Efficient and Stable Silicon Microwire Photocathodes with a Nickel Silicide Interlayer for Operation in Strongly Alkaline Solutions

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* Supporting Information

ABSTRACT: Most photoanodes commonly applied in solar fuel research (e.g., of Fe₂O₃, BiVO₄, TiO₂, or WO₃) are only active and stable in alkaline electrolytes. Silicon (Si)-based photocathodes on the other hand are mainly studied under acidic conditions due to their instability in alkaline electrolytes. Here, we show that the induction of nickel into a 3D Si structure, upon thermal annealing, yields a thin (sub-100 nm), defect-free nickel silicide (NiSi) layer. This has allowed us to design and fabricate a Si microwire photocathode with a NiSi interlayer between the catalyst and the Si microwires. Upon electrodeposition of the catalyst (here, nickel molybdenum) on top of the NiSi layer, an efficient, Si-based photocathode was obtained that is stable in strongly alkaline solutions (1 M KOH). The best-performing, all-earth-abundant microwire array devices exhibited, under AM 1.5G simulated solar illumination, an ideal regenerative cell efficiency of 10.1%.

In a complete photoelectrochemical cell, a photocathode and -anode are coupled together, preferably in one electrolyte, which is either acidic or alkaline. A major shortcoming of photoelectrochemical (PEC) cells that operate in an acidic electrolyte is the limited range of materials for the oxygen evolution reaction (OER) catalyst. The vast majority of PEC cell-compatible OER catalysts in acidic electrolyte is based on oxides of ruthenium (Ru) and, especially, iridium (Ir), which are very scarce noble metals. Furthermore, McCrory et al. benchmarked the overpotential to produce 10 mA/cm² for many known earth-abundant OER and hydrogen evolution reaction (HER) catalysts for 2 h in both acidic (1 M H₂SO₄) and alkaline (1 M KOH) electrolytes. According to McCrory et al., the best earth-abundant HER/OER catalyst combination in acidic electrolyte (i.e., NiMo for the HER and Ni for the OER) requires an overpotential of 1.14 V, while the best HER/OER combination in alkaline electrolyte (i.e., NiMo for the HER and NiMoFe for the OER) only requires an overpotential of 430 mV. McKone et al. showed that NiMo, which is the best-performing earth-abundant HER catalyst in acidic electrolyte, is only stable up to 10 h of operation, while the same catalyst is stable >100 h in alkaline electrolyte. Therefore, there is a strong drive to produce HER photocathodes, based on earth-abundant materials, that are stable and active in an alkaline medium.

Silicon (Si) is a widely investigated material as a photoabsorber in a photocathode. However, crystalline Si has a high stability in acidic media, but it is etched quickly (∼2 μm/h) in alkaline solutions. Therefore, the majority of research for Si as a photocathode is conducted in an acidic environment. This problem can potentially be overcome by introducing an intermediate closed layer between the catalyst and the n⁺-Si emitter. Both Kast and Bae et al. showed the necessity to protect planar Si photocathodes with an intermediate layer of titanium oxide (TiO₂). However, they employed a thin layer (∼2 nm) of a precious metal catalyst (Ir or Pt) to overcome the...
light absorption limitations that are encountered with earth-abundant catalyst materials. Earth-abundant catalysts require higher mass loadings of catalyst to achieve the same catalytic activity. High mass loadings of catalyst lead to parasitic optical absorption losses of the photon absorber (Si) underneath, limiting the photon current density ($J_{sc}$) and concomitantly the efficiency ($\eta$) of the device.\textsuperscript{5,9}

Our previously fabricated n$^+$/p-Si microwire array photocathodes, in part based on existing microwire research of others,\textsuperscript{6,7} with spatioselectively deposited nickel molybdenum (NiMo) surpassed the latter problem.\textsuperscript{10} By carefully adjusting the design parameters, we reported one of the highest reported efficiencies (i.e., $\eta_{rec} = 10.8\%$) in acidic electrolyte. In the fabrication process of these photocathodes, the majority of the microwires are passivated by silicon-rich silicon nitride (SiN$_x$) and protected from the harsh alkaline electrolyte.\textsuperscript{\textdegree} Unfortunately, spatioselectively deposited NiMo does not provide a conformal coverage over the Si structure, and thus, the underlying Si substrate in the catalyst-covered areas will be etched in an alkaline electrolyte, reducing the lifetime of Si/NiMo microwire photocathodes substantially.\textsuperscript{10,12} Passivation techniques, as employed by Kast and Bae et al., are mostly limited to planar substrates due to the limitations of sputtering or evaporation.\textsuperscript{6,7} Si microwire substrates require a deposition technique that is suitable for high-aspect-ratio structures. Atomic layer deposition (ALD) of TiO$_2$ has been used successfully to coat micropillars conformally,\textsuperscript{13} but its applicability in spatioselective deposition has so far not been tested.

Therefore, the proposed intermediate has to meet several requirements: (i) be deposited spatioselectively only on the interface between the silicon and the NiMo overlayer, (ii) be electrically conductive between the n$^-$-Si emitter and the catalyst on top, (iii) be stable in alkaline solution, (iv) be defect free, and (v) have deposition techniques that are compatible with high-aspect-ratio structures. In order to comply with all requirements for defect-free interlayer formation, we envisaged the use of a spatioselectively electrodeposited Ni layer (stable between pH 5 and 14)\textsuperscript{9,14} that is transformed into nickel silicide (NiSi) at locations where it is in contact with Si, in a self-aligned and repairing process. NiSi is an effective and proven masking material for selective Si etching in KOH, in which it is not being etched at a noticeable rate, and NiSi is highly conductive.\textsuperscript{15,16} More importantly, the formation mechanism of NiSi provides the opportunity to repair possible defects introduced in the preceding step of the electrodeposition of Ni because Ni diffuses into the Si substrate following Fick’s law of diffusion. Therefore, NiSi as an interlayer can comply with all four requirements stated above.

Both Pinaud and Shaner et al. have pointed out that PEC cells could become more efficient and commercially attractive than a PV–electrolyzer combination when the production cost can be reduced, which can be addressed by using earth-abundant materials and by improving the overall efficiency and the operational durability.\textsuperscript{17,18} The work described in our study addresses steps in all of these directions.

Here we show the chemical resistivity and applicability of NiSi as an interlayer for the protection of an efficient Si microwire photocathode in alkaline electrolyte for prolonged periods of time. We apply the NiSi interlayer in a photocathode that is functional in alkaline media by the fabrication of a Si microwire array with a radial n$^+$/p-junction, the spatioselective formation of a conformal interlayer of NiSi, and the subsequent electrodeposition of NiMo as an active and stable HER catalyst in alkaline medium.\textsuperscript{7} By the spatioselective functionalization of the Si microwire with a catalyst, light blocking due to the catalyst is kept to a minimum.\textsuperscript{9} The activity and stability of the photocathode are assessed for prolonged periods of time under strong alkaline conditions.

Development of a NiSi Interlayer. The fabrication of silicon nitride (SiN$_x$)-passivated microwires with a radial n$^+$/p junction of ∼900 nm, a diameter of 4 μm, a length of 40 μm, a pitch of 12 μm, and the spatioselective retracting of the SiN$_x$ layer was performed as previously reported (see Materials and Methods).\textsuperscript{19–21} The fabrication scheme of the microwire arrays with spatioselectively deposited Ni or NiSi interlayers is schematically depicted in Scheme 1.

First, we fabricated microwire arrays with spatioselectively electrodeposited Ni (Scheme 1A). The deposition of conformal Ni caps is discussed in detail in the SI. These Ni caps were used as is, or the Ni cap was transformed into NiSi by means of rapid thermal annealing (RTA, 485 °C, and a holding time of 120 s; see Scheme 1C and Figure S1). NiSi is a widely studied material in solid-state devices for electronic applications, owing
to its properties: its ease in formation due to a broad temperature range (400–700 °C) (as opposed to other silicides, e.g., TiSi, CoSi, RhSi), its chemical resistivity in KOH, and a low resistivity (∼10–18 μΩ cm).\textsuperscript{24,25} NiSi has been found to grow by a diffusion-controlled mechanism, whereby the Ni atoms diffuse through the growing NiSi layer with an activation energy between ∼1.75 and 1.85 eV.\textsuperscript{25} The pre-exponential factor, $D_0$, for the diffusion of Ni is mainly dependent on the pretreatment of the Si sample before Ni deposition (e.g., with native oxide or stripped in 1% HF) and is in the range of 1–2 cm$^2$/s.\textsuperscript{26}

In order to test the chemical resistivity of each material (i.e., Ni, SiN$_x$, NiSi, and Si) separately, we used 1 M KOH (2 wt %) at room temperature, which resembles the intended operating condition of a solar-to-fuel device. The etch rates in Table S1 clearly show the necessity of protecting Si: Si etches at a high rate, although doping of Si (which is required for the emitter formation) reduces the etch rate significantly.\textsuperscript{27} Even at these reduced etch rates, unprotected microwire arrays would be etched completely within a couple of hours. In contrast, both Ni and NiSi show a very high chemical resistivity under these conditions.

SEM images were acquired after immersing passivated microwire array samples in a 1 M KOH solution for 24 h, with either Ni or NiSi as the interlayer. Figure 1A,B shows SEM images of a sample that was only protected by a spatiotselective Ni layer on top of the microwire. Figure 1A shows an overview of the array, and most of the microwires were affected, etched, or completely removed. Figure 1B shows a zoom-in of Figure 1A, and only hollow sleeves of SiN$_x$ are visible, whereas the Ni caps are absent. For samples with a slightly larger Ni capping layer (upper ∼2 μm), released Ni caps were found all over the substrate (see Figure S2). Scallops resulting from the fabrication process of the microwires are clearly visible within the caps, further indicating the stability of Ni under the alkaline test conditions (as also from Table S1), confirming that only Si has been etched while leaving the Ni structure intact. Furthermore, the SiN$_x$ layer showed great chemical resistance, as indicated in Table S1. Therefore, these results indicate that the instability of the Si structures occurs at the interface between SiN$_x$ and Ni or at possible pinholes in the Ni layer.

Figure 1C shows an overview of microwires with a NiSi interlayer after 24 h in 1 M KOH. All of the microwires are still intact, which indicates that NiSi provides continuous protection of the underlying silicon under the harsh alkaline conditions. Figure 1D shows a close-up of the microwires in Figure 1C, clearly confirming that the microwires are undamaged. Defects within the Ni layer are clearly detrimental for the stability of the underlying Si microwire array. Pinholes are most likely still present within several of the millions of microwires/cm$^2$. Even a single pinhole could eventually lead to dissolution of the complete silicon device and should therefore be prevented. Annealing the sample by RTA does not only form a chemically resistive NiSi layer, it may also (i) repair defects within the layer and (ii) seal off the interface at the top edge of the SiN$_x$ protection layer, both attributed to the diffusion process of the Ni atoms into the Si material at the Ni–Si interface. In order to show the above-mentioned effects, we
produced two test structures. Figure 2A,B shows SEM images in order to visualize the repair of defects (i), and Figure 2C,E shows images to visualize sealing of the interface between the protective SiN$_x$ layer and underlying Si (ii).

Figure 2A shows a cross section of a Si microwire with sputtered Ni, and Figure 2B shows that after annealing the sample by RTA. Sputtering of Ni (bright contrast in Figure 2A) resulted in a nonconformal layer over the Si microwire array, in particular, at the side walls where scallops are present, thus providing induced defects. The top of a scallop causes a shadowing effect for the incoming sputtered material, and as a result of the high directionality of the material flux during sputtering, no material is found within the troughs of the scallops. After annealing and stripping the remaining Ni layer, a conformal NiSi layer is visualized by the SEM image in Figure 2B. Ni diffused not only orthogonally inward but also into the troughs of the scallops where no Ni source was present at the Si interface, thereby forming a conformal and closed NiSi layer. A diffusion distance of $\sim 100$ nm is apparently sufficient to seal the defects induced by the scalloping.

Figure 2C shows a SEM image of a 5 $\mu$m long microwire, whereby the upper 2.5 $\mu$m was spatioselectively functionalized with electrodeposited Ni and the lower 2.5 $\mu$m is SiN$_x$. Figure 2D shows a cross-sectional image of a spatioselectively functionalized Si microwire after Ni diffusion, of which Figure 2E shows a zoom-in at the interface of Si, SiN$_x$, and NiSi. A conformal layer of NiSi is formed completely over the top of the microwire (light gray), as in Figure 2B. More importantly, the zoom-in (Figure 2E) clearly visualizes that a NiSi layer is formed in between the Si and SiN$_x$ layer. To aid in the visualization, Figure S3A shows EDX mapping of this interface in combination with a line scan (see Figure S3B). Furthermore, we performed X-ray diffraction, which further supported the 1:1 stoichiometry of NiSi (see Figure S4). This indicates that Ni has diffused downward in between the conformal SiN$_x$ layer and the Si microwire, thereby effectively protecting the underlying Si against the alkaline electrolyte. Generally, as long as the defects are smaller than twice the diffusion distance of Ni during the RTA step, defects occurring in the preceding Ni deposition step will be repaired.

**Photocathodes with a NiSi Interlayer.** After successful development of the NiSi interlayer for providing alkaline-stable Si microwire arrays, NiMo was deposited as a catalyst on top of microwire arrays with Ni as well as NiSi as the interlayer. Electrodeposition was employed in order to cover all microwires with a catalyst layer. NiMo was deposited by contacting the n$^+$-emitter, as was performed for the preceding Ni deposition step. Successful structures of NiMo-coated wires with Ni and NiSi interlayers are shown in Figure S5. The deposition of NiMo on both substrates (i.e., Figure SSA for Ni, Figure SSB for NiSi) resulted in an open granular structure. This highlights even further the necessity for a sealed interlayer as NiMo alone is not adequate to protect the underlying Si microwire. Furthermore, Figure S6 shows that the spatioselective electrodeposition of NiMo is possible over large areas of microwires, as long as the interlayers are conductive.
The activity of functionalized substrates was assessed using dark $JE$ measurements for HER electrocatalysis at planar Si substrates, tested in 1 M KOH (Figure 3). The influence of the doping level of n-Si is included because Wong et al. showed the presence of a Schottky barrier at the interface of n-type Si and NiSi. This barrier can be reduced by increasing the doping level of n-type Si (see Figure S7). Although the band edge position of Si straddles the H+/H2 redox couple, planar Si shows almost no catalytic activity over a large overpotential range (not shown in Figure 3), which underlines the requirement for a catalyst. Furthermore, unprotected n-Si is etched rapidly ($\sim2$ $\mu$m/h) under these conditions (see Table S1). The addition of a smooth Ni film on the surface improves the catalytic activity substantially, as shown in Figure 3. By electrodepositing NiMo on top of the already deposited Ni (Scheme 1C), the activity is increased even further (see Figure 3, NiMo$-$Ni on n$^+$-Si). However, from the above-mentioned KOH immersion experiments, it is known that Ni alone does not protect the interface of the Si microwires, and NiSi is required to preserve the microwires.

NiSi was prepared as described on samples with different doping levels. After removal of the remaining Ni, NiMo was deposited on top (see Scheme 1D), and the resulting dark $JE$ behavior was characterized (Figure 3). For n-Si and n$^+$-Si, the activity was less than that for the NiMo$-$Ni (on n$^+$-Si) sample. This is due to the Schottky barrier formed at lower doping levels, as described in more detail in the SI. By increasing the doping level, this barrier is overcome, and the activity of NiMo$-$NiSi on n$^+$-Si appeared to be the same as NiMo on a metallic Ni layer. Therefore, a doping level of $10^{21}$ cm$^{-3}$ was applied for the n-emitters.

Previously, we optimized Si microwire photocathodes with respect to (optimum values between brackets): the doping depth of the emitter (900 nm), microwire length (40 $\mu$m), pitch (12 $\mu$m), and catalyst coverage (upper $\sim$100 nm). Here, we used these settings to fabricate a microwire array photocathode, but now with an emitter doping level of $10^{21}$ cm$^{-3}$ to ensure Ohmic contact between the catalyst and the NiSi interlayer while using NiMo as the HER catalyst. $JE$ measurements for Si microwire arrays with spatioselectively deposited NiMo catalyst on a NiSi interlayer were performed in a 1 M KOH electrolyte under AM 1.5G illumination, and the results are presented in Figure 4A. Here, the photocathode is characterized as an ideal regenerative cell (IRC).

The values of the fill factor (FF), open-circuit voltage ($V_{oc}$), and photocurrent density ($J_{ph}(E_{H2/H+})$) are referenced to the equilibrium potential of the half-reaction being performed at the photocathode, and $P_{in}$ is the light power input (AM 1.5G, 100 mW/cm$^2$). All relevant values of the photocathode are presented in Figure 4A. Although microwires are employed here, we do note that the planar bottom accounts for half of the generated photocurrent ($\sim15$ mA/cm$^2$), as was demonstrated in our previous study, where we studied the influence of catalyst coverage. To our knowledge, this half-cell gave the highest $V_{oc}$, short-circuit current ($J_{sc}$) and FF values reported so far for an all-earth-abundant photocathode in alkaline conditions, with an overall efficiency of 10.1%.

**Figure 3.** Plots of the current density vs potential for planar Si devices with and without NiMo catalyst on a Ni or NiSi interlayer, at different doping levels as stated.

**Figure 4.** (A) $JE$ measurements of microwire photocathodes with a NiSi interlayer and functionalized with NiMo catalyst; see Scheme 1D. The average of four different samples prepared with the same settings is shown, and the standard deviation is in light blue (the four individual graphs are given in Figure S8 and their characteristic parameters in Table S2). (B) Recorded current density under a supplied potential of 500 mV vs RHE of a Si microwire array photocathode under continuous AM 1.5G simulated sunlight.
The NiMo catalyst is expected to have long stability in alkaline conditions. To assess the durability of this catalyst in the microwire configuration, we measured the current density at a constant potential vs RHE. An applied bias of 500 mV vs RHE resulted in a current density of ~10 mA/cm² and was maintained for 12 days under AM 1.5G light (see Figure 4B). These values for potential and current density are in good agreement with the JE measurement given in Figure 4A. The average recorded current density was stable over the entire period of time, and the current only oscillated slightly, which is most probably due to H₂ bubble formation and detachment. The decrease in current density in the first day is most likely due to an increase of the temperature of the whole PEC cell by the solar irradiation. This will lead to a negative shift of the Vₜₚ of the photocathode. The shift in Vₜₚ has been observed by performing JE measurements at controlled cell temperatures (Figure S9A). Plotting the Vₜₚ as a function of the PEC cell temperature revealed a shift of ~2.2 mV/°C (Figure S9B). Thereby, a small change of the Vₜₚ has a large effect on the current density at constant potential. Furthermore, the Si microwire arrays were unaffected by immersion in 1 M KOH for prolonged periods of time (see Figure S10), which indicates the excellent passivation properties of the NiSi interlayer, positioned between the Si microwires and the NiMo catalyst.

In conclusion, we have designed, fabricated, and experimentally validated a broadly applicable photoelectrode architecture that not only circumvents the trade-off between catalytic activity and optical absorption but also provides stability in harsh alkaline electrolyte. For the latter reason, an interlayer of NiSi was developed to effectively shield the underlying Si microwire from the alkaline electrolyte, in which Si microwires normally are being etched rapidly. By annealing a sample with spatiotemporally electrodeposited Ni, pinholes within the Ni layer were repaired effectively by Ni diffusion during the NiSi formation step. To ensure Ohmic behavior between the microwire array and the NiSi interlayer, a high doping level of the Si emitter layer is required to overcome an undesirable Schottky barrier. Lastly, by spatially decoupling light absorption and catalytic activity on high-aspect-ratio silicon microwires with a radial n+/p-junction, an efficient, i.e., ηIRC = 10.1%, solar-driven Si photocathode that is stable in alkaline electrolyte was achieved, which maintained constant activity for several days of operation.

Furthermore, the etch rates of the materials exposed to KOH (i.e., Si₅N₃, NiSi, and NiMo⁶) have been evaluated. This analysis indicates, together with known thicknesses of the SiNₓ and NiSi layers, that the device should be stable for at least 6 operating years. This lifetime is most likely limited by the SiNₓ layer, and its stability can potentially be further improved by using stoichiometric SiNₓ and/or a larger layer thickness.

Our future research will focus on the integration of these Si microwires with spatiotemporal catalyst deposition in a full solar-to-fuel device. The improved chemical resistivity of these Si microwires in alkaline electrolyte should enable the identification of a suitable combination with a higher-bandgap photoanode.

**ACKNOWLEDGMENTS**

This work is part of the research program of the Foundation for Fundamental Research on Matter (FOM, Project 13CO12-2), which is part of The Netherlands Organization for Scientific Research (NWO). Dr. D. Dubbink is gratefully acknowledged for his insights, discussions, and expertise in characterizing the NiSi layer by XRD.

**REFERENCES**

(1) Reier, T.; Nong, H. N.; Teschner, D.; Schlogl, R.; Strasser, P. Electrocatalytic Oxygen Evolution Reaction in Acidic Environments - Reaction Mechanisms and Catalysts. Adv. Energy Mater. 2017, 7, 1601275.

(2) McCorry, C. C.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Janamillo, T. F. Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. J. Am. Chem. Soc. 2015, 137, 4347–4357.

(3) Carino, M.; Fritz, D. L.; Mergel, J.; Stolten, D. A Comprehensive Review on PEM Water Electrolysis. Int. J. Hydrogen Energy 2013, 38, 4901–4934.

(4) Turekian, K. K.; Wedepohl, K. H. Distribution of the Elements in Some Major Units of the Earth’s Crust. Geol. Soc. Am. Bull. 1961, 72, 175–192.

(5) McKone, J. R.; Saddler, B. F.; Werlang, C. A.; Lewis, N. S.; Gray, H. B. Ni–Mo Nanopowders for Efficient Electrochemical Hydrogen Evolution. ACS Catal. 2013, 3, 166–169.

(6) Kast, M. G.; Enman, L. J.; Gurnon, N. J.; Nadarajah, A.; Boettcher, S. W. Solution-deposited F:SnO2/TiO2 as a Base-stable Protective Layer and Antireflective Coating for Microtextured Buried-junction H2-evolving Si Photocathodes. ACS Appl. Mater. Interfaces 2014, 6, 22830–22837.

(7) Bae, D.; Shayestehaminzadeh, S.; Thorsteinsson, E. B.; Pedersen, T.; Hansen, O.; Seger, B.; Vesborg, P. C. K.; Olafsson, S.; Chorkendorff, I. Protection of Si Photocathode Using TiO2 Deposited by High Power Pulse Magneton Sputtering for H₂ Evolution in Alkaline Media. Sol. Energy Mater. Sol. Cells 2016, 144, 758–765.

(8) Shaner, M. R.; McKone, J. R.; Gray, H. B.; Lewis, N. S. Functional Integration of Ni-Mo Electrocatalysts with Si Microwire Array Photocathodes to Simultaneously Achieve High Fill Factors and Light-limited Photocurrent Densities for Solar-driven Hydrogen Evolution. Energy Environ. Sci. 2015, 8, 2977–2984.

(9) Boettcher, S. W.; Warren, E. L.; Putnam, M. C.; Santori, E. A.; Turner-Evans, D.; Kelzenberg, M. D.; Walter, M. G.; McKone, J. R.; Brunschwig, B. S.; Atwater, H. A.; Lewis, N. S. Photoelectrochemical Hydrogen Evolution using Si Microwire Arrays. J. Am. Chem. Soc. 2011, 133, 1216–1219.

(10) Visselaar, W.; Westerik, P.; Vreebeek, J.; Tiggelaar, R. M.; Berenschot, E.; Tas, N. R.; Gardeniers, H. J.; Huskens, J. Spatial Decoupling of Light absorption and Catalytic Activity of NiMo-loaded High-aspect-ratio Silicon Microwire Photocathodes. Nature Energy 2018, 3, 185–192.

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**Notes**

The authors declare no competing financial interest.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.8b00267.
(11) Williams, K. R.; Gupta, K.; Wasilk, M. Etch Rates for Micromachining Processing - Part II. J. Microelectromech. Syst. 2003, 12, 761−778.
(12) McKone, J. R.; Warren, E. L.; Bierman, M. J.; Boettcher, S. W.; Brunschwig, B. S.; Lewis, N. S.; Gray, H. B. Evaluation of Pt, Ni, and Ni-Mo Electro catalysts for Hydrogen Evolution on Crystalline Si Electrodes. Energy Environ. Sci. 2011, 4, 3573−3583.
(13) Shaner, M. R.; Hu, S.; Sun, K.; Lewis, N. S. Stabilization of Si Microwire Arrays for Solar-Driven H2O Oxidation to O2(g) in 1.0 M KOH(aq) Using Conformal Coatings of Amorphous TiO2. Energy Environ. Sci. 2015, 8, 203−207.
(14) Boubatra, M.; Azizi, A.; Schmerber, G.; Dinia, A. The Influence of pH Electrolyte on the Electrochemical Deposition and Properties of Nickel Thin Films. I onics 2012, 18, 425−432.
(15) Bhaskaran, M.; Sriram, S.; Sim, L. W. Nickel Silicide Thin Films as Masking and Structural Layers for Silicon Bulk Micro-machining by Potassium Hydroxide Wet Etching. J. Micromech. Microeng. 2008, 18, 095002.
(16) Bhaskaran, M.; Sriram, S.; Holland, A. S.; Evans, P. J. Characterisation of Nickel Silicide Thin Films by Spectroscopy and Microscopy Techniques. Micron 2009, 40, 99−103.
(17) Pinaud, B. A.; Benck, J. D.; Seitz, L. C.; Forman, A. J.; Chen, Z. B.; Deutsch, T. G.; James, B. D.; Baum, K. N.; Baum, G. N.; Ardo, S.; Wang, H. L.; Miller, E.; Jaramillo, T. F. Technical and Economic Feasibility of Centralized Facilities for Solar Hydrogen Production via Photocatalysis and Photoelectrocatalysis. Energy Environ. Sci. 2013, 6, 1983−2002.
(18) Shaner, M. R.; Atwater, H. A.; Lewis, N. S.; McFarland, E. W. A Comparative Technoeconomic Analysis of Renewable Hydrogen Production Using Solar Energy. Energy Environ. Sci. 2016, 9, 2354−2371.
(19) Elbersen, R.; Tiggelaar, R. M.; Milbrat, A.; Mul, G.; Gardeniers, H.; Huskens, J. Controlled Doping Methods for Radial p/n Junctions in Silicon. Adv. Energy Mater. 2015, 5, 1401745.
(20) Elbersen, R.; Vrijelaar, W.; Tiggelaar, R. M.; Gardeniers, H.; Huskens, J. Fabrication and Doping Methods for Silicon Nano- and Micropillar Arrays for Solar-Cell Applications: A Review. Adv. Mater. 2015, 27, 6781−6796.
(21) Elbersen, R.; Vrijelaar, W.; Tiggelaar, R. M.; Gardeniers, H.; Huskens, J. Effects of Pillar Height and Junction Depth on the Performance of Radially Doped Silicon Pillar Arrays for Solar Energy Conversions. Adv. Energy Mater. 2016, 6, 1501728.
(22) Vrijelaar, W.; Elbersen, R.; Tiggelaar, R. M.; Gardeniers, H.; Huskens, J. Photo-Electrical Characterization of Silicon Micropillar Arrays with Radial p/n Junctions Containing Passivation and Anti-Reflection Coatings. Adv. Energy Mater. 2017, 7, 1601497.
(23) Westerik, P. J.; Vrijelaar, W. J. C.; Berenschot, J. W.; Tas, N. R.; Huskens, J.; Gardeniers, J. G. E. Sidewall Patterning - a New Wafer-scale Method for Accurate Patterning of Vertical Silicon Structures. J. Micromech. Microeng. 2018, 28, 015008.
(24) d’Heurle, F.; Petersson, C. S.; Baglin, J. E. E.; La Placa, S. J.; Wong, C. Y. Formation of Thin Films of NiSi: Metastable Structure, Diffusion Mechanisms in Intermetallic Compounds. J. Appl. Phys. 1984, 55, 4208−4218.
(25) Tang, W.; Nguyen, B.-M.; Chen, R.; Dayeh, S. A. Solid-state Reaction of Nickel Silicide and Germanide Contacts to Semiconductor Nanochannels. Semicond. Sci. Technol. 2014, 29, 054004.
(26) Borel, J. P. La Diffusion Dans les Solides. Phys. Status Solidi B 1966, 13, 3−23.
(27) Palik, E. D. Study of the Etch-Stop Mechanism in Silicon. J. Electrochem. Soc. 1982, 129, 2051−2059.
(28) Detavernier, C.; Jordan-Sweet, J.; Lavoie, C. Texture of NiSi Films on Si(001), (111), and (110) Substrates. J. Appl. Phys. 2008, 103, 113526.
(29) Wong, H. S.; Chan, L.; Sainudra, G.; Yeo, Y. C. Sub 0.1 eV Effective Schottky-barrier Height for NiSi on n-type Si (100) using Antimony Segregation. IEEE Electron Device Lett. 2007, 28, 703−705.
(30) Coridan, R. H.; Nielander, A. C.; Francis, S. A.; McDowell, M. T.; Dix, V.; Chatman, S. M.; Lewis, N. S. Methods for Comparing the Performance of Energy-conversion Systems for Use in Solar Fuels and Solar Electricity Generation. Energy Environ. Sci. 2015, 8, 2886−2901.
(31) Chander, S.; Purohit, A.; Sharma, A.; Arvind; Nehra, S. P.; Dhaka, M. S. A Study on Photovoltaic Parameters of Mono-Crystalline Silicon Solar Cell with Cell Temperature. Energy Rep. 2015, 1, 104−109.
(32) Wen, C.; Fu, C.; Tang, J.; Liu, D.; Hu, S.; Xing, Z. The Influence of Environment Temperatures on Single Crystalline and Polycrystalline Silicon Solar Cell Performance. Sci. China: Phys., Mech. Astron. 2012, 55, 235−241.