Targeted positioning of quantum dots inside 3D silicon photonic crystals observed by synchrotron X-ray fluorescence tomography

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It is a major challenge in nanotechnology to precisely position active nanoparticles, like quantum dots, inside a three-dimensional (3D) nanostructure in order to realize novel functions. This is notably relevant to tune and control spontaneous emission and lasing of embedded quantum emitters [1,2]. Here, we study 3D photonic band gap crystals made from silicon that are infiltrated with PbS nanocrystal quantum dots that emit in the near infrared including telecom. Our crystals have the inverse woodpile structure and exhibit a broad full 3D band gap. Such crystals strongly inhibit emission of semiconductor quantum dots [3]. The material distribution in the crystals is defined by two perpendicular arrays of pores (Fig. 1(A)), running in the Z and X-directions. The crystal are made by CMOS-compatible means by deep reactive ion-etching through tailored masks. The PbS nanocrystals are covalently bonded to polymer brush layers that are grafted to the Si-air interfaces inside the 3D nanostructure using surface-initiated atom transfer radical polymerization (SI-ATRP) [4].

Once the 3D positioning is done, the challenge arises how to non-destructively verify where the nanoparticles reside in the 3D nanostructure. These nanomaterials are from the outset opaque, hence optical microscopy has insufficient penetration depth, apart from limited resolution. While scanning electron microscopy (SEM) offers fantastic nm spatial resolution, it has a small penetration depth hence only the sample surface is viewed (see Fig. 1), but not the bulk. X-ray techniques are promising tools for Nanophotonics, in view of excellent penetration depth, non-destructive character, and nm spatial resolution.

The functionalized 3D nanostructures are probed by X-ray fluorescence tomography at the ESRF (beamline ID-16NI). The study was done at 17 keV photon energy to obtain large penetration depths and efficient excitation of the elements of interest. X-rays are sharply focussed (23×37 nm^2). We collect fluorescence images while rotating the crystal from 0 to 180°. On the projection maps we perform tomographic reconstruction (Radon transform) to obtain the 3D atom density distribution with 50 nm resolution for each individual element.

Fig. 1(B) shows a projection map of the Pb atoms. The field of view contains the 3D photonic crystal that is surrounded by bulk silicon. A closer inspection after tomographic reconstruction reveals two sets of pores running in the Z and the X-directions, matching the design. The quantum dots are located throughout the whole crystal volume positioned on a thin polymer brush layer. We conclude that 3D X-ray fluorescence tomography is a fantastic method to solve many research questions on optical metamaterials for applications, including cavity arrays, physically unclonable functions, quantum emitters as qubits and for enhanced lighting efficiency.

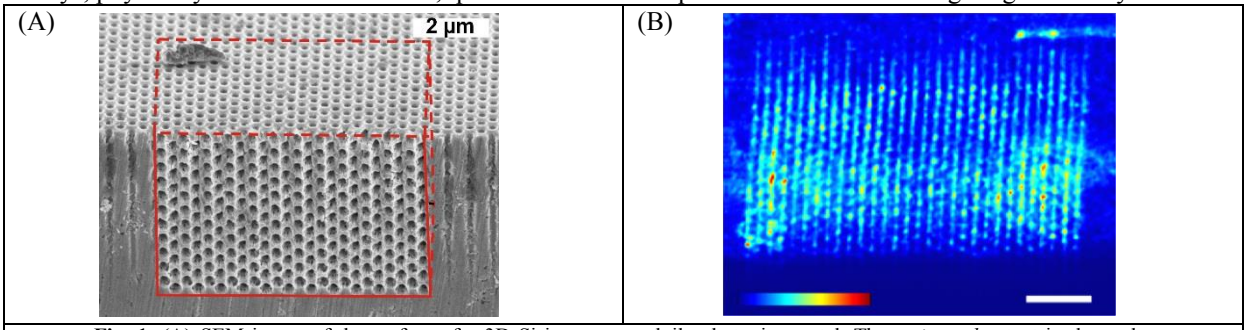

Fig. 1. (A) SEM image of the surface of a 3D Si inverse woodpile photonic crystal. The *estimated* extent is shown by dashed lines. The 3D crystal is surrounded by a large 2D array of pores that is first etched in the Z-direction. From Ref. [5] **(B)** Projection maps of the number of Pb atoms per pixel (area 50 x 50 nm) and integrated along the propagation direction of the beam, for the sample orientation at θ=-47°. The colour scale is the areal atomic densitiy $N_{a,Pb}$ (in units atoms/pixel area) ranging from 0 to 420000 lead atoms per pixel. The scale bar represents 2 µm as in Fig. 1(A).

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