Supplementary information

Three-dimensional fabrication and characterisation of core-shell nano-columns using electron beam patterning of Ge-doped SiO_2

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Methods

Thin Ge-doped amorphous SiO_2 films were deposited onto a Si substrate using plasma-enhanced chemical vapor deposition (PECVD). The reaction gases were SiH_4, GeH_4 and N_2O. By varying the ratio between SiH_4 and GeH_4, the Ge concentration in the film was adjusted to achieve a concentration of 33 mol%, confirmed using Rutherford backscattering spectroscopy (RBS). The deposition time was 15 min, resulting in film thicknesses of 1.1 μm. After deposition, the films were heated at 1100 ^{o}C for 4 hours in N_2 for consolidation. For transmission electron microscopy (TEM) examination, two pieces of the films were glued together with epoxy and milled using Ar in a Gatan Precision Ion Mill System (PIPS^{TM}) to a thickness of 200 nm. The sample was uncoated for TEM observation.

The electron beam current in the TEM experiments was kept constant (measured using a Whenelt cup) at 0.6 nA with beam diameters of 0.2-0.3 nm. These settings correspond to a current density of 85 pA/Å^2. The dwell time for electron tomography was 20 μs/pixel (20 sec/ image), corresponding to an electron dose of 106 e^-/Å^2 at each specimen tilt angle.

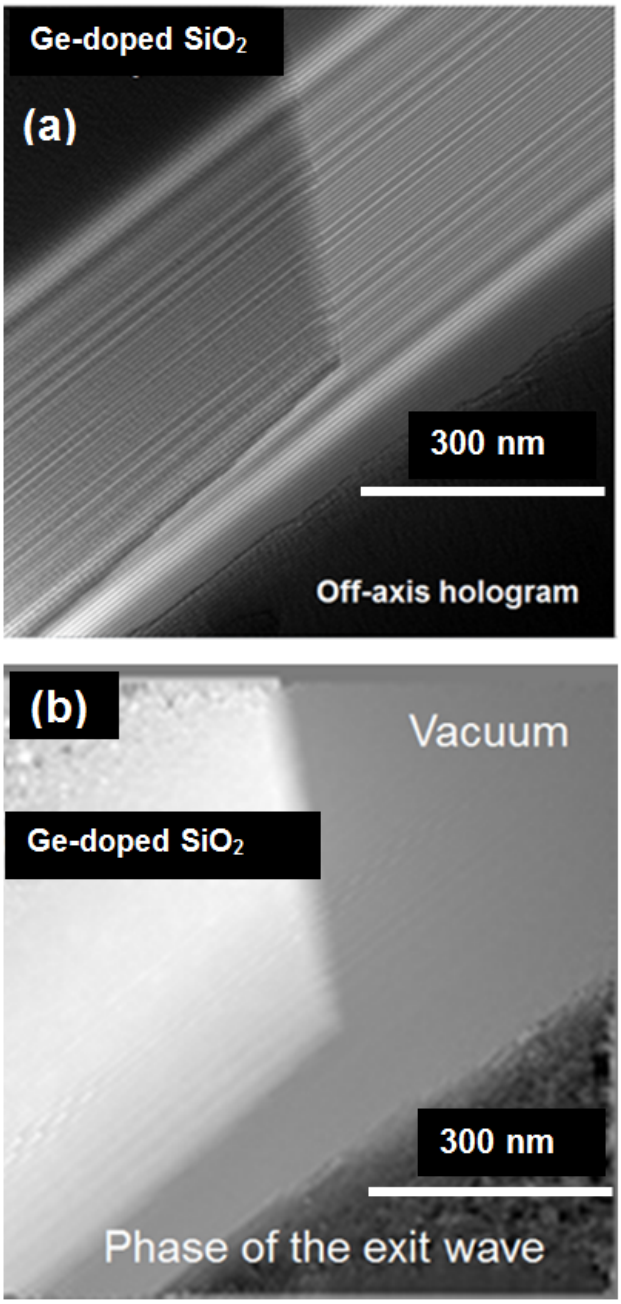

FIGURE 1. (a) Off-axis electron hologram acquired from the same area of the Ge-doped SiO_2 sample that was used for the electron irradiation experiments. (b) Phase of the electron wave recovered from the specimen electron hologram and from a vacuum reference electron hologram (see also Fig. 1(f) in main text). The phase contains information about the mean inner potential and thickness of the material and the presence of electromagnetic fields. A slope in the phase in vacuum is associated with electrostatic charging of the sample.

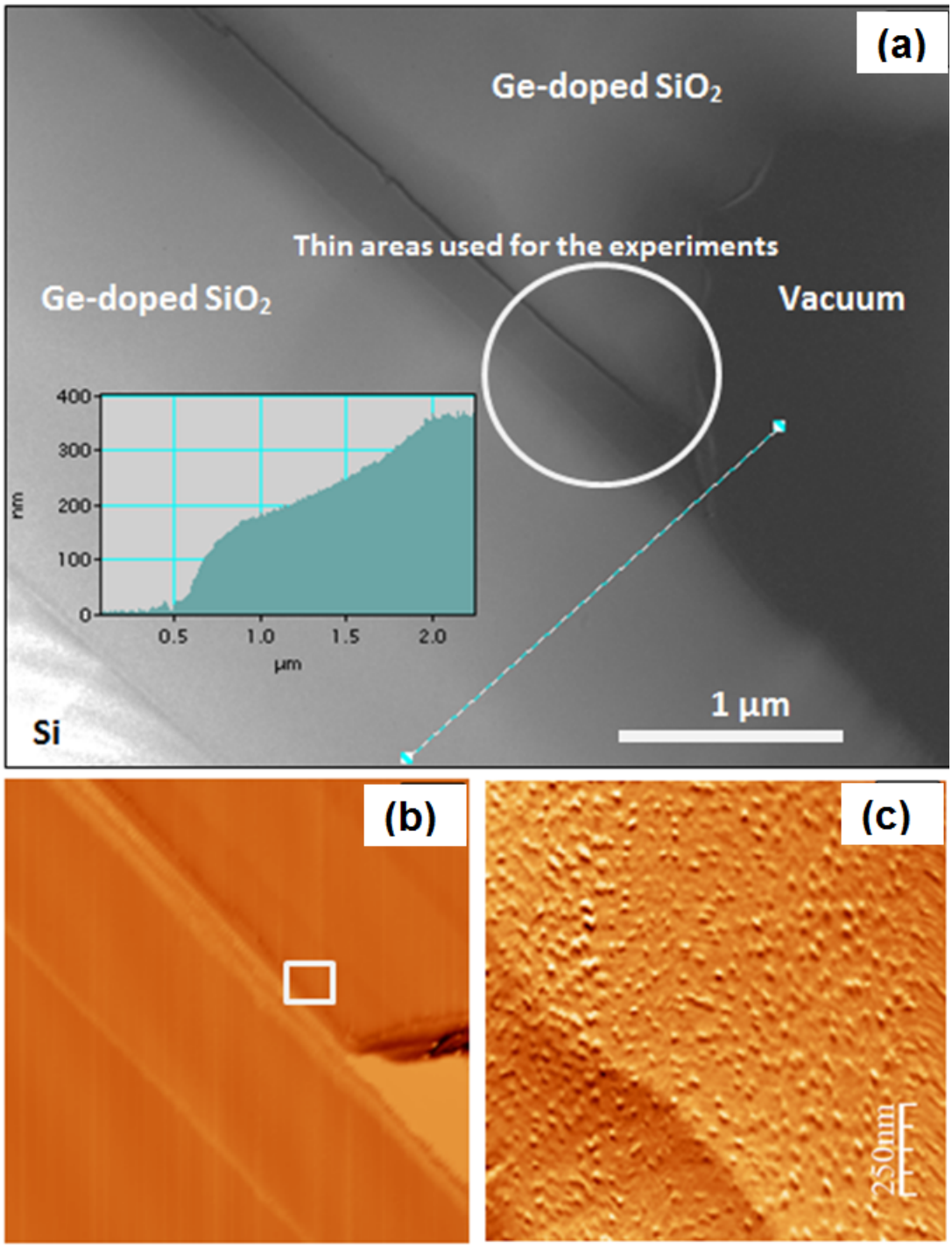

FIGURE 2. Scanning transmission electron microscopy (STEM) and atomic force microscopy (AFM) images of particles at the surface of the sample: (a) High-angle annular dark-field (HAADF) STEM image of the sample at low-magnification. Two pieces of Ge-doped SiO_2 supported on Si were glued together and thinned down to 200 nm. (b) AFM image of the topography of the same area shown in (a). (c) AFM image corresponding to the squared inset in (b). Particles are present on the surface in the area irradiated using the TEM.

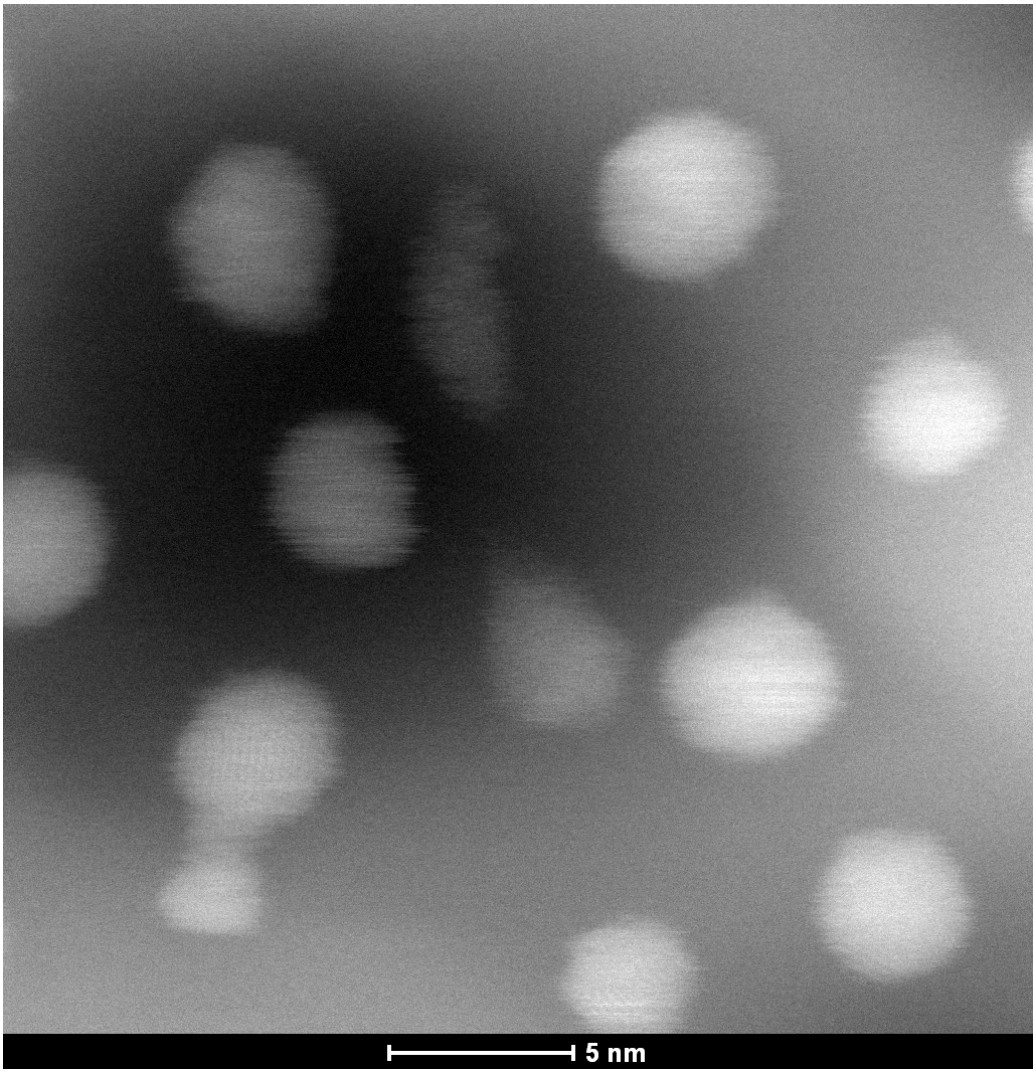

FIGURE 3. STEM images of particles close to the surfaces of the Ge-doped SiO_2 specimen.

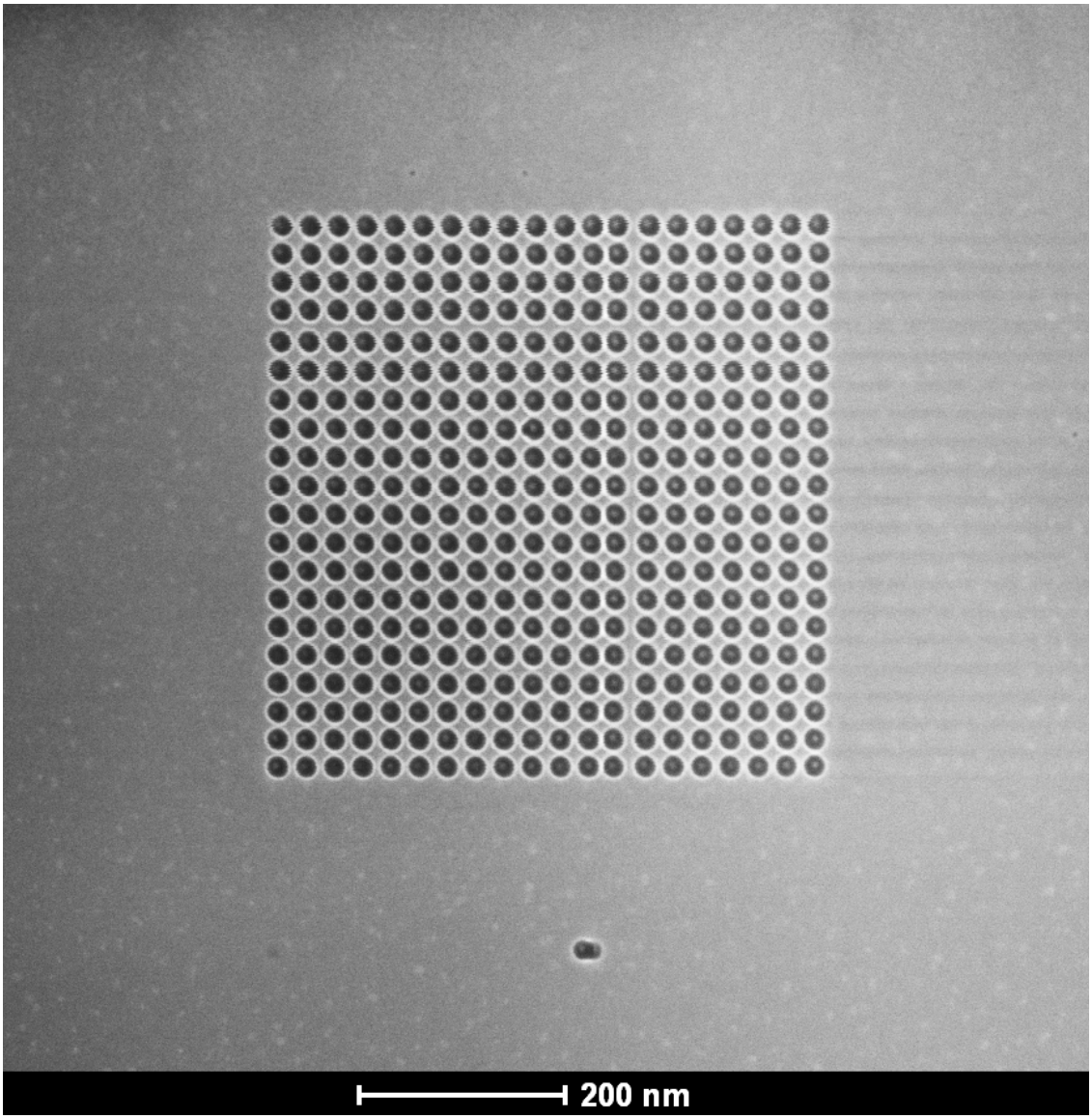

FIGURE 4. HAADF STEM image of regular array of core-shell cylinders. In some cases the cylinders display a bright core.