Electronic supplementary information

Germanium Nanocrystal Doped Inverse Crystalline Silicon Opal

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Experimental Procedures

Materials. Anhydrous ethanol was purchased from Brampton and used as received. Colloidal germanium nanocrystals (ncGe) suspended in ethanol (0.002 g/mL) were prepared similarly to our previous report.[10] Monodisperse silica microspheres with 360 nm diameter were synthesized by a modified Stöber process[17] and sonicated in anhydrous ethanol before use. Sapphire wafer was purchased from University wafer and cleaned using a piranha solution. Disilane (99.99 %) was purchased from Gelest and used as received. Hydrofluoric acid aqueous solution ($HF_{(aq)}$, 2 wt%) was prepared from a solution (48 wt%) purchased from Aldrich.

Preparation of ncGe-o. In a typical experiment, a silica opal with 5 wt% of ncGe (5wt%-ncGe-o) was prepared as follows. Colloidal ncGe ethanol solution (0.625 mL) was added to a vial and diluted to 7.75 mL with anhydrous ethanol and sonicated for 2 h. Then a silica microsphere ethanol solution (0.1 g/mL, 0.25 mL) was added to the solution and sonicated for 2 h. A sapphire wafer was placed vertically into the solution at an ambient temperature of 35 ^{o}C for 3 days to allow the self-assembly of ncGe and silica microspheres via ethanol evaporation. The procedure was repeated twice to give 5wt%-ncGe-o deposited on the sapphire wafer. 3wt%-ncGe-o and 7wt%-ncGe-o were prepared from 0.375 and 0.875 mL of ncGe ethanol solution similarly as described above.

Preparation of i-ncGe-cSi-o. Amorphous Si was deposited in the interstices of the ncGe-o via dynamic chemical vapor deposition (CVD) from disilane precursor. The ncGe-o was heated to 450 ^{o}C in a custom-built CVD reactor with the pressure maintained at 0.5 mTorr. Then disilane gas was flowed over the ncGe-o with a pressure of ca. 370 mTorr for 3.5 h. The amorphous Si

over-layer was removed by unidirectional reactive ion etching (RIE) with CHF_3 plasma. Then the silica opal was chemically etched in $HF_{(aq)}$ (2 wt%) for 3 h. The resulting inverse amorphous Si opal was annealed 630 ^oC in a tube furnace under flowing hydrogen (5 %)/argon (95 %) atmosphere for 20 h, and subsequently under nitrogen for 20 h, to give i-ncGe-cSi-o. Hydrogen-plasma passivation of i-ncGe-cSi-o was carried out via plasma-enhanced CVD. The i-ncGe-cSi-o was set into a dc saddle-field plasma-enhanced CVD reactor. Hydrogen gas was flowed into the reactor at 280 sccm with the pressure at 1 Torr and then plasma passivation was done at the dc power of 0.08 W/cm^2 at 300 ^oC for 2 h.

Characterization. Field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDX) were performed on a Hitachi S-5200. The ncGe-o sample was carbon-coated to improve the resolution. Reflectance and absorption spectra for ncGe-o were measured by a Shimadzu UV-3100PC UV-vis-NIR scanning spectrophotometer. Reflectance spectra for i-ncGe-cSi-o were obtained on a Perkin Elmer UV-vis-NIR spectrometer Lambda 900. Transmission electron microscopy (TEM) and EDX were performed at the Canadian Centre for Electron Microscopy at McMaster University using a FEI Titan electron microscope. TEM samples of i-ncGe-cSi-o were scratched from the sapphire wafer and deposited onto carbon-coated copper grids. Powder X-ray diffraction patterns (PXRD) of i-ncGe-cSi-o were obtained on a sapphire wafer and acquired using a Siemens D5000. X-ray photoelectron spectroscopy (XPS) was acquired using a Thermo Scientific Theta Probe utilizing monochromatic Al K_α radiation. The spectra were calibrated to the C1s peak (284.8 eV) arising from adventitious carbon. Raman spectroscopy was performed using a 532 nm diode laser and calibrated using a crystalline Si wafer. DC electrical photo and dark conductivities (σ_{ph}, σ_d) were measured by the two probe method. Aluminum coplanar electrodes at a separation of 1 mm and a width of 5 mm were deposited on the samples using an Ulvac EBH-6. Yokogawa Hewlett Packard 4140B pA meter/dc voltage source was used for all electrical measurements. Ohmic contacts between the aluminum and the i-cSi-o film were confirmed from *I-V* curves which were linear. Each current was recorded with the voltage at 50 V under AM 1.5 condition (100 mW/cm^2) using a Wacom WXS-1140S-L2F AM1.5G or in a dark box. The σ_{ph} and σ_d were calculated from the currents at 50 V with the equation $\sigma = LI/WdV$ [S/cm], where L [cm] is the gap length between two electrodes, I [A] is the measured current, W [cm] is the width of the

electrodes, *d* [cm] is the thickness estimated from cross section SEM images of the samples which contain void spaces, and *V* [V] is the voltage.

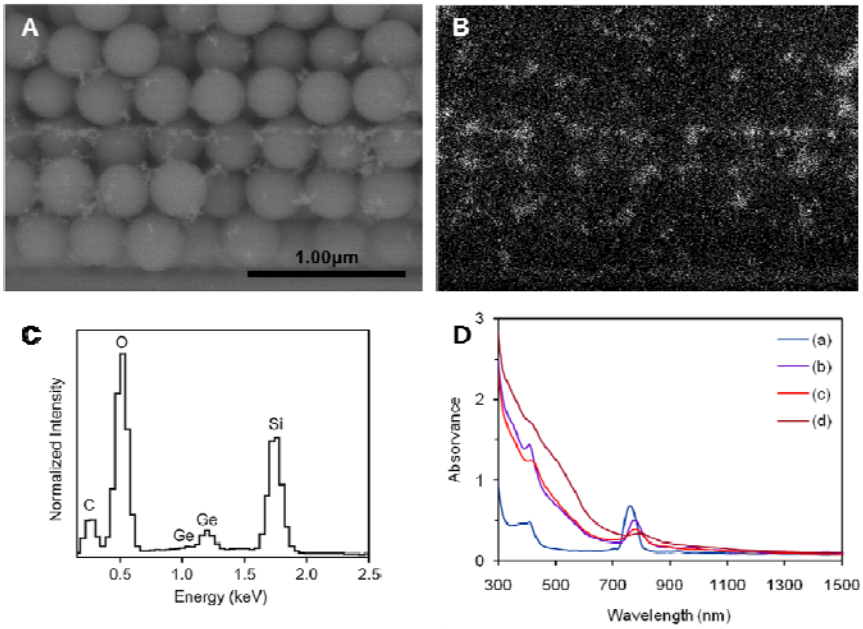

Fig. S1. Elemental Ge map and EDX spectrum of 5wt%-ncGe-o from FE-SEM and optical absorption spectra of ncGe-o. (A) SEM image. (B) Elemental Ge mapping image. (C) EDX spectrum. (D) Absorption spectra of ncGe-o with pure silica opal as a reference: (a) silica opal, (b) 3wt%-ncGe-o, (c) 5wt%-ncGe-o and (d) 7wt%-ncGe-o.

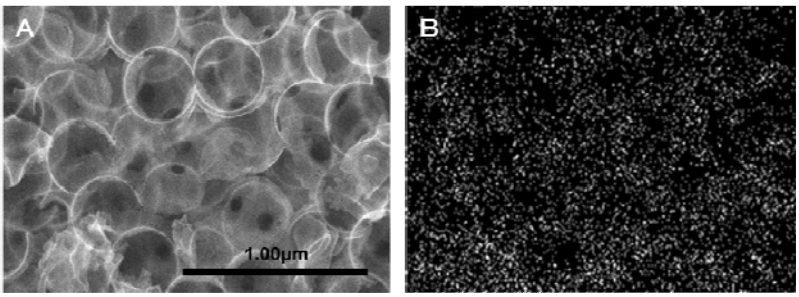

Fig. S2. (A) TEM image and (B) Elemental Ge mapping image of i-5wt%-ncGe-cSi-o.

Table S1. Dark and photo conductivities of i-ncGe-cSi-o and i-cSi-o as a reference

sample	thickness (nm)[a]	current (A)[b]		conductivity (S/cm)[e]		photo sensitivity (σ_{ph}/σ_d)
		dark[c]	photo[d]	σ_d	σ_{ph}	
i-cSi-o	1502	1.64E-05	2.16E-05	4.36E-04	5.74E-04	1.32
i-3wt%-ncGe-cSi-o	1892	7.08E-07	1.19E-06	1.50E-05	2.52E-05	1.68
i-5wt%-ncGe-cSi-o	2643	7.33E-07	1.20E-06	1.11E-05	1.82E-05	1.64
i-7wt%-ncGe-cSi-o	2986	5.48E-08	9.82E-08	7.34E-07	1.32E-06	1.79

[a]Estimated from cross section FE-SEM images of the samples which contain void spaces. [b]Average of 3 measurements at 50 V. [c]Recorded in dark box. [d]Recorded under AM 1.5 condition (100 mW/cm^2). [e]$\sigma = LI/WdV$ [S/cm], where L [0.1 cm] is the gap length between two electrodes, I [A] is the measured current, W [0.5 cm] is the width of the electrodes, d [cm] is the thickness estimated by FE-SEM, and V [50 V] is the voltage.

References

17 W. Stöber, A. Fink, E. Bohn, *J. Colloid. Interface. Sci.*, 1968, **26**, 62.