Modification of the silicon structural properties by ultrasonication

Ekaterina V. Skorb†, Helmuth Möhwald

Max Planck Institute of Colloids and Interfaces
Am Mühlenberg 1, Golm 14476 (Germany); skorb@mpikg.mpg.de

The propagation of ultrasonic waves in a liquid medium may lead to acoustic cavitation, which is the formation, growth, and rapid implosive collapse of a vapor filled microbubble. Rapid bubble implosion induces localized extreme conditions inside the bubble in terms of temperature and pressure ("hot spots") estimated to be about 5000 K and 0.1 GPa, respectively. In addition, a part of the vaporized molecules can be dissociated to form radical species, such as OH• and H• for water sonolysis, then be able to react rapidly in the center. These conditions are combined with a very fast cooling rate (up to 10^{10} K s^{-1}) and thus offer the opportunity of working at room temperature with extreme conditions.[1] When the collapse of the surrounding bubbles leads to the emission of shock waves the pressure reaches several GPa with a starting shock velocity of 4000 m s^{-1}. In addition, imploding in the vicinity of a solid boundary (heterogeneous cavitation), the bubble collapse becomes asymmetric and leads to a specific phenomenon (liquid jets): an inrush of liquid passes through the bubble, penetrates the opposite bubble interface, and strikes the surface with a high velocity (ca. few hundred meters per second). Study and application of high intensity ultrasound for silicon modification is an area of our interest.

The main goals of the work are: (1) to understand and to control the formation of cavitation bubbles and processes on its interface; (2) to understand the influence of the collapsing bubble on the silicon surface; (3) to make use of defined surface treatment in constructing of porous silicon, silicon with hydrogen terminated bonds, change silicon crystal structure.

We measure effect of cavitation assisted processes on the interfaces by studying the impact on silicon surface after its removal from the reactor. Reactor conditions are controlled precisely allowing us to find optimal conditions for regulating the process of silicon modification: reactor shape, sonotrode position; frequency; intensity of ultrasonic treatment; temperature; pressure; concentrations of chemical species due to variation of solution (polar protic solvents, non-polar, polar aprotic, ionic liquid) and additives (hydrogen donor material; μ- and nano-particles). As model silicon substrates n- and p- types of silicon wafers (100 and 111); amorphous layer of silicon and polycrystalline Si are used.

It was shown that surface modification by ultrasonication results from the interplay of conceptually different mechanisms. 1 - there is physical impact primarily responsible for the enhancement of chemical reactions include (a) improvement of mass transport from turbulent mixing and acoustic streaming, (b) the generation of surface damage at liquid-solid interfaces by shock waves and microjets, and (c) the fragmentation of friable solids to increase the surface area; while 2 – the extreme temperatures and pressures create highly reactive radicals derived from solvent and additives (for example, hydrogen donor materials).[1-3] Obviously, the silicon modification demonstrated here relies on both mechanisms. In particular in the work was demonstrated the formation of developed, porous silicon by the "green" method of ultrasonication: i) one-step formation of silicon with different porous structure (25-40% in the case of aqueous and its increase to 60-70% in the case of mixing water with alcohol (Fig.a) and 40-50% in the case of ionic liquid used as a solution during sonication), ii) formation of photoluminescent centers (Fig.b), defect states, quantum dots and hydrogen terminated bonds which could be centers for charge separation and iii) possibility of patterned surface exposure to localize the effect of modification.[4-5]

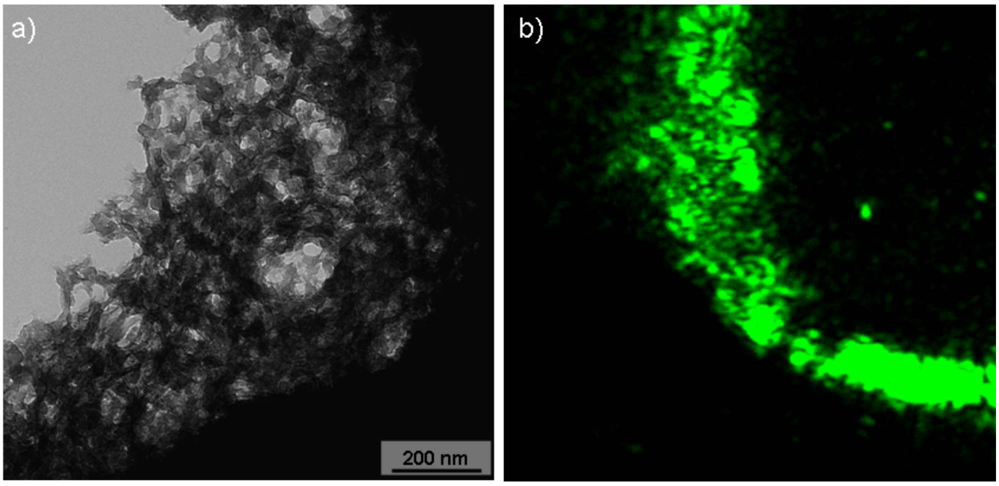

Figure. (a) TEM image and (b) confocal fluorescent modes of photoluminescence of porous silicon from sonochemically modified silicon at 57 W/cm^2 exposure in water-alcohol solution in the presence of magnesium after 30 min of exposure.

The proposed novel method of ultrasound assisted modification of silicon which is applicable on a large range of materials providing a basis for many types of applications in chemistry, materials science, photovoltaic and optics where the structure and properties of silicon can be easily controlled by ultrasound conditions.

[1] Suslick, K. S.; Price, G. J. *Annu. Rev. Mater. Sci*. **1999**, *29*, 295.

[2] Skorb, E. V.; Shchukin, D. G.; Möhwald, H.; Andreeva, D. V. *Nanoscale* **2010**, *2*, 722.
[3] Skorb, E. V.; Shchukin, D. G.; Möhwald, H.; Andreeva, D. V. *Langmuir* **2010**, *26*, 16973.
[4] Skorb, E. V.; Möhwald, H., European Patent Application N. 10014157.1.
[5] Method for modifying the structural properties of silicon by ultrasonication; **in preparation**.