

Stabilization of Nanocrystalline 2D Structures of Silicon with Perfluorophenyl Ligands

A. S. Orekhov^a, S. V. Savilov^b, V. N. Zakharov^b, A. V. Yatsenko^b, and L. A. Aslanov^{b, *}

^a*Institute of Crystallography, Russian Academy of Sciences, Leninskii pr. 59, Moscow, 119991 Russia*

^b*Moscow State University, Moscow, Russia*

**e-mail: aslanov.38@mail.ru*

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Abstract—Use of perfluorophenyl ligands for stabilization of silicon nanocrystals gives rise to 2D structures with an area up to $50 \times 15 \text{ nm}^2$ and a thickness of about 3 nm. Their formation can be explained by specific interactions of perfluorophenyl ligands.

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INTRODUCTION

In the last three to four years, two-dimensional nanocrystals of semiconductors have been of stable interest [1–8]. It has been stated in [9] that one-atom-thick silicon layers (like graphene) cannot be obtained without using a substrate; i.e., all 2D structures of silicon will have a certain thickness. We managed to dispense with substrates in the synthesis of flat silicon nanocrystals sandwiched between the outer layers of perfluorophenyl ligands. With other (phenyl, carbene, alkyl, perfluorobutyl, and halide) ligands, such sandwich structures were not detected.

EXPERIMENTAL

Bromo(pentafluoro)benzene (99.98%, SIA S&M-Invest), 1,2-dimethoxyethane (>99%, Sigma-Aldrich), metallic potassium (99.5%, Sigma-Aldrich), tetrabromosilane, tetrachlorosilane (99.99%, Sigma-Aldrich), mercury (99.9%, Alfa Aesar), and granulated lithium (99%, Alfa Aesar) were used.

Silicon nanocrystals (nc-Si) with perfluorophenyl ligands on their surface (FPh-ncSi) were obtained in several steps.

The synthesis of a dispersion of nc-Si with bromide ligands was carried out in a Schlenk vessel equipped with a magnetic stirrer. The vessel was purged with argon and charged with dry 1,2-dimethoxyethane (50 mL) and metallic potassium (2.62 g, 68 mmol). The reaction mixture was heated to 85°C. The potassium became divided into particles 1–3 mm in diameter. Then a solution of SiBr_4 (5.43 g, 15 mmol) in dimethoxyethane (10 mL) was added under argon. After 1 h, a yellow-brown dispersion formed; the total reaction time was 2 h.

The bromide content of the nc-Si surface was determined by titrating a sample (1 mL) of the disper-

sion obtained with 0.04 M KOH. The content of surface bromide ions was 0.2 mol/L. Bromo(pentafluoro)benzene (20% excess with respect to the bromide ligands of nc-Si) and amalgamated lithium (10% excess with respect to $\text{C}_6\text{F}_5\text{Br}$) were used to prepare perfluorophenyllithium, an alkylating agent.

Lithium was amalgamated in a Schlenk vessel. The vessel was purged with argon, charged with mercury (31.13 g, 155 mmol) and metallic lithium (0.092 g, 13 mmol), and heated on an oil bath to 200°C. Both the metals were stirred to homogenization and the resulting amalgam was cooled to room temperature.

Perfluorophenyllithium was synthesized at -17°C in the Schlenk vessel used to prepare amalgamated lithium. Dimethoxyethane (5 mL) and bromo(pentafluoro)benzene (0.74 mL, 1.65 mmol) were added, and the reaction mixture was stirred with a magnetic stirrer for 50 min.

The bromide ligands on the nc-Si surface were replaced by perfluorophenyl ones in the same Schlenk vessel at -17°C . The vessel was charged with the dispersion (25 mL) of bromide-containing nc-Si obtained at the first step. The reaction mixture was stirred for 1 h. The color of the dispersion was intense dark yellow.

The resulting dispersion of nc-Si with a shell of perfluorophenyl ligands was treated with dry gaseous HCl for 1 min to remove the excess of perfluorophenyllithium. A yellow dispersion of nc-Si with perfluorophenyl ligands formed over mercury.

The synthesis with SiCl_4 was carried out according to the same procedure.

IR spectra were recorded on a Tensor 27 FTIR spectrometer (Bruker) (resolution 1 cm^{-1} , signal averaging over 32 scans). Samples were dissolved in 1,2-dimethoxyethane and their films deposited on a ZnSe

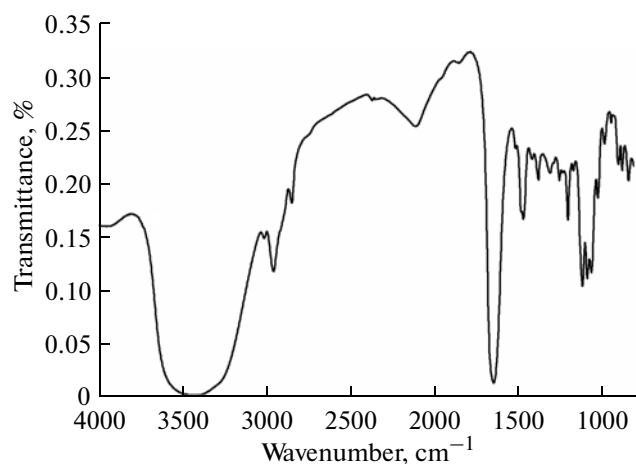


Fig. 1. IR spectrum of nanosilicon stabilized by perfluorophenyl ligands.

MNPVO crystal and a KBr window were dried in vacuo at 80°C.

To verify the reproducibility of the results, the samples were independently examined by two specialists using high-resolution transmission electron microscopy (TEM). Those studies were performed with a TITAN 80–300 microscope (FEI, USA) with a spherical aberration corrector in the light and dark field modes and a JEOL JEM 2100F/Cs microscope (JEOL Co. Ltd.) with a field emission gun fitted with a spherical aberration corrector (CEOS GmbH, Germany), a Tridiem energy filter, and an electron energy loss spectrum analyzer (Gatan Inc., USA). The accelerating voltages for the above microscopes were 300 and 200 kV, respectively. Experimental data were processed and interpreted with the DigitalMicrograph (Gatan Inc.), TIA (FEI), and JEMS program packages (Switzerland).

The dispersion of nc-Si obtained was also studied by atomic force microscopy with a Nanopix 2000 microscope in the intermittent mode. The dispersion of nc-Si was deposited in a thin layer on a substrate of single-crystal silicon, and the layer was dried. In most solvents, the formation of agglomerates was observed. Agglomeration was avoided by employing bromo(pentafluoro)benzene as a dispersive medium in which small-area silicon lamellas were dispersed.

Photoemission spectra of solid-state samples were recorded on a PerkinElmer LS-55 spectrometer.

RESULTS AND DISCUSSION

Attachment of perfluorophenyl ligands to the surface of silicon nanoparticles was confirmed by IR spectroscopy (Fig. 1): the absorption bands at 1459 and 1243 cm^{-1} correspond to the Si–C vibrations [10, 11]. The wide bands at 3420 and 2100 cm^{-1} are due to the O–H and Si–H vibrations, respectively [12, 13]. The abundance of OH groups is not surprising because

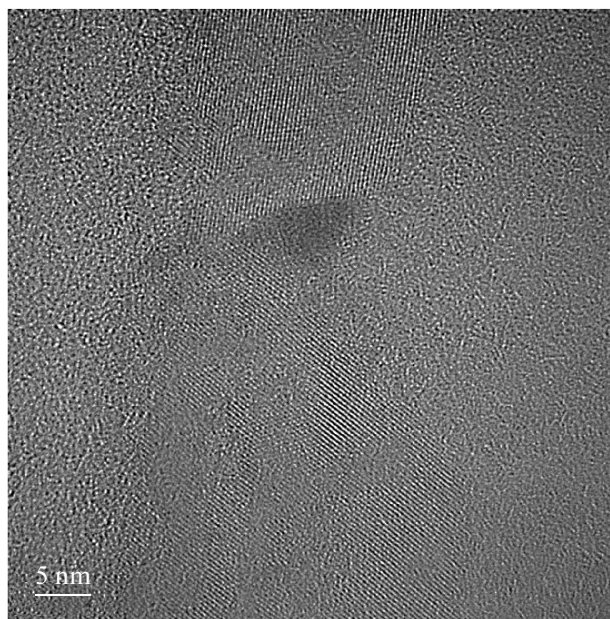


Fig. 2. High-resolution TEM image of 2D silicon structures stabilized by perfluorophenyl ligands.

electron-withdrawing perfluorophenyl ligands favor a nucleophilic attack of atmospheric moisture on silicon nanoparticles. The intense band at 1635 cm^{-1} suggests the presence of water molecules in the sample and is due to the bending vibrations of physically sorbed water [13]. The absorption band at 1077 cm^{-1} can be attributed to the Si–O stretching vibrations [11, 12]. The peaks at 2947 and 2838 cm^{-1} (CH_2 stretching) are due to the residual amounts of octane used as a dispersive medium in the final step of sample preparation.

A TEM study revealed that the samples obtained contain nanoparticles of two types characterized by large and small sizes. The average diameter of small nanoparticles is 4.0 ± 0.5 nm. A diffraction analysis showed that small silicon nanoparticles are amorphous: the electron diffraction pattern contains only haloes characteristic of amorphous particles.

Sample scans also produced dot patterns, thus suggesting the presence of crystalline nanoparticles. The arrangement of reflections on electron diffraction patterns corresponds to the cubic unit cell of silicon. High-resolution images were obtained for areas with dot patterns (Fig. 2). One can see that crystalline particles have linear dimensions of 25 nm and more in the plane of nanocrystals. Analysis of the contrast of the images near the (crystalline particle)/(carbon substrate) boundaries suggests that the particles are thin plates (2D structures). The thickness of lamellar nanocrystals was estimated using atomic force microscopy. Its average value is about 3 nm.

Energy-dispersive X-ray spectroscopy (Fig. 3) showed that flat silicon nanoparticles contain not only the expected silicon, carbon, and fluorine but also

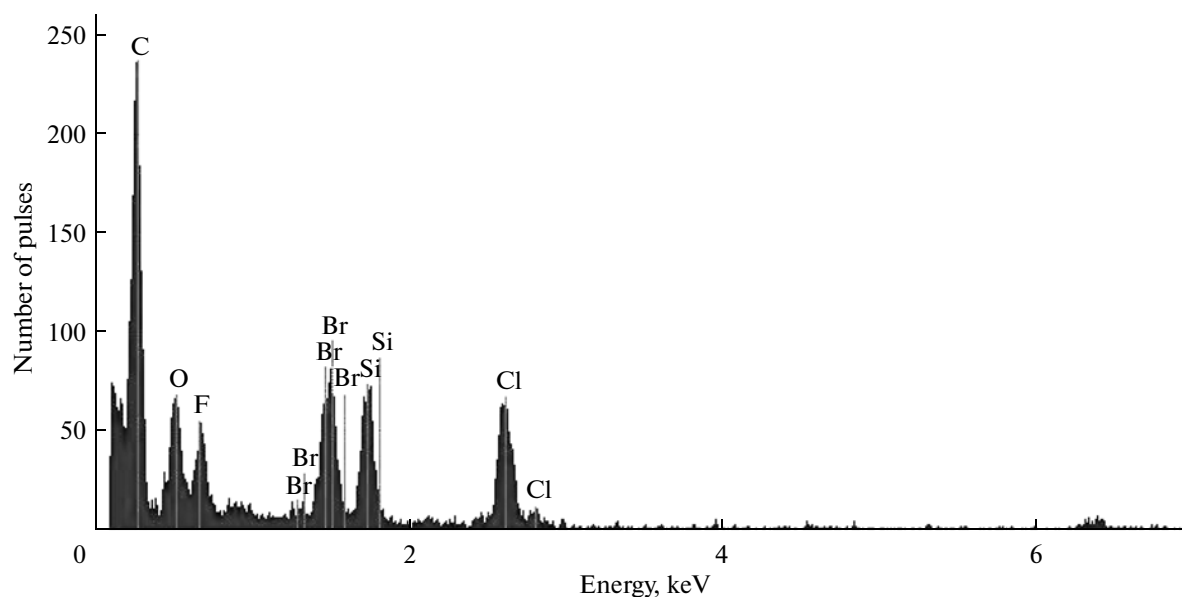


Fig. 3. Energy-dispersive spectrum of 2D silicon structures stabilized by perfluorophenyl ligands.

some oxygen. Bromine and chlorine seem to be present as impurities of lithium bromide and lithium chlorides.

Apparently, lamellar nanocrystals form when the bromide ligands on the surface of small silicon nanoparticles are replaced by perfluorophenyl ligands with subsequent aggregation of small silicon nanoparticles into plates. In our opinion, the formation of such plates is due to specific interactions of ligands. The perfluorophenyl ligands are united into layers as a result of self-assembly, which makes small silicon nanoparticles become aggregated into crystalline layers framed by perfluorophenyl ligands on two sides. Therefore, there is a relationship between small and large silicon nanoparticles: flat plates are formed by aggregation of small nanoparticles.

The carbon atoms of the perfluorophenyl groups bear a considerable positive charge because their electrons are attracted by the fluorine atoms. In turn, the F atoms become negatively charged and the perfluorophenyl groups are thus attracted to each other by virtue of the interacting unlike charges on the C and F atoms of adjacent rings [14]. The crystal structure of pentafluorobenzoic acid [15] distinctly shows attraction of parallel perfluorophenyl rings. These rings are shifted relative to each other in such a way as to minimize the C...F distances for the atoms of the adjacent rings (the interplanar spacings are 3.30 and 3.23 Å). This means that the specific electron density distribution in perfluorophenyl ligands is responsible for the attraction between such ligands; note that these interactions cannot be classified among those occurring in normal π – π stacking.

Nanosilicon remaining on the glass substrate after evaporation of the solvent shows photoemission

(Fig. 4). Amorphous particles do not luminesce because of numerous broken bonds, while the emission peak of perfluorophenyl ligands appears in the UV range. For instance, the photoemission band of hexafluorobenzene extends from 300 to 470 nm, with a maximum at 365 nm. The spectrum of hexafluorobenzene is featureless and independent of the exci-

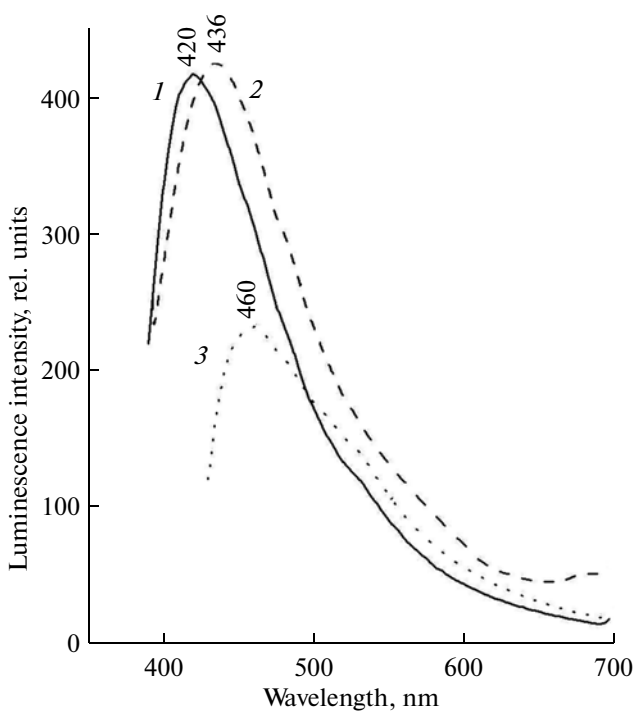


Fig. 4. Photoemission spectra of nanosilicon stabilized by perfluorophenyl ligands at λ_{exc} = (1) 350, (2) 375, and (3) 400 nm.

tation wavelength in the 220–270 nm range [16]. That is why only 2D nanocrystals of silicon can produce luminescence when exposed to exciting radiation with the wavelengths used.

To sum up, we were the first to discover that the use of perfluorophenyl ligands gives rise to nanocrystalline 2D structures of silicon with blue photoluminescence. Such structures offers considerable scope for preparation of p – n junctions by doping techniques adopted in modern microelectronic industry.

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