

Supporting Information For:

Enhancement of Light Absorption in Silicon Nanowire Photovoltaic Devices with Dielectric and Metallic Grating Structures

*Jin-Sung Park, Kyoung-Ho Kim, Min-Soo Hwang, Xing Zhang, Jung Min Lee, Jungkil Kim,
Kyung-Deok Song, You-Shin No, Kwang-Yong Jeong, James F. Cahoon, Sun-Kyung Kim, and
Hong-Gyu Park*

This file includes:

Methods

Supplementary Figures S1–S6

Supplementary References

Methods

Fabrication of NW PV devices with Si₃N₄ or Ag gratings. Core/shell p/in Si NWs were synthesized by vapor-liquid-solid growth of a p-type core and the subsequent vapor-solid growth of intrinsic and n-type shells in a chemical vapor deposition (CVD) reactor. Over the grown NWs, a conformal layer of SiO₂ with a thickness of ~40 nm was deposited using plasma-enhanced chemical vapor deposition (PECVD). The NWs were shear-transferred, from the substrates on which they were grown, onto a 200-nm-thick Si₃N₄-coated quartz substrate. 500-nm-thick SU-8 2000.5 layer was spin-coated on the device substrate, and electron-beam lithography (EBL) was performed to define the SU-8 etch masks on the shell regions of NWs. The device substrate was dipped into BHF solution for 20 s and subsequently immersed in a KOH solution (18.0 g KOH in 60 ml H₂O and 20 ml isopropanol at 60°C) for 16–20 s. The SU-8 etch mask was removed using a UV/ozone dry stripper (Samco UV-1). Electrical contacts were selectively patterned on the n-type and p-type regions of individual NWs using EBL with the PMMA/MMA resist. The device substrate was treated with BHF for ~5 s to remove the oxide layer of the Si NW and then, ~5 nm of Ti and 300–400 nm of Pd were deposited using a thermal evaporator. In parallel, Si₃N₄ gratings were fabricated from a Si₃N₄/SiO₂/Si substrate. Grating patterns were defined using EBL and reactive ion etching (RIE). Ag gratings with a thickness of ~100 nm were fabricated on a SiO₂/Si substrate using EBL and thermal evaporation of Ag. The Si₃N₄ or Ag gratings were detached from the substrates by wet-etching of the SiO₂ layer after coating PMMA on the gratings. Then, the PMMA/grating layer floating on water was transferred to the n-type shell region of the NW PV device. The device was baked to fix the position of the grating, and the PMMA layer was removed by acetone.

Device measurements. A solar simulator (150 W, Newport Oriel) with AM 1.5G filter and calibrated 1-sun intensity was used in conjunction with a probe station (MST-4000, MS Tech) and semiconductor parameter analyzer (4156C, Agilent Technologies) to obtain the device transport characteristics. Polarization-resolved external quantum efficiency (EQE) spectra were obtained using a home-built optical setup. We used a Quartz Tungsten Halogen lamp (1000 W, Newport) as the illumination source and a spectrometer (SpectraPro 2300i, Acton Research) with a 1200 g/mm grating. An uncoated Glan-Thompson calcite polarizer (10GT04, Newport) and Si photodetector (918D-UV-OD3, Newport) were used to obtain absolute EQE spectra. The

illumination power was measured from 380 to 1000 nm in 5 nm increments through a 1.0 mm diameter circular aperture to confirm the uniformity and accuracy of the power density. The current density and absolute EQE were calculated using the photocurrent data and the projected area of the Si NWs, which was measured by SEM. All EQE spectra were measured when light was illuminated on the NWs through a transparent quartz substrate. The J - V characteristics in Figure 3b and Supporting Information Figure S5 were measured when light was illuminated on the NWs through the grating.

Numerical simulations. We used finite element method (FEM) (COMSOL Multiphysics) to calculate EQE. NWs were placed on a 200-nm-thick Si_3N_4 -coated quartz substrate. First, we calculated the absorption efficiency of the Si NWs for TE- and TM-polarized normal incident light coming through the quartz substrate. Then, EQE was obtained by multiplying the absorption efficiency by internal quantum efficiency (IQE), where IQE was assumed to be 0.7 (for the NW with Si_3N_4 grating) or 0.9 (for the NW with Ag grating). The structural parameters used in the simulations were determined based on the SEM images of the fabricated NW PV devices. For the NW with Si_3N_4 grating (Figure 2d–f and Supporting Information Figure S3d–f), the diameter of the hexagonal NW, SiO_2 outer-shell thickness, and thickness of the Si_3N_4 grating were 330, 60, and 100 nm, respectively. For the NW with Ag grating (Figure 4e–f), the NW diameter, SiO_2 outer-shell thickness, thickness of the Ag grating, and pitch of the Ag grating were 310, 70, 100, and 620 nm, respectively. The widths of individual grating grooves were half of the given pitch for both Si_3N_4 and Ag gratings. The refractive indices and extinction coefficients of Si and Ag were taken from the literature.^{S1,S2} The refractive indices of Si_3N_4 and quartz were set to 2 and 1.45, respectively.

Supplementary Figures

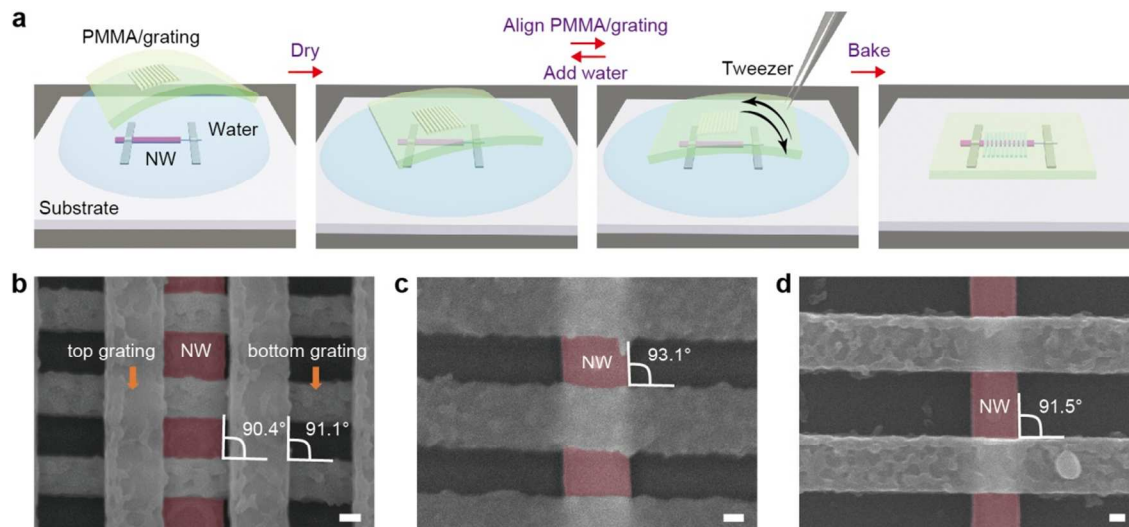


Figure S1. (a) Schematic of alignment process of gratings. The PMMA/grating layer floating on water is transferred to the substrate with the NW device. The volume of the water between the PMMA/grating and substrate is reduced by natural drying. We then slightly move the PMMA/grating layer using tweezers, to precisely adjust the relative position and angle between the NW device and grating. If the PMMA/grating layer does not move, water is added between the PMMA/grating and substrate using pipet. After repeating this fine alignment process, the position of the grating is fixed by baking the substrate on hot plate. The temperature of hot plate is slowly increased up to 230°C. (b)–(d) Magnified SEM images of Si NW PV devices (pink; false color) with Si_3N_4 gratings. We examine the devices of Figure 1d (b), Figure 2b (c) and Figure 2c (d), to measure the angles between the gratings and underlying NWs. The misalignment of the grating in angle is $< \sim 3^\circ$ with respect to the axis of the underlying NW in each device. All scale bars, 100 nm.

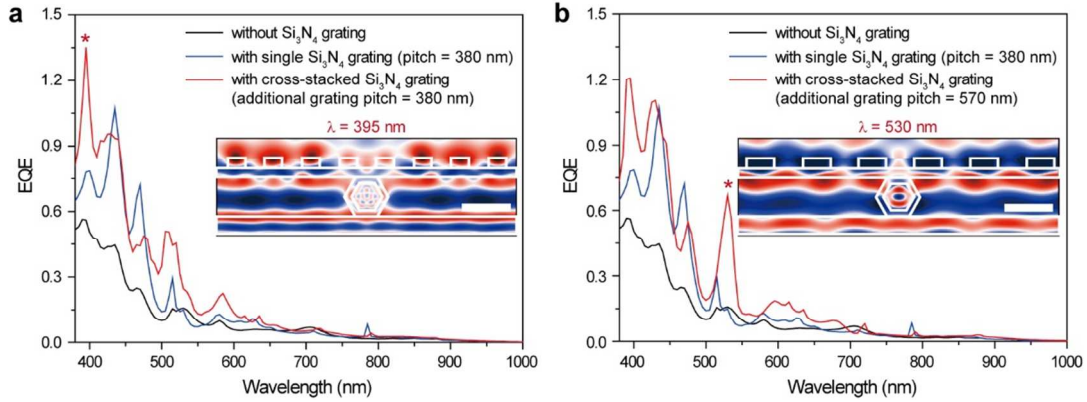


Figure S2. Calculated TE-polarized EQE spectra of a Si NW without a grating (black), a Si NW with a single Si_3N_4 grating with a pitch 380 nm (blue), and a Si NW with a vertically cross-stacked Si_3N_4 grating (red). In the cross-stacked grating, the pitches of the bottom and top gratings are 380 and 380 nm (a), and 380 and 570 nm (b), respectively. Light is incident on the NW through the Si_3N_4 -coated quartz substrate. Insets, the electric field profiles calculated at 395 (a) and 530 nm (b), which are the wavelengths denoted by *. Scale bars, 500 nm. The calculated absorption spectra of the Si NWs with cross-stacked gratings indicate enhanced light absorption compared to those of the Si NWs without grating and with single grating. In particular, a significant enhancement was observed near the wavelengths that correspond to the pitch of the top grating. The electric field profiles (insets) demonstrate that the absorption enhancement in the Si NWs with cross-stacked grating originates from the incorporation of resonant NW modes and diffracted light from the grating.

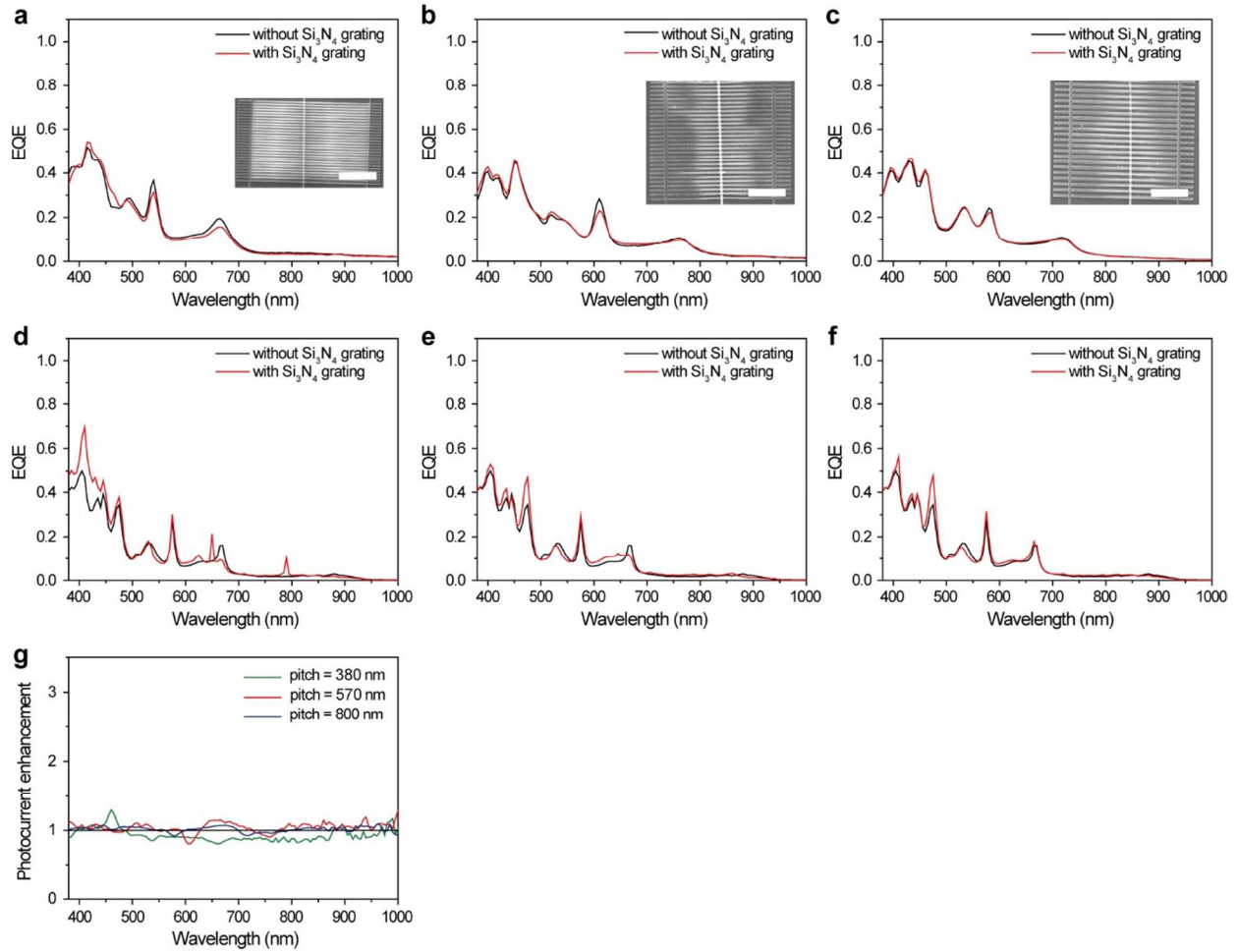


Figure S3. (a)–(c) Measured TM-polarized EQE spectra of a Si NW PV device without (black) and with (red) Si₃N₄ grating. The grating pitches and widths of the grating grooves are 380 and 190 nm (a), 570 and 320 nm (b), and 800 and 380 nm (c), respectively. Insets show SEM images of the Si₃N₄ gratings on Si NW PV devices. All scale bars, 5 μ m. The NW diameters are 290 (a), 340 (b), and 300 nm (c). In each panel, the measurements were performed using the same NW PV device before and after transferring the grating. (d)–(f) Calculated TM-polarized EQE spectra of a Si NW PV device without (black) and with (red) the Si₃N₄ grating. The grating pitches are 380 (d), 570 (e), and 800 nm (f). The width of an individual grating groove is half of the given pitch. (g) Measured photocurrent enhancement as a function of the wavelength for the grating pitches of 380 (green), 570 (red), and 800 nm (blue). The photocurrent enhancement is defined as the ratio of the EQE of a NW PV with grating to that of a bare NW PV. Data were taken from Figure S3a–c.

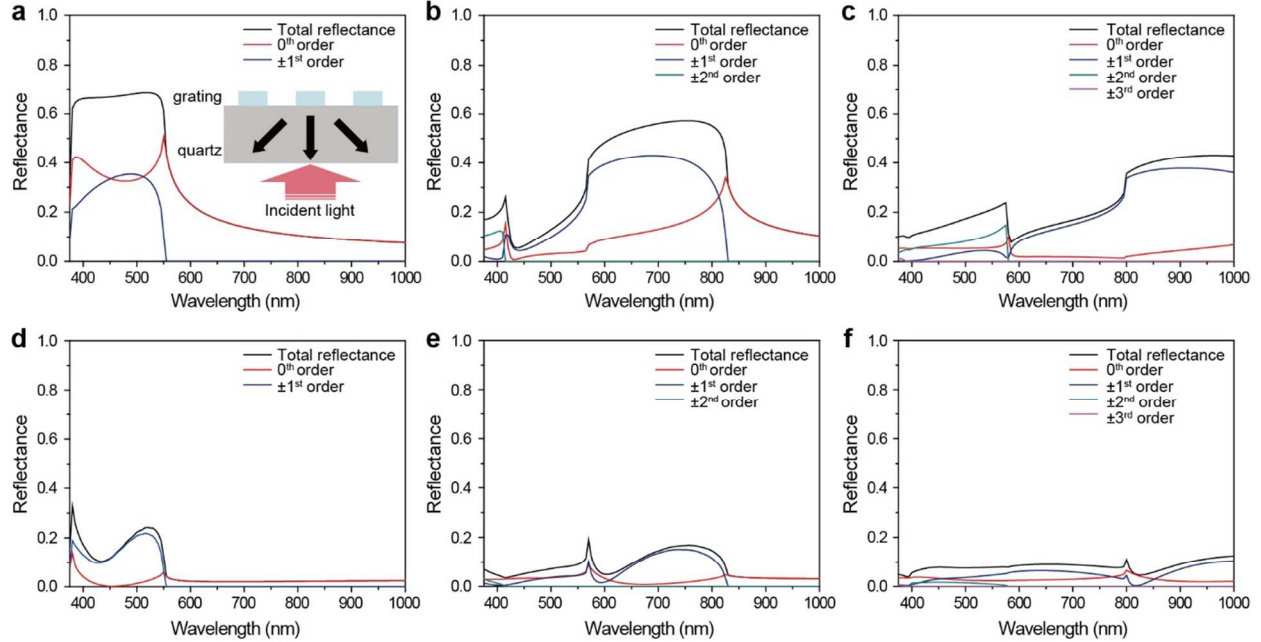


Figure S4. Calculated reflectance spectra of the diffracted light by the Si_3N_4 grating on a quartz substrate. Vertically incident TE-polarized (a–c) and TM-polarized (d–f) light is injected into the grating through the quartz substrate (Figure S4a, inset). Grating pitches of 380 (a, d), 570 (b, e) and 800 nm (c, f) were used. We calculated the total reflectance of diffraction (black), which is the ratio of the total reflected power by the grating to that of the incident power. We also calculated the reflectance of the diffracted light for a given order, which is the ratio of the reflected power of a given order to that of the incident power. The 0th order (red), the sum of ± 1 st order (blue), the sum of ± 2 nd order (green), and the sum of ± 3 rd order (purple) reflectances are shown. The 2nd and 3rd order reflectance for a pitch of 380 nm (a, d) and the 3rd order reflectance for a pitch of 570 nm (b, e) are zero in the visible spectral range. We note that the relatively high reflectance of the diffracted light is observed for the TE polarization and the wavelength of the maximum diffraction depends on the grating pitch.

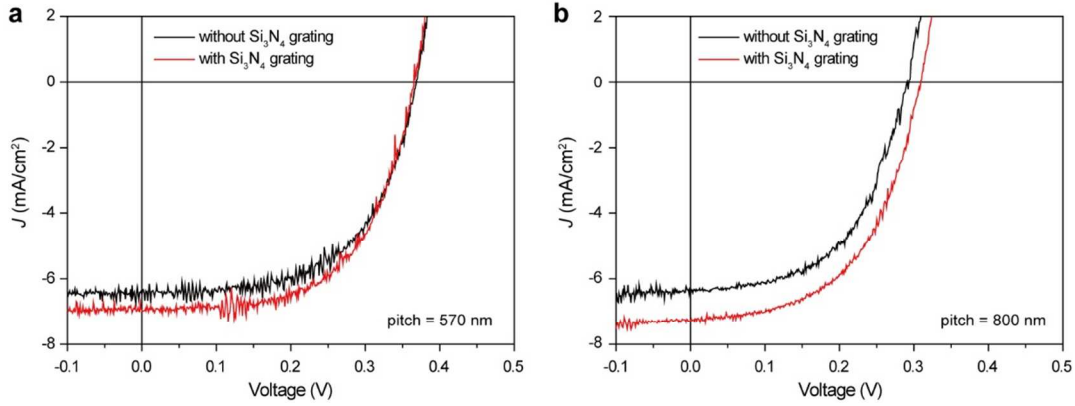


Figure S5. Measured current density J versus voltage characteristics, under 1-sun AM 1.5G illumination, for a Si NW PV device without (black) and with (red) the Si_3N_4 grating. The NW diameters are 340 (a) and 300 nm (b). The grating pitches are 570 (a) and 800 nm (b). (a) The J_{SC} values are 6.48 and 6.95 mA/cm^2 without and with the grating, respectively. V_{OC} is 0.37 V in both cases. (b) The J_{SC} values are 6.51 and 7.26 mA/cm^2 and the V_{OC} values are 0.29 and 0.31 V without and with the grating, respectively.

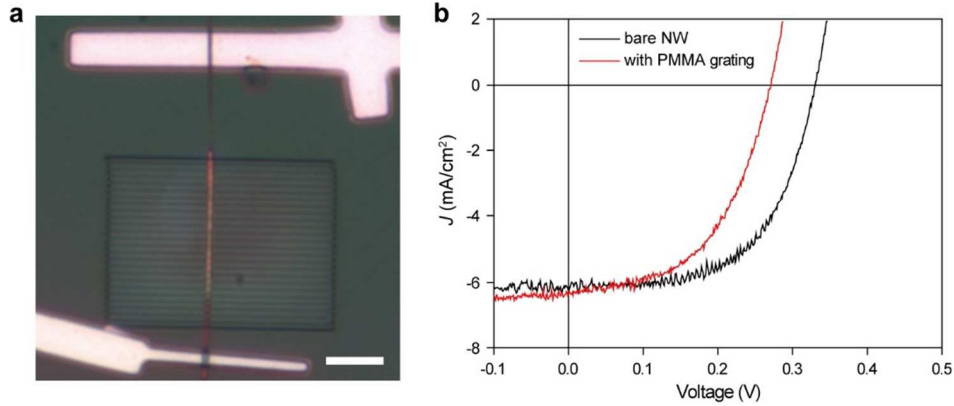


Figure S6. A Si NW PV device with a PMMA grating. (a) Optical micrograph of the PV device with a PMMA grating. The grating was fabricated by electron-beam lithography. The NW diameter, grating pitch, and width of the grating groove are 290, 580, and 320 nm, respectively. The PMMA thickness is ~ 500 nm. Scale bar, 5 μm . (b) The measured current density J versus voltage characteristics, under 1-sun AM 1.5G illumination, for a Si NW PV device without (black) and with (red) the PMMA grating. The J_{SC} values are 6.26 and 6.38 mA/cm^2 without and with the grating, respectively. V_{OC} decreased significantly from 0.33 to 0.27 V. Such deterioration of the electrical property is mainly attributed to the damage of the NW during the fabrication of large-area grating by high-dose electron-beam lithography.

Supplementary References

S1. Green, M. A. *Sol. Energy Mater. & Sol. Cells* **2008**, *92*, 1305–1310.

S2. Johnson, P. B.; Christy, R. W. *Phys. Rev. B* **1972**, *6*, 4370–4379.