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## DESCRIPTION JPH0964417A

#### [0001]

13 TECHNICAL FIELD The present invention relates to a method for forming a thin film of a siloxene compound that emits light in the visible wavelength range on a silicon substrate.

#### [0002]

- 18 2. Description of the Related Art Bulk silicon such as an ingot or substrate is an indirect transition semiconductor.
- 20 Therefore, a change in momentum is required when the excited carriers fall to the ground state, and the luminous efficiency is low, making this material unsuitable for use as a material for light-emitting devices. On the other hand, it is well known that Si has excellent properties as a material for electronic devices and is widely used in electronic information processing devices such as DRAMs and LSIs. In recent years, there has been much research into silicon-based luminescent materials, such as hydrogenated and hydroxide compounds with a layered silicon skeleton, such as siloxene (Si6O3H6), porous silicon, and hydrogenated amorphous silicon. All of these luminescent materials retain part of the silicon skeletal structure, and therefore are materials that are highly compatible with Si substrates.

#### [0003]

- 32 [Problem to be solved by the invention] If it is possible to fabricate a light-emitting device on a Si substrate using these materials, it will be possible to fabricate a light-emitting device on the same substrate as an electronic device with excellent characteristics, the benefits of which will be immeasurable.
- 36 Among these materials, siloxene-based compounds exhibit strong photoluminescence (PL) in the visible range and are therefore promising materials for light-emitting devices on Si

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substrates. However, it has been difficult to deposit a thin film of a siloxene compound on a Si substrate using conventional techniques.

#### [0004]

- 45 Siloxene compounds can be obtained by soaking granular CaSi2 in hydrochloric acid, but this method only produces powdered siloxene compounds.
- <sup>47</sup> In an example of forming a siloxene-based compound on a silicon substrate, a method has been reported in which metallic Ca is deposited on the silicon substrate by vapor deposition, the substrate is heated to diffuse the silicon from the substrate, and then a hydrochloric acid treatment is performed ("New growth technique for luminescent layers on silicon": M.S. Brandt, et al.; Applied Physics A, Vol. 54, pp. 567-569, 1992) 
  In this case, however, Si is supplied only from the substrate side at the stage of obtaining the CaSi2 thin film, so the composition distribution in the film thickness direction is not uniform. In addition, metallic Ca is highly reactive, and when stored in air, an oxide film forms on its surface. It also gradually absorbs moisture and forms carbonates or hydroxides, so it must be stored in a dry, inert atmosphere or in oil, etc., making handling complicated during production.

### [0005]

60 The present invention has been made to solve the problems of the prior art described above, and has an object to provide a method for producing a siloxene-based compound thin film that uses calcium silicide, which can be easily handled in air, as a main raw material and that can form a siloxene-based compound thin film with a uniform composition distribution in the film thickness direction on a Si substrate.

#### [0006]

- 68 In order to achieve this object, the method for producing a siloxene compound thin film of the present invention is characterized by using a vapor deposition method using CaSi2 and Si as evaporation sources, a rapid heating method, and a chemical treatment method using hydrochloric acid.
- 72 That is, the present invention relates to a method for producing a siloxene-based compound thin film, which comprises depositing two or more layers of CaSix (0<x<2) thin films and Si thin films alternately on a silicon (Si) substrate in a vacuum using one of calcium disilicide (CaSi2), calcium silicide (CaSi) or dicalcium silicide (Ca2Si) as a calcium silicide and Si as an evaporation source, heating the CaSix/Si multilayer thin film-deposited Si substrate in a vacuum or in an inert atmosphere to form a CaSi2 single crystal thin film on the Si substrate, and treating the CaSi2 single crystal thin film-deposited Si substrate with hydrochloric acid to form a siloxene-based compound thin film on the silicon substrate.

#### [0007]

- *s2* DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT The method according to the present invention involves three process steps.
- 85 The first step is the so-called deposition method.
- 86 That is, in a vacuum chamber, calcium silicide, for example, CaSi2, is evaporated as an evaporation source. At this time, due to phase equilibrium, when the evaporated CaSi2 reaches the opposing Si substrate, it is always accompanied by a loss of Si, and an amorphous CaSix (0<x<2) thin film is deposited on the Si substrate. Next, a thin Si film is deposited on the CaSix in the same manner using Si as the evaporation source. There are two methods for heating the evaporation source: resistance heating and electron beam heating. It is preferable to use resistance heating for calcium silicide, which has a relatively low melting point, and electron beam heating for silicon, which has a high melting point. CaSix/Si multi-layer thin films are stacked according to the required film thickness. At this time, it is important to adjust the thickness ratio of the CaSix thin film and the Si thin film so that it finally matches the composition of CaSi2. When CaSi2 is used as the evaporation source, the composition x of the CaSix evaporated film depends on the heating temperature and the shape of the apparatus, but the composition for x = 1 is more stable than other compositions, so a thin film of this composition can be easily obtained under a relatively wide range of conditions. Therefore, the thickness ratio of CaSix to Si should be approximately 1:1. The film thickness is preferably set to 200 Å or less, taking into consideration the mutual diffusion length of each element (Ca and Si). The second stage is a rapid heating method in which the substrate is irradiated with infrared rays to rapidly heat it to 800 ° C. or higher at a rate of about 120 ° C./min. If the thin film is then held at a temperature of 800 ° C or higher for an appropriate period of time, the CaSix/Si multilayer thin film becomes a single crystal thin film of CaSi2 due to interdiffusion of the elements. In this case, because CaSix and Si are deposited alternately, a thin CaSi2 film can be obtained with a short heat treatment. In addition, since each layer after deposition is a thin film of 200 Å or less, it is possible to obtain a CaSi2 thin film with an extremely uniform composition distribution in the film thickness direction after heat treatment. The third step is chemical treatment with hydrochloric acid. That is, in order to suppress the generation of fumes from hydrogen chloride, the piece is immersed in hydrochloric acid that is kept at a temperature below room temperature for 2 hours to 5 days. The CaSi2 single crystal thin film has Ca extracted by the hydrochloric acid, and instead hydrogen (H) and hydroxyl groups (OH) terminate the silicon skeleton of the CaSi2, changing it into a siloxane compound thin film. At this time, the required treatment time and the type of the obtained siloxene compound will vary depending on the concentration and temperature of the hydrochloric acid used for treatment.
- 118 For example, when the hydrochloric acid concentration is low (approximately 1N) and the temperature is high (approximately room temperature), the required processing time for a film 1 μ m thick is approximately 2 hours. The resulting thin film is a type of siloxene in which oxygen has penetrated the silicon skeleton, known as Kautskii siloxene (Figure 4b). On the other hand, when a similar film is treated in concentrated hydrochloric acid at 0 ° C for 5 hours, a thin film of a compound called Wyeth-type siloxene (Figure 4a), which has a more

conductive structure and in which the silicon skeleton is not oxidized, is obtained. Furthermore, treatment in concentrated hydrochloric acid at -20 ° C or below for 3 to 5 days produces a thin film of a siloxane-based compound (Figure 4c) called chlorinated polysilane (SiH1-xClx), which does not contain oxygen or hydroxyl groups but contains chlorine instead. Chlorinated polysilanes contain less oxygen in the silicon planar backbone and are therefore more conductive than Kautzki or Weiss siloxanes. In FIG. 4, (a) is a schematic diagram of a single layer of silicon planar skeleton structure of Weiss-type siloxene, (b) is a schematic diagram of a single layer of silicon planar skeleton structure of Kautzki-type siloxene, and (c) is a schematic diagram of a single layer of silicon planar skeleton structure of chlorinated polysilane (SiH1-xClx). As a result of the above, a thin film of a siloxene compound is formed on the Si substrate.

#### [0008]

- 144 Example 1 FIG. 1 is a schematic diagram of a resistance heating/electron beam heating hybrid evaporation apparatus used in the first step of the present invention.
- 146 Here, 101 is an evaporation chamber, 102 is a substrate holder, 103 is a substrate shutter, 104 is a substrate heating unit (see FIG. 2), 105 is an electron beam heating evaporation source (Si), 107 is an electron beam heating generation unit (filament), 108 is an electron beam evaporation source (Si), 107 is an electron beam heating generation unit (filament), 108 is an electron beam evaporation source (CaSi2 grains), 111 is a resistance heating evaporation shutter, and 112 is a silicon substrate. The CaSi2 of the evaporation source 110 is in granular form with a purity of 99.5% or more. The Si is in pellet form with a purity of 99.99999% or more. The degree of vacuum in the chamber 101 under normal conditions is 1 × 10 7 Torr or less. The resistance heating portion 109 is a boat-shaped resistor made of tungsten, and can be heated to 1200 ° C. or higher by passing electricity through it. The electron beam heating section consists of a water-cooled crucible (commonly known as hearth) 105 and a tungsten filament 107. Electrons generated from the filament 107 are redirected 270 ° by an external magnetic field and irradiated onto a target 105 in the hearth, capable of heating an evaporation source 106 up to 1800 ° C or higher.

#### [0009]

- 164 FIG. 2 is a schematic diagram of a substrate heating section 104 used in the second stage of the present invention.
- 166 Generally, the deposition apparatus has a heating device for heating the substrate, and FIG. 2 shows this portion in an enlarged scale from FIG. Here, reference numeral 21 denotes a lamp house, 22 denotes a thermocouple, 23 denotes a tungsten filament, 24 denotes a quartz filament cover, 25 denotes a substrate holder, 26 denotes a substrate pressing plate, 27 denotes a silicon substrate, and 28 denotes a substrate shutter. An infrared lamp is used as the heat source, and a heating rate of 5 ° C/sec or more can be achieved at temperatures

#### [0010]

- 182 FIG. 3 is a schematic diagram of an inert atmosphere low temperature chemical processing apparatus used in the third step of the present invention.
- 184 Here, 301 is a positive pressure glove box, 302 is a bath box, 303 is a nitrogen gas flow meter, 304 is a check valve, 305 and 306 are stop valves, 307 is a low-temperature constant temperature water bath, 308 is a non-aqueous refrigerant (methanol, etc.), 309 is a flask, 310 is hydrochloric acid, 311 is a CaSi2 thin film laminated Si substrate, and 312 is a rubber stopper. The atmosphere is made inert because, if oxygen is present in the atmosphere during the hydrochloric acid treatment, the oxygen is likely to penetrate into the silicon planar skeleton of the siloxene compound, resulting in a decrease in electrical conductivity. A CaSi2 single crystal thin film laminated Si substrate 311 introduced through a pass box 302 into a glove box 301 whose atmosphere has been completely replaced with nitrogen is treated with hydrochloric acid in a flask 309 whose temperature is kept constant in a lowtemperature thermostatic bath 307. At this time, a low processing temperature below 0 ° C. makes it possible to obtain a siloxane compound thin film with a lower degree of oxidation of the silicon skeleton (i.e., with higher electrical conductivity), so a liquid with a low melting point such as methanol or ethylene glycol is used as the coolant 308 in the thermostatic water bath 307. Nitrogen is constantly flowing into the glove box 301 to prevent the intrusion of oxygen, and a rubber stopper 312 is placed on the flask 309 to prevent hydrogen chloride gas from evaporating from the hydrochloric acid 310 in the flask and dissipating it.

#### [0011]

- 205 FIG. 5 is a schematic cross-sectional view of a CaSi2 thin film on a Si substrate after the second step produced using the apparatus shown in FIGS.
- 207 The planar Si skeleton of CaSi2 extends in a direction parallel to the Si substrate surface, and the planar skeleton is layered in the film thickness direction. Therefore, the siloxene compound thin film after the third step is also laminated in a similar manner.

#### [0012]

- 213 FIG. 6 shows a typical X-ray diffraction spectrum of the CaSi2 thin film/(111) Si substrate structure after the second stage of processing.
- 215 As can be seen from the figure, in addition to the peak from the Si substrate, a clear peak from the CaSi2 thin film is observed. The preparation conditions at each stage for several different samples are shown in Table 1.

#### [0013]

- 220 FIG. 7 shows photoluminescence (PL) emission of sample numbers 1-3 among the samples shown in Table 1 after the treatment up to the third stage was completed.
- 223 The PL measurements were performed using the 325 nm line of a helium-cadmium (He-Cd) laser as the excitation light source, and the samples were measured in air at room temperature. In addition, all samples except for a few emit strong PL light in the visible range. In addition, by changing the temperature in the third stage of the CaSi2 thin film processing, the emission color can be changed from green (~510 nm) to red-orange (~600 nm) in the visible range. As shown in Table 1, the film thickness is 1.0 µm, which is sufficient for use as an active layer in a light-emitting device.

#### [0014]

233 As described above in detail, the present invention makes it possible to easily form a thin film of a siloxene compound on a Si substrate, which was difficult to achieve with the conventional techniques.

#### [0015] 239 BRIEF DESCRIPTION OF THE DRAWINGS

#### [0016]

243 FIG. 1 is a schematic diagram of a resistance heating/electron beam heating hybrid evaporation apparatus used in the first step of the method of the present invention.

#### [0017]

248 2 is a schematic diagram of a substrate heating section used in the second stage of the method of the present invention.

#### [0018]

253 FIG. 3 is a schematic diagram of an inert atmosphere low-temperature scientific processing apparatus used in the third step of the method of the present invention.

#### [0019]

258 4 is a schematic diagram showing a silicon planar skeleton structure in a siloxene compound.

#### [0020]

262 Figure 5: Schematic diagram of a Si substrate on which a CaSI2 thin film is layered.

#### [0021]

266 6 is an X-ray diffraction spectrum of the sample after the second step of the method of the present invention.

#### [0022]

271 FIG. 7 shows the PL emission spectrum of the siloxene compound thin film/Si substrate according to the present invention.

#### [0023]

276 Explanation of symbols

#### [0024]

280 101 1. Vapor deposition chamber 102, substrate holder 103, substrate shutter 104, substrate heating section 105, evaporation source crucible 106, silicon pellets 107, electron gun (electron beam source) 108, evaporation source shutter 1 109, resistance heating boat 110, evaporation source shutter 2 111, silicon substrate 21, lamp house 22, thermocouple 23, tungsten filament 24, quartz filament cover 25, substrate holder 26, substrate pressing plate 27, silicon substrate 28, substrate shutter 301, positive pressure glove box 302, pass box 303, nitrogen gas flow meter 304, check valves 305, 306, stop valve 307, low temperature thermostatic water bath 308, non-aqueous refrigerant (methanol, etc.) 309, flask 310, hydrochloric acid 311, CaSi2 thin film laminated Si substrate 312, rubber stopper