and was comparable to that of typical protected Si photoanodes that contained buried Si p-n junctions.

**Broader context:**

Thick (> 50 nm) multifunctional $NiO_x$ coatings enable the use of small-band-gap non-oxide semiconductors as photoanodes in fully integrated, intrinsically safe, and efficient photoelectrosynthetic water-splitting systems. The equivalent open-circuit voltage generated by such protected n-type semiconductor heterojunction structures is however significantly lower than that obtained from homogeneous $np^+$ buried junctions. We demonstrate herein that deposition of a thin cobalt oxide film onto n-Si substrates prior to deposition of a thick multifunctional $NiO_x$ coating significantly improves the performance of such protected n-type Si photoanodes. The approach provides a route

to formation of stabilized, high-performance Si photoanodes without requiring the formation of buried p-n homojunctions, potentially simplifying the photoelectrode processing and thus reducing the cost of monolithically integrated solar-driven water-splitting devices.

**Graphical Abstract:**

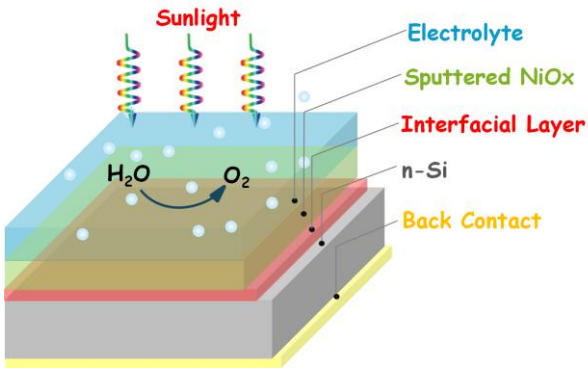


Table of contents: n-Si/$SiO_x$/$CoO_x$/$NiO_x$ photoanodes show high water oxidation current, and 1700 h stability in 1.0 M KOH biased at 1.63 V versus RHE under 1 Sun illumination of 100 mW $cm^{-2}$.

**Main text:**

Although $SrTiO_3$, $KTaO_3$, and TaON have been used in stable wired or "wireless" configurations to effect direct solar-driven water splitting,[1] all known smaller-band-gap, non-oxide semiconductors require protection from corrosion for use in stable, intrinsically safe, efficient photoelectrosynthetic or photovoltaic-(PV) biased electrosynthetic water-splitting cells.[2, 3] When the protective layer fully prevents

contact between the electrolyte and the semiconductor, effective charge separation in the light absorber requires a mechanism for establishing a significant electric field at the semiconductor surface. Semiconductor/metal Schottky barriers;[4, 5] p-n homojunctions on planar electrodes,[6-10] spherical electrodes,[11] and radial emitters on microwires;[12] metal-insulator-semiconductor contacts;[13, 14] in situ formation of emitter layers by carrier inversion;[15-18] heterojunctions;[19-21] and mixed barrier-height semiconductor/metal/oxide/liquid systems[22] have all been investigated in either wired or "wireless" photoelectrosynthetic or PV-biased electrosynthetic systems. Generally tandem structures or triple junctions are required to provide the open-circuit voltage ($V_{oc}$) necessary to effect unassisted water splitting in either a wired or monolithically integrated ("wireless") configuration,[23-28] with noble metals or earth-abundant electrocatalysts[28] used in the full water-splitting system. The electrode surfaces require both protection or stabilization against corrosion and the deposition of an effective catalyst for use in either the photoelectrochemical anodic (water oxidation) or cathodic (fuel formation) half reactions.

Ni-oxide films formed by reactive sputtering have recently been shown to form protecting layers on a variety of semiconductor surfaces, including Si, InP, amorphous hydrogenated Si (a-Si:H), and CdTe.[29-31] The $NiO_x$ is optically transparent in the visible region and has an index of refraction that makes the $NiO_x$ a near-optimal anti-reflective coating on a variety of semiconductor surfaces. Furthermore, $NiO_x$ is chemically stable at high pH, and upon activation forms a surface layer that is catalytic for the

oxygen-evolution reaction (OER), with overpotentials of ~330 mV at 10 mA $cm^{-2}$ in 1.0 M KOH(aq).[29] $NiO_x$ coatings on semiconductors that form passive films under photoanodic conditions have produced high photocurrent densities for solar-driven OER from water for months of continuous operation under simulated 1 Sun conditions.[29-31]

However, due to nonoptimal energetics at the interface between the $NiO_x$ and the semiconductor, formation of a direct heterojunction contact between the n-type absorber and the p-type $NiO_x$ layer yields relatively low $V_{oc}$ values. [29-31] Significantly higher $V_{oc}$ values for such stabilized systems have been obtained from electrodes formed by deposition of a $NiO_x$ coating onto a buried p-n homojunction.[29, 30] For example, freshly etched n-Si and $np^+$-Si photoanodes protected by a multifunctional layer of $NiO_x$ yielded equivalent open-circuit voltages (see Supplementary Information) of 180 mV and 510 mV, respectively.[29] The formation of heterojunctions between n-Si coated with a layer of $SiO_x$ (either native or introduced by processing steps) and thin (< 20 nm) films of Ni,[22] $MnO_x$,[32] and $TiO_2$[33] offers some protection against corrosion to n-Si photoanodes, and in some cases yields photoanodes exhibiting $V_{oc} \geq 500$ mV. The ideal regenerative solar-to-$O_2$ conversion efficiency[34] of these heterogeneous systems is relatively low compared to values exhibited by $NiO_x$ protected $np^+$-Si photoanodes.[29, 35] The solar-to-fuel conversion efficiency is thus limited when such protected photoanodes are used in a tandem photochemical diode design.[3, 36]

For technologically well-developed semiconductors such as Si and the III-V materials, p-n homojunctions can be formed to provide $V_{oc}$ values that can approach the Shockley

diode bulk recombination/diffusion limit.[2, 3] Many semiconductors of interest for use in photoelectrochemical cells, however, cannot be doped to form high-quality homojunctions. Moreover, the doping/diffusion process generally requires high temperatures, and adds complexity to the formation of a functional photoelectrode, relative to electrodeposition or spray pyrolysis of the active semiconductor layer onto a suitable substrate. For small grain-size polycrystalline films, dopants often migrate preferentially along grain boundaries, especially during the drive-in step, producing majority-carrier shunts that degrade the performance of the resulting photoelectrode.[37] Hence methods which allow large $V_{oc}$ values and high efficiencies to be obtained from protected semiconductor photoelectrodes in contact with aqueous electrolytes, but which do not require the formation of diffused homojunctions, are desirable.

We demonstrate herein that introduction of a thin, compositionally controlled, interfacial cobalt oxide layer between the n-Si absorber and the protective, multifunctional $NiO_x$ film can yield $V_{oc}$ values close to the Shockley diode limit for moderately doped n-Si(100) photoelectrodes. The performance and stability of such materials used as PV-biased electrosynthetic systems for water oxidation are comparable to that observed from diffused Si p-n homojunctions protected by the $NiO_x$ overlayer. Such "interfacial engineering" of the junction energetics demonstrates that protection schemes can be implemented to yield high-performance photoelectrodes without the complexity of the requirement to form a diffused homojunction, while concurrently obtaining efficient separation of photogenerated charges in the semiconducting

photoelectrode.

To form the desired interfacial layers, n-Si (100) (0.1–1 ohm-cm resistivity, 525 μm thick) was first etched in an RCA SC-2 etchant solution for 10 min at 75 °C to produce a thin $SiO_x$ layer on the Si surface (n-Si/$SiO_{x,RCA}$). Thin films of $CoO_x$ were then deposited by atomic-layer deposition (ALD) onto the Si/$SiO_{x,RCA}$. After ALD growth of the $CoO_x$ layer, $NiO_x$ was deposited by reactive radio-frequency sputtering onto the $CoO_x$, with the Si substrates maintained at 300 °C (n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$). Sixty ALD cycles of $CoO_x$ deposition were found to optimize the photocurrent-onset potentials relative to the formal potential, $E^{o'}(Fe(CN)_6^{3-/4-})$ for the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ devices (Figure S1) and were thus used in the fabrication of all of the devices described herein.

Figure 1A shows a high-resolution transmission-electron microscopy (TEM) image of the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ interface. An amorphous ~ 2 nm thick layer of $SiO_x$ was observed on the surface of the crystalline Si, with a 2–3 nm thick layer of $CoO_x$ between the $SiO_x$ and $NiO_x$ layers. The low difference in contrast between the $CoO_x$ and $NiO_x$ layers is due to the similar densities of the metal oxide films. Figure 1B shows the results of a scanning transmission-electron microscopy (STEM) energy-dispersive spectroscopy (EDS) line scan across the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ interface. A Co X-ray signal was evident at the interface between the Si and Ni signals, and confirmed the presence of the thin $CoO_x$ layer, which was also detected using X-ray photoelectron spectroscopy (XPS) (Figure S2A, B). Peak-fitting of the XP spectra in the Co $2p_{3/2}$ region

showed the co-presence of Co(II) and Co(III), possibly in the forms of CoO, $Co_2O_3$, $Co_3O_4$ and $Co(OH)_2$/CoOOH.[38, 39] Grazing incidence X-ray diffractometry (GIXRD) showed that the film was polycrystalline with peak positions consistent with $Co_3O_4$, and indicated that annealing the film under the deposition conditions did not result in any significant changes to the structure, crystallinity, or preferred orientation of the film (Figure S2C). The root-mean-squared (rms) surface roughness of the n-Si/$SiO_{x,RCA}$ and n-Si/$SiO_{x,RCA}$/$CoO_x$ surfaces was 0.403 nm and 0.453 nm, respectively (Figure S3). A low-magnification high-angle annular dark-field (HAADF) STEM image of a cross-section of the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ film (Figure 1C) showed that the $NiO_x$ film consisted of short columns with an average diameter of ~20 nm and an average height of ~102 nm, with a mean density of ~2500 columns $\mu m^{-2}$.

Figure 2A shows the current-density versus potential (*J*-*E*) behavior of n-Si/$SiO_{x,RCA}$/$NiO_x$ photoanodes with and without an interfacial layer of $CoO_x$, in contact with 1.0 M KOH(aq), illuminated by 1 sun of simulated solar illumination, and without correction for resistance losses in the system. The photocurrent-onset potentials were -239 ± 3 mV and -74 ± 12 mV relative to the formal potential for water oxidation ($E^{o'}(O_2/H_2O)$ = 1.23 V versus a reversible hydrogen electrode, RHE, at pH = 14) for the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ and n-Si/$SiO_{x,RCA}$/$NiO_x$ photoanodes, respectively, with three electrodes of each type measured. Thus, the presence of the interfacial $CoO_x$ layer between the n-Si/$SiO_{x,RCA}$ and the $NiO_x$ resulted in a -165 mV shift in the

photocurrent-onset potential of the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanode relative to the n-Si/$SiO_{x,RCA}$/$NiO_x$ electrode that did not contain the $CoO_x$ layer. The *J-E* behavior for the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ electrode exhibited a larger slope (~ 140.0 mA $cm^{-2}$ $V^{-1}$ measured between 1.00 V and 1.15 V versus RHE) than the *J-E* behavior of the n-Si/$SiO_{x,RCA}$/$NiO_x$ electrode (slope ~100 mA $cm^{-2}$ $V^{-1}$ measured between 1.25 V and 1.45 V vs RHE). The increased slope is attributable to a reduced series resistance and/or reduced surface recombination velocity, which could indicate that the $CoO_x$ layer prevents further oxidation of the Si and/or damage to the existing $SiO_{x,RCA}$ junction layer during sputter-deposition of the $NiO_x$ film. The photocurrent density for the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanode structure was 27.7 ± 0.4 mA $cm^{-2}$ at $E^{o'}(O_2/H_2O)$, and the solar-to-$O_2$(g) ideal regenerative-cell conversion efficiency[34] ($\eta_{IRC}$, see Supplementary Information) was 2.1 ± 0.2 %, while for the n-Si/$SiO_{x,RCA}$/$NiO_x$ photoanode structure the photocurrent density was 6.3 ± 1.5 mA $cm^{-2}$ at $E^{o'}(O_2/H_2O)$, and the $\eta_{IRC}$ for solar-to-$O_2$(g) was 0.11 ± 0.04 %, each with three electrodes of each type tested. A load-line analysis based on an equivalent-circuit model consisting of a photodiode connected in series with a dark electrolysis cell indicated that obtaining a shift in the *J-E* behavior equivalent to that observed for the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanode relative to the $p^+$-Si/$NiO_x$ anode would require a 12.3 ± 0.3 % efficient photodiode with a $V_{oc}$ of 565 ± 3 mV and a short-circuit photocurrent density ($J_{sc}$) of 32.5 ± 0.3 mA $cm^{-2}$.[34] The performance of the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanode was modestly better than that reported for a homogeneous buried-junction $p^+$n-Si electrode

that had been freshly etched and directly sputtered with $NiO_x$ (photocurrent-onset potential of -180 ± 20 mV relative to $E^{o'}(O_2/H_2O)$ and a photocurrent density of 29 ± 1.8 mA $cm^{-2}$ at $E^{o'}(O_2/H_2O)$), and was significantly improved relative to the performance of an HF-etched n-Si electrode that had been directly sputtered with $NiO_x$ (photocurrent-onset potential of +150 ± 20 mV relative to $E^{o'}(O_2/H_2O)$ and negligible photocurrent density at $E^{o'}(O_2/H_2O)$).[29]

With these same n-Si substrates at a comparable light-limited current density, a high-quality semiconductor/liquid junction formed between a freshly etched n-Si photoanode[17] and a non-aqueous solution containing a reversible, one-electron redox couple (e.g., $CH_3OH$-0.20 M 1,1'-dimethylferrocene ($Me_2Fc^0$)-0.010 M $Me_2Fc^+$) which forms an in-situ emitter by virtue of carrier inversion[40] yielded a photocurrent-onset potential of -640 mV relative to $E^{o'}(Me_2Fc^{+/0})$ (Figure S4). We therefore expect that improvements upon the 0.56 V $V_{oc}$ yielded by the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ structure could be obtained through decreasing the defect densities at the Si surface and by yet further increases in the band bending in the Si.

Figure 2B shows the wavelength-dependent external quantum yield ($\Phi_{ext}$) for electrons collected from n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ and $np^+$-Si/$NiO_x$[29] photoanodes, respectively, in contact with 1.0 M KOH(aq) while under potentiostatic control at 1.93 V versus RHE. Figure 2B also displays the observed absorptance spectrum of an n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanode in air for light at normal incidence. The shape of

the $\Phi_{ext}$ versus wavelength behavior for the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ electrode was consistent with the absorptance spectrum of the $NiO_x$-coated Si substrate measured in air.[29] The n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanodes exhibited higher $\Phi_{ext}$ values at wavelengths < 500 nm relative to those of $np^+$-Si/$NiO_x$ photoanodes, indicating that the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ heterojunction had lower parasitic absorption losses in the near-surface layer. In the homojunction device, short-wavelength light is significantly absorbed by the thin, non-photoactive, highly doped emitter layer,[29] while in commercial high-efficiency Si photovoltaic devices, short-wavelength light is absorbed primarily by the heterogeneous passivation layers.[41] For the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanodes, $\Phi_{ext}$ was > 0.9 in the wavelength range of 550–780 nm, which compared favorably to $\Phi_{ext}$ values of ≤ 0.75 across the wavelength range of 400–1100 nm reported for n-Si/$SiO_{x,RCA}$/$TiO_2$/Ni photoanodes measured under similar conditions.[42] The increased $\Phi_{ext}$ for the $NiO_x$-coated photoanodes at wavelengths > 550 nm was due to the anti-reflective behavior of the $NiO_x$ coating. Consistently, $NiO_x$-coated n-Si photoanodes produced light-limited current densities under 1 Sun simulated AM1.5 illumination that were ~ 4.5 mA $cm^{-2}$ greater the light-limited current densities observed under such conditions from n-Si/$SiO_{x,RCA}$/$TiO_2$/Ni photoanodes.

Electrochemical impedance spectroscopy was used to determine the differential capacitance (*C*) of the n-Si/$SiO_{x,RCA}$/$NiO_x$, n-Si-E/$CoO_x$/$NiO_x$ (where n-Si-E indicates n-Si which was freshly etched in buffered HF (aq) before the next processing step), and

n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ electrodes, with Mott-Schottky plots ($C^{-2}$ vs $E$) indicating flat-band potentials ($V_{fb}$) of -0.67 ± 0.02 V, -0.69 ± 0.03 V, and -0.83 ± 0.02 V versus ($Fe(CN)_6^{3-/4-}$), respectively (Figure 2C). The slopes in the linear regions of the $C^{-2}$ vs $E$ plots yielded a doping density of ~ $10^{17}$ $cm^{-3}$ for all electrodes, which implies a corresponding resistivity of ~ 0.09 ohm cm, close to the range of 0.1 – 1 ohm cm specified by the manufacturer of the Si wafer. Kelvin-probe force microscopy (KPFM, Figure 2D) showed that the work function of the $CoO_x$ layer was 120 mV greater than that for n-Si/$SiO_{x,RCA}$ surfaces, indicating that the energy-band structure at the n-Si/$SiO_{x,RCA}$/$CoO_x$ interface was significantly different than that at the n-Si/$SiO_{x,RCA}$ interface. The negative shift in $V_{fb}$ for the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ electrode relative to the n-Si/$SiO_{x,RCA}$/$NiO_x$ electrode is in accord with the KPFM data, as well as with the *J-E* behavior observed in 1.0 M KOH(aq) (Figure 2A). The barrier height within the Si of n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ as calculated from the 0.83 V ± 0.02 V flat-band potential was 0.98 V ± 0.02 V (see Supplementary Information), close to the band gap of Si. This large band bending would likely result in the formation of a strong inversion layer at the surface of n-Si,[43] and thus would result in large observed photovoltages due to the associated improvements in charge-carrier separation and collection, as well as due to a reduction in the rate of electron-hole recombination and improvement in diffusion of charge carriers.[44]

The reverse-saturation current density and the diode quality factor for the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanode, extracted by a linear fit of the dependence of the photocurrent-onset potentials relative to $E^{o'}(Fe(CN)_6^{3-/4-})$ on the logarithm of photocurrent density ($J_{ph}$) (Figure S5), were $1.50\times10^{-7}$ mA $cm^{-2}$ and 1.09, respectively. The diffusion current was ~ $10^{-10}$ mA $cm^{-2}$, thus the thermionic emission current was the dominant contributor to the reverse-saturation current. Given a Richardson constant of 120 A $cm^{-2}$ $K^{-2}$ and a barrier height of 0.98 ± 0.02 V (see Supplementary Information), the transmission coefficient, $\alpha$, was estimated to be on the order of unity.

Figure 3A shows the chronopotentiometric data for an n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanode in contact with 1.0 M KOH(aq) and held at 1.63 V versus RHE while under simulated 1 sun illumination of 100 mW $cm^{-2}$. The current density was 30 ± 2 mA $cm^{-2}$ for 1700 h of continuous operation, at which point the experiment was stopped. Cyclic voltammograms were collected every 10 h during the stability test (Figure 3B), and showed that the *J-E* behavior for the photoanode gradually shifted anodically throughout the experiment. The photocurrent-onset potential relative to $E^{0'}(O_2/H_2O)$ shifted from -239 mV to -214 mV, -198 mV, and -185 mV while the photocurrent density at $E^{0'}(O_2/H_2O)$ decreased from 27.9 mA $cm^{-2}$ to 24.6 mA $cm^{-2}$, 21.4 mA $cm^{-2}$ and 16.2 mA $cm^{-2}$ after 500 h, 1000 h and 1500 h respectively. Hence the solar-to-$O_2$(g) value for $\eta_{IRC}$[34] decreased from 2.2% to 1.5%, 1.1%, and 0.74% after 500 h, 1000 h and 1500 h of operation, respectively. The gradual decrease in performance may result from the

generation of $SiO_x$ islands at pinholes in the sputtered $NiO_x$ film and/or from an increase in resistivity arising from thickening of the $SiO_x$ layer in the interface, as well as from the slow electrochemical conversion of $CoO_x$ to $Co(OH)_2$ and then to ion-permeable CoOOH (Figure S6) and the loss of catalytic activity. The stability of n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanodes was comparable to the reported stability of $np^+$-Si/$NiO_x$ photoanodes,[29] demonstrating that the interfacial $CoO_x$ layer did not adversely affect the stability of the $NiO_x$ coating.

Figure 3C shows the mass of $O_2$(g) generated, as determined using a calibrated oxygen probe, by an n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanode in contact with 1.0 M KOH(aq) under galvanostatic control for 30 min at a current density of 0.5 mA $cm^{-2}$. The measured mass of $O_2$(g) was in agreement with that calculated based on the charge passed, assuming 100% Faradaic efficiency for the generation of $O_2$(g). The total charge passed during the stability test was $1 \times 10^7$ greater than the total charge needed to dissolve the $CoO_x$ interfacial layer, and was $1 \times 10^2$ greater than the charge required to dissolve the entire Si substrate (see Supplementary Information). Assuming a 20% solar capacity factor, the 1700 h of stable water oxidation measured for the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanode in contact with 1.0 M KOH(aq) represented the same amount of anodic charge density as would be passed in approximately one year of operation in the field at a maximum photocurrent density of 30 mA $cm^{-2}$.

The thin layer of chemically grown silicon oxide present on the n-Si substrates prior to further processing by ALD and sputtering contributes to the improvement in performance observed when comparing n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanodes to n-Si/$CoO_x$/$NiO_x$ photoanodes (Figure 2C, S7). Both ALD and sputtering result in the growth of a thin layer of $SiO_x$ on freshly etched silicon surfaces. The properties of the $SiO_x$ layers produced by the different processing methods vary, and affect the performance of devices. The chemically grown $SiO_x$ layer may result in fewer trap states at the Si/$SiO_x$ interface than are produced by the sputtered $SiO_x$, and/or may serve to protect the underlying silicon from arcs and surface roughening during the RF sputtering process. In addition, the $SiO_x$ layer likely contributes to the initiation and conformity of the ALD growth process for the $CoO_x$ interfacial films, which on freshly etched Si surfaces would be expected to proceed via inhomogeneous island growth that can result in rough films as well as in interfacial silicon oxides or silicates,[45] and in reduced values for the built-in voltage and photovoltage of the junction.

Although this work has focused on the use of interfacial layers of ALD-grown $CoO_x$, other transition-metal oxides, including $FeO_x$ and $NiO_x$, also hold promise for use as interfacial layers on Si photoanodes protected by sputtered $NiO_x$ (Figure S7).

This work clearly demonstrates that the introduction of ALD layers of cobalt oxide improves the equivalent open-circuit voltage of protected n-Si photoanodes to values comparable to that obtainable from photoanodes fabricated using homogeneous p-n

buried Si junctions. Interfacial cobalt oxide layers increase the band bending at the interface and thereby offer a route to high-performance photoanodes, potentially simplifying the photoelectrode processing and allowing for the use of inexpensive polycrystalline absorbers while maintaining high photoelectrode performance.

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**Author contribution:**

X.Z., R.L., K.S., K.M.P, B.S.B and N.S.L designed the experiments and wrote the manuscript. X.Z., R.L. K.S., D.F., M.T.M, Y.F., S.T.O. A.C.N., S.Y. performed the experiments.

**Figures:**

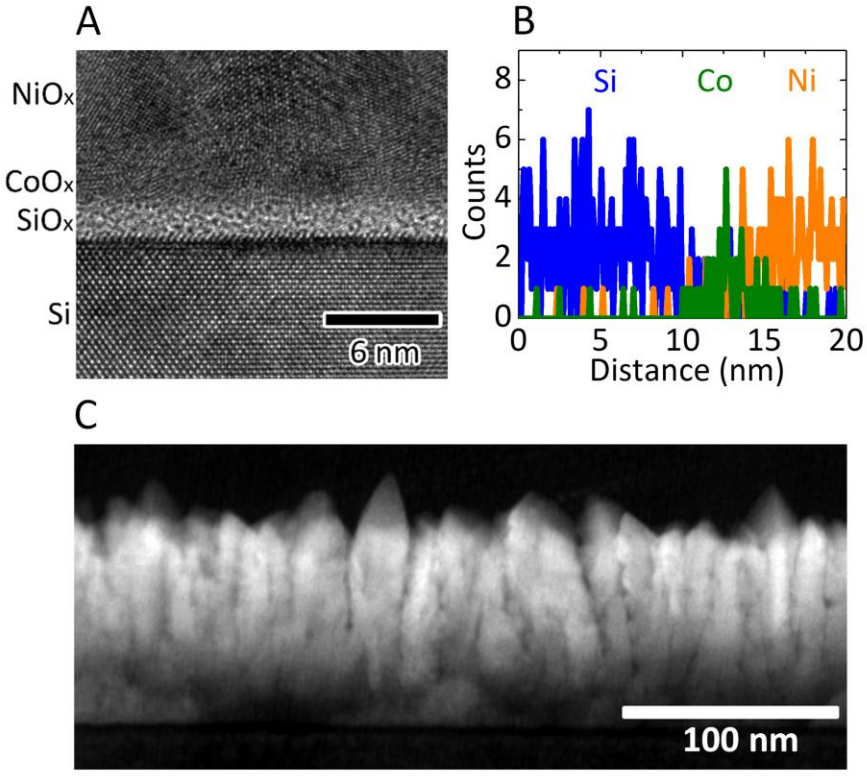


**Figure 1**. (A) High-resolution transmission-electron microscope (TEM) image of a cross-section of an n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ sample. The lighter region at the surface of the Si is $SiO_x$. The $CoO_x$ layer is incorporated into the highly polycrystalline region between the $SiO_x$ and the larger $NiO_x$ grains at the top of the image. (B) Energy-dispersive spectroscopy (EDS) line-scan across the Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ interface in which the $K\alpha$ X-rays from Si, Co, and Ni are displayed as a function of distance. (C) Low-magnification HAADF-STEM cross-sectional image of an n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ electrode. The bright film is the polycrystalline $NiO_x$ layer, which grew in a columnar

fashion with vertical grain boundaries. The Si wafer is the dark layer at the bottom of the image.

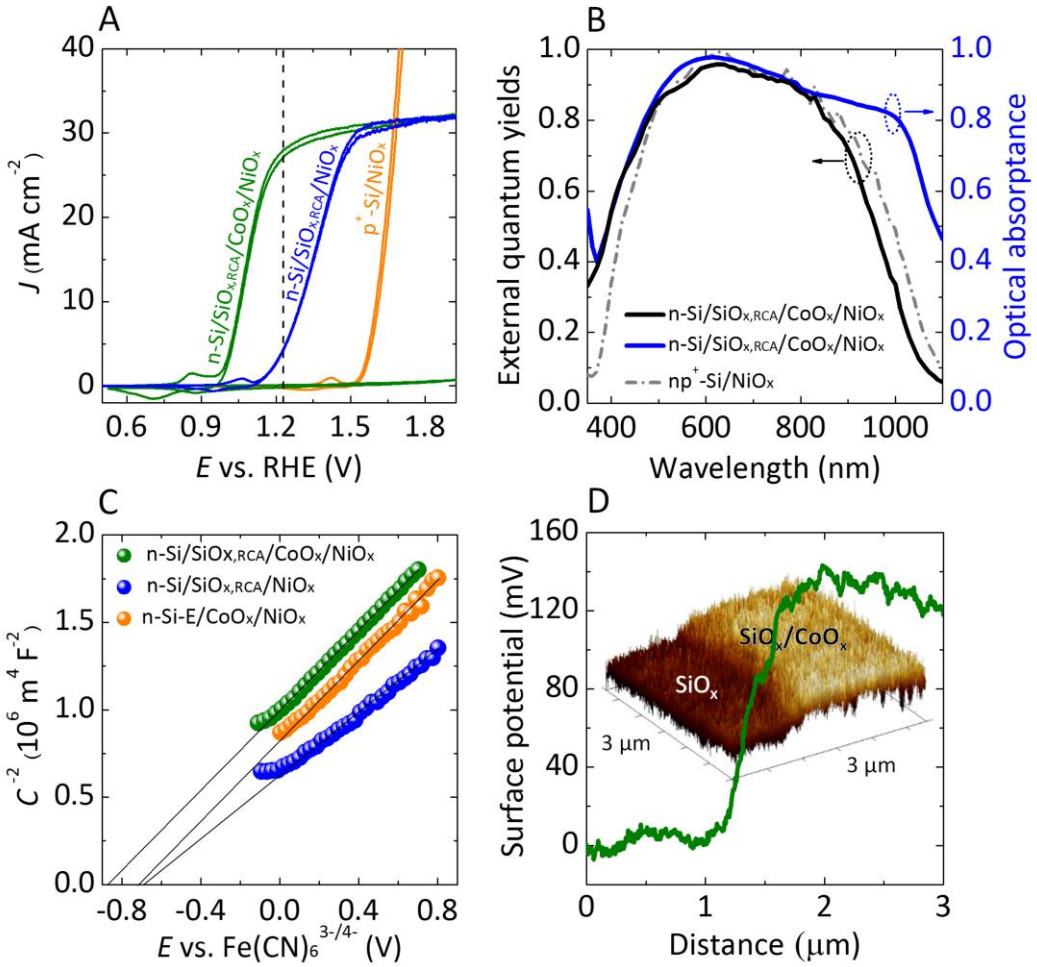


**Figure 2**. (A) Representative current-density versus potential (*J-E*) behavior of n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ and n-Si/$SiO_{x,RCA}$/$NiO_x$ photoanodes in contact with 1.0 M KOH (aq) in the dark (See Supplementary Information) and under 100 mW $cm^{-2}$ of simulated AM1.5G solar illumination. The *J-E* behavior of a non-photoactive $p^+$-Si/$NiO_x$ electrode is also shown. The dark dashed line indicates the formal potential for water oxidation, $E^{o'}(O_2/H_2O)$. (B) Wavelength-dependent external quantum yield for

n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ (black) and $np^+$-Si/$NiO_x$ (gray dash and dot) photoanodes in contact with 1.0 M KOH(aq) and held potentiostatically at 1.93 V versus a reversible hydrogen electrode (RHE) while illuminated by light that had been passed through a monochromator. The data for the $np^+$-Si/$NiO_x$ photoanode are extracted from reference 29. The optical absorptance for the n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanode is shown in blue. (C) Mott-Schottky ($C^{-2}$ vs $E$) plots of the inverse of the differential capacitance of the electrode vs potential for an n-Si/$SiO_{x,RCA}$/$NiO_x$ photoanode (blue), an n-Si-E/$CoO_x$/$NiO_x$ photoanode (orange, n-Si-E indicates the n-Si was freshly etched in buffered HF (aq) before the next processing step), and an n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanode (green). (D) Kelvin probe force microscopy images showing the change in potential as the probe was scanned from the n-Si/$SiO_{x,RCA}$ surface to the n-Si/$SiO_{x,RCA}$/$CoO_x$ surface.

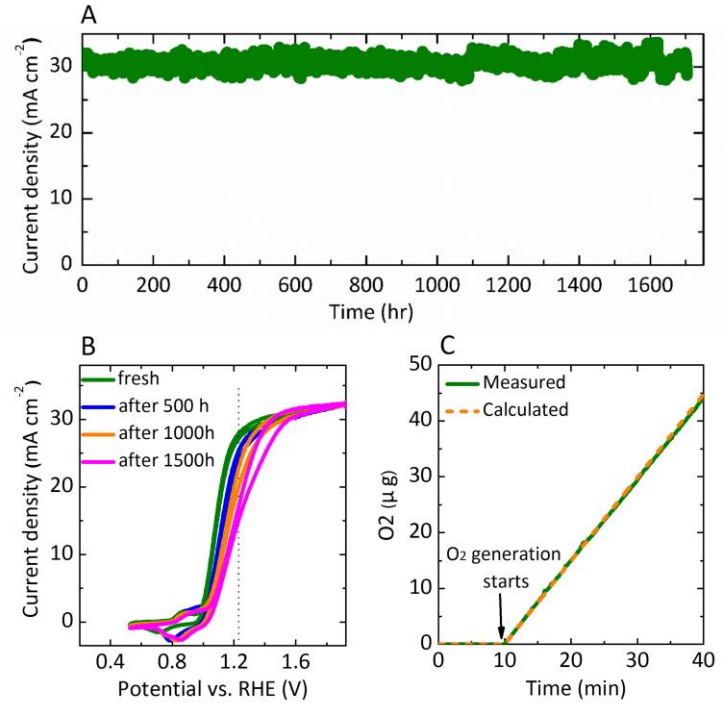


**Figure 3** (A) Chronoamperometry of n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanodes biased at 1.63 V vs. RHE under 1 Sun of simulated 1.5G solar illumination from an ENH-type tungsten-halogen lamp. (B) Representative *J-E* behavior for an n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanode in contact with 1.0 M KOH(aq) under 100 mW $cm^{-2}$ of AM 1.5G simulated solar illumination collected before, and after 500 h, 1000 h and 1500 h of continuous operation at 1.63 V vs RHE. (C) Mass of $O_2$ (g) generated (green line) by an n-Si/$SiO_{x,RCA}$/$CoO_x$/$NiO_x$ photoanode held at a constant current density of 0.5 mA $cm^{-2}$ for 30 min while under AM 1.5G simulated illumination and in contact with 1.0 M KOH(aq), as determined by a calibrated $O_2$ probe and as calculated based on the charge passed assuming 100% Faradaic efficiency for $O_2$ generation (orange dashed line).

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