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 °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 °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 CHF₃ plasma. Then the silica opal was chemically etched in HFₐq (2 wt%) for 3 h. The resulting inverse amorphous Si opal was annealed 630 °C 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/cm² at 300 °C 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 Kα 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 (σₚₑ, σ₅) 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/cm²) using a Wacom WXS-1140S-L2F AM1.5G or in a dark box. The σₚₑ and σ₅ 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

<table>
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<th>sample</th>
<th>thickness (nm)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>current (A)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>conductivity (S/cm)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>photo sensitivity (&lt;sup&gt;σ&lt;/sup&gt;ph/&lt;sup&gt;σ&lt;/sup&gt;d)</th>
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</table>

<sup>a</sup>Estimated from cross section FE-SEM images of the samples which contain void spaces. <sup>b</sup>Average of 3 measurements at 50 V. <sup>c</sup>Recorded in dark box. <sup>d</sup>Recorded under AM 1.5 condition (100 mW/cm²). <sup>e</sup><sup>σ</sup> = LI/WdV [S/cm], where <sup>L</sup> [0.1 cm] is the gap length between two electrodes, <sup>I</sup> [A] is the measured current, <sup>W</sup> [0.5 cm] is the width of the electrodes, <sup>d</sup> [cm] is the thickness estimated by FE-SEM, and <sup>V</sup> [50 V] is the voltage.

References