Methods for producing nanostructured silicon and silicon-germanium via solid state metathesis (SSM). The method of forming nanostructured silicon comprises the steps of combining a stoichiometric mixture of silicon tetraiodide (SiI₄) and an alkaline earth metal silicide into a homogeneous powder, and initiating the reaction between the silicon tetraiodide (SiI₄) with the alkaline earth metal silicide. The method of forming nanostructured silicon-germanium comprises the steps of combining a stoichiometric mixture of silicon tetraiodide (SiI₄) and a germanium based precursor into a homogeneous powder, and initiating the reaction between the silicon tetraiodide (SiI₄) with the germanium based precursors.
References Cited

OTHER PUBLICATIONS


* cited by examiner
FIG. 10
RAPID SOLID-STATE METATHESIS ROUTES TO NANOSTRUCTURED SILICON-GERMANIUM

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority from provisional patent application U.S. Ser. No. 61/352,499 entitled “RAPID SOLID-STATE METATHESIS ROUTES TO NANOSTRUCTURED SILICON-GERMANIUM,” filed Jun. 8, 2010 hereby incorporated by reference.

This invention was made with Government support under Grant No. 1308818, awarded by the Jet Propulsion Laboratory/NASA, Grant No. NNX09AM26H awarded by NASA, and Grant No. 0805357 awarded by the National Science Foundation. The Government has certain rights in this invention.

FIELD

The present disclosure relates generally to nanostructured silicon and silicon-germanium, and more particularly to methods of producing nanostructured silicon and silicon-germanium via solid state metathesis (SSM).

BACKGROUND

Nanostructured silicon and silicon-germanium are attractive materials for a variety of applications due to their abundance, stability and low toxicity. Recently, nanostructured silicon and silicon-germanium have been utilized in several applications from thermoelectrics, photovoltaics, solar cell batteries and biological imaging. Several methods exist for producing silicon, such as the pyrolysis of silane, pulsed laser ablation, MOCVD, MBE, plasma etching and electrochemistry. However, these aforementioned methods are inherently limited due to the expense, complex equipment, toxic precursors and difficulty of scaling up the reactions to produce on a commercial scale. An alternative method of producing nanostructured silicon involves a solution-based synthetic technique. The drawback of the solution-based synthetic technique is the use of a long chain hydrocarbon capping ligand necessary to prevent particle agglomeration. The capping ligand, however, adds additional processing steps prior to use of the nanostructured silicon for applications where electron transfer is critical, such as in thermoelectrics or in solar cells.

Thus, there is a need for a new method for producing nanostructured silicon and nanostructured silicon-germanium, which is relatively inexpensive, does not require expensive equipment or toxic precursors and is capable of being scaled-up efficiently to produce commercial amounts of the reaction product.

SUMMARY

The present disclosure relates generally to nanostructured silicon and silicon-germanium, and more particularly to methods of producing nanostructured silicon and silicon-germanium via solid state metathesis (SSM). The method of forming nanostructured silicon comprises the steps of combining a stoichiometric mixture of silicon tetraiodide (SiI₄) and an alkaline earth metal silicide into a homogeneous powder, and initiating the reaction between the silicon tetraiodide (SiI₄) with the germanium-based precursors. Other systems, methods, features and advantages of the example embodiments will be or will become apparent to one with skill in the art upon examination of the following figures and detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is powder X-ray diffraction pattern of nanostructured Si made from SiI₄ using (a) CaSi and (b) Mg₂Si.

FIGS. 2a, 2c and 2f are images of nanostructured silicon produced from the solid state metathesis of SiI₄ and 2CaSi. FIG. 2b is an EDS image of the nanostructured silicon shown in FIGS. 2a, 2c and 2f.

FIGS. 3a, 3c and 3d are images of nanostructured silicon produced from the solid state metathesis of SiI₄ and Mg₂Si. FIG. 3b is an EDS image of the nanostructured silicon shown in FIGS. 3a, 3c and 3d.

FIG. 4 illustrates crystallite size and calculated maximum adiabatic temperature as a function of NaCl addition mol% according to the reaction of SiI₄ and 2CaSi.

FIG. 5 is time-lapse photography images of the reaction between Mg₂Si and SiI₄ initiated by a drop of ethanol.

FIGS. 6a is an image of nanostructured germanium produced using a germanium-based precursor. FIG. 6b is an EDS image of the nanostructured germanium shown in FIG. 6a.

FIG. 7 is an SEM image of nanostructured silicon-germanium using germanium in the solid state metathesis reaction of SiI₄ and 2CaSi.

FIGS. 8a and 8d are images of nanostructured silicon-germanium using germanium in the solid state metathesis reaction of SiI₄ and 2CaSi. FIGS. 8b and 8c are EDS images of the nanostructured silicon-germanium shown in FIGS. 8a and 8d.

FIGS. 9a and 9b are images of nanostructured silicon using tin in the solid state metathesis of SiI₄ and 2CaSi. FIG. 9c is an EDS image of the nanostructured silicon shown in FIGS. 9a and 9b.

FIGS. 10a and 10b are images of nanostructured silicon-germanium produced using a germanium-based precursor.

DETAILED DESCRIPTION

The term, “EDS,” as used herein refers to energy dispersive spectroscopy, which is an analytical technique used for the elemental analysis or chemical characterization of a sample. As used herein, the term “nanoparticle” is a microscopic particle with at least one dimension less than 100 nm. Nanoparticle can comprise multiple configurations or morphology and be referred to synonymously with the terms nanowire, nanocluster, nanocrystal or nanowires. The term, as used herein, “nanowire” is a nanostructure or nano-morphology, with the diameter of the order of a nanometer (10⁻⁹ meters). Alternatively, nanowires can be defined as structures that have a thickness or diameter constrained to tens of nanometers or less and an unconstrained length. Typical nanowires exhibit aspect ratios (length-to-width ratio) of 1000 or more.

As used herein “Powder X-ray Diffraction” refers to a scientific technique using X-ray, on powder samples for structural characterization of materials. In the example embodiments, the dried products were examined by powder X-ray diffraction (XRD) using a PANalytical Powder X-ray diffractometer using Cu Kα (λ=1.5408 Å) radiation. The X-ray scans were conducted with a range of 10°≤θ≤100° at 0.033 degree intervals and 25.13 second count times.
The term, "precursor," as used herein, is a compound that participates in the chemical reaction that produces another compound. The precursors used in the methods of the present embodiments include, but are not limited to, alkaline earth silicide precursors (Mg$_2$Si or CaSiMg, or CaSi$_2$), germanium-based precursors (Mg$_2$Ge or GeC$_6$), alkali silicides or germanides (Li$_2$Si or Na$_4$Si) and the like.

As used herein, the term "solid state metathesis" or "SSM" refers to the method of synthesizing compounds from two solids where one portion of one molecule is transferred to the other molecule. In the present embodiments, SSM reactions are highly exothermic double displacement reactions, driven by not only the formation of the product but the thermodynamically favorable formation of a salt. The salt is washed away with water or acid leaving behind the desired product. The SSM reactions in present embodiments can utilize two metathesis initiation techniques, such as resistivity heated nickel wire initiation, or can be initiated mechanochemically by a high-energy ball mill.

The term, TEM, as used herein refers to transmission electron microscopy, which is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, which is a crystallographic experimental technique that can be performed inside a transmission electron microscope (TEM).

The methods of the present embodiments have an advantage over the current method because the methods can be scaled up from milligram quantities to gram scale reactions, since these SSM reactions can be initiated mechanochemically by a high-energy ball mill. Another advantage of the ball milling initiation method is that all of the reactants can be consumed during the reaction due to the continuous injection of energy into the reaction. One problem with other metathesis initiation techniques, such as resistivity heated nickel wire initiation, is that it often leads to incomplete reaction propagation and a significant amount of the starting material remains.

A significant feature of the method described herein is the solid state metathesis reaction between precursors and silicon tetraiodide (SiI$_4$). In one embodiment, an alkaline earth silicide precursor (Mg$_2$Si or CaSi or CaSi$_2$) is reacted with silicon tetraiodide (SiI$_4$). In other embodiments, other compounds and alloys such as nanostructured germanium and nanostructured silicon-germanium can be produced utilizing other precursors.

The idealized reactions between silicon tetraiodide and the alkaline earth silicide precursors are:

\[
2 \text{CaSiI}_4(s) + \text{SiI}_4(s) \rightarrow 3 \text{SiI}_6(s) + 2 \text{CaI}_2(s) \quad \quad [1]
\]

\[
\text{Mg}_2\text{Si}(s) + \text{SiI}_4(s) \rightarrow 2 \text{SiI}_6(s) + 2 \text{MgI}_2(s) \quad \quad [2]
\]

When the two reactants, shown in reactions 1 and 2 are homogenously mixed and initiated, a double displacement reaction occurs yielding nanostructured silicon and a salt as the end products. The salts in the respective reactions, 2CaI$_2$(s) and 2MgI$_2$(s), are washed away with either water or ethanol. Depending on which silicide precursor is used, two different morphologies are obtained, either nanoparticles or dendritic nanowires.

For the calcium silicide reactions, shown in reactions 1, which yield nanostructured silicon with the nanoparticle morphology, the reactions can either be initiated using a resistivity heated nichrome wire or using the mechanochemical technique of high-energy ball milling. The nichrome wire is heated to a temperature of above 800° C. In the high-energy ball milling method, each of the reagents or chemicals is all added separately at one time and subsequently ball milled together.

For the magnesium silicide reaction, shown in reaction 2, which yields the nanowire morphology, the precursors are ball milled to obtain a high surface area and a homogenous reaction mixture. The actual reaction does not occur in the ball mill, but is initiated via a drop of ethanol. The mechanism by which the nanowire morphology is produced is speculated to be a two-step mass transfer kinetic process. The first step of the mass transfer kinetic process involves the ethanol droplet reacting with the high surface area Mg$_2$Si precursor to oxidize it to MgO and SiH$_4$ (Equation 3):
reaction (6):

\[ \text{WMg}_{2}\text{Ge}+\text{XGeSi}+\text{YSi}_{2}+\text{ZGeI}_{4} \rightarrow \text{Si}_{1-x}\text{Ge}_{x}+\text{MgI}_{2} \]  

Additionally, a composite or an alloy can be made by a mixture of the germanide and silicide precursors (reaction 7):

\[ \text{WMg}_{2}\text{Ge}+\text{XGeSi}+\text{YSi}_{2}+\text{ZGeI}_{4} \rightarrow \text{Si}_{1-x}\text{Ge}_{x}+\text{MgI}_{2} \]

In addition, the method described herein can include the use of alkaline earth silicides (such as \( \text{Mg}_{2}\text{Si} \) and \( \text{CaSi} \)) and silicon tetrasilide. It could be expanded to utilize alkali based precursors such as alkali silicides or germanides (\( \text{Li}_{2}\text{Si} \) or \( \text{Na}_{2}\text{Si} \)) and other silicon tetrahalides (or germanium tetrahalides) such as \( \text{SiCl}_{4} \) or \( \text{SiBr}_{4} \). Due to the fact that the end product is isolated in air, a native oxide layer may exist on the nanostructured silicon. However, the native oxide layer may be removed from the nanostructured end product by an etching treatment with hydrofluoric acid or a similar treatment known to one of ordinary skill in the art.

**EXAMPLE EMBODIMENTS**

The example embodiments are made using the following reagents: \( \text{SiI}_{4} \) (99% available from Alfa Aesar, Ward Hill, Mass.), \( \text{CaSi} \) (99.5% available from GPS Chemicals, Inc. Powell, Ohio), \( \text{CaSi}_{2} \) (95% available from Strem Chemicals, Inc. Newburyport, Mass.), \( \text{Mg}_{2}\text{Si} \) (99.5% available from Materion Corporation, Mayfield Heights, Ohio) \( \text{Mg}_{2}\text{Ge} \) and \( \text{GeI}_{4} \) (Alfa Aesar/Ward Hill, Mass.).

Example 1 illustrates the solid state metathesis of nanostructured silicon by reacting \( \text{SiI}_{4} \) and \( 2\text{CaSi} \). The reaction of Example 1 is performed using the following idealized reaction:

\[ 2\text{CaSi}(s)+\text{SiI}_{4}(s) \rightarrow 3\text{Si}(s)+2\text{CaI}_{2}(s) \]

Stoichiometric mixtures of the precursor materials were ground to a homogeneous powder in an argon—or helium-filled glove box. The reactions in Example 1 are initiated using a resistively heated nichrome wire. For reaction using the nichrome initiated method the precursor amounts were measured and have a total precursor mass of 2 grams (~0.25 g yield of the Si product via CaSi and CaSi_{2} synthesis). The powders were then subjected to a resistively heated nichrome wire, which is heated to more than 800 °C, to initiate the reaction. It is noted that solid state metathesis reactions are extremely exothermic and may initiate upon grinding. Safety precautions should be taken prior to conducting these types of reactions or when scaling up. The resultant product of the embodiment of Example 1 is characterized by one or more of the following features, including powder X-ray Diffraction; Scanning Electron Microscopy (SEM); Transmission Electron Microscopy (TEM); Energy dispersive spectroscopy (EDS) or selected area (electron) diffraction (SAED).

FIG. 1 illustrates the powder X-ray diffraction pattern of nanostructured Si made from \( \text{SiI}_{4} \) using CaSi marked (a) at the bottom. The stick pattern overlay is the JCPDS file 00-027-1402 for silicon. FIGS. 2a, 2c, and 2d are images of nanostructured silicon produced from the solid state metathesis of \( \text{SiI}_{4} \) and \( 2\text{CaSi} \). As shown in FIGS. 2a, 2c, and 2d, the reaction of Example 1 yields the nanostructured silicon that comprises a nanoparticle morphology.

FIG. 2a is a SEM image of the dried product from the reaction of \( \text{SiI}_{4} \) and \( \text{CaSi} \), which shows aggregates of Si nanoparticles ranging from submicron to micron-sized particles. The EDS image in FIG. 2b, confirms that the end product is composed mainly of Si with some surface oxides and a slight Ca impurity. FIG. 2c is the transmission electron microscopy image demonstrating that the large silicon nanoparticles are actually aggregates of smaller Si nanoparticles ranging from 30 to 50 nm in size, which is in agreement with the crystallite size calculated from XRD. The TEM diffraction pattern from...
reactions. The reactants were loaded into tungsten carbide vials with several tungsten carbide balls (SPEX CertiPrep Inc., Metuchen, N.J.) and milled for several hours. In the synthesis involving Mg$_2$Si and SiI$_4$, the precursor materials were ball milled to a homogeneous powder and the reaction was initiated using approximately 200 microliters of ethanol. It is also noted that solid state metathesis reactions are highly exothermic and should be handled in a fume hood or glove box. This step involves the evolution of molecular iodine. The final products were washed with 50% 6 M HCl/50% ethanol to remove the salt by-product, then washed with ethanol and finally dried in air. All three of the reactions had over 90% yield in the product. The resultant product of the embodiment described in Example 5 is characterized by one or more of the following techniques, including powder X-ray Diffraction; Scanning Electron Microscopy (SEM); Transmission Electron Microscopy (TEM); Energy dispersive spectroscopy (EDS) or selected area (electron) diffraction (SAED).

FIG. 1 illustrates the powder X-ray diffraction pattern of nanostructured Si made from SiI$_4$ using Mg$_2$Si marked (b). FIGS. 3a, 3c and 3d are images of nanostructured silicon produced from the solid state metathesis of SiI$_4$ and Mg$_2$Si. In the reaction of Example 5, the resultant nanostructured silicon has nanowire morphology.

FIG. 3a is an SEM image that shows nanowire bundles, several microns in size, that resemble groups of oriented dendritic wires composed of nanowires with diameters of approximately 50 nm. FIG. 3b is an EDS image of the nanostructured silicon shown in FIGS. 3a, 3c and 3d. A TEM image in FIG. 3c shows that the silicon nanowires are 40 nm in diameter with a 10 nm thick oxide layer, which is in agreement with the crystallite size calculated from XRD. Selected area electron diffraction (SAED) in FIG. 3d of the nanowires demonstrates that they are highly crystalline with a diffraction pattern oriented generally along the 111 direction. The silicon nanowires average 50 nm in diameter and the product is mainly Si with some oxygen and residual Mg. FIG. 3c is a TEM image of the silicon nanowires, the lighter area is believed to correspond to a 10 nm thick oxide layer on the nanowires. In FIG. 3d is the SAED pattern of the nanowires showing that they grow in the (111) direction. In order to form the Si nanowires, a drop of ethanol or approximately 500 microliter is used to initiate the reaction. FIG. 5 is time-lapsed photographs of a Mg$_2$Si+SiI$_4$ reaction. The ethanol droplet initiates the reaction and in less than 1 minute the reaction reaches completion. A large violet plume of iodine vapor is observed approximately 3 seconds into the reaction.

Example 6 illustrates the solid state metathesis of nanostructured germanium by reacting Mg$_2$Si(Si$_4$)+SiI$_4$. The reaction of Example 6 is performed using the following idealized reaction:

\[
\text{Mg}_2\text{Si(Si$_4$)+SiI$_4$} \rightarrow \text{Mg}_2\text{Si(Si$_4$)} + \text{SiI$_4$} + \text{SiI$_4$}
\]

For mechanochemically initiated reactions, the precursor material total mass was scaled up to 8 grams to yield 0.83 g of Si product via Mg$_2$Si and 1.25 g of Si product via CaSi reactions. The reaction products were loaded into tungsten carbide vials with several tungsten carbide balls (SPEX CertiPrep Inc., Metuchen, N.J.) and then loaded onto a Spex 8000D mixer mill (SPEX CertiPrep Inc., Metuchen, N.J.) and milled for several hours. In the synthesis involving Mg$_2$Si and SiI$_4$, the precursor materials were ball milled to a homogeneous powder and the reaction was initiated using a drop of ethanol. It is also noted that solid state metathesis reactions are highly exothermic and should be handled in a fume hood or glove box. This step involves the evolution of molecular iodine. The final products were washed with 50% 6 M HCl/150% ethanol to remove the salt by-product, then washed with ethanol and finally dried in air. All three of the reactions had over 90% yield in the product.
precursor materials were ball milled to a homogeneous powder. The amount of germanium used is 20% by mole of the reaction product that one is attempting to produce.

FIG. 7 is an SEM of nanostructured silicon-germanium produced using germanium in the solid state metathesis reaction of SiI₄ and 2CaSi. The SEM image in FIG. 7 shows the nanostructure of the silicon is nanowire morphology. It is believed that the added elemental germanium is acting as a heat sink to control the reaction temperature by dissipating the heat of reaction, thus, more time for nanowire formation.

FIGS. 8a and 8c are images of the nanostructured silicon-germanium produced using germanium in the solid state metathesis reaction of SiI₄ and 2CaSi. FIGS. 8a and 8c are SEM images showing a nanowire morphology. The EDS image in FIGS. 8b and 8d confirm that the end product is composed mainly of silicon-germanium.

Example 8 illustrates solid state metathesis of nanostructured silicon-germanium produced using elemental tin (Sn) to the reaction of SiI₄ and 2CaSi. The reaction of Example 8 is performed using the following idealized reaction:

\[2\text{CaSi(s)} + \text{SiI}_4(s) + \text{Sn(s)} \rightarrow \text{Si}_3\text{Ge(s)} + 2\text{CaI}_2(s)\]  

The reaction of Example 8 is performed in the same manner as Example 1, with the addition of tin (Sn) to the reaction product that one is attempting to produce. FIGS. 9a and 9b are images of nanostructured silicon using tin in the solid state metathesis of SiI₄ with the CaSi step comprises resistively heating the powder using a nichrome wire. FIGS. 9c and 9d confirm that the end product is composed mainly of Si with some surface oxides and a slight Sn impurity.

Example 9 illustrates the solid state metathesis of nanostructured silicon-germanium by reacting Mg₂Si with an alkaline earth metal silicide into a homogeneous powder, and initiating the reaction between the silicon tetraiodide SiI₄ with the alkaline earth metal silicide. FIGS. 10a and 10b are images of nanostructured silicon-germanium produced using a germanium based precursor. FIG. 10a shows that the nanostructure of silicon-germanium is a nanowire morphology. The bright spots in the SEM image of FIG. 10b are germanium.

The reaction of Example 9 is characterized by one or more of the following techniques, including powder X-ray Diffraction; Scanning Electron Microscopy (SEM); Transmission Electron Microscopy (TEM); Energy dispersive spectroscopy (EDS) or selected area (electron) diffraction (SAED).

What is claimed is:

1. A method of forming nanostructured silicon comprising the steps of:
   a) combining a stoichiometric mixture of silicon tetraiodide SiI₄ and an alkaline earth metal silicide into a homogeneous powder, and
   b) initiating the reaction between the silicon tetraiodide SiI₄ with the alkaline earth metal silicide.

2. The method of claim 1, wherein the alkaline earth metal silicide is selected from the group consisting of: Mg₂Si, CaSi₂, and CaSi.

3. The method of claim 2, wherein the initiating the reaction of the SiI₄ with the Mg₂Si step comprises adding a predetermined amount of ethanol.

4. The method of claim 3, wherein the initiating the reaction of the SiI₄ with the CaSi step comprises ball milling the SiI₄ and CaSi together.

5. The method of claim 2, wherein the initiating the reaction of the SiI₄ with the CaSi step comprises resistively heating the powder using a nichrome wire.

6. The method of claim 1, wherein the nanostructured silicon formed by the method comprises a morphology selected from the group consisting of nanoparticles, nanopowders, nanoclusters, nanocrystals, nanowires and mixtures thereof.

7. The method of claim 1, wherein the method further comprises the step of washing a salt by-product from the nanostructured silicon with a solution selected from the group consisting of water, alcohol and mixtures thereof.

8. The method of claim 1, wherein the method further comprises the step of etching a native oxygen layer from the nanostructured silicon by using a treatment comprising:
   a) the steps of:
      i) removing the salt by-product, then washed with ethanol and
      ii) adding elemental tin as Example 1 with the addition of tin (Sn) to the reaction product that one is attempting to produce.

9. A method of forming nanostructured silicon comprising the steps of:

(a) grinding a stoichiometric mixture of silicon tetraiodide SiI₄ and an alkaline earth metal silicide into a homogeneous powder, and
(b) reacting the silicon tetraiodide SiI₄ with the alkaline earth metal silicide.

10. The method of claim 9 wherein the alkaline earth metal silicide is selected from the group consisting of Mg₂Si, CaSi₂, and CaSi.

11. The method of claim 10 wherein the step of reacting the SiI₄ with the CaSi comprises resistively heating the powder using a nichrome wire.

12. The method of claim 10, wherein the step of reacting the SiI₄ with the Mg₂Si comprises adding a predetermined amount of ethanol.

13. The method of claim 10, wherein the step of reacting the SiI₄ with the Mg₂Si comprises ball milling the SiI₄ and Mg₂Si together.

14. A method of forming nanostructured silicon comprising the step of
(a) ball milling a mixture of silicon tetraiodide SiI₄ and an alkaline earth metal silicide into a homogeneous powder, and
(b) reacting the silicon tetraiodide SiI₄ with the alkaline earth metal.

15. The method of claim 14 wherein the alkaline earth metal silicide is selected from the group consisting of Mg₂Si, CaSi₂, and CaSi.

16. The method of claim 15 wherein the step of reacting the SiI₄ with the Mg₂Si comprises adding a predetermined amount of ethanol.

17. A method of forming nanostructured silicon-germanium comprising the steps of:
(a) combining a stoichiometric mixture of SiI₄ and a germanium based precursor into a homogeneous powder, and
(b) initiating a reaction between the SiI₄ and the germanium based precursor.

18. The method of claim 17 wherein the germanium based precursor is selected from the group consisting of Mg₂Ge and GeI₄.

19. The method of claim 17, wherein the combining step (a) comprises grinding the stoichiometric mixture of SiI₄ and an germanium based precursor into a homogeneous powder.

20. The method of claim 17, wherein the grinding the stoichiometric mixture of SiI₄ and an germanium based precursor into a homogeneous powder is done in a glove box filled with argon and helium.

21. The method of claim 17, wherein the combining step (a) comprises ball milling the mixture of silicon tetraiodide and the germanium based precursor into a homogeneous powder.

22. The method of claim 17, wherein the initiating the reaction of the SiI₄ with the germanium based precursor comprises step comprises resistively heating the homogenous powder using a nichrome wire.

23. The method of claim 17, wherein the initiating the reaction of the SiI₄ with the germanium based precursor comprises step comprises adding a predetermined amount of ethanol.

24. The method of claim 17 wherein the nanostructured silicon-germanium formed by the method comprises a morphology selected from the group consisting of nanoparticles, nanopowders, nanoclusters, nanocrystals, nanowires and mixtures thereof.

25. The method of claim 17, wherein the method further comprises the step of washing a salt by-product from the nanostructured silicon-germanium with a solution selected from the group consisting of water, alcohol and mixtures thereof.

26. The method of claim 17, wherein the method further comprises the step of etching a native oxygen layer from the nanostructured silicon by using a treatment comprising hydrofluoric acid.

27. A method of forming nanostructured silicon comprising the steps of:
(a) combining a stoichiometric mixture of SiI₄ and an alkaline earth metal silicide into a homogeneous powder, (b) adding tin to the homogeneous powder, and (c) initiating a reaction between the SiI₄ and the alkaline earth metal silicide.

28. A method of forming nanostructured silicon comprising the steps of:
(a) grinding a stoichiometric mixture of SiI₄ and an alkaline earth metal silicide into a homogeneous powder, (b) adding tin to the homogeneous powder, and (c) reacting the SiI₄ with the alkaline earth metal silicide.

29. A method of forming nanostructured silicon comprising the steps of:
(a) ball milling a mixture of SiI₄ and an alkaline earth metal silicide into a homogeneous powder, (b) adding tin to the homogeneous powder, and (c) reacting the SiI₄ with the alkaline earth metal silicide.

* * * * *