

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 March 2008 (06.03.2008)

PCT

(10) International Publication Number
WO 2008/027101 A1

(51) International Patent Classification:

C01B 33/035 (2006.01) **C01B 33/03** (2006.01)

(21) International Application Number:

PCT/US2007/013905

(22) International Filing Date: 14 June 2007 (14.06.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

11/512,853 30 August 2006 (30.08.2006) US

(71) Applicant (*for all designated States except US*): **HEMLOCK SEMICONDUCTOR CORPORATION** [US/US]; 12334 Geddes Road, Hemlock, MI 48626 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **ARVIDSON, Arvid, Neil** [US/US]; 4710 North Verity, Sanford, MI 48657 (US). **MOLNAR, Michael** [US/US]; 11363 Moorfield Drive, Freeland, MI 48623 (US).

(74) Agent: **BROWN, Catherine, U.**; Patent Department-Mail CO1232, Dow Corning Corporation, 2200 West Salzburg Road, Midland, MI 48686-0994 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(54) Title: SILICON PRODUCTION WITH A FLUIDIZED BED REACTOR INTEGRATED INTO A SIEMENS-TYPE PROCESS

(57) Abstract: A fluidized bed reactor and a Siemens reactor are used to produce polycrystalline silicon. The process includes feeding the vent gas from the Siemens reactor as a feed gas to the fluidized bed reactor.



WO 2008/027101 A1

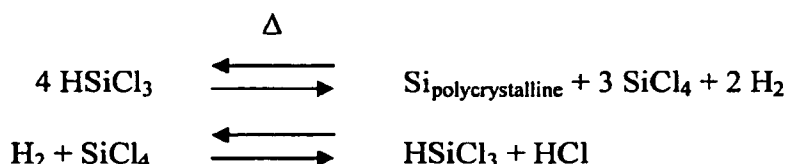
SILICON PRODUCTION WITH A FLUIDIZED BED REACTOR INTEGRATED INTO A SIEMENS-TYPE PROCESS

CROSS-REFERENCE TO RELATED APPLICATIONS

- 5 [0001] This application claims the benefit of U.S. Patent Application No. 11/512,853 filed 30 August 2006 under 35 U.S.C. §120. U.S. Patent Application No. 11/512,853 is hereby incorporated by reference.

BACKGROUND

- [0002] It is known that silicon can be made in rod form by a process referred to as the Siemens process. A mixture comprising hydrogen and silane (SiH_4) or a mixture comprising hydrogen and trichlorosilane is fed to a decomposition reactor containing, substrate rods which are kept at a temperature of more than 1000 °C. Silicon is deposited on the substrate and by-product gas mixtures exit in a vent stream. When a mixture comprising hydrogen and trichlorosilane is used, the vent stream may include hydrogen, hydrogen chloride, chlorosilanes, silane, and silicon powder. For purposes of this application, the term 'chlorosilanes' refers to any silane species having one or more chlorine atoms bonded to silicon and includes, but is not limited to monochlorosilane (H_3SiCl), dichlorosilane (H_2SiCl_2), trichlorosilane (HSiCl_3), silicon tetrachloride (SiCl_4), and various chlorinated disilanes such as hexachlorodisilane and pentachlorodisilane. In the vent stream, hydrogen and chlorosilanes such as silicon tetrachloride and trichlorosilane may be present both from un-reacted feed gas and reaction product from the decomposition. The vent stream is passed through a complex recovery process where condensations, scrubbing, absorption and adsorption are unit operations often used to facilitate the capture of feed material trichlorosilane and hydrogen for recycle. One problem associated with the Siemens process is that it is difficult to achieve a high yield of polycrystalline silicon product to silicon fed due to the chemical equilibria and kinetics that control this reaction process.



Quite often only 50%, or less, of the maximum theoretical yield of polycrystalline silicon is achieved.

[0003] An alternate process is to feed the mixture comprising hydrogen and silane or the mixture comprising hydrogen and trichlorosilane to a fluidized bed containing silicon nearly spherical beads that are maintained also at high temperature. The beads grow in size, and when large enough, are passed out the bottom of the fluidized bed reactor as product. The vent gases exit the top of the reactor and are sent through a recovery process similar to the one described above for the Siemens process. Yield in this system may be nearly 90 % of theoretical maximum, as compared to the 50 % for the Siemens process.

[0004] One problem with the fluidized bed reactor process is that one must heat the beads to a temperature higher than the average bed temperature to facilitate heat transfer. That can be done, for example, by use of hot walled reactor, microwave energy, or infrared radiation. All heating methods have unique operating problems. One problem, however, is that the bottom of the fluidized bed reactor may be hot, and the feed gas is reactive when it contains only trichlorosilane and hydrogen. As a result, the feed gas distributor, large beads, and reactor side walls are prone to rapid deposition of silicon. Those deposits subsequently disrupt the proper feed distribution, product separation, and heat transfer of the system. Another problem with the fluidized bed reactor process is the product quality is generally insufficient for use in integrated circuit manufacture; however, the product of the fluidized bed reactor process may be used in solar grade applications.

[0005] There is a need in the polycrystalline silicon industry to improve efficiency of polycrystalline silicon production and reduce by-products.

SUMMARY

[0006] A process comprises feeding a vent gas stream from a Siemens reactor to a fluidized bed reactor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 is a flow diagram of a process described herein.

[0008] Figure 2 is a flow diagram of an alternative process described herein.

Reference Numerals

101 Siemens feed gas stream

102 Siemens reactor

comprise trichlorosilane, silicon tetrachloride, or combinations thereof. Polycrystalline silicon is deposited from the feed gas stream(s) 104, 106 onto the silicon seed particles. Polycrystalline silicon product in bead form is removed from the fluidized bed reactor 105 in product stream 107. A vent gas stream 108 may comprise hydrogen, hydrogen chloride, and chlorosilanes, e.g., trichlorosilane and silicon tetrachloride, is removed from the fluidized bed reactor 105 and sent to recovery system 109. Hydrogen may be recovered and sent back to the Siemens reactor 102 through line 110. Chlorosilanes may be recovered through line 111 and recycled or sold. Hydrogen chloride may be recovered and sold. Silicon tetrachloride may be hydrogenated or otherwise converted to trichlorosilane, and the resulting trichlorosilane may be recycled to the Siemens reactor 102.

Siemens Reactor

[0011] The Siemens reactor used in this invention may be a conventional Siemens reactor, such as a Siemens reactor disclosed in U.S. Patents 2,999,735; 3,011,877; 3,862,020; or 3,961,003. For example, operation of the Siemens reactor may be performed as follows.

Polycrystalline silicon seed rods are placed upright and parallel to one another in the Siemens reactor. Two or more of these seed rods may be connected to one another by a bridge, thereby forming a U-rod. The U-rods are heated until they reach a temperature ranging from 700 °C to 1,400 °C, alternatively 1,000 °C to 1,200 °C, alternatively 1,100 °C to 1,150 °C. The Siemens reactor may be operated at a pressure ranging from 13 kPa (2 psig) to 3450 kPa (500 psig), alternatively 6 kPa (1 psig) to 1380 kPa (200 psig), and alternatively 100 kPa (1 bar) to 690 kPa (100 psig).

[0012] The Siemens feed gas is fed to the Siemens reactor through an inlet in the base. The Siemens feed gas may comprise hydrogen and trichlorosilane. The Siemens feed gas may optionally further comprise silicon tetrachloride. Silicon is deposited from the feed gas onto the U-rod, thereby increasing the diameter of the U-rod. The Siemens feed stream may comprises 5 % to 75 % trichlorosilane. The Siemens feed gas may comprise 0.015 moles of trichlorosilane per mole of hydrogen to 0.3 moles of trichlorosilane per mole of hydrogen. Alternatively, the Siemens feed gas may comprise 0.03 moles of trichlorosilane per mole of hydrogen to 0.15 moles of trichlorosilane per mole of hydrogen. Without wishing to be bound by theory, it is thought that the amount of polycrystalline silicon product ranging from

20 % to 40 % based on the total quantity of silicon contained in the Siemens feed gas may be obtained from the Siemens reactor.

[0013] The vent gas stream from the Siemens reactor may be fed directly to the fluidized bed reactor without intervening treatment steps (without any unit operations between the Siemens reactor and the fluidized bed reactor). Alternatively, the vent gas stream from the Siemens reactor may be treated to remove certain species before being fed into the fluidized bed reactor. Figure 2 shows a process flow diagram of this process. The vent gas stream 104 from the Siemens reactor 102 may be treated, for example, by feeding the vent gas stream 104 through a dust removing apparatus 201, which is cooled with fluid such as service water, thereby removing fine silicon powder, disilanes, or combinations thereof through line 202. The dust removing apparatus 201 may comprise a sintered metal blowback filter, a contact condenser, or a combination thereof (for example, a sintered metal blowback filter located either upstream or downstream of a contact condenser in the stream 104 line. The resulting treated vent gas stream 203 comprising trichlorosilane (*i.e.*, with fine silicon powder, disilanes, or both, removed) may then be heated, using for example, a vaporizer 204. The overhead vapor from the contact condenser 205 comprises hydrogen and non-condensable chlorosilanes. The overhead vapor 205 and the treated vent gas stream 203 may optionally then be recombined and fed to the fluidized bed reactor 105. Without wishing to be bound by theory, it is thought that although this treatment step requires more energy and capital than directly feeding the vent gas stream 104 from the Siemens reactor 102 to the fluidized bed reactor 105, it is still more efficient than building a stand-alone process because existing capital assets from the Siemens technology can be used.

Fluidized Bed Reactor

[0014] The fluidized bed reactor used in this invention may be a conventional fluidized bed reactor, such as a fluidized bed reactor disclosed in U.S. Patent 5,077,028. For example, operation of the fluidized bed reactor may be performed as follows. Seed particles of silicon are placed in a fluidized bed reactor and fluidized. Sources of seed particles are known in the art. For example, seed particles may be obtained by mechanical attrition of granular polycrystalline silicon or by crushing polycrystalline silicon produced in a Siemens reactor. The gas used to fluidize the bed may comprise the vent gas stream from the Siemens reactor; a diluent gas such as hydrogen, argon, helium, nitrogen; or a combination thereof. Silicon is

deposited on the surface of the seed particles, increasing their diameters. The resulting product in bead form may be removed from the fluidized bed, and more seed particles may be introduced.

[0015] The temperature inside the fluidized bed reactor may range from 900 °C to 1420 °C, alternatively 1100 °C to 1300 °C, and alternatively 1100 °C to 1250 °C. Feeding the vent gas stream from the Siemens reactor directly into the fluidized bed reactor may offer the advantage of energy savings by having to provide less heat to the fluidized bed reactor. The concentration of chlorosilanes in the feed stream to the fluidized bed reactor may range from 20 mol% to 50 mol%. Without wishing to be bound by theory, it is thought that excessive amounts of fine powder may form if the concentration of chlorosilanes is higher than 50 %. The average diameter of the fluidized silicon particles may range from 0.5 mm to 4 mm, alternatively 0.6 mm to 1.6 mm. The residence time of the fluidized particles may range from 0.5 second to 2 seconds. The minimum fluidization velocity and design operational velocity may be determined by one of ordinary skill in the art based on various factors. The minimum fluidization velocity may be influenced by factors including gravitational acceleration, fluid density, fluid viscosity, solids density, and solids particle size. The operational velocity may be influenced by factors including heat transfer and kinetic properties, such as height of the fluidized bed, total surface area, flow rate of silicon precursor in the feed gas stream, pressure, gas and solids temperature, concentrations of species, and thermodynamic equilibrium point.

[0016] One skilled in the art will recognize that the Siemens reactor operates in a batch process, and the fluidized bed reactor operates in a continuous process. Furthermore, the vent gas composition leaving the Siemens reactor may vary during the course of a batch.

Therefore, one skilled in the art would recognize that vent gases from multiple (two or more) Siemens reactors may be combined to form a vent gas stream fed to the fluidized bed reactor, or the feed gas stream to the fluidized bed reactor may be supplemented with additional trichlorosilane, silicon tetrachloride, hydrogen, or a combination thereof, for example, to minimize variability of the feed gas stream to the fluidized bed reactor. Furthermore, the vent gas stream from the Siemens reactor may be fed to one or more fluidized bed reactors configured in parallel. Without wishing to be bound by theory, it is thought that supplementing the feed gas stream to the fluidized bed reactor with chlorosilanes comprising

trichlorosilane may increase silicon production rate. Without wishing to be bound by theory, it is thought that supplementing the feed gas stream to the fluidized bed reactor with silicon tetrachloride may prevent undesired deposition such as on heater walls and feed distributors.

[0017] Without wishing to be bound by theory, the fluidized bed reactor may have

5 deposition of the difference of yield, 90 % to 50%, or 40 % of theoretical maximum. Without wishing to be bound by theory it is thought that another advantage of this process is that the partially-converted feed gases from the Siemens reactor are of a composition that is not able to deposit silicon at temperatures above 1250 °C. That detail allows for design of heating system by a hot wall reactor, resistively-heated feed tube, or other means more efficient than
10 commonly used in a fluidized bed reactor process.

[0018] The disclosure of ranges includes the range itself and also anything subsumed therein, as well as endpoints. For example, disclosure of a range of 700 to 1,400 includes not only the range of 700 to 1,400, but also 700, 850, 1000 and 1400 individually, as well as any other number subsumed in the range. Furthermore, disclosure of a range of, for example, 700
15 to 1400 includes the subranges of, for example, 1000 to 1400 and 1000 to 1100, as well as any other subrange subsumed in the range. Similarly, the disclosure of Markush groups includes the entire group and also any individual members and subgroups subsumed therein. For example, disclosure of the Markush group hydrogen, trichlorosilane, tetrachlorosilane, and hydrogen chloride includes the member hydrogen individually; the subgroup
20 trichlorosilane and tetrachlorosilane; and any other individual member and subgroup subsumed therein.

Recovery System

[0019] The vent gas stream from the fluidized bed reactor may be recovered by any conventional means. The vent gas stream from the fluidized bed reactor may be cooled using
25 conventional equipment. Fine silicon powder may be removed using conventional equipment such as a contact condenser, sintered metal blowback filtration assembly, or a combination of a cyclone and filter assembly.

[0020] Alternatively, the vent gas stream from the fluidized bed reactor may be fed to a contact condenser to knock down the solids in liquid chlorosilanes and thereafter spray dry
30 the fine silicon powder may be spray dried in a spray dryer. The resulting silicon powder may be neutralized and sold. Alternatively, the fine silicon powder and chlorosilanes may be

recovered and converted to chlorosilanes for use as a feed stream to the Siemens reactor. One skilled in the art would be able to select a suitable recovery system without undue experimentation.

Industrial Applicability

- 5 **[0021]** The combined benefits of no duplicity of feed and recovery systems and easier heating of the process may make the integral fluidized bed reactor with a Siemens reactor process more manageable and economic. The polycrystalline silicon product of the Siemens reactor may be suitable for either solar cell or integrated circuit applications. The polycrystalline silicon product of the fluidized bed reactor may be suitable for solar cell
10 applications.

CLAIMS

1. A process comprising: 1) feeding a vent gas stream from one or more Siemens reactors to one or more fluidized bed reactors.
- 5 2. The process of claim 1, where the vent gas stream comprises hydrogen and chlorosilanes.
3. The process of claim 1, where the vent gas stream comprises hydrogen and silane.
- 10 4. The process of claim 2, further comprising supplementing the vent gas stream with additional chlorosilanes.
5. The process of claim 4, where the additional chlorosilanes comprise trichlorosilane, silicon tetrachloride, or a combination thereof.
- 15 6. The process of claim 1, further comprising using silicon produced by the Siemens reactor for integrated circuits, for solar cells, or both.
7. The process of claim 1, further comprising using silicon produced by the fluidized bed
20 reactor for solar cells.
8. The process of claim 2, where the vent gas stream comprises trichlorosilane, silicon tetrachloride, hydrogen, hydrogen chloride and silicon powder and the process further comprises removing silicon powder from the vent gas stream before feeding the vent gas
25 stream to the fluidized bed reactor.
9. The process of claim 2, where the vent gas stream is optionally supplemented with additional trichlorosilane to form a feed gas stream to the fluidized bed reactor, and the feed gas stream to the fluidized bed reactor comprises a concentration of chlorosilanes ranging
30 from 20 mol% to 50 mol%.

10. The process of claim 2, further comprising: 2) feeding a second vent gas stream from the fluidized bed reactor to a recovery system.

5 11. The process of claim 10, where the second vent gas stream comprises: hydrogen, trichlorosilane, tetrachlorosilane, and hydrogen chloride.

12. The process of claim 10, further comprising: 3) recovering hydrogen, trichlorosilane, or both, and feeding the hydrogen, trichlorosilane, or both, to the Siemens reactor in step 1).

10 13. The process of claim 10, further comprising 3) recovering tetrachlorosilane, converting the tetrachlorosilane to trichlorosilane, and feeding the trichlorosilane to the Siemens reactor in step 1).

15 14. A process comprising: i) feeding a vent gas stream from multiple Siemens reactors directly to one or more fluidized bed reactors without intervening treatment steps.

15. The process of claim 14, where the vent gas stream comprises hydrogen and chlorosilanes.

20 16. The process of claim 14, where the vent gas stream comprises hydrogen and silane.

17. The process of claim 14, further comprising using silicon produced by the Siemens reactor for integrated circuits, for solar cells, or both.

25 18. The process of claim 14, further comprising using silicon produced by the fluidized bed reactor for solar cells.

19. The process of claim 15, where the vent gas stream comprises trichlorosilane, silicon tetrachloride, hydrogen, hydrogen chloride and silicon powder.

30

20. The process of claim 15, further comprising: ii) feeding a second vent gas stream from the fluidized bed reactor to a recovery system.
21. The process of claim 20, where the second vent gas stream comprises: hydrogen,
5 trichlorosilane, tetrachlorosilane, and hydrogen chloride.
22. The process of claim 20, further comprising: iii) recovering hydrogen, trichlorosilane, or both, and feeding the hydrogen, trichlorosilane, or both, to the Siemens reactor in step i).
- 10 23. The process of claim 20, further comprising iii) recovering tetrachlorosilane, converting the tetrachlorosilane to trichlorosilane, and feeding the trichlorosilane to the Siemens reactor in step i).

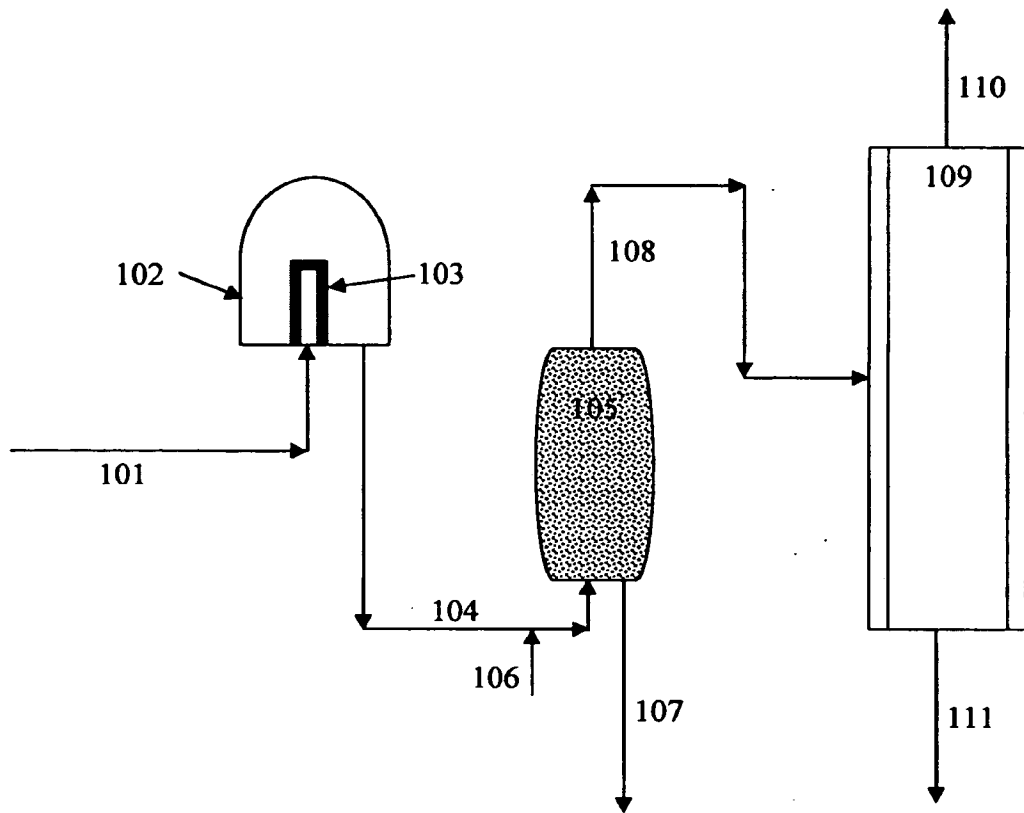


Figure 1

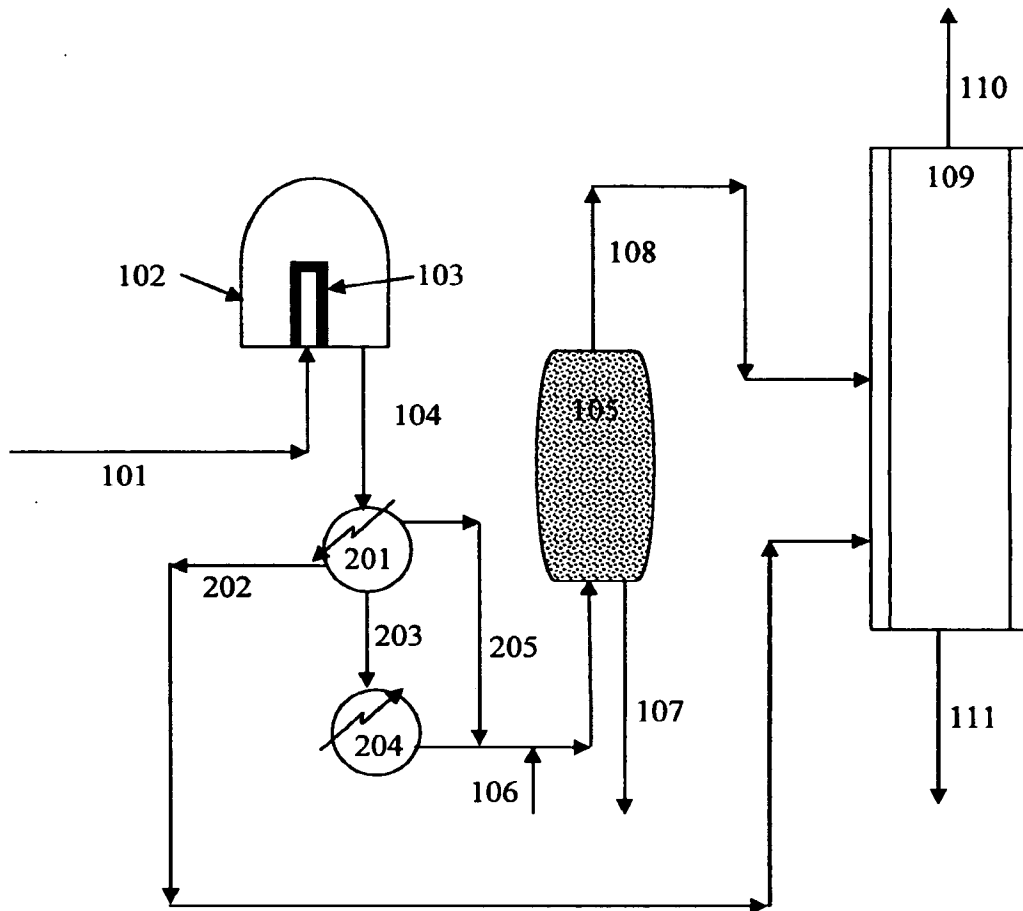


Figure 2

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2007/013905

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B33/035 C01B33/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, INSPEC, COMPENDEX, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02/100776 A (HEMLOCK SEMICONDUCTOR CORP [US]; KENDIG JAMES EDWARD [US]; LANDIS DAVI) 19 December 2002 (2002-12-19) claims 1,3,14,16 page 1, line 12 - page 2, line 2 page 2, line 19 - line 22 page 3, line 30 - page 6, line 13	1
A	GB 2 028 289 A (SCHUMACHER CO J C) 5 March 1980 (1980-03-05) page 1, line 19 - line 40	1
A	US 4 491 604 A (LESK ISRAEL A [US] ET AL) 1 January 1985 (1985-01-01) claims 1-11 column 1, line 9 - line 28 figure 4	1
	----- -/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

21 December 2007

Date of mailing of the international search report

03/01/2008

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Rigondaud, Bernard

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2007/013905

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 481 232 A (OLSON JERRY M [US]) 6 November 1984 (1984-11-06) column 2, line 11 - line 24 -----	1
A	US 6 007 869 A (SCHREIEDER FRANZ [DE] ET AL) 28 December 1999 (1999-12-28) column 2, line 12 - line 36 -----	1
A	US 4 818 495 A (IYA SRIDHAR K [US]) 4 April 1989 (1989-04-04) column 2, line 6 - line 65 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2007/013905

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 02100776	A	19-12-2002	AT 276969 T DE 60201354 D1 DE 60201354 T2 EP 1392601 A1 JP 2004532786 T US 2002187096 A1	15-10-2004 28-10-2004 16-02-2006 03-03-2004 28-10-2004 12-12-2002
GB 2028289	A	05-03-1980	CA 1145117 A1 DE 2919086 A1 DE 2954368 A1 FR 2433479 A1 IT 1193203 B JP 1428904 C JP 55027890 A JP 62028083 B	26-04-1983 06-03-1980 12-07-1984 14-03-1980 15-06-1988 09-03-1988 28-02-1980 18-06-1987
US 4491604	A	01-01-1985	JP 59123227 A	17-07-1984
US 4481232	A	06-11-1984	CA 1207985 A1 DE 3419656 A1 FR 2547571 A1 JP 1717458 C JP 3080723 B JP 60036317 A	22-07-1986 10-01-1985 21-12-1984 14-12-1992 25-12-1991 25-02-1985
US 6007869	A	28-12-1999	CN 1216288 A DE 19735378 A1 EP 0896952 A1 JP 3122643 B2 JP 11139817 A	12-05-1999 18-02-1999 17-02-1999 09-01-2001 25-05-1999
US 4818495	A	04-04-1989	NONE	