Supporting Information:

Self-Patterned Nanoparticle Layers for Vertical Interconnects: Application in Tandem Solar Cells

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Methods

Thin-film Si tandem cell deposition

Boron-doped ZnO (ZnO:B) front electrodes were deposited on clean glass substrates by means of low-pressure chemical vapor deposition (LP-CVD), using diethylzinc, diborane, and water as precursors. To smoothen the rough surfaces of the as-grown ZnO:B layers with thicknesses of 2.5, 3.5, and 5 μm , the layers were treated with an Ar plasma for 4, 7, and 10 minutes, respectively. The amorphous silicon (a-Si) component cell was deposited on top of the ZnO:B front electrode by plasma-enhanced CVD (PE-CVD) in a reactor with a parallel plate configuration. This cell comprised a p-type hydrogenated microcrystalline Si ($\mu\text{c-Si:H}$) layer, a p-type a-SiC:H window layer, an intrinsic a-Si:H layer with a thickness of 180–230 nm, an n-type a-Si:H layer, and an n-type $\mu\text{c-Si:H}/\mu\text{c-SiO}_x\text{:H}$ layer. The SiO_2 nanoparticle (NP) intermediate reflector layer was deposited on top of the a-Si cell by spin coating from a stable dispersion containing SiO_2 NPs ~ 40 nm in diameter. By tuning the spin speed, the thickness of the SiO_2 NP layer could readily be adjusted. Thick SiO_2 NP layers were obtained at a spin speed of 1000 rpm, thin SiO_2 NP layers at 5000 rpm. In both cases, the spin coating duration was set to 60 s. The samples were then annealed in air on a hot plate at 150 $^\circ\text{C}$ for 10 minutes to completely dry the SiO_2 NP layer. The $\mu\text{c-Si}$ cell was deposited in an industrial PE-CVD reactor with a parallel-plate configuration, either on top of the SiO_2 NP layer, or directly on the a-Si cell for reference cells without an intermediate reflector. The layer stack of the $\mu\text{c-Si}$ cell consisted of a p-type $\text{SiO}_x\text{:H}$ layer, a 1.2- to 1.6- μm -thick intrinsic $\mu\text{c-Si:H}$ layer, and an n-type $\mu\text{c-SiO}_x\text{:H}/\mu\text{c-Si:H}$ layer. Finally, a 2.5- μm -thick ZnO:B rear electrode was deposited by LP-CVD. The photoactive area with a size of 1.2 cm^2 was defined by lift-off of the ZnO:B rear electrode and SF_6/O_2 reactive-ion etching of the Si layers.

Characterization

The short-circuit current density (J_{sc}) of thin-film Si tandem cells was determined from external quantum efficiency (EQE) measurements by convolution of the EQE curves with the AM1.5g solar spectrum. The EQE curves of the a-Si and $\mu\text{c-Si}$ component cells were measured without applying a bias voltage, utilizing near-infrared and blue bias light, respectively, to generate a high photocurrent in the component cell not being measured. The current-density–voltage ($J(V)$) characteristics, from which the open-circuit voltage (V_{oc}) and fill factor (FF) were obtained, were measured using a four-lamp class AAA WACOM sun simulator (WXS-220S-L2 AM1.5G) with an AM1.5g irradiance spectrum at 1000 Wm^{-2} . A detached white dielectric back reflector was mounted behind the ZnO rear electrode for all $J(V)$ and EQE measurements. $J(V)$ measurements were performed with a black mask to define an illuminated area of 1.05 cm^2 . Current-matching measurements were performed with the same solar simulator, in combination with a 15% intensity filter and light-emitting diodes to replace the removed light with either blue or near-infrared light [M. Bonnet-Eymard et al., *Sol. Energy Mater. Sol. Cells* 117, 120–125 (2013)]. Total reflectance measurements were conducted using a spectrophotometer (Perkin Elmer Lambda 900) equipped with an integrating sphere. The refractive index of SiO_2 NP layers spin-coated on polished Si wafers was determined by variable-angle spectroscopic ellipsometry (Horiba Jobin Yvon UVISSEL). Sample cross sections were prepared for scanning electron microscopy (SEM) analysis by using ion milling polishing (Hitachi IM4000). SEM observations were performed on a Zeiss Merlin with an in-lens detector and an acceleration voltage of 2 kV. The SiO_2 NP size distribution was determined from top-view SEM

images (JEOL JSM-7500 TFE) by grain analysis using Gwyddion 2.30. Conductive atomic force microscopy (c-AFM) with a Dimension ICON (Bruker) equipped with a PeakForce TUNA module was used to map the conductivity of the surface of an a-Si cell coated with SiO₂ NPs. SCM-PIT c-AFM tips were used (Bruker, spring constant: 1-5 N m⁻¹, tip radius: 20 nm, coated on the front and back side with platinum/iridium). In the PeakForce TUNA mode, force curves were acquired at a frequency of 1 kHz and the sample was scanned at a rate of 0.5 Hz (scan size: 10 μm × 10 μm, 512 lines). The ScanAsyst option was selected to automatically control the integral and proportional gains and the peak force set point (typical value: 30 nN). For current measurements, a bias of +1 V was applied between the tip and the sample. During each force curve, the contact-averaged current was recorded (average current when the tip is in contact with the surface, from the snap-in until the pull-off). The image was then treated to obtain a 3D superposition of the topography and the contact current map.

Refractive index of the SiO₂ NP layer

Figure S1: Real (n) and imaginary (k) parts of the refractive index of a SiO₂ NP multilayer deposited by solution processing on a polished Si wafer, measured using variable-angle spectroscopic ellipsometry.

Influence of the ZnO front electrode thickness

The J_{a-Si} and $J_{\mu c-Si}$ of tandem cells with 2.5-, 3.5-, and 5-μm-thick ZnO front electrodes are shown in Figure S2a. The EQE measurements used to determine these current densities are shown in Figure S3. J_{a-Si} is strongly enhanced for tandem cells with SiO₂ NP layers, confirming that these layers act as efficient intermediate reflectors. With increasing ZnO front electrode thickness the SiO₂ intermediate reflectors become less effective, resulting in a smaller boost of J_{a-Si} . This can be explained by the fact that for the same spin coating conditions a smaller percentage of the a-Si cell surface will be covered by the NPs when the surface feature size increases, leading to less efficient reflection. However, when the surface features are too small, the complete a-Si cell surface is covered by the SiO₂ NPs at low spin speeds,

limiting the possibilities to adjust the intermediate reflector's optical properties by tuning the NP layer thickness.

The $\mu\text{c-Si}$ material growth is strongly influenced by the substrate morphology and, hence, the ZnO front electrode thickness. This is shown in Figure S2b for 2.5-, 3.5-, and 5- μm -thick ZnO front electrodes. The V_{oc} of all tandem cells decreases with increasing ZnO layer thickness. However, for all substrates, the SiO_2 NP intermediate reflectors leads to an increased V_{oc} , confirming the enhanced electrical performance of the $\mu\text{c-Si}$ component cell upon surface smoothing. The V_{oc} enhancement is stronger for the thicker SiO_2 NP layer, which leads to high V_{oc} values even for very rough substrates.

Figure S2: a) Current densities of the component cells of a-Si (230-nm-thick intrinsic layer)/ $\mu\text{c-Si}$ (1.6- μm -thick intrinsic layer) tandem solar cells, obtained from EQE measurements. Tandem devices on ZnO front electrodes with thicknesses of 2.5, 3.5, and 5 μm , without an intermediate reflector (IR), with a thin SiO_2 NP layer, or with a thick SiO_2 NP layer are compared. b) V_{oc} of the tandem cells presented in (a).

Figure S3: EQE spectra of a-Si (230-nm-thick intrinsic layer)/ $\mu\text{c-Si}$ (1.6- μm -thick intrinsic layer) tandem cells without an intermediate reflector, with a thin SiO_2 NP layer, or with a thick SiO_2 NP layer, for ZnO front electrode thicknesses of a) 2.5, b) 3.5, and c) 5 μm .

Light-induced degradation

Figure S4: Normalized efficiency decay curves of a-Si/ μ c-Si tandem solar cells with an epoxy/glass encapsulation under light soaking (AM1.5g illumination at 1 sun intensity, 50 °C). All three cells—the cell without an intermediate reflector and the cells with either a thin or a thick SiO₂ NP intermediate reflector layer—show a similar relative decay. The cells used for these stability tests feature thinner a-Si (180 nm) and μ c-Si (1.2 μ m) component cells than the cells presented in the main text (230 nm and 1.6 μ m, respectively). Therefore, their light-soaking stability is slightly higher (~7% relative degradation instead of ~10%).