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(71) Applicant(s):
Westfälische Wilhelms-Universität Münster
(Incorporated in the Federal Republic of Germany)
Schlossplatz 2, 48149 Münster,
Federal Republic of Germany

(72) Inventor(s):
Hartmut Bracht
Sebastian Knebel

(74) Agent and/or Address for Service:
24IP Law Group Sonnenberg Fortmann
Medius House LG, 2 Sheraton Street,
LONDON, W1F 8BH, United Kingdom

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Yang, H et al. (2002) Sol-gel preparation of Ge nanocrystals embedded in SiO2 glasses. Journal of Crystal Growth 236, 371-375.
Yang, H. et al (2002) Photoluminescence of Ge nanoparticles embedded in SiO2 glasses fabricated by a sol-gel method. Applied Physics Letters 81(27), 5144-5146.
Nogami, M. and Abe, Y. (1994) Sol-gel method for synthesising visible photoluminescence nanosized Ge-crystal-doped silica glasses. Applied Physics Letters 65(20) 2545-2547
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Yang, H. et al. (2003) Sol-gel preparation and photoluminescence of size controlled germanium nanoparticles embedded in a SiO2 matrix. Journal of Physical Chemistry B 107, 13319-13322.

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(54) Abstract Title**: Synthesis of germanium nanoparticles in thin Si02 films**

(57) A method for synthesis of germanium nanoparticles 105 in thin Si0$_2$ films 104 comprising: preparing a solution comprising silicon esters, germanium tetrachloride ($GeCl_4$) or germanium esters, methyl- or higher alcohols, and water; applying the solution to a surface of a substrate; consolidating the solution on the surface of the substrate, thereby obtaining a glass comprising silicon dioxide and germanium dioxide; selectively reducing the germanium dioxide to form germanium nanoparticles. The consolidation may be achieved by heating in an oxidising atmosphere to a temperature over 400 °C. The selective reduction may be achieved by heating in a reducing atmosphere of hydrogen mixed with an inert gas such as nitrogen at a temperature of between 800 and 1200 °C. The substrate may be silicon. The silicon ester may be tetraethoxysilane (TEOS).

Also disclosed is a device comprising a substrate having a first layer of silicon dioxide and a second layer of silicon dioxide with germanium nanocrystals.

FIG. 1

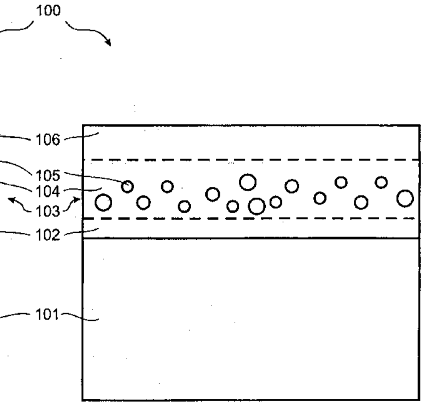

FIG. 2

FIG. 1

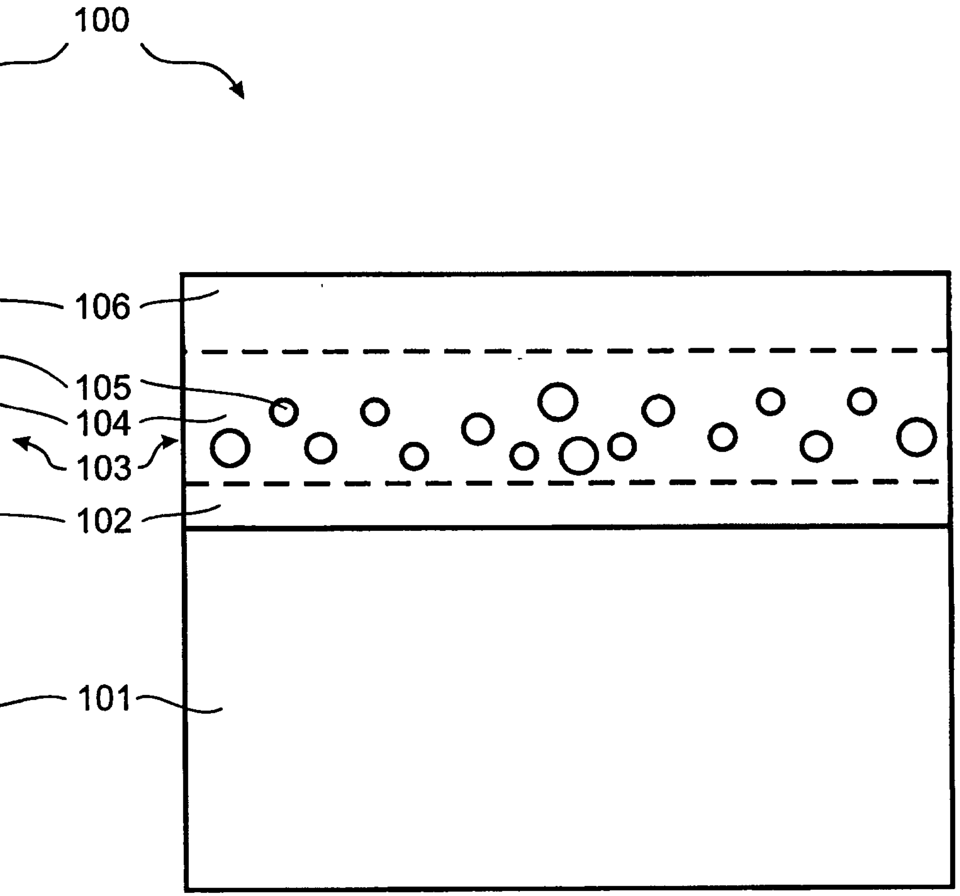

FIG. 2

Title: Condensed Materials

Description

Introduction

The functional properties of materials such as crystalline elemental and compound semiconductors, ion conducting homogeneous and nanostructured glasses, and silica layers are strongly affected by defects. The understanding about the properties of defects is of fundamental significance for the fabrication of materials with desired features. These defects may be for example group IV nanocrystals that are embedded in SiO_2. In the past, one focus has been on silicon nanocrystals in SiO_2, but also germanium nanocrystals have been studied. Nanocrystals of this kind show at least two interesting effects. Firstly, it could be shown that nanocrystals can serve as efficient light emitters and are, therefore, interesting for optical applications. Secondly, compatibility with silicon-based electronics can be maintained when using these materials which is of particular interest when the nanoparticles are to be created in a thin film applied to the silicon-based electronic.

Prior Art

A number of methods for producing nanoparticles in oxide films are known. These methods typically need technically sophisticated equipment and are relatively cost-intensive.

Films that were created by sputtering and heat treatment were reported by Jensen et al. in "*Ge nanocrystals in magnetron sputtered SiO_2*", Appl. Phys. A 83, 41 – 48 (2006), and by Kan et al. in "*Effect of annealing profile on defect annihilation, crystallinity and size distribution of germanium nanodots in silicon oxide matrix*", Appl. Phys. Lett. 83, 2058 (2003). In both papers the production of germanium nanodots by sputtering SiO_2 and Ge at the same time and subsequent thermal annealing is described.

Molecular beam epitaxy (MBE) was reported by Kanjilal et al. in "*Structural and electrical properties of silicon dioxide layers with embedded germanium nanocrystals grown by* *molecular beam epitaxy*", Appl. Phys. Lett. 82, 1212 (2003). This paper describes the fabrication of crystalline Ge-nanodots in amorphous SiO_2 by MBE and subsequent rapid thermal processing under oxidizing and reducing atmospheres. This method allows to produce a sheet with defined distance to the substrate that contains all dots.

Chemical vapor deposition (CVD) is described by Ağan et al. in "*Synthesis and size differentiation of Ge nanocrystals in amorphous SiO_2*", Appl. Phys. A 83, 107 – 110 (2006), and by Kanoun et al. in "*Charging effects in Ge nanocrystals embedded in SiO_2 matrix for non volatile memory applications*", Materials Science and Engineering C 26 (2006) 360 – 363. In the first paper by Ağan et al. a mixed SiO_2-GeO_2 glass is produced by plasma enhanced CVD and subsequent heat treatment in an inert gas atmosphere. The second paper by Kanoun et al. describes the fabrication of germanium nanocrystals on Si nuclei that were deposited firstly on a SiO_2 surface.

Ion implantation is described by Markwitz et al. in "*Microstructural investigations of ion beam synthesized germanium nanoclusters embedded in SiO_2 layers*", Nuclear Instruments and Methods in Physics Research B 142 (1998) 338 – 348, and by Bonafos et al. in "*An electron microscopy study of the growth of Ge nanoparticles in SiO_2*", Appl. Phys. Letters 76, 3962. Both papers describe the fabrication of Ge nanodots embedded in SiO_2 by implantation of Ge^+ ions in a SiO_2 layer and subsequent thermal annealing.

Nogami et al. proposed a sol-gel process for the synthesis of Ge nanodots in sol-gel derived massive bulk glasses by thermal annealing in a reducing atmosphere in "*Sol-gel method for synthesizing visible photoluminescent nanosized Ge-crystal-doped silica glasses*", Appl. Phys. Lett. 65 (20) 2545. However, this paper does not consider Ge nanodot formation in thin films. The same is true for European Patent EP 1 113 987 B1, because it is directed at the formation of thick films, i.e. films that are thicker than 1 μm.

Summary of the Invention

The method suggested by the inventors for synthesis of germanium nanoparticles in thin SiO_2 films comprises

preparing a solution comprising silicon esters, germaniumtetrachloride ($GeCl_4$) or germanium esters, methyl- or higher alcohols, and water;

applying the solution to a surface of a substrate;
consolidating the solution on the surface of the substrate, thereby obtaining a glass comprising silicon dioxide and germanium dioxide;
selectively reducing the germanium dioxide to form germanium nanoparticles.

Accordingly, the method implements the sol-gel route to produce thin layers of glasses with Ge-nanoparticles, i.e. germanium nanoparticles. The method allows the generation of nanoparticles from materials of which the oxides are less stable than the matrix. The wet chemical based sol-gel technique is technologically simple and a fast method to produce germanium nanoparticles and, in particular, germanium nanocrystals. The method does not require technically sophisticated equipment, as it is the case for other proposed routes to synthesise germanium nanocrystals in silicon dioxide, such as ion implementation, chemical vapor deposition (CVD), sputter deposition, or molecular beam epitaxy (MBE). The preparation of nanoparticles in SiO_2 with the sol-gel technique and a subsequent appropriate treatment is easily manageable and by far less cost-intensive than the other preparation techniques.

The term "silicon esters" may also mean a single type of silicon ester. The same applies to the terms "germanium esters" and "methyl- or higher alcohols". The term "glass" also comprises gels.

The silicon ester(s) reacts with water to SiO_2 networks under the influence of H^+-ion and alcohol (methyl- or higher alcohols) concentrations. This reaction is usually named condensation. It can be easily observed, because the condensated silicon ester(s) forms a network that leads to a stiff gel. The $GeCl_4$ decomposes rapidly to germanium dioxide (GeO_2) and hydrochloric acid (HCl).

The process for the production of the germanium nanoparticles comprises the selected reduction of germanium and its segregation to nanospheres. The term "selected reduction" or "selectively reducing" means that the reduction affects mostly the germanium dioxide and not (or hardly) the silicon dioxide. This is due to the fact that SiO_2 is much more stable towards reduction than GeO_2.

The consolidation may comprise heating the substrate, i.e. it is a heat treatment. The consolidation serves several aims:

- The water and the ethanol should be removed.
- The residual carbon hydrates should be oxidized and removed.
- The porous glass is sintered.

After the heat treatment the glass cannot be removed by usual solvents such as acetone or ethanol. In contrast, the unconsolidated layers can be removed with little mechanical grating by acetone.

During consolidation, the substrate may be heated under oxidizing atmosphere above 400°C. For example, the coated substrate is heated under air atmosphere up to 600°C with heating rates below 1°C/min.

The application may comprise spin coating the solution to the surface of the substrate. Spin coating of the solution to the surface of the substrate produces a thin and homogeneous film on the surface. Other methods of applying the solution to the surface may also be contemplated.

One of the silicon esters may be Tetraethoxy-orthosilane (TEOS). One of the methyl- or higher alcohols may be ethanol. It could be experimentally demonstrated that the method works with Tetraethoxy-orthosilane and ethanol. However, other silicon esters and methyl- or higher alcohols may be suited for the method as well.

A condensation speed of the esters may be controlled by the H^+-ion concentration via the pH value of the solution. Controlling the H^+-ion concentration of the solution provides an indirect control facility that is usually easy to manipulate.

The reduction may be performed under a gas atmosphere consisting of hydrogen and inert gas at temperatures between 800°C and 1200°C. The heat treatment reduces a high part of the germanium dioxide without reducing the silicon dioxide. This may be achieved by optimizing the heat treatment which also serves for controlling the size of the germanium nanocrystals. It is also possible to add a second annealing phase under inert gas atmosphere or under a vacuum. The used gas mixture is well suited for industrial applications because it is not as explosive as pure hydrogen.

The substrate may be a silicon substrate. Silicon is suited as substrate material since SiO_2 is much more stable towards reduction than GeO_2. Therefore, SiO_2 is not reduced in noteworthy amounts during the reduction phase. The first SiO_2 layer is not affected by the reduction.The silicon dioxide film containing the nanocrystals may be regarded as an electrical structure or component. Circuits for connecting this electrical structure with other electrical or electronic components may be formed in the silicon, for example by means of known lithography methods. It may also be contemplated to form e.g. driving electronics for the electrical structure in the silicon matrix.

The method may further comprise

- preparing an additive solution comprising diethoxydimethylsilane and ethanol;
- adding said additive solution to said solution that comprises Tetraethoxy-orthosilane, germaniumtetrachloride ($GeCl_4$) or germanium esters, ethanol, and water.

The presence of hydrolyzed diethoxydimethylsilane lowers the condensation rate of hydrolyzed germaniumtetraethoxide. The additive prevents the solutions containing useful concentrations of $(Ge(OC_2H_5)_4$ from geling too fast, thereby making it suitable for a subsequent coating procedure.

The invention is also directed at a product that is produced according to the method described above.

The invention is furthermore directed at such a device that comprises a substrate having a first layer of silicon dioxide on the surface of the substrate and a second layer of silicon dioxide with germanium nanocrystals. The silicon dioxide of the first layer is a dielectric material that prevents unwanted electron flow.

The first layer of SiO_2 develops when the sol-gel layer is consolidated. A thinner first layer can be obtained, if the duration of the heat treatment is shortened, the peak temperature of the heat treatment is decreased, or the oxygen content is reduced during the consolidation phase.

The second layer may have a thickness from 20 nm to 200 nm. The size of the germanium nanocrystals may be smaller than 20 nm. In order for the second layer to have the desired effects, it is important that the nanocrystals have a certain average size and maintain a certain distance to each other and to the silicon substrate. The embedded nanocrystals represent a deep potential well within the dielectric matrix. Especially for quantum-sized particles a behavior can be observed that is much different from the bulk crystal.

The invention is also directed at a non-volatile memory, an optical switch, a photoluminescence device, or a capacitor made from the device described above.

One example of a non-volatile memory is a field effect transistor (FET) in which the germanium nanoparticles are disposed in the control oxide between the gate and the channel of the field effect transistor. A thin tunneling oxide separates the inversion surface of an n-channel silicon field-effect transistor from a distributed film of nanoparticles that covers the entire surface channel region. A thicker tunneling oxide separates the nanoparticles from the control gate of the FET. The non-volatile memory device formed in this manner utilizes direct tunneling and storage of electrons in three-dimensionally confined nanoparticles. The effect of the germanium nanoparticles is comparable to the effect of a floating gate. In particular, bi-stability in the conduction of the transistor channel is achieved. The fabrication of a non-volatile memory cell requires control of four main parameters: (i) the tunnel oxide thickness, (ii) the nanocrystal density, (iii) the nanocrystal diameter, and (iv) the control oxide thickness. This is, to a large extent, possible, if the film structure of the non-volatile memory is obtained through the method proposed in this application.

Silicon dioxide glasses with embedded germanium nanoparticles also have potentials for non-linear optical devices. When small-sized semiconductor particles are embedded in the dielectric matrices, the wave functions of photoexcited electron-hole carriers and excitons are confined in a deep potential well of the matrix.

Description of the Drawing

Figs. 1 and 2 show a cross section through a structure 100 obtained with the method proposed by the inventors. Fig. 1 shows a transmission electron photo of an actually produced structure 100. Fig. 2 schematically shows the layers of structure 100. The structure is based on substrate 101 which in the present case is silicon. A layer 102 of silicon dioxide is situated on top of substrate 101. This layer 102 is exempt from germanium nanoparticles and may serve as a tunneling oxide. On top of layer 102 is situated a layer 103 of silicon dioxide 104 with embedded germanium nanoparticles 105. Another layer 106 of silicon dioxide that is exempt from germanium nanoparticles is found on top of layer 103. All three layers 102, 103, and 106 are formed during the heat treatment which include the consolidation and reduction treatment. In a non-volatile memory device this layer 106 may serve as control oxide, i.e. it is interposed between e.g. a control gate of a field effect transistor and layer 103 containing the nanoparticles 105.

Example 1

Tetraethoxyorthosilane (TEOS), germaniumtetrachloride ($GeCl_4$) and ethanol in at least p.a.-purity and highly purified water were used as starting materials. The solution was spin-coated in order to form homogeneous layers. The coated substrates are heated under air atmosphere up to 600°C with heating rates below 1°C/min. Selected reduction of germanium and its segregation to nanospheres took place under a gas atmosphere consisting of 10 vol% hydrogen and 90 vol% nitrogen at 1000°C for several hours. Under this condition germanium precipitated in form of spheres that were embedded in the glass. The heat treatment needed to be optimized in order to reduce a high part of the germanium dioxide without reducing the silicon dioxide and to control the size of the germanium nanoparticles. The nanoparticles were about 5nm in diameter. The layer of silicon dioxide in immediate contact with the silicon substrate that was exempt from germanium nanoparticles measured about 8 nm in thickness. The layer of silicon dioxide containing the germanium nanoparticles measured about 40 nm in thickness.

Example 2

Tetraethoxysilane, germaniumtetraethoxide ($Ge(OC_2H_5)_4$, ethanol, diethoxydimethylsilane ($(CH_3)_2Si(OC_2H_5)_4$, hydrochloric acid (HCl), and highly purified water were used here as starting materials.

The diethoxydimethylsilane was diluted with ethanol. Then it was hydrolyzed with water and hydrochloric acid for several hours. The hydrolysis was done under continuous stirring in a closed bottle at 5°C. Afterwards a part of the solution described above and water were added to a solution consisting of tetraethoxysilane, germaniumtetraethoxide and ethanol. This new solution was aged for several hours under the same conditions that were applied for the hydrolysis of diethoxydimethylsilane as described above. Slices of silicon wafers were dip coated with this solution. The thermal treatment was the same as used in example 1.

The presence of hydrolyzed diethoxydimethylsilane lowers the condensation rate of hydrolyzed germaniumtetraethoxide. Without this additive the solutions containing useful concentrations of $(Ge(OC_2H_5)_4$ gelate too fast for any coating procedure.

Claims

1. Method for synthesis of germanium nanoparticles in thin SiO_2 films comprising:
   preparing a solution comprising silicon esters, germaniumtetrachloride ($GeCl_4$) or germanium esters, methyl- or higher alcohols, and water;
   applying the solution to a surface of a substrate;
   consolidating the solution on the surface of the substrate, thereby obtaining a glass comprising silicon dioxide and germanium dioxide;
   selectively reducing the germanium dioxide to form germanium nanoparticles.

2. Method of claim 1, wherein the consolidation comprises heating the substrate.

3. Method of claim 2, wherein said substrate is heated under oxidizing atmosphere above 400°C.

4. Method of any one of claims 1 to 3, wherein said application comprises spin coating said solution to the surface of said substrate.

5. Method of any one of claims 1 to 4, wherein one of said silicon esters is Tetraethoxy-orthosilane (TEOS).

6. Method of any one of claims 1 to 5, wherein one of said methyl- or higher alcohols is ethanol.

7. Method of any one of claims 1 to 6, wherein a condensation speed of said esters is controlled by the H^+-ion concentration of the solution.

8. Method of any one of claims 1 to 7, wherein said reduction is performed under a gas atmosphere consisting of hydrogen and inert gas at temperatures between 800°C and 1200°C.

9. The method of any one of the above claims, wherein the substrate is a silicon substrate.

10. The method of any one of claims 6 to 9, further comprising

preparing an additive solution comprising diethoxydimethylsilane and ethanol;

adding said additive solution to said solution that comprises Tetraethoxy-orthosilane, germaniumtetrachloride ($GeCl_4$) or germanium esters, ethanol, and water, prior to applying said solution to the surface of said substrate.

11. A product processed according to any one of claims 1 to 10.

12. A device comprising a substrate having a first layer of silicon dioxide on the surface of the substrate and a second layer of silicon dioxide with germanium nanocrystals.

13. The device of claim 12, wherein the thickness of the second layer is between 20nm and 200nm.

14. The device of claim 12 or 13, wherein the size of the germanium nanocrystals is smaller than 20nm.

15. A non-volatile memory, an optical switch, a photoluminescence device, a capacitor made from the device of one of claims 12 to 14.

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Application No:	GB0624634.2	**Examiner:**	Nicholas Mole
Claims searched:	1-10	**Date of search:**	9 July 2007

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
Y	1-7, 9	Yang, H et al. (2002) Sol-gel preparation of Ge nanocrystals embedded in SiO2 glasses. Journal of Crystal Growth 236, 371-375.
Y	1-7, 9	Yang, H. et al (2002) Photoluminescence of Ge nanoparticles embedded in SiO2 glasses fabricated by a sol-gel method. Applied Physics Letters 81(27), 5144-5146.
Y	1-7, 9	Nogami, M. and Abe, Y. (1994) Sol-gel method for synthesising visible photoluminescence nanosized Ge-crystal-doped silica glasses. Applied Physics Letters 65(20) 2545-2547
Y	1-9	Nogami, M. and Abe, Y. (1997) Sol-gel synthesis of Ge nanocrystals-doped glass and its photoluminescence. Journal of Sol-Gel Science and Technology 9(2), 139-143.
Y	1-7, 9	Yang, H. et al. (2003) Sol-gel preparation and photoluminescence of size controlled germanium nanoparticles embedded in a SiO2 matrix. Journal of Physical Chemistry B 107, 13319-13322.
Y	1-9	EP 1113987 A (GEL DESIGN) see esp. page 6 lines 3-14
Y	1-9	EP 0693580 A (SUMITOMO) see esp. example 4

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category	P	Document published on or after the declared priority date but before the filing date of this invention
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

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Worldwide search of patent documents classified in the following areas of the IPC

B05D; B82B; C01B; C03C; H01L

The following online and other databases have been used in the preparation of this search report

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International Classification:

Subclass	Subgroup	Valid From
C03C	0014/00	01/01/2006
B05D	0003/04	01/01/2006
H01L	0021/316	01/01/2006