Supplementary Information

Section I: Experiments on Si samples coated with perforated Au films

Stability of Au in HF Solution

A macroscopic Au wire was placed in close proximity with a P-Si substrate in H_2O_2/ HF solution for 10 min, following the procedures of Geyer *et. al*[1] (Fig. S1a). The two materials were separated by a 400 nm thick perforated photoresist film. Unlike the case when an Ag wire was used, no Au nanoparticles or etching was observed on the Si surface (Fig. S1b). This shows that Au is stable in the etching solution, unlike Ag, which undergoes dissolution and re-deposition in the presence of HF. This result is consistent with those from previous reports[2, 3].

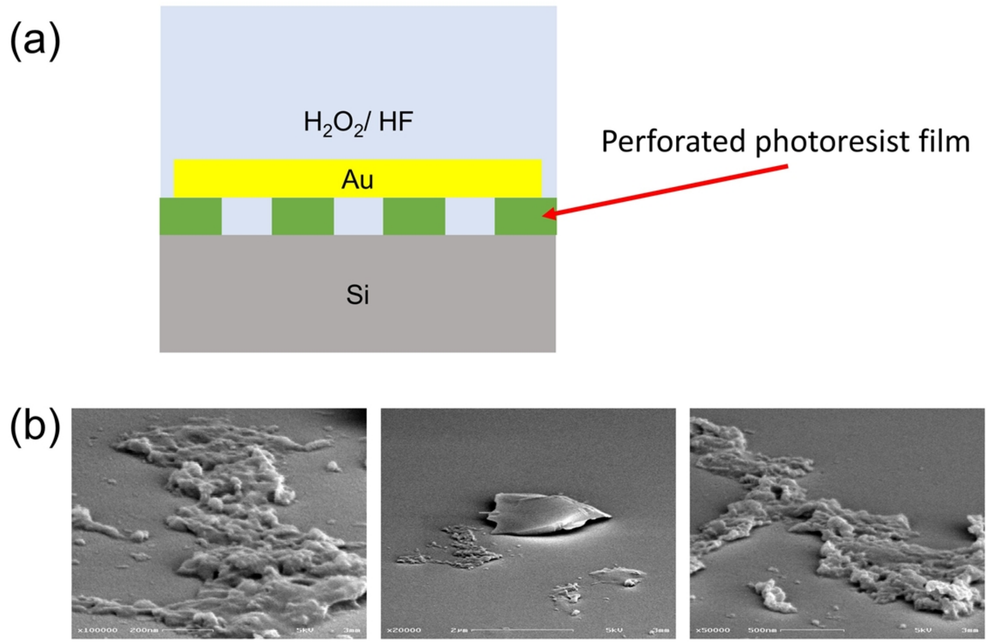

Figure S1: (a) Schematic diagram showing a macroscopic Au wire placed in close proximity with a P type Si substrate in 0.2M H_2O_2/4M HF solution, separated by a perforated photoresist film. (b) SEM images at various magnifications showing that no etching occurred after 10 min. The artifacts in the pictures are photoresist that have not been properly removed.

The images are taken around these artifacts as they assist the user in finding the right depth of field, which is difficult to do when the surface, such as in this case, is too smooth.

Verification of the Schottky Barrier Height for the Au/Si interface using the Mott-Schottky Plot

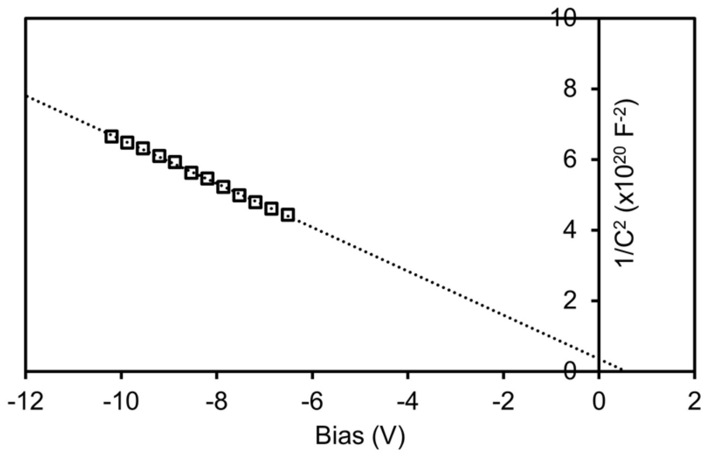

Figure S2: Mott-Schottky plot of Au/N-Si. The measurements were conducted at 1 MHz using Agilent 4980A.

From Fig. S2, it can be seen that the x-intercept of the plot, which corresponds to the built-in potential of the Au/N-Si interface, is 0.56V. Given that the doping concentration of the substrate is $10^{15}/cm^3$, the energy difference between the conduction band and the Fermi level can be calculated to be 0.26eV.[4] Therefore, according to the Mott-Schottky plot, the Schottky barrier height, ϕ_N, can be calculated to be 0.26 eV + 0.56 eV = 0.82 eV, which is exactly the same as that obtained through the J-V_a plot in the main text.

Uniformity of Etching

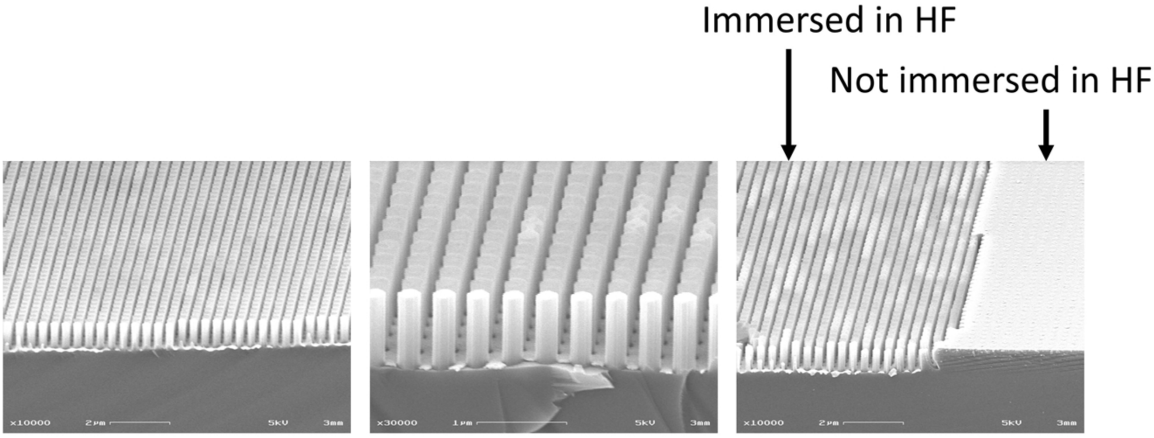

Figure S3: SEM pictures of n-Si nanowires taken at different locations along the entire length of the sample. MAAE was carried out at 1.4 mA/cm^2 for 8min, and the anodic contact was made through the perforated Au film.

The etching of the Si samples using MAAE was highly uniform, as can be seen from Fig. S3. This uniformity persists up to the boundary between the immersed and non-immersed parts of the sample. The boundary occurs because only part of the sample is immersed in the HF etching solution when the anodic contact was made through the perforated Au mesh (see Fig. 1b in main text).

P-Si, perforated Au contact

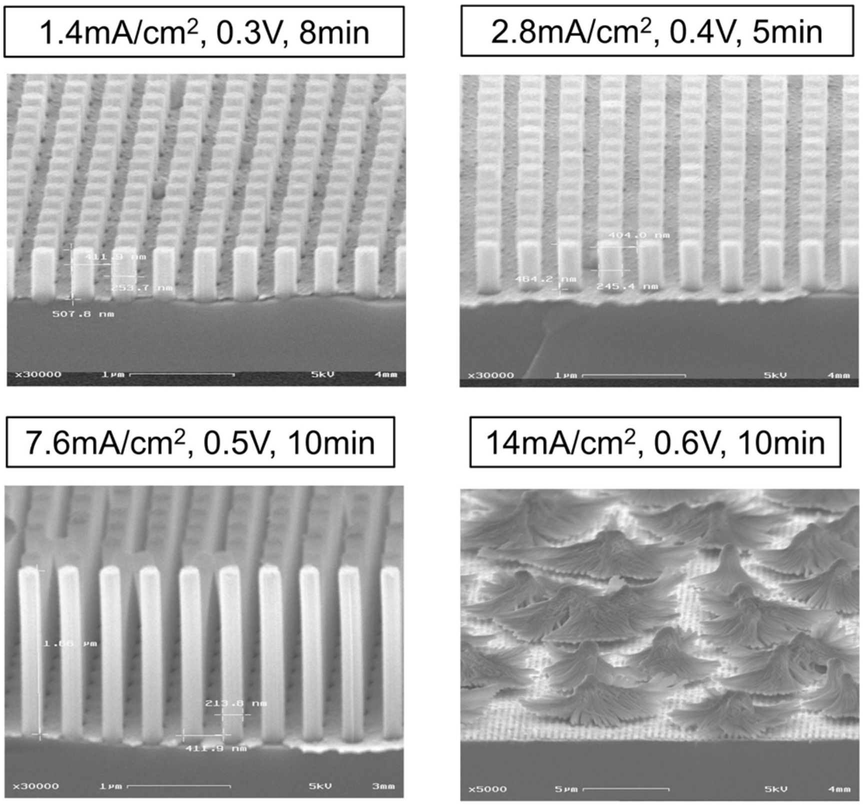

Figure S4: SEM images showing the morphology of nanowires obtained by electrochemical etching of P-type Si substrates with the anodic contact made through a perforated Au film. Etching parameters are given for each image.

P-Si, Si contact

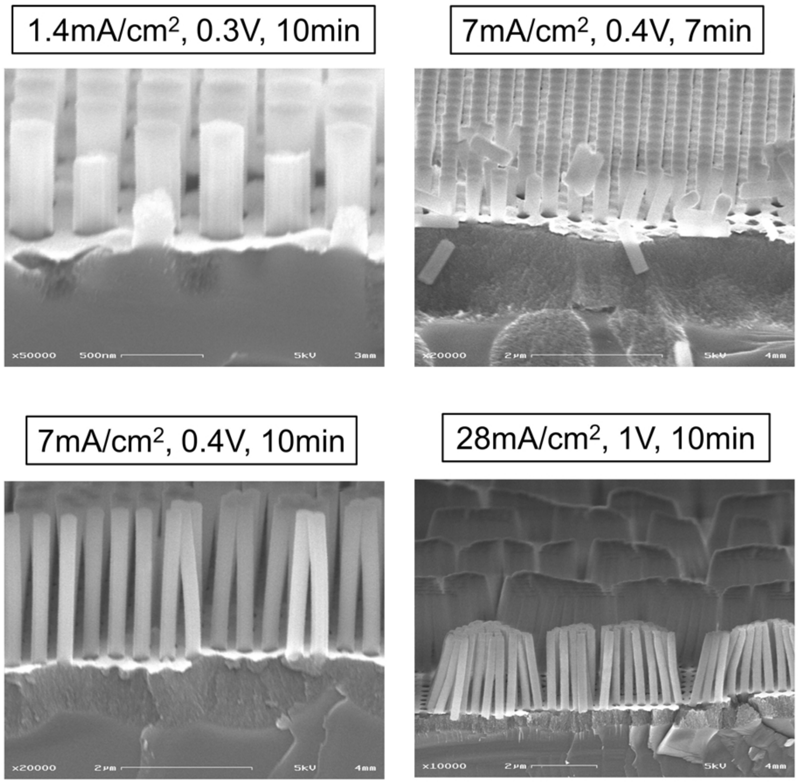

Figure S5: SEM images showing the morphology of nanowires obtained by electrochemical etching of P-type Si substrates with the anodic contact made through the Si substrate. Etching parameters are given for each image. As seen in the top right and bottom left images, the length of the nanowires and thickness of the porous layer are different even when the same etching parameters were used, suggesting that reaction rates of regular anodic etching and MAAE may be governing the overall morphology when both reactions take place simultaneously.

N-Si, Au mesh contact

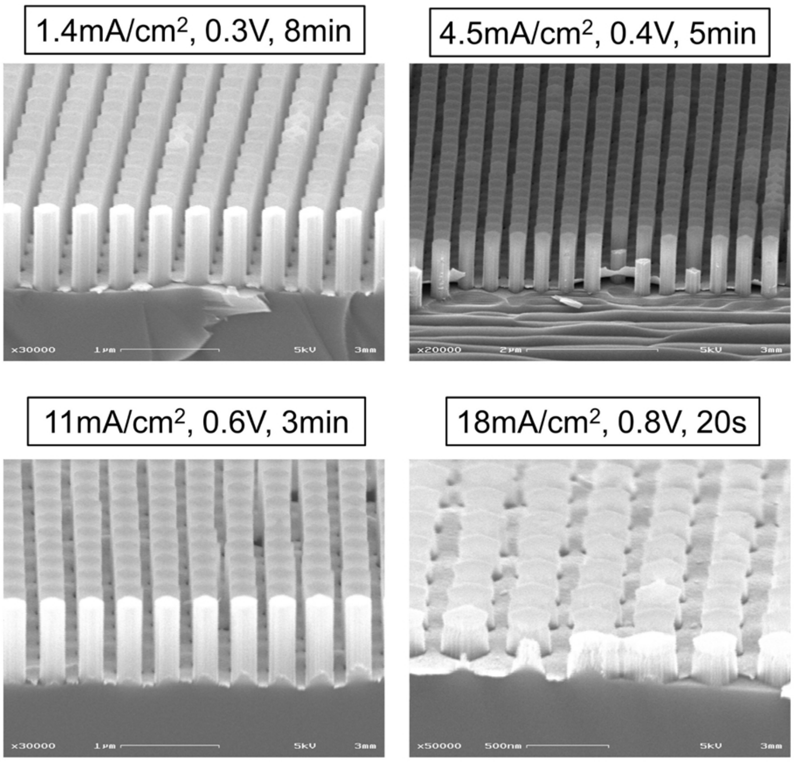

Figure S6: SEM images showing the morphology of nanowires obtained by electrochemical etching of N-type Si substrates with the anodic contact made through the perforated Au film. Etching parameters are given for each image.

N-Si, Si contact

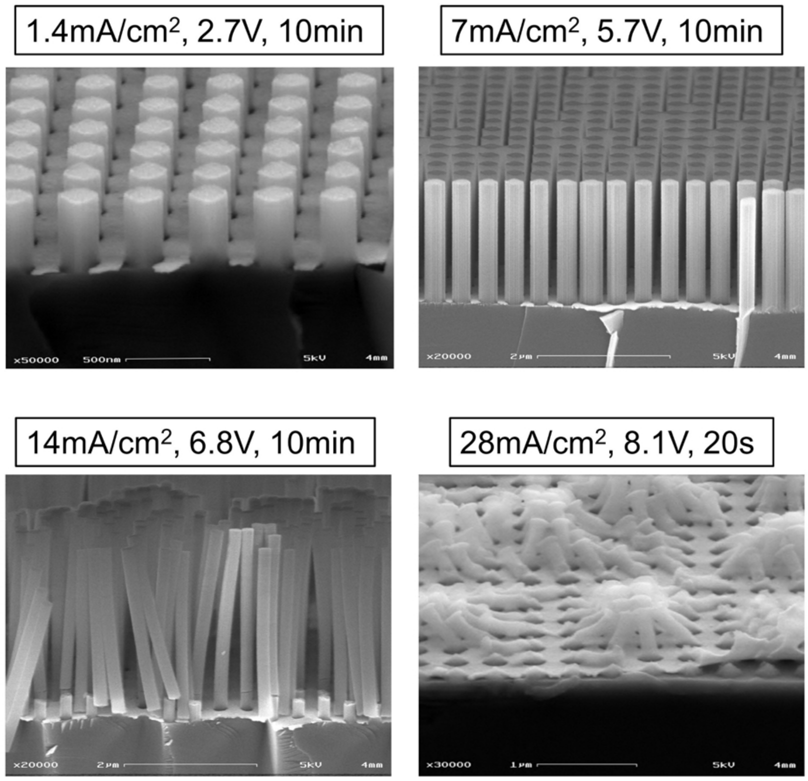

Figure S7: SEM images showing the morphology of nanowires obtained by electrochemical etching of N-type Si substrates with the anodic contact made through the Si substrate. Etching parameters are given for each image.

P+-Si, Au mesh contact

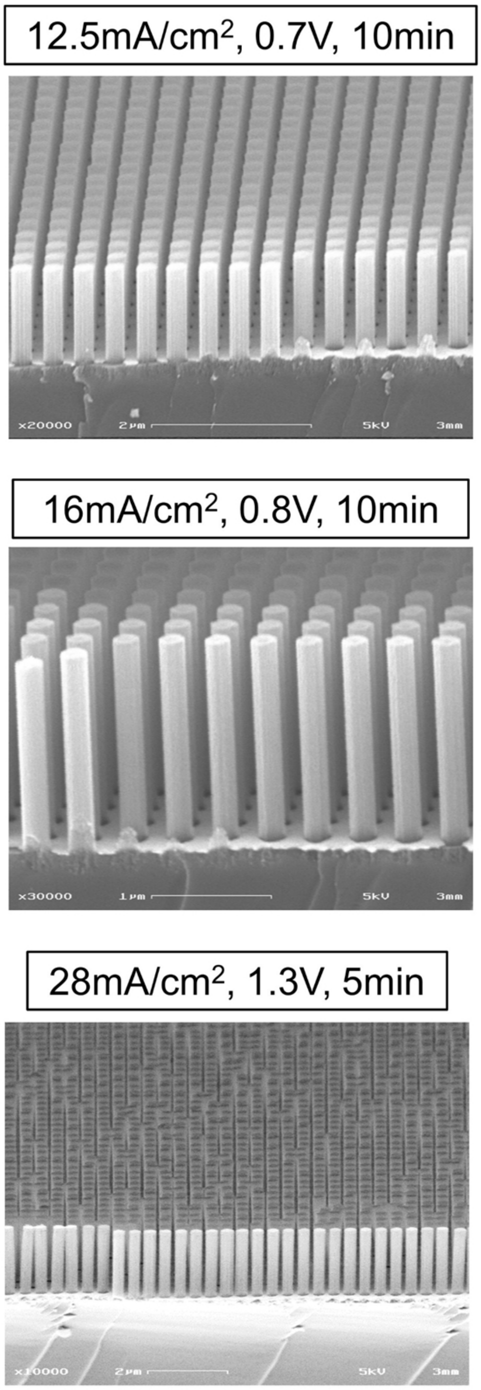

Figure S8: SEM images showing the morphology of nanowires obtained by electrochemical etching of P+-type Si substrates with the anodic contact made through the perforated Au film. Etching parameters are given for each image.

P+-Si, Si contact

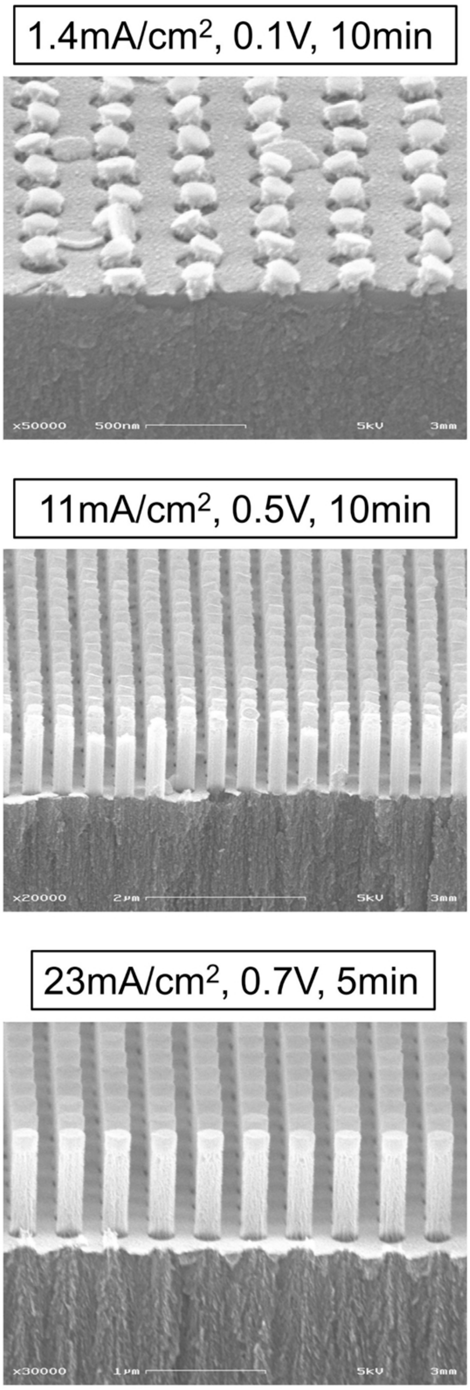

Figure S9: SEM images showing the morphology of nanowires obtained by electrochemical etching of P+-type Si substrates with the anodic contact made through the Si substrate. Etching parameters are given for each image.

N+-Si, Au mesh contact

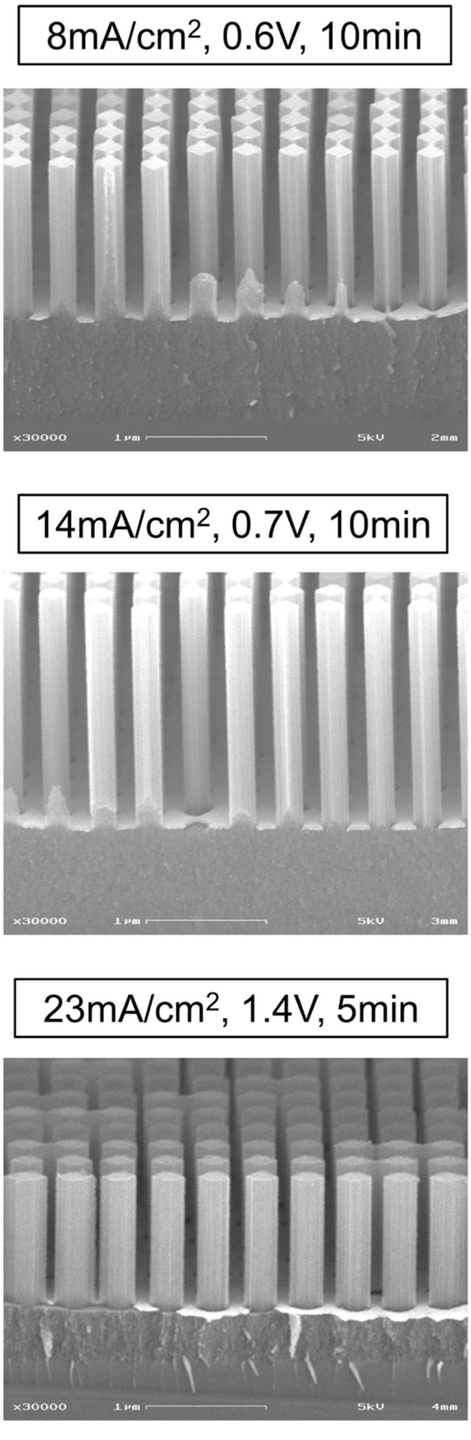

Figure S10: SEM images showing the morphology of nanowires obtained by electrochemical etching of N+-type Si substrates with the anodic contact made through the perforated Au film. Etching parameters are given for each image.

N+-Si, Si contact

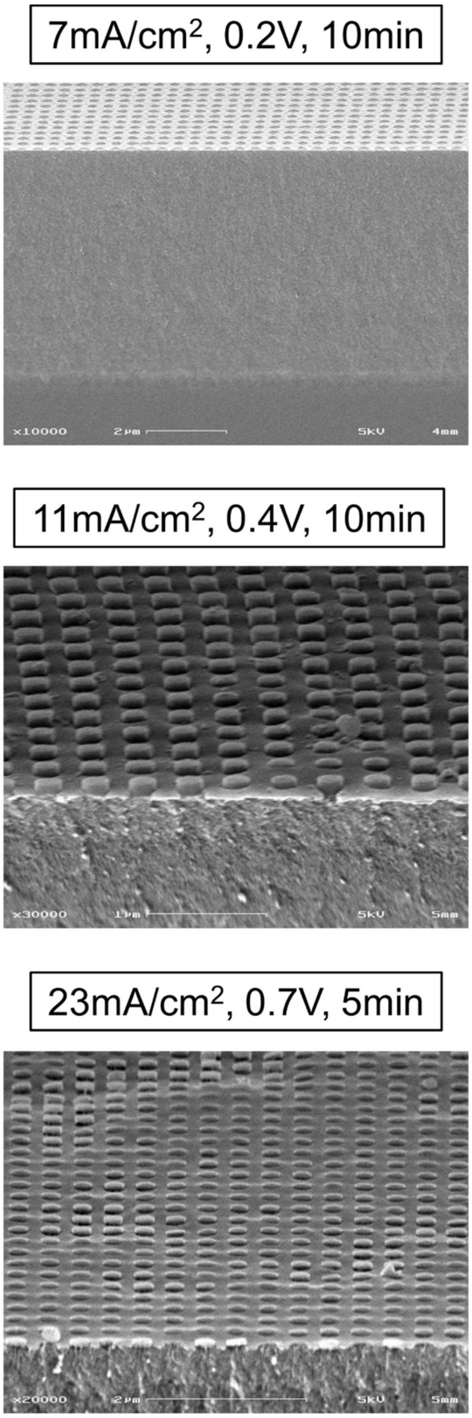

Figure S11: SEM images showing the morphology of nanowires obtained by electrochemical etching of N+-type Si substrates with the anodic contact made through the Si substrate. Etching parameters are given for each image.

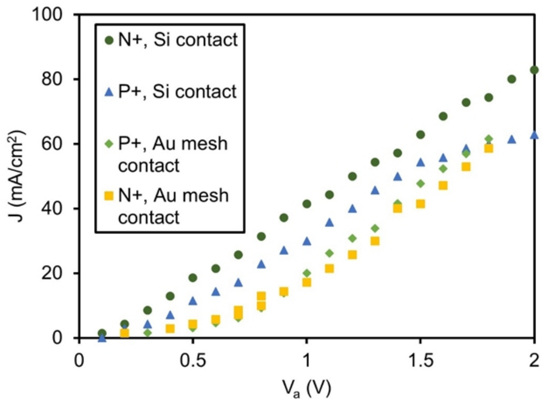

Figure S12: Current density –applied voltage, J-V_a, plots for electrochemical etching of heavily doped Si substrates.

Section II: Experiments on Si samples coated with perforated Pt films

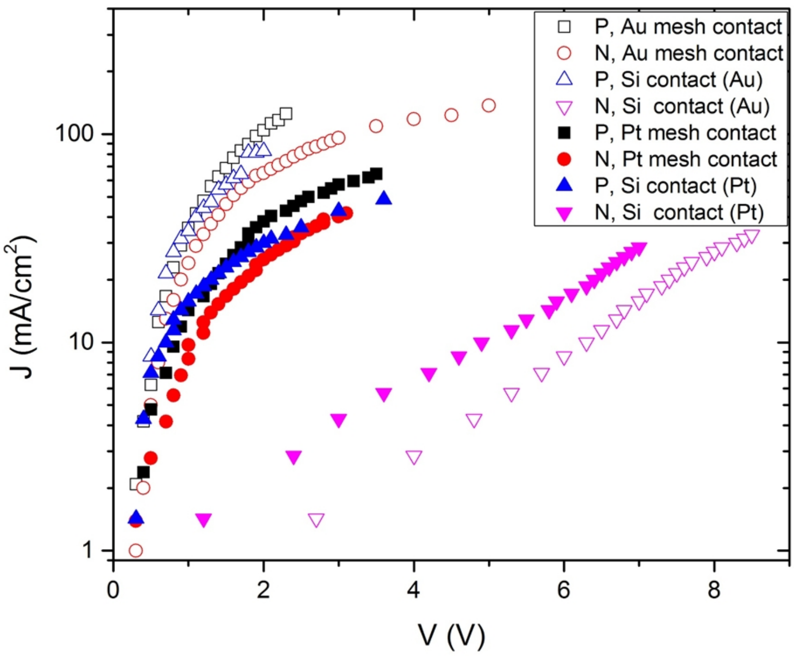

Figure S10: Current density-applied voltage, J-V_a, plots for electrochemical etching of lightly doped Si substrates, etched using Au or Pt.

To further test our model for MAAE, we replaced Au with Pt and repeated the same experiments. Au and Pt show very different catalytic activities in the conventional MACE process. However, Au and Pt behave similarly for MAAE, for all tested configurations.

Table S1: Schottky barrier heights and breakdown voltage V_{BR} (N-Si, Si contact) determined from experimental J-V_a trends obtained for Au and Pt.

Experimental configuration	Au	Pt
P-Si, metal contact	0.76eV	0.77eV
P-Si, Si contact	0.76eV	0.77eV
N-Si, metal contact	0.82eV	0.89eV
N-Si, Si contact	V_{BR}=8.5V	V_{BR}=5.6V

We determined the barrier heights for Pt using the same methods used for Au. In our model, for P-Si, the barrier mainly remains at HF-P-Si interface regardless of where the contact is, as both Pt-P-Si and Au-P-Si contacts are ohmic. Therefore, this barrier should not be affected by the metal, which is consistent with the data shown in Table S1. Both Au and Pt yield a barrier around 0.76eV for P-Si.

Both Au/N-Si and Pt/N-Si form rectifying contacts, so the voltage is mainly dropped across this metal-Si interface when anodic contact is made through the metal. Therefore, the measured barrier heights are the Schottky barrier heights for the metal-N-Si contacts. We obtained 0.82eV for Au, and 0.89eV for Pt, which are consistent with values reported in literature[5-8].

For N-Si, when anodic contact is made through Si, we assume the rate limiting step is the generation of holes through reverse bias breakdown. A quantitative analysis of the breakdown voltage for Pt, using the same method described in the main text for Au, indicates a breakdown voltage of 5.6V. This is in good agreement with the range of breakdown voltages previously reported[9].

In summary, experiments on Pt-based MAAE are consistent with our results for Au, and support the discussions of mechanisms in the text based on results on Au. The SEM images shown in Figures S11 to S14 below also show similar morphologies for Pt-based MAAE compared to Au-based MAAE.

P-Si, Pt mesh contact

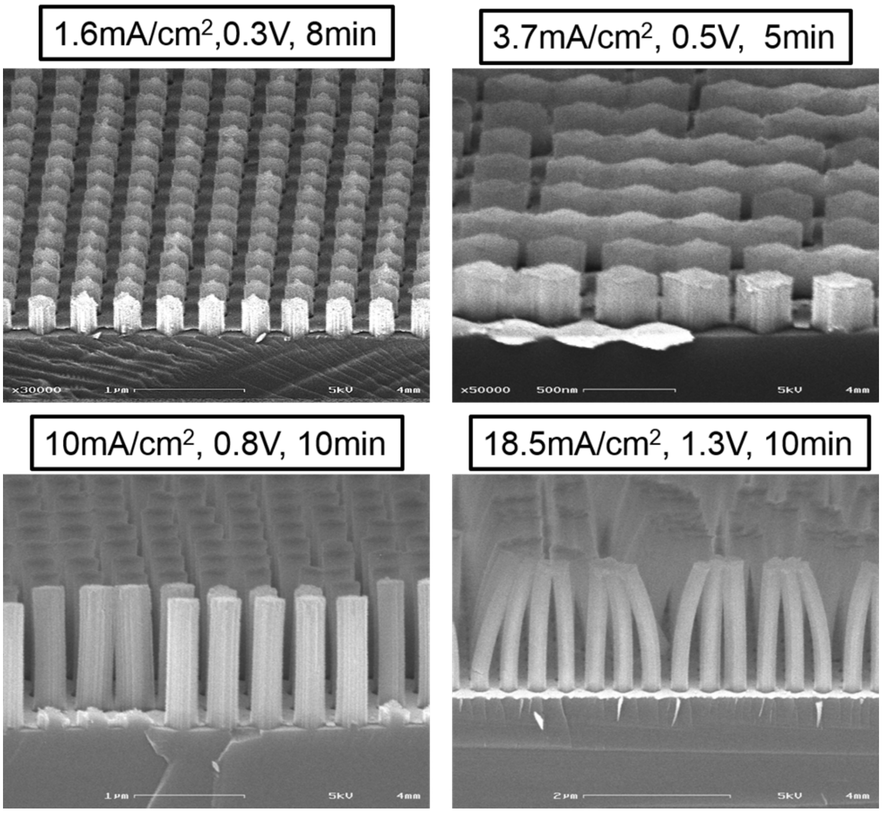

Figure S11: SEM images showing the morphology of nanowires obtained by electrochemical etching of P-type Si substrates with the anodic contact made through the perforated Pt films. Etching parameters are given for each image.

<u>P-Si, Si contact</u>

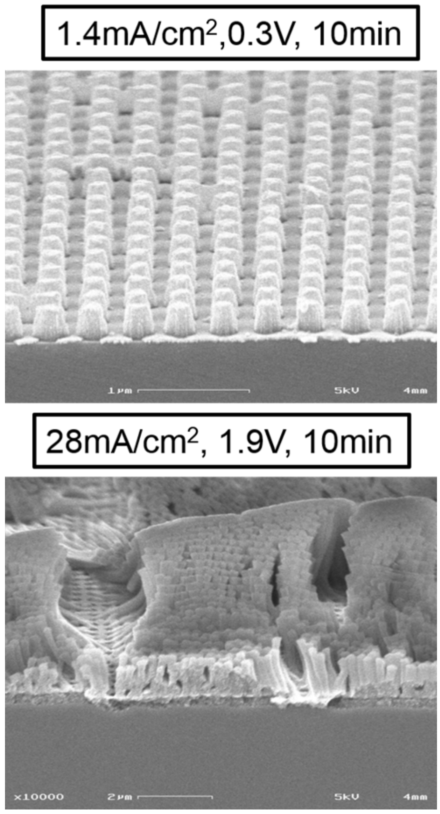

Figure S12: SEM images showing the morphology of nanowires obtained by electrochemical etching of P-type Si substrates (with Pt on the front surface), with the anodic contact made through the Si substrate. Etching parameters are given for each image.

N-Si, Pt mesh contact

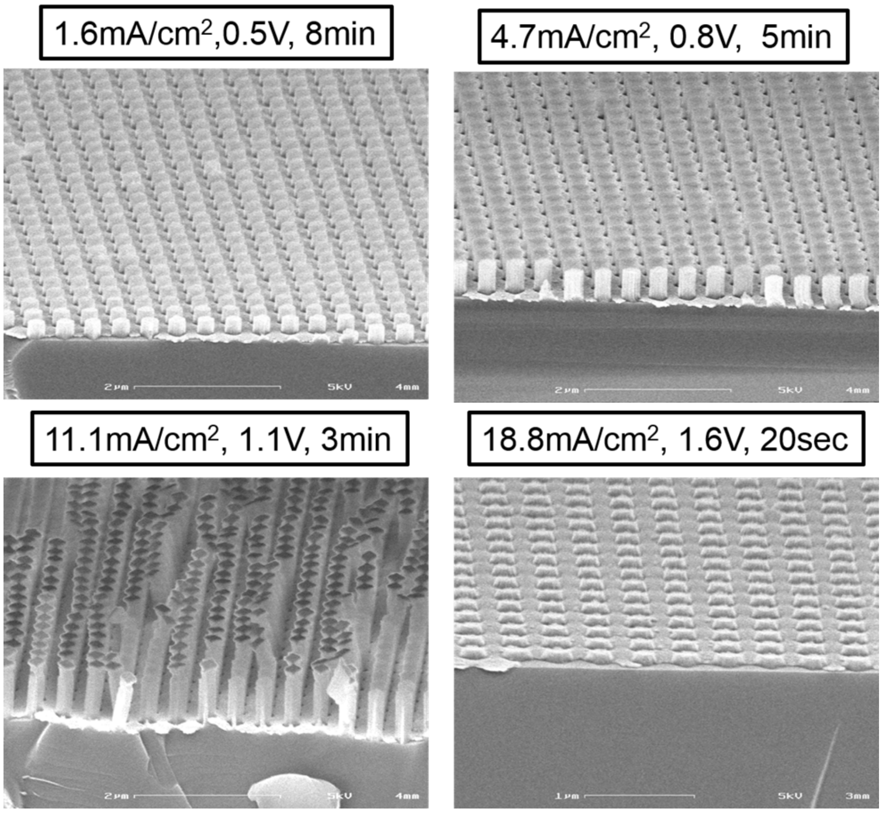

Figure S13: SEM images showing the morphology of nanowires obtained by electrochemical etching of N-type Si substrates with the anodic contact made through the perforated Pt film. Etching parameters are given for each image.

N-Si, Si contact

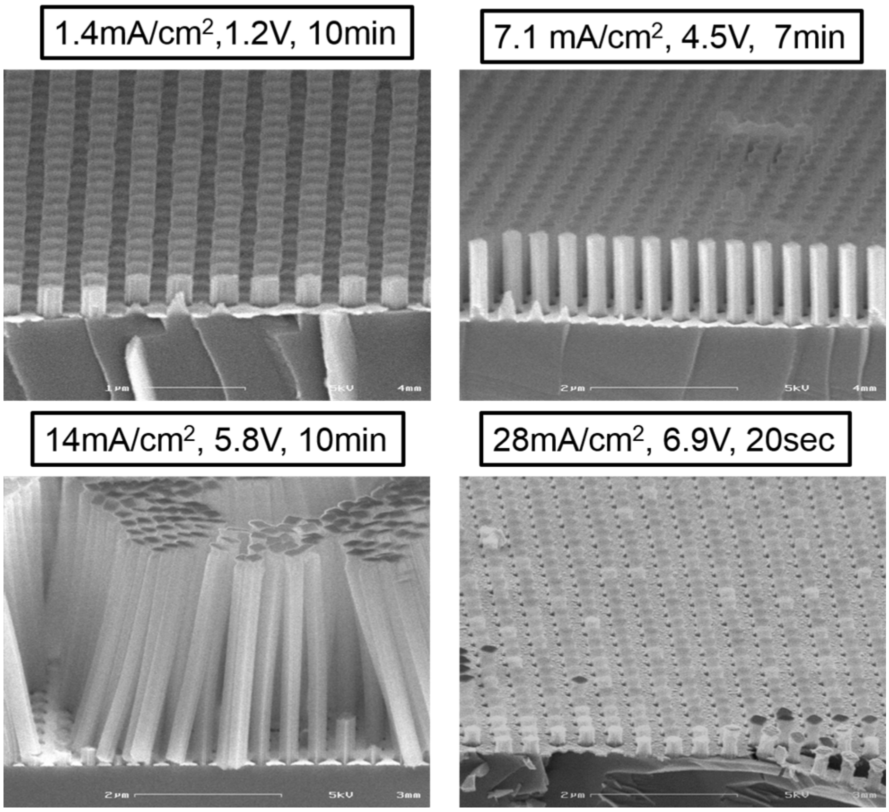

Figure S14: SEM images showing the morphology of nanowires obtained by electrochemical etching of N-type Si substrates (with Pt on the front surface) with the anodic contact made through the Si substrate. Etching parameters are given for each image.

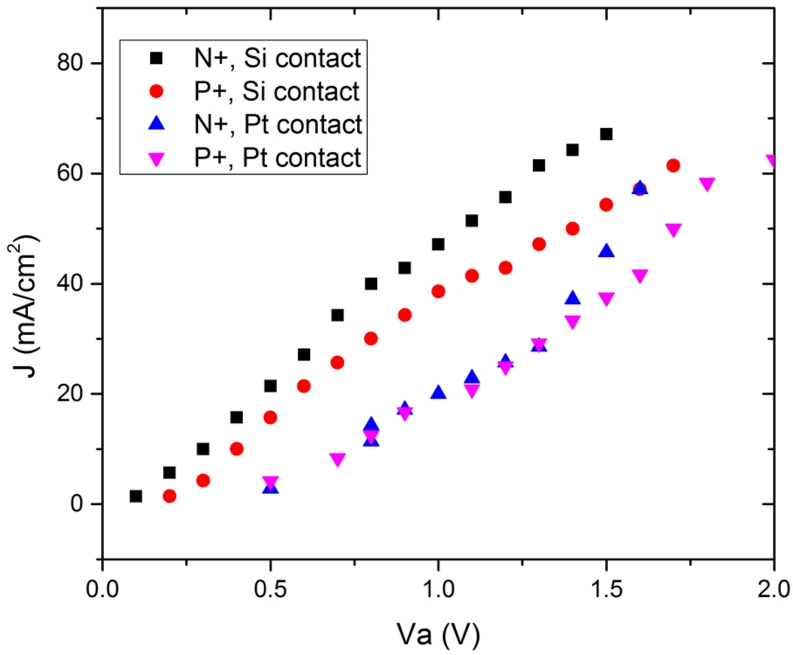

Figure S15: Current density-applied voltage, J-V_a, plots for electrochemical etching of heavily doped Si substrates with Pt.

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