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# Formation of threadlike nanostructures of silicon and silicon carbide by chemical vapor deposition

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**Synthesis of threadlike nanostructures of silicon and silicon carbide by chemical vapor deposition (CVD) using dichlorosilane pyrolysis in the presence of $CCl_4$ and $CF_2Cl_2$ in nitrogen has been carried out. Nitrogen molecules react on active surface areas of the substrate originating during etching with a gaseous mixture of 7.5% $SiH_2Cl_2$–7.5% $CCl_4$–85% $N_2$.**

Continuous progress in the characteristics of electronic devices is in many respects caused by reduction of the sizes of active elements of integrated microcircuits. The miniaturization of transistors to a scale of about 10 nm requires the replacement of monocrystalline semiconductor materials with other physical objects, as well as the use of nanofilms as active layers (in field-effect transistors and optoelectronic devices) and isolating layers.[1]

The threadlike nanocrystalline structures of Si, GaAs, GaP and other semiconductors possessing unique electrophysical properties are also promising as new materials along with carbon nanotubes.[2–4] Metal organic vapor-phase epitaxy at 1300–1400 K in the presence of metal nanoparticles (Au, Pt, Cu, Ni, *etc.*) deposited on a substrate surface as a catalyst is, as a rule, used for the synthesis of such threadlike nanostructures of silicon, gallium phosphide and other semiconductors. It has been established[4] that it is possible to grow up successfully such anisotropic materials as Si, Ge, GaP, InP, SiC and GaAs in the form of threads; the threads under the specified conditions are cylindrical. However, it is practically impossible to grow up threadlike nanocrystalline Si and GaP in the presence of drops of bismuth, antimony and some other metals. It was assumed[4] that, in case of threadlike crystallization, the closed boundary of three phases takes main part in the growth mechanism as a source of generation of the steps of vapor → dropping liquid → crystal that is qualitatively similar to the dislocation mechanism of growth.

Silicon carbide and silicon carbonitride are also prospective as new thin-film materials along with silicon oxide and silicon nitride[5] for processing active elements of optoelectronic devices.[1,6,7] Various modifications of gas-phase plasma-enhanced chemical vapor deposition (PCVD, PECVD, afterglow PECVD) are used for the synthesis of materials. Recently, interest has essentially increased to studying silicon sub oxide films $SiO_x$ as initial materials for the processing of silicon light emitting structures. Silicon nanoparticles in oxide matrix are formed under thermal decomposition of amorphous $SiO_x$ on Si and $SiO_2$.[7] A similar method is used to obtain silicon carbide nanofibers (recrystallisation of a powder of amorphous silicon carbide in the presence of a catalyst[8]). Note that the gas-phase CVD without physical stimulation as radio-frequency discharge is more preferable as it excludes radiation damages in product materials.

The nanofiber synthesis of SiC is also carried out using gas-phase CVD from $SiMeCl_3$ in the presence of a catalyst.[9,10] However, only polynanocrystalline nanotubular fibers of SiC consisting of bounded disoriented nanogranules can be obtained.

The present work is aimed at the synthesis of anisotropic nanostructures of silicon and silicon carbide by CVD. For this purpose, the gas-phase pyrolysis of dichlorosilane (DCS) and the reactions of DCS with $CCl_4$ and $CF_2Cl_2$ vapors in mixtures with nitrogen were used. The presence of nitrogen in gaseous mixtures allowed us to obtain silicon carbonitride under experimental conditions.†

The micrograph of a surface fragment of the sample obtained by pyrolysis of DCS in nitrogen (15% DCS–85% $N_2$, 1000 K, total pressure of 1 atm) (Figure 1) indicates the formation of threadlike nanostructures (conic needles 200 nm in diameter

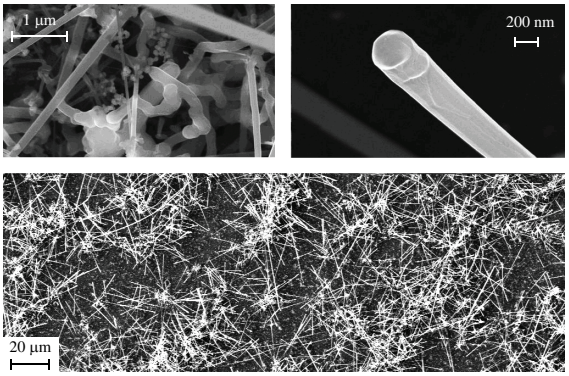


**Figure 1** Micrograph of a surface fragment of the sample obtained in the pyrolysis of DCS in $N_2$ (15% DCS + $N_2$, 1000 K, total pressure of 1 atm).

† The experiments were performed using a static vacuum installation[11] at 1000–1100 K and atmospheric pressure. The reactor was a horizontal quartz cylinder 3.6 cm in diameter and 25 cm in length, equipped with inlets for connection of vacuum communications at both butt-ends. The reactor temperature was set to within ±1 K by means of a KVA-501 temperature gauge. Mixtures of 7.5% DCS–7.5% $CCl_4$–85% $N_2$, 7.5% DCS–7.5% $CF_2Cl_2$–85% $N_2$, 15% DCS–85% $N_2$ were prepared before the experiment. Two plates of silicon 100 (3 cm in length and 0.4 cm in width) were placed in the reactor. The reactor was heated to 1000 or 1100 K with pumping, then filled with the reaction mixture and kept for 1 h at the above temperature. Then, the heating was turned off and when the temperature in the reactor had reached 300 K, the silicon plates were extracted.

When the saturated vapor of $Mo(CO)_6$ (0.17 Torr[12]) was passed through the heated reactor under pumping before the reaction mixture was bled in, a leaky layer of molybdenum metal was deposited on reactor walls and plate surfaces.

The samples obtained were investigated with an Electron Probe X-ray Micro analyzer JCXA-733 Superprobe electronic microscope (JEOL).

The reactor was pumped out by means of a 2NVR-5D pump to $10^{-2}$ Torr after each experiment. The pressure was measured by a gas-discharge manometer and a vacuum gauge. Chemically pure gases ($N_2$ and $CF_2Cl_2$), liquid $CCl_4$ and solid $Mo(CO)_6$ were used in experiments.

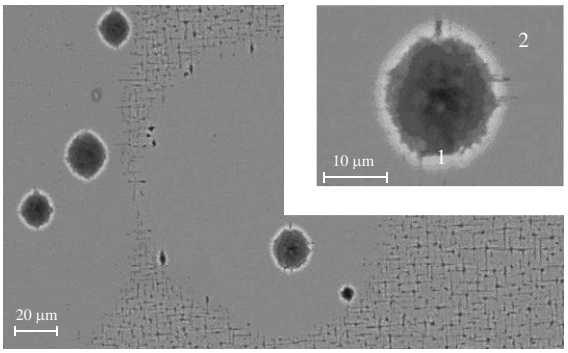


**Figure 2** Micrograph of a surface fragment of the sample obtained in the pyrolysis of a 15% DCS–7.5% $CCl_4$–77.5% $N_2$ mixture at 1000 K (total pressure of 1 atm).

and 10–30 μm in length). The elemental analysis of a needle gives Si, 97.2% and O, 2.8%. Therefore, the CVD allows us to obtain threadlike structures of nanocrystalline silicon. The attempt to obtain such nanostructures on the substrate covered with a leaky layer of molybdenum was unsuccessful. This result is in accordance with published data[4] on impossibility of growing up threadlike nanocrystalline Si in the presence of metal drops.

The micrograph of a surface fragment of the sample obtained by pyrolysis of the mixture of 7.5% DCS–7.5% $CCl_4$–85% $N_2$ (1000 K, total pressure of 1 atm) (Figure 2) shows the formation of etch patterns on the sample surface. The elemental analysis proves that chemical reaction occurs along the borders of etch patterns, *i.e.*, on the most active sites of a surface with excess of free energy.[5] The elemental analysis of site 1 gives C, 12.55%; N, 1.39%; O, 3.88%; Si, 81.64% and other impurities, 0.54%, whereas that of site 2 gives 100% Si (Figure 2); the error of the measurements is < 10%.

Thus, the change in surface state (*e.g.*, covering the surface with a leaky metal layer) makes the formation of threadlike nanostructures impossible, *i.e.*, the material and state of the surface play a considerable role in the process of CVD.

Note that the presence of the fluorine-containing compound in the gas mixture ($CF_2Cl_2$) leads to silicon oxycarbide and carbide formation. As is seen from micrograph of a surface fragment of the sample obtained with the use of reaction mixture of 7.5% DCS–7.5% $CF_2Cl_2$–85% $N_2$ (1000 K, 1 atm) (Figure 3), some threadlike nanostructures are formed on silicon substrate. According to the elemental analysis, the SiC film is deposited on a substrate (C, 32.19%; O, 12.06%; Si, 54.43%; F, 0.9%; Cl, 0.43% Cl and other impurities, 0.27%). The threadlike nanostructures have approximately the same composition: 4–13% O for different sites of the sample at a constant Si/C ratio. The latter means that the presence of oxygen in the sample could be caused by small leakage of atmospheric air during the experiment. Elemental analysis also shows that nitrogen (which forms in

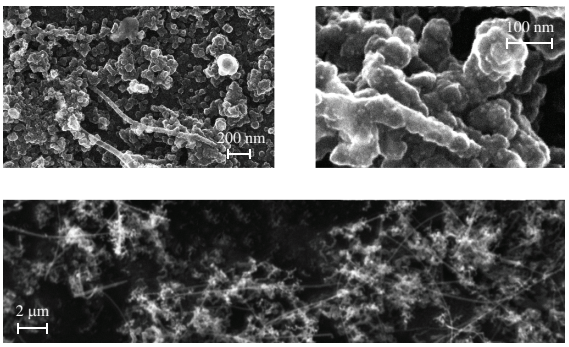


**Figure 3** Micrograph of a surface fragment of the sample obtained in the pyrolysis of a 15% DCS–7.5% $CF_2Cl_2$–77.5% $N_2$ mixture at 1000 K (total pressure of 1 atm).

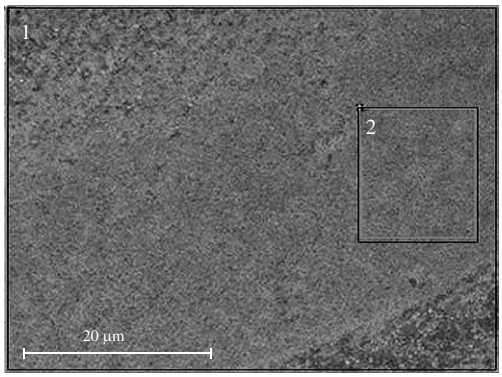


**Figure 4** Micrograph of a nanocrystalline film of silicon carbide obtained by the pyrolysis of a 7.5% DCS–7.5% $CF_2Cl_2$–85% $N_2$ mixture at 1100 K, total pressure of 1 atm). Elemental analysis (%): (1) C, 26.32; O, 6.05; Si, 66.15; Cl, 1.48; (2) C, 32.16; O, 5.65; Si, 60.8; Cl, 1.38.

reaction of the substrate with reactive gas mixture) is missing in the deposited film.

Experiments with the same gas mixture at 1100 K demonstrated that the formation of threadlike nanostructures of silicon oxycarbide no longer occurs; only a nanocrystalline film of silicon carbide forms. Figure 4 exhibits the micrograph of the substrate fragment with both completely and partially covered areas, the average size of crystallites forming this covering is ~30 nm. The elemental analysis data for the film material are close to those for the film obtained at 1000 K.

Thus, the capability of CVD for the synthesis of threadlike nanostructures on the basis of silicon and silicon carbide has been established. Note that the Si–C bond of silicon carbide is formed directly during the synthesis, in contrast to the methods described previously,[9,12] in which it is directly included into the precursor structure (*e.g.*, $MeSiCl_3$). The material and substrate temperature along with gas mixture composition play a determining role in the formation of threadlike nanostructures. Silicon threadlike nanostructures can be obtained only from dichlorosilane as a precursor over a silicon substrate; those of silicon carbide, only from a gaseous mixture of $SiH_2Cl_2$–$CF_2Cl_2$ (1:1) over the silicon substrate at 1000 K.

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