Supporting Information

Plasmonically Enhanced Spectral Upconversion for Improved Performance of GaAs Solar Cells under Nonconcentrated Solar Illumination

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1. Supplementary Methods

Fabrication of Ultrathin GaAs Microscale Solar Cells. Epitaxial stacks of ultrathin GaAs solar cells were grown on a (100) semi-insulating wafer by molecular beam epitaxy (MBE)[1]. The preparation of ultrathin GaAs microcells started with the formation of an n-type metal contact (Pd/Ge/Au = 5 nm/35 nm/80 nm) by electron-beam evaporation (Temescal) and liftoff process. Active cell areas (~500 × 500 μm^2) were defined by photolithography (AZ1518, Merck KGaA) and successive wet chemical etching of n^+-GaAs top contact layer in a mixture (4:1, by volume) of citric acid (150 g of citric acid monohydrate (≥ 99.0%, Sigma-Aldrich) in 124.5 mL deionized (DI) water) and hydrogen peroxide (H_2O_2, 30-32%, Macron), n-$Al_{0.4}Ga_{0.6}As$ window in citric acid /H_2O_2 (20:1, by volume), and n-GaAs (50 nm) / p-GaAs (150 nm) in citric acid / H_2O_2 (4:1, by volume). Subsequently, a recessed p-type contact (~240 × 40 μm^2) was made within the cell boundary by depositing metals (Pt/Ti/Pt/Au = 10 nm/40 nm/10 nm/80 nm) on the $Al_{0.3}Ga_{0.7}As$ back-surface field layer and thermal annealing (175°C in N_2 atmosphere, 1 h), followed by the formation of additional mesa structures (~580 × 580 μm^2) to isolate individual microcells. The selective etching of $Al_{0.95}Ga_{0.05}As$ sacrificial layer was performed in HCl/DI water (1:6, by volume) with a photoresist anchor structure and etch holes located outside of the active junction area. After the completion of undercut etching microcell were individually released by an elastomeric stamp with relief features (~600 × 600 μm^2) made of PDMS (Sylgard 184, Dow Corning), followed by wet chemical etching of p^+-GaAs in citric acid/H_2O_2 (4:1, by volume).

Fabrication of Plasmonically Engineered Upconversion Solar Module. A plasmonic reflector consisting of hole-post hybrid silver nanostructure was fabricated through previously reported procedures[2, 3]. Starting with the soft-imprinting of hexagonally periodic nanohole arrays (p_{hole} =

~700 nm, h_{hole} = ~300 nm, D_{hole} = ~570 nm) on a 1.5-μm-thick thermally curable polymer (SU-8 2, Microchem) spin-coated on a silicon substrate, the hole-post hybrid silver nanostructure (p_{hole} = ~700 nm, h_{hole} = ~550 nm, D_{hole} = ~490 nm, h_{post} = ~260 nm, D_{post} = ~340 nm) was formed by angled (~15°) electron beam deposition of Cr/Ag (15 nm/550 nm). β-phase $NaYF_4$: Yb^{3+}, Er^{3+} upconversion nanocrystals in toluene solution (~3 wt%) prepared by previously reported procedures[2] was spin-coated (1000 rpm, 10 s) on a plasmonic reflector and baked on a hot plate (70°C, 30 s), followed by spin-coating of PMMA (M_n = 996,000 g/mol, Sigma-Aldrich, ~13.7 wt% in toluene, 3000 rpm, 30 s) and baking (120°C, 30 min). Subsequently, thermally curable epoxy (SU-8 2005) was spin-coated (3000 rpm, 30 s) as a transparent waveguiding layer, followed by UV exposure (UVP B-100AP, 5 min) and baking (95°C, 5 min; 120°C, 30 min). Retrieved micro cells with an etched bottom contact were then printed on the composite substrate using a thin (~1 μm) photocurable adhesive. To implement a condition of confined illumination, Cr/Au (10 nm/200 nm) was deposited by electron beam evaporation, followed by photolithography and wet chemical etching (gold etchant TFA, Transene; CR-7, KMG Chemicals).

Optical and Photovoltaic Characterization. Total (*i.e.* specular + diffuse) reflectance spectra of plasmonic substrates were obtained by a UV/Vis spectrophotometer (LAMBDA 950, PerkinElmer) with an angle of incidence of 8˚, where a silver mirror was used as 100% reflectance standard. Photoluminescence spectra of upconversion nanocrystals were measured using 968 nm continuous-wave laser (average power = 1.5 W, intensity = 12 W/cm^2), where the excitation light was illuminated at near-normal incidence (< 5°) to the sample through a collimating lens (EFL = 10 mm). The emitted light was filtered by a 750 nm short-pass filter (Thorlabs) and collected by a spectrometer (Acton SP2500, Princeton Instruments). The current-voltage characteristics of GaAs microcells were obtained by a semiconductor parameter analyzer (4156C, Agilent technologies) and a full-spectrum solar simulator (94042A, Oriel).

Optical Modeling. Reflectance spectra, as well as the local electric-field intensity distribution of hole-post hybrid silver nanostructures were numerically calculated by a finite-difference time-domain method (FDTD, Lumerical Solutions) through procedures adapted from our previous work[2, 3]. For the reflectance spectra with 8° incident light, a BFAST (broadband fixed angle source technique) was employed to implement a light source, and the reflectance values were obtained using a broadband frequency-domain power monitor. The refractive index of surrounding medium were fixed at 1 and 1.49, for the case of in air and in PMMA, respectively.

2. Supplementary Figures

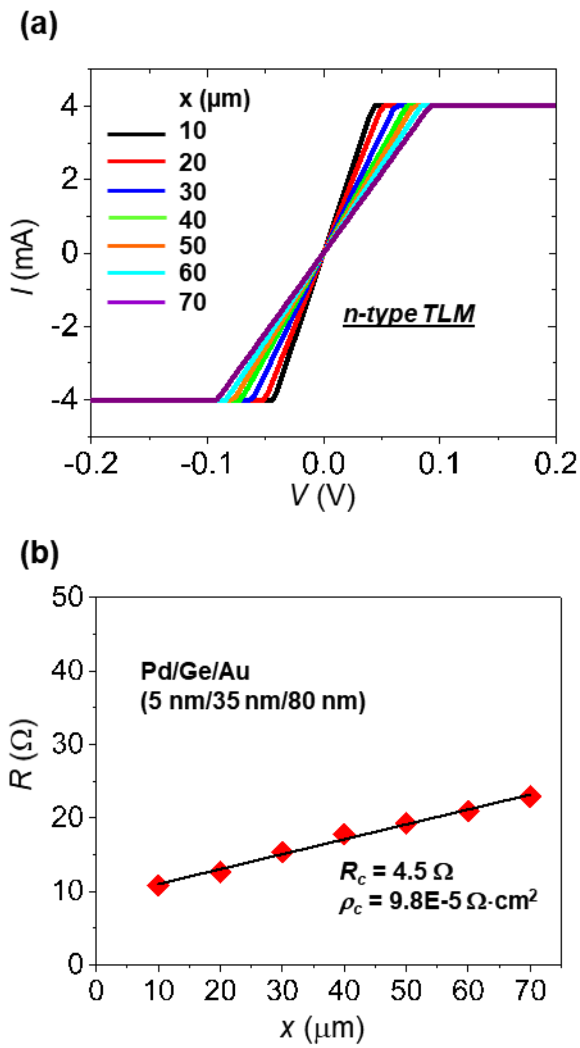

Figure S1. (a) Representative current (I)-voltage (V) curves measured between metal pads with varying distances (x), and (b) total resistance (R) as a function of x from standard transmission line model (TLM) measurements, where Pd/Ge/Au (5 nm/35 nm/80 nm) were deposited on n^+-GaAs contact layer and annealed under 175°C, 60 min in 100% N_2 atmosphere.

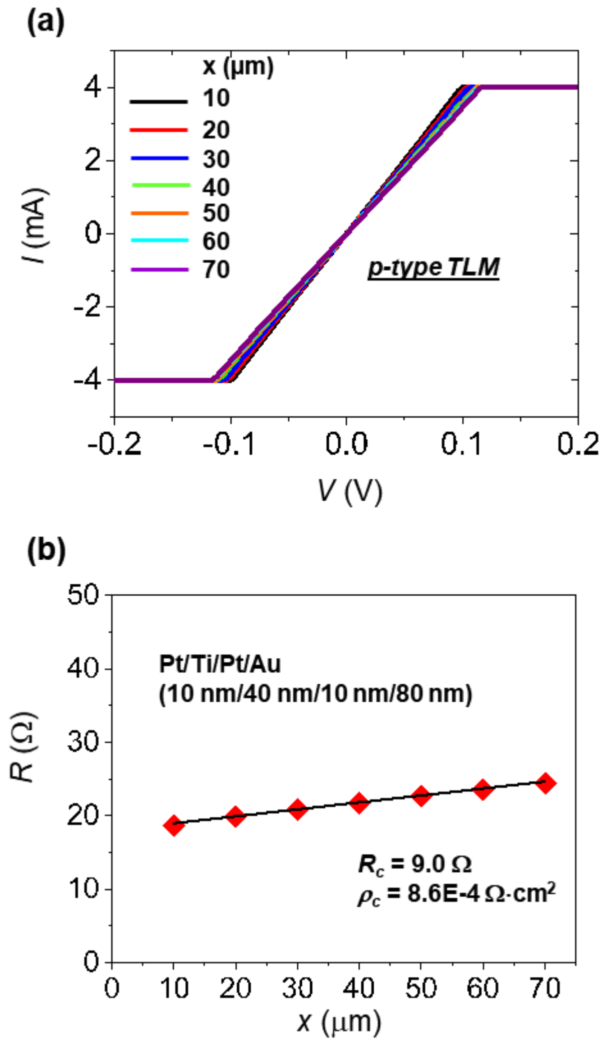

Figure S2. (a) Representative current (*I*)-voltage (*V*) curves measured between metal pads with varying distances (*x*), and (b) total resistance (*R*) as a function of *x* from standard transmission line model (TLM) measurements, where Pt/Ti/Pt/Au (10 nm/40 nm/10 nm/80 nm) were deposited on p^+-$Al_{0.3}Ga_{0.7}As$ back-surface field layer, and annealed under 175°C, 60 min in 100% N_2 atmosphere.

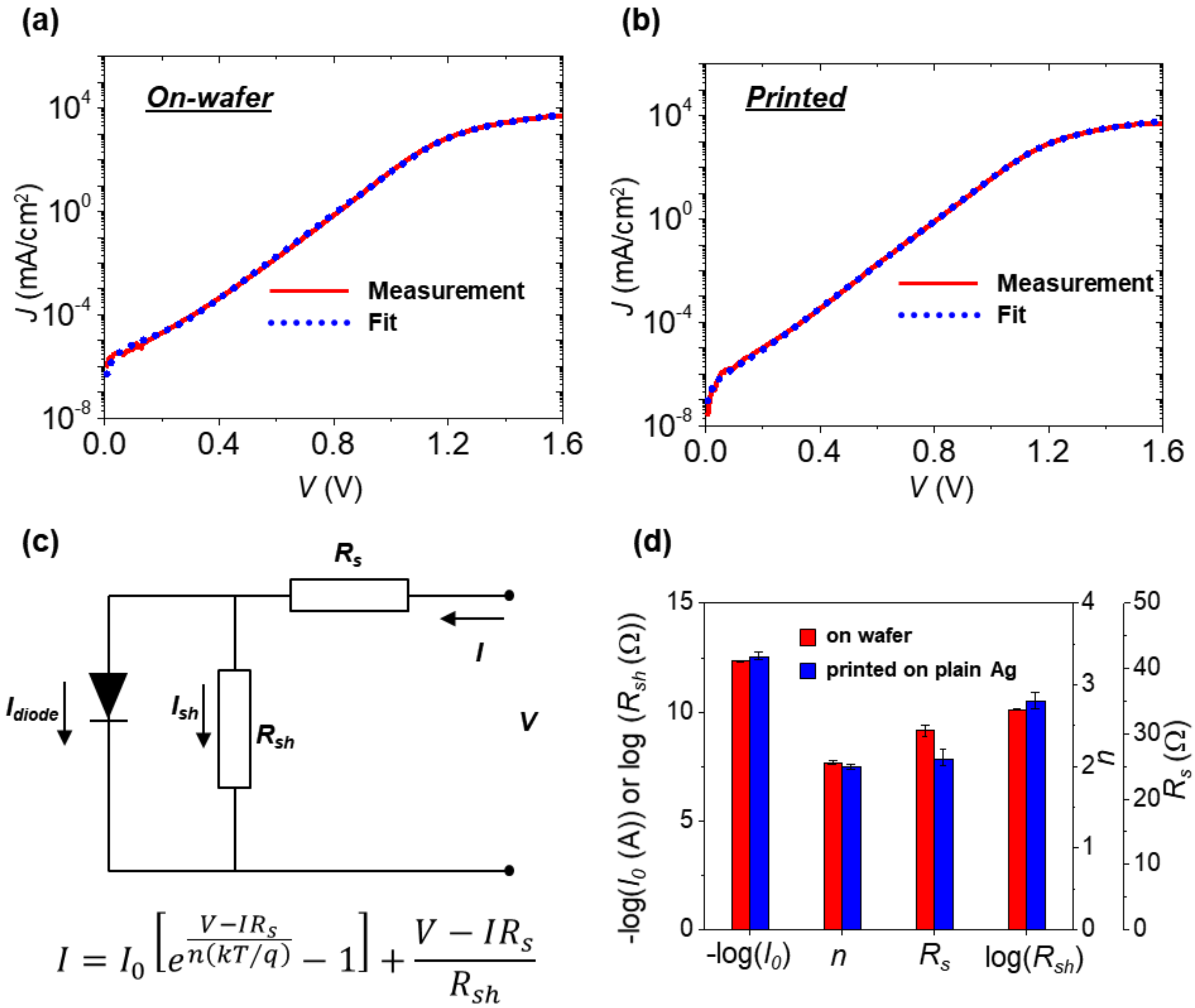

Figure S3. Representative dark current density (J)-voltage (V) curves of GaAs solar cells measured (a) on wafer and (b) after transfer printing on a plain silver reflector without removing a bottom contact layer. (c) A single-diode model used to fit the experimental data in (a) and (b), where I_0, n, k, T, q, R_s, and R_{sh} are reverse-bias saturation current, diode ideality factor, Boltzmann constant, absolute temperature, electronic charge, series resistance, and shunt resistance, respectively. (d) Fitted parameters of single-diode model extracted from (a) and (b). Error bars show maximum and minimum values of the error from the average value.

3. Supplementary Table

	I_0 (A)	$-log\ (I_0$ (A))	n	R_s (Ω)	R_{sh} (Ω)
on wafer	4.74E-13	12.33	2.05	30.5	3.84E+10
printed on plain Ag	3.01E-13	12.53	2.00	26.2	4.83E+10

Table S1. Fitted parameters of single-diode model (Figure S3(c)) extracted from dark *IV* measurements of GaAs microcells on wafer and after printing on a plain silver reflector, including reverse-bias saturation current (I_0), ideality factor (n), series resistance (R_s), and shunt resistance (R_{sh}).

4. Supplementary References

1. Lee, S.-M.; Kwong, A.; Jung, D.; Faucher, J.; Biswas, R.; Shen, L.; Kang, D.; Lee, M. L.; Yoon, J. High Performance Ultrathin GaAs Solar Cells Enabled with Heterogeneously Integrated Dielectric Periodic Nanostructures. *ACS Nano* **2015**, *9*, 10356-10365.

2. Lee, S. M.; Li, W. G.; Dhar, P.; Malyk, S.; Wang, Y.; Lee, W.; Benderskii, A.; Yoon, J. High-Performance Flexible Nanostructured Silicon Solar Modules with Plasmonically Engineered Upconversion Medium. *Advanced Energy Materials* **2015**, *5*, 1500761.

3. Lee, S.-M.; Dhar, P.; Chen, H.; Montenegro, A.; Liaw, L.; Kang, D.; Gai, B.; Benderskii, A. V.; Yoon, J. Synergistically Enhanced Performance of Ultrathin Nanostructured Silicon Solar Cells Embedded in Plasmonically Assisted, Multispectral Luminescent Waveguides. *ACS Nano* **2017**, *11*, 4077-4085.