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Description

Nano-wires made of novel precursors and method for the production thereof

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The present invention relates to nanowires which consist of or comprise semiconductor materials and which serve for applications in photovoltaics and electronics, and also to a method for production thereof. A feature of the nanowires is that they are obtained by an innovative method using innovative precursors. The precursors constitute compounds or mixtures of compounds each having at least one direct Si-Si and/or Ge-Si and/or Ge-Ge bond, with substituents which consist of halogen and/or hydrogen and with a composition in which the atomic ratio of substituents to metalloid atoms is at least 1:1.

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Prior art:

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Described in the prior art, for the production of silicon nanowires, is the thermal decomposition of gaseous silicon precursor compounds. Here, besides various silicon compounds, catalytically active metals are employed. Generally speaking, catalyst metal agglomerates of a few nanometers in diameter are produced first of all, and then act catalytically on the decomposition of the silicon compounds and contribute to the ordered deposition of the elemental silicon formed. Depending on the reaction conditions, the resulting nanowires are crystalline or wholly or partly amorphous. It is preferred to use metals which exhibit eutectic mixtures with a low melting temperature with silicon. The model conception says that, under the reaction conditions, a liquid metal/Si mixture is formed, from which, finally, solid Si deposits as a result of further uptake of Si from the

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precursor compounds as they decompose. However, a comparable growth behavior is also observed even at temperatures below the eutectic melting point. Silicon nanowires are deposited predominantly on substrates
5 such as silicon or such as metal oxides, an example being Al_2O_3 .

For example, E.C. Garnett, W. Liang, and P. Yang, Advanced Materials 2007, 79, 2946, describe the
10 production of silicon nanowires by CVD deposition from SiCl_4/H_2 with Pt as catalyst metal, under atmospheric pressure and at 805°C . Y. Zhang, Q. Zhang, N. Wang, Y. Yan, H. Zhou, and J. Zhu, Journal of Crystal Growth 2006, 221, 185, use a similar method under atmospheric
15 pressure with an optimized temperature of 900°C , with Ni as catalyst metal.

It is found that for the epitaxial deposition of silicon nanowires on crystalline silicon it is
20 necessary first of all to remove the oxide layer of the substrate. Where chlorosilanes are used as precursor compounds, there is formation, together with hydrogen additionally present, of HCl, which reacts with the oxide layer (S. Ge, K. Jiang, X. Lu, Y. Chen, R. Wang,
25 and S. Fan, Advanced Materials 2005, 17, 56). When chlorine-free precursor silanes are used, the same effect can be achieved by admixing HCl (S. Sharma, T.T. Kamins, and R.S. Williams, Journal of Crystal Growth 2004, 261, 613). For example, WO 2001/136412,
30 after the production of suitable catalyst metal agglomerates, claims the successive use of at least two different precursor gas mixtures, of which the first mixture comprises either a chlorine-containing silane or, in addition to a silane, another chlorine source,
35 and which ensures the start of growth, but requires comparatively high temperatures for the decomposition. Thereafter the reaction temperature is lowered and a

second precursor gas is used, which has a lower decomposition temperature. Suitable precursor compounds cited are SiH_4 , Si_2H_6 , SiCl_4 , and SiH_2Cl_2 . Examples of suitable catalyst metals are Au, Al, Pt, Fe, Ti, Ga, Ni, Sn, or In. In addition to the conventional CVD technique for producing silicon nanowires, there are also references to Plasma Enhanced Sputter Deposition and Plasma Enhanced CVD, which allow a reduction in the reaction temperature.

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W.I. Park, G. Zhenq, X- Jiang, B. Tian, and C.M. Lieber, Nano Letters 2008, 8, 3004, describe how at 400°C and 10 torr pressure, the growth rate of silicon nanowires with Au as catalyst is 130 times greater for disilane, Si_2H_6 , than for SiH_4 . Even with reaction temperatures optimized for SiH_4 , the growth rate lags behind that starting from disilane by a factor of 31. S. Akhtar, A. Tanaka, K. Usami, Y. Tsuchiya, and S. Oda, Thin Solid Films 2008, 517, 317, show that nanowires can be produced from $\text{Si}_2\text{H}_6/\text{H}_2$ using Au catalyst even at a temperature of 350°C and under a pressure of 3 torr. For example, JP 2006117475 A and JP 2007055840 A describe the production of Si nanowires at temperatures as low as 250-300°C, using disilane and trisilane as silicon sources, employing the metals Au, Ag, Fe, and/or Ni as catalysts, and setting a pressure during the reaction of 1-5 torr.

30 H.-Y. Tuan, D.C. Lee, T. Hanrath, and B.A. Korgel, Nano Letters 2005, 5, 681, show that the formation of Si nanowires takes place even without a substrate in supercritical organic solvents at 400-520°C and a pressure of 14.3 - 23.4 MPa. The catalyst metal used is Ni, and, in addition to trisilane, Si_3H_8 , the precursor compounds employed include octylsilane and phenylsilane. A.T. Heitsch, D.D. Fanfair, H.-Y. Tuan,

and B.A. Korgel, Journal of the American Chemical Society 2008, 130, 5436, show that for trisilane as precursor molecule, this reaction leads to Si nanowires even under atmospheric pressure and at boiling
5 temperature (420-430°C) with high-boiling organic solvents.

A disadvantage of the use of silanes ($\text{Si}_n\text{H}_{2n+2}$) is their pyrophoric properties (self-ignitability in air), which
10 hinder handling.

Objective:

The object on which the present invention is based is
15 that of providing innovative nanowires by a new method from suitable precursors of the specified kind that are new for this purpose. The intention, moreover, is to provide a method for producing such nanowires.

20 Definitions:

Precursors for the growth of nanowires are silicon and/or germanium-containing compounds which are converted into elemental silicon and/or germanium under
25 the process conditions.

Polysilanes in the sense of the invention are compounds having at least one Si-Si bond. According to one embodiment of the invention, polysilanes are
30 halogenated and hydrogenated polysilanes and also polysilanes having organic substituents, and the corresponding partially halogenated and partially hydrogenated polysilanes, having the following general formula: $\text{Si}_n\text{X}_a\text{H}_b$, where $a+b$ is greater than or equal to
35 $2n$ and less than or equal to $2n+2$, a and b are each greater than or equal to 0, and X = halogen, amine substituent or organic radical, such as alkyl radicals,

for example, more particularly methyl. It is also possible, furthermore, to use polysilanes with organic substituents for SiC nanowires, or with amine substituents for SiN nanowires. It is also possible, furthermore, to use polysilanes having (transition) metal substituents.

Polygermanes in the sense of the invention are compounds having at least one Ge-Ge bond. According to one embodiment of the invention, the polygermanes are halogenated and hydrogenated polygermanes and also the corresponding partially halogenated and partially hydrogenated polygermanes, having the following general formula: $\text{Ge}_n\text{X}_a\text{H}_b$, where $a+b$ is greater than or equal to $2n$ and less than or equal to $2n+2$, a and b each being greater than or equal to 0, and X = halogen, amine substituent or organic radical, such as alkyl radicals, for example, more particularly methyl. Furthermore, polygermanes with organic substituents can also be used for GeC nanowires, or, with amine substituents for GeN nanowires. It is also possible, furthermore, for polygermanes having (transition) metal substituents to be used.

Polygermasilanes in the sense of the invention are compounds having at least one Si-Ge bond. According to one embodiment of the invention, polygermasilanes are halogenated and hydrogenated polygermasilanes, and also the corresponding partially halogenated and partially hydrogenated polygermasilanes, having the following general formula: $\text{Si}_{n-z}\text{Ge}_z\text{X}_a\text{H}_b$ or $\text{Si}_z\text{Ge}_{n-z}\text{X}_a\text{H}_b$, where $a+b$ is greater than or equal to $2n$ and less than or equal to $2n+2$, a and b each being greater than or equal to 0, n is greater than z , and X = halogen, amine substituent or organic radical, such as alkyl radicals, for example, more particularly methyl. Additionally it is also possible to use polygermasilanes having organic

substituents for SiGeC nanowires, or having amine substituents for SiGeN nanowires. Additionally it is also possible to use polygermasilanes having (transition) metal substituents.

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By p-doped precursors is meant that the respective compound/the mixture comprises a fraction of p-doping atoms such as boron, aluminum, gallium, or indium, preferably boron atoms, that is useful for the desired semiconductor properties of the deposition product (e.g., Fermi level), it being possible for these atoms either to be incorporated into the precursor molecules or to be admixed as separate compounds to the precursors.

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By n-doped precursors is meant that the respective compound/the mixture comprises a fraction of n-doping atoms such as nitrogen, phosphorus, arsenic, antimony, or bismuth, preferably phosphorus atoms, that is useful for the desired semiconductor properties of the deposition product (e.g., Fermi level), it being possible for these atoms either to be incorporated into the precursor molecules or to be admixed as separate compounds to the precursors.

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Further doping elements may be taken from the groups of the Periodic Table of the Elements to the left and right of main group 4 (group 14), preferably from groups 13 and 15.

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Monosilanes and monogermanes are all compounds having in each case only one silicon atom or one germanium atom. SiX_aH_b and GeX_aH_b , where $a+b$ is 4, and a and b are each greater than or equal to 0.

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The term "metalloid atoms" refers to atoms of the semimetals silicon and germanium.

The expressions "...consist of halogen..." or "...consist of hydrogen..." mean that apart from minor other constituents (< 1% by mass), the substituents consist
5 exclusively of halogen or of hydrogen, respectively.

By "predominantly" is meant that the constituent in question is present in the mixture to an extent of more than 80% by mass.

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"Virtually no[ne]" means that a secondary constituent is present at less than 5% by mass in a mixture.

Description:

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The nanowires produced in accordance with the invention are notable for the fact that the innovative precursors used are liquid under standard conditions (room temperature, atmospheric pressure) with one exception
20 (Si_2H_6) and are soluble in numerous solvents, meaning that they can be handled more easily and securely than many conventional precursors, such as monosilane, for example. Examples of solvents which are inert relative to the precursors are monochlorosilanes, such as SiCl_4 ,
25 liquid alkanes, such as hexane, heptane, pentane, and octane, and also aromatics, such as benzene, toluene, and xylene, for example.

In certain embodiments of the invention, particularly
30 preferred precursors are the highly chlorinated polysilanes, polygermanes, polygermasilanes, more particularly $\text{Si}_n\text{Hal}_{2n+2}$ with $\text{Hal} = \text{Cl}, \text{F}, \text{Br}, \text{or I}$, preference being given to using $\text{Si}_n\text{Cl}_{2n+2}$ with $n = 2 - 10$, more preferably with $n = 2 - 5$. Polygermanes which can
35 be used are, generally, compounds of the general formula $\text{Ge}_n\text{Hal}_{2n+2}$, with $\text{Hal} = \text{Cl}, \text{F}, \text{Br}, \text{or I}$, preferably $\text{Ge}_n\text{Cl}_{2n+2}$. Polygermasilanes which can be used

are compounds of the general formula $\text{Si}_{n-x}\text{Ge}_x\text{Hal}_{2n+2}$ or $\text{Si}_x\text{Ge}_{n-x}\text{Hal}_{2n+2}$ with $n > x$, it being possible for the parameter n in the case of the polygermanes and polygermasilanes to be $n = 2 - 10$, more preferably
5 $n = 2 - 5$.

According to a further embodiment of the invention, the nanowires may be obtained from precursors which contain virtually no rings, the amount of rings, based on the
10 overall product mixture, being below $< 2\%$ by mass.

According to a further embodiment of the invention, the nanowires may be obtained from precursors which contain virtually no branched chains, the amount of branching
15 sites, based on the overall product mixture, being below $< 5\%$ by mass, preferably $< 2\%$ by mass. It is possible, for example, to use halogenated polysilanes having a low fraction of rings and having chains with low degrees of branching, these polysilanes being of
20 the kind described in PCT application WO2009/143823 A2, hereby incorporated in full by reference in relation to their properties and synthesis.

Furthermore, the nanowires may be obtained from
25 precursors which consist predominantly of branched chains. It is possible, for example, to use halogenated polysilanes having a high fraction of rings and having branched chains, of the kind described in PCT application WO 2009/143824 A1, hereby incorporated in
30 full by reference in relation to their properties and synthesis.

According to another embodiment of the invention it is possible to obtain nanowires from precursors whose
35 substituents consist exclusively of hydrogen. In this case, for example, polysilanes, polygermanes or polygermasilanes of the general formulae $\text{Si}_n\text{H}_{2n+2}$,

$\text{Ge}_n\text{H}_{2n+2}$ and/or $\text{Si}_{n-x}\text{Ge}_x\text{H}_{2n+2}$ or $\text{Si}_x\text{Ge}_{n-x}\text{H}_{2n+2}$ with $n > x$ with $n = 3 - 10$, more preferably with $n = 3 - 5$, can be used as precursors. It is also possible to use cyclic polysilanes, polygermanes and polygermasilanes having
5 the general formulae Si_nH_{2n} , Ge_nH_{2n} and/or $\text{Si}_{n-x}\text{Ge}_x\text{H}_{2n}$ or $\text{Si}_x\text{Ge}_{n-x}\text{H}_{2n}$, with $n > x$ with $n = 3 - 10$, more preferably with $n = 4 - 6$.

The gas mixture (precursor and carrier gas and/or
10 hydrogen) used in the context of the method of the invention may additionally be diluted with an inert gas, such as helium, neon, argon, krypton, xenon, or nitrogen, for example, and/or may comprise further admixtures (additives), such as doping additives,
15 examples being liquid or solid boron compounds, metallic compounds or phosphorus compounds, for example. Examples are BBR_3 , TiCl_4 , or PCl_3 . In the context of the method of the invention, the admixing of inert gases is, however, not mandatory.

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The deposition temperatures in the method of the invention lie between $250 - 1100^\circ\text{C}$, preferably between 330 to 950°C .

25 Some embodiments of the method of the invention are notable for the fact that nanowires can be obtained from the precursors of the invention without the presence of hydrogen in free or bonded form being necessary during the deposition, since there are other
30 semiconductor-yielding reactions present, as for example: $\text{Si}_3\text{Cl}_8 \rightarrow 2 \text{SiCl}_4 + \text{Si}$, $\text{Ge}_3\text{Cl}_8 \rightarrow 2 \text{GeCl}_4 + \text{Ge}$, $3 \text{GeSi}_2\text{Cl}_6 \rightarrow 4 \text{SiCl}_4 + 2 \text{GeCl}_4 + \text{GeSi}_2$. In the case of certain embodiments of the invention, this is possible through use of highly halogenated, more particularly
35 highly chlorinated, polysilanes of the general formula $\text{Si}_n\text{Cl}_{2n+2}$ with $n = 2 - 10$, more preferably with $n = 2 - 5$, or by using the corresponding highly halogenated, more

particularly high chlorinated, polygermanes or polygermasilanes.

5 The reaction pressures in the case of the method of the invention are situated in the range from 0.1 hPa to 2200 hPa, preferably at 1 hPa to 1100 hPa, more preferably between 200 hPa and 1100 hPa.

10 The partial pressures of the precursors of the invention may be adjusted in a simple way by varying the temperatures of the reservoir vessel and also by admixing further gas components.

15 Metallic catalysts employed for the deposition of the nanowires of the invention include metals such as bismuth, preferably transition metals, such as Cu, Ag, Ni, and Pt, for example, or else Au, or mixtures thereof.

20 By using the precursors of the invention it is possible to employ catalysts which do not affect the electronic properties of the nanowires. Ni and Pt particularly are compatible with typical metal oxide semiconductor technologies.

25 According to a further embodiment of the invention, the innovative precursors are able to be decomposed over the metallic catalysts to form the corresponding elements, as for example Si or Ge, and/or alloys, as
30 for example Si-Ge alloys, and so form the nanowires.

The particle sizes (diameters) of the catalysts are 5 nm to 1000 nm, preferably 20 nm - 200 nm, and can be determined by means of an electron microscope, for
35 example.

The nanowires of the invention possess diameters in the

range from 50 to 1200 nm and lengths in the range from 100 to 100 000 nm, and other dimensions are obtainable as well by varying the growth times.

- 5 The growth rates are situated in the range from 5 nm to 5000 nm per minute.

By using the precursors of the invention and/or at low process temperatures of below 600°C during the
10 formation of the nanowires, the growth of the nanowires of the invention can also be carried out without formation of hydrogen halide, thereby exerting an influence also on the etching behavior and the epitaxially associated orientation of the nanowires.

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The precursors of the invention are preferably suitable both for the gas/liquid/solid phase growth process and for the gas/solid/solid phase growth process. In the case of the gas/liquid/solid phase growth process, a
20 liquid eutectic mixture is formed from the metal and the semimetal element (e.g., gold/silicon), from which silicon deposits on the solid wire and in which fresh silicon dissolves by decomposition of the precursors in the gas phase. In the case of the gas/solid/solid phase
25 growth process, a solid alloy of the semimetal element in the metal is formed by the dissolution of the element after decomposition of the precursor and also by the deposition from the solid alloy onto the nanowire as a result of diffusion processes in the
30 solid alloy.

In the case of certain embodiments of the invention, by using the precursors of the invention, such as the highly halogenated polysilanes, polygermanes or
35 polygermasilanes, for example, it is possible to obtain hydrogen-free nanowires, since the use of hydrogen is not necessary for producing the nanowires.

A further feature of the nanowires produced in accordance with the invention is that the innovative precursors used may be designed preferably as single-
5 source precursors for doped semiconductor regions. As a result of this it is possible to do away with the use of toxic or otherwise hazardous dopants, such as phosphine and diborane, for example, which in conventional doping processes necessitate the use of
10 costly gas supply and safety systems. According to one embodiment of the invention, therefore, it is possible to produce the nanowires using exclusively the precursors, without additional reactive gases, such as hydrogen, for example.

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Moreover, a feature of the nanowires produced in accordance with the invention is that the innovative precursors used can be used in temporal alternation, i.e., for example, p-doped and n-doped precursors
20 alternately, for the growth, with the precursors being switched at least once during the process. In this way it is possible to obtain, for example, differently doped regions preferably in alternation in the longitudinal direction, more particularly p/n
25 junctions, which are important, for example, for the photovoltaic effect. In a corresponding way it is also possible, furthermore, to produce alternating regions having different Si:Ge ratios.

30 In addition it is possible to obtain nanowires having compositions which alternate in growth direction. For this purpose, different precursors/precursor mixtures can be provided in alternation during growth. As a result it is possible to obtain, for example, different
35 dopings or alloys in a crystal of a nanowire.

A further feature of the method of the invention for

producing nanowires is that during the deposition of the nanowires, besides the nanowires, less than 10% of pulverulent by-products, comprising, for example, the elemental semimetals Si or Ge, are deposited in the
5 deposition region of the nanowires. These unwanted by-products may be formed as a result of unwanted, uncatalyzed decomposition of the precursors.

All of the precursors of the invention can also be used
10 for the epitaxial growth of nanowires on crystalline Si substrates.

Working example:

15 Using highly chlorinated polysilanes of the formula $\text{Si}_n\text{Cl}_{2n+2}$ with $n = 2 - 10$, such as Si_3Cl_8 , for example, as precursors, and with Au as metallic catalyst, nanowires can be produced with decomposition of the precursors at temperatures between 400°C to 900°C . Besides the
20 precursors, only helium, as inert gas, was present, and so the nanowires were produced in particular in the absence of hydrogen or other reactive gases. The nanowires had dimensions of $2\text{ }\mu\text{m}$ to $20\text{ }\mu\text{m}$ in length, and a width of 50 nm to 500 nm .

Claims

1. Nanowires which consist of or comprise semiconductor materials and serve for applications in photovoltaics and electronics, characterized in that they are produced from precursors which constitute compounds or mixtures of compounds each having at least one direct Si-Si and/or Ge-Si and/or Ge-Ge bond, with substituents consisting of halogen and/or hydrogen and with a composition in which the atomic ratio of substituents to metalloid atoms is at least 1:1.
2. The nanowires according to claim 1, characterized in that they are obtained from precursors which for deposition do not require the presence of hydrogen in free or bonded form.
3. The nanowires according to either of the preceding claims, characterized in that they are obtained from precursors which contain virtually no rings, the amount of rings, based on the overall product mixture, being below < 2% by mass.
4. The nanowires according to any of the preceding claims, characterized in that they are obtained from precursors which contain virtually no branched chains, the amount of branching sites, based on the overall product mixture, being below < .5% by mass, preferably < 2% by mass.
5. The nanowires according to any of claims 1 to 3, characterized in that they are obtained from precursors which consist predominantly of branched chains.
6. The nanowires according to any of the preceding

claims, characterized in that they are obtained from precursors whose substituents consist exclusively of halogen, more particularly chlorine.

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7. The nanowires according to any of claims 1 to 5, characterized in that they are obtained from precursors whose substituents consist exclusively of hydrogen.

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8. The nanowires according to any of claims 1 to 4 or 6, 7, characterized in that they are obtained from precursors which consist predominantly of linear chains.

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9. The nanowires according to any of the preceding claims, characterized in that they are obtained from precursors which possess an average chain length of $n = 2-6$, preferably $n = 2-5$.

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10. The nanowires according to any of the preceding claims, characterized in that they are obtained from precursors which are readily soluble in inert solvents.

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11. The nanowires according to any of the preceding claims, characterized in that they are obtained from precursors which are not pyrophoric, such as, for example, highly halogenated polysilanes, the halogen being more particularly Cl and/or Br.

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12. The nanowires according to any of the preceding claims, characterized in that they contain less than 1 atom% of hydrogen.

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13. The nanowires according to any of the preceding claims, characterized in that they contain 10 ppb

to 50 000 ppm, preferably 10 ppb to 100 ppm, of halogen, preferably chlorine.

- 5 14. The nanowires according to any of the preceding claims, characterized in that they are obtained from precursors which have an H content of less than 5 atom%, preferably less than 2 atom%.
- 10 15. The nanowires according to any of the preceding claims, characterized in that they are obtained from precursors which comprise p-doping atoms incorporated in the precursor molecules.
- 15 16. The nanowires according to any of the preceding claims, characterized in that they are obtained from precursors which comprise n-doping atoms incorporated in the precursor molecules.
- 20 17. The nanowires according to any of the preceding claims, characterized in that they are obtained from precursors which comprise p-doping additions as separate additives in the mixture.
- 25 18. The nanowires according to any of the preceding claims, characterized in that they are obtained from precursors which comprise n-doping additions as separate additives in the mixture.
- 30 19. The nanowires according to any of the preceding claims, characterized in that they are obtained from precursors which comprise doping additions from the groups of the Periodic Table of the Elements to the left and right of main group 4 (group 14), preferably from groups 13 and 15.
- 35 20. The nanowires according to any of the preceding claims, characterized in that they are obtained

from the precursors, with admixtures from the group of the monosilanes and/or the monogermanes having been added additionally.

- 5 21. The nanowires according to any of the preceding
claims, characterized in that they are obtained
from precursors which are decomposed over
catalysts for the deposition of the nanowires of
the invention, with catalysts employed being
10 metals, preferably transition metals, or mixtures
thereof.
22. The nanowires according to any of the preceding
claims, characterized in that they are obtained
15 from precursors which are suitable both for the
gas/liquid/solid phase growth process and for the
gas/solid/solid phase growth process.
23. A method for producing nanowires according to any
20 of the preceding claims by reacting precursors, or
precursors and hydrogen, characterized in that a
precursor:hydrogen mixing ratio of 1:0 to 1:1 000
000 is operated.
- 25 24. The method according to preceding claim 23,
characterized in that the deposition takes place
without presence of hydrogen in elemental or
bonded form.
- 30 25. The method according to any of the preceding
claims, characterized in that less than 10% of
pulverulent by-products occur in the deposition of
the nanowires.
- 35 26. The method according to any of the preceding
claims, characterized in that a pressure range of
0.1 - 2200 hPa, preferably 1 to 1200 hPa is

operated.

27. The method according to any of the preceding claims, characterized in that the deposition takes place at a temperature of 250°C to 1100°C, preferably 300°C to 950°C, more preferably, in particular 350°C to 900°C.
28. A method for producing nanowires according to any of the preceding claims by reacting precursors, or precursors and hydrogen, characterized in that different precursors for the growth are used in temporal alternation, the precursors being switched at least once during the process.
29. A method for producing nanowires according to any of the preceding claims by reacting precursors, or precursors and hydrogen, characterized in that nanowires having compositions which alternate in growth direction are obtained.