Black silicon with functional luminescent organic monolayer enabled by direct femtosecond-laser printing

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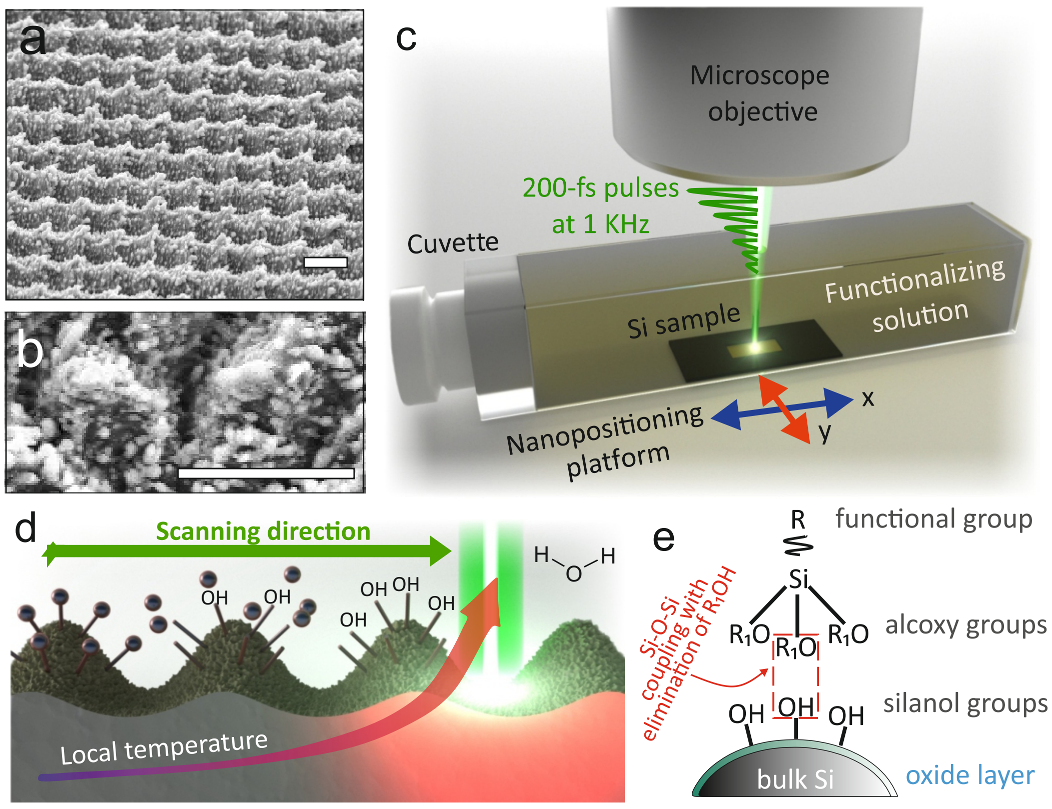
Introduction

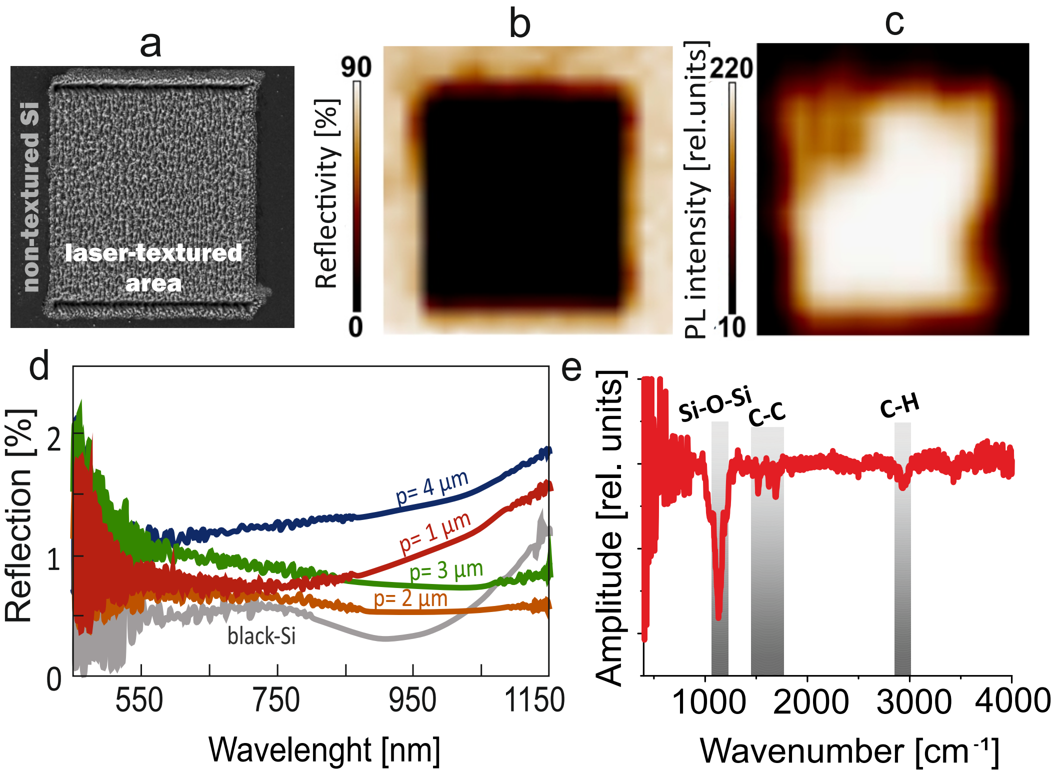
Nanotextured surfaces structures with dimensions smaller than the optical wavelength allows to create compact, efficient and highly sensitive optical sensors due the ability of sharply amplifying weak electromagnetic fields incident on the surface. Modification of the silicon surface, as material widely used for optoelectronic and photonic applications, using femtosecond laser radiation is an inexpensive high-rate technological process of homogeneous nanotextured surfaces exhibiting feature size below the optical diffraction limit. Here, we proposed single-step technology allowing to locally bind the organic light-emitting nanolayer in the process of Si surface nanotexturing by fs-laser pulses. Resulting anti-reflecting nanostructures facilitate excitation of the Rhodamine 6G resulting in multi-fold enhancement of its spontaneous emission rate making the developed approach promising for realization of chemosensor arrays.

Fabrication



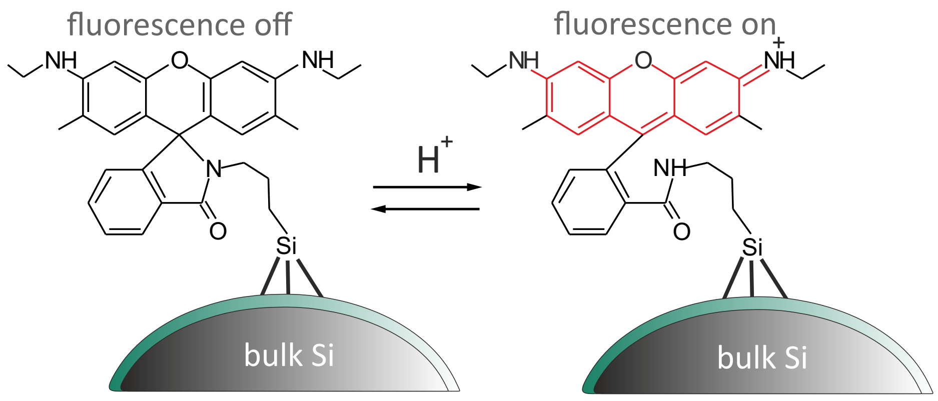
(a, b) Side-view (view angle of 45°) SEM images of the chemically functionalized Rhodamine 6G ultra-black Si surface, scale bar indicates 2 μm; (c) artistic representation of the setup for liquid-assisted fs-laser texturing and functionalization of Si surface; (d) scheme of surface functionalization during fs-laser processing; (e) scheme of surface chemical reaction.

Characterization

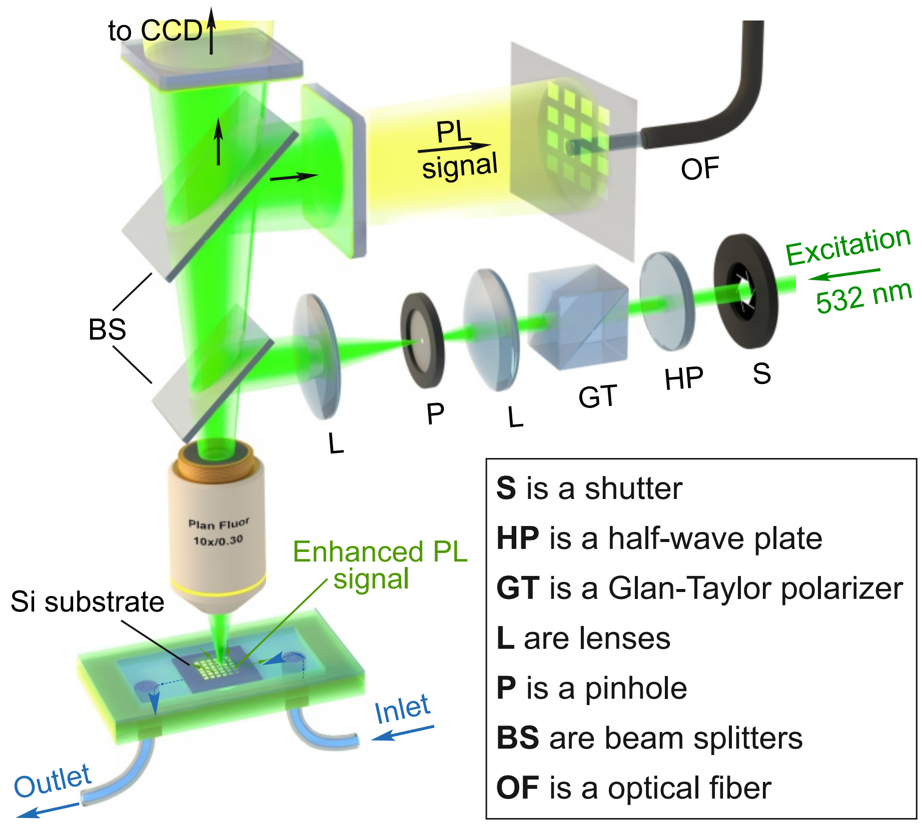


Correlated (a) SEM image, (b) confocal laser reflection and (c) photoluminescence (PL) maps (the laser pump at 473 nm was used) of the laser-textured area functionalized with Rhodamine 6G nanolayer. The laser-textured area size is 50×50 μm^2; (d) FTIR reflection spectra measured from nanotextured surfaces at varied lateral intervals between scanning lines *p*; (e) normalized FTIR reflection spectrum of the functionalized laser-textured Si surface.

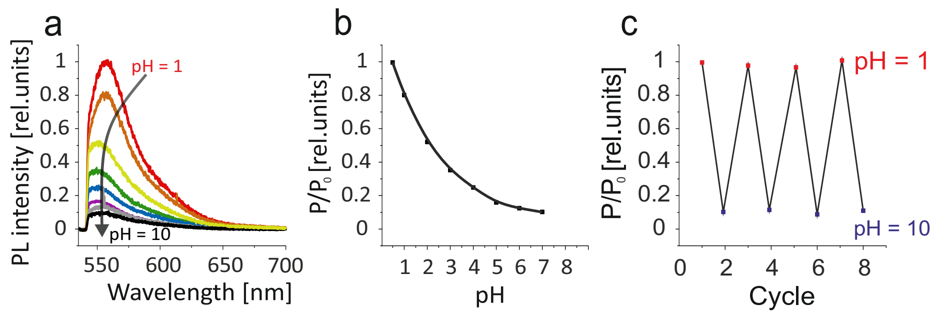
PL measurements and pH sensing tests



Spirolactam ring-opening reaction. Rhodamine 6G spirolactam derivative display a red color change and strong PL in acidic solution by activating a carbonyl group in its spirolactam moiety.



Experimental setup for PL measurements and pH sensing tests.



(a) a series of PL spectra of the pH sensitive laser-textured surface upon successive acidification of the surrounding solution; (b) change in signal intensity upon cyclic filling of the microfluidic cell with basic (pH = 10) and acidic (pH = 1) solutions; (c) change in signal intensity upon cyclic filling of the microfluidic cell with basic (pH = 10) and acidic (pH = 1) solutions. dependence of the normalized PL intensity P/P_0 on pH value.

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