



(51) International Patent Classification:

H01L 21/469 (2006.01)

(21) International Application Number:

PCT/US201 1/001 117

(22) International Filing Date:

23 June 2011 (23.06.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/398,980	2 July 2010 (02.07.2010)	US
61/402,191	24 August 2010 (24.08.2010)	US

(71) Applicant (for all designated States except US): **MATHESON TRI-GAS, INC.** [US/US]; 150 Allen Road, Basking Ridge, NJ 07920 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **TORRES, Robert, Jr.** [US/US]; 16392 Maple Rock Ct., Parker, CO 80134

(US). **FRANCIS, Terry, Arthur** [US/US]; 3112 Lone Pine Road, Schenectady, NY 12303-5006 (US). **HASAKA, Satoshi** [JP/JP]; Toyo Building, 1-3-26, Koyama, Shinagawa-ku, Tokyo 142-8558 (JP). **BRABANT, Paul, David** [US/US]; 42 Shelterwood Road, East Greenbush, NY 12061 (US).

(74) Agent: **PETERSEN, Steven, C**; 7198 Celome Ct., San Diego, CA 92129 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, 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, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

[Continued on nextpage]

(54) Title: THIN FILMS AND METHODS OF MAKING THEM USING CYCLOHEXASILANE

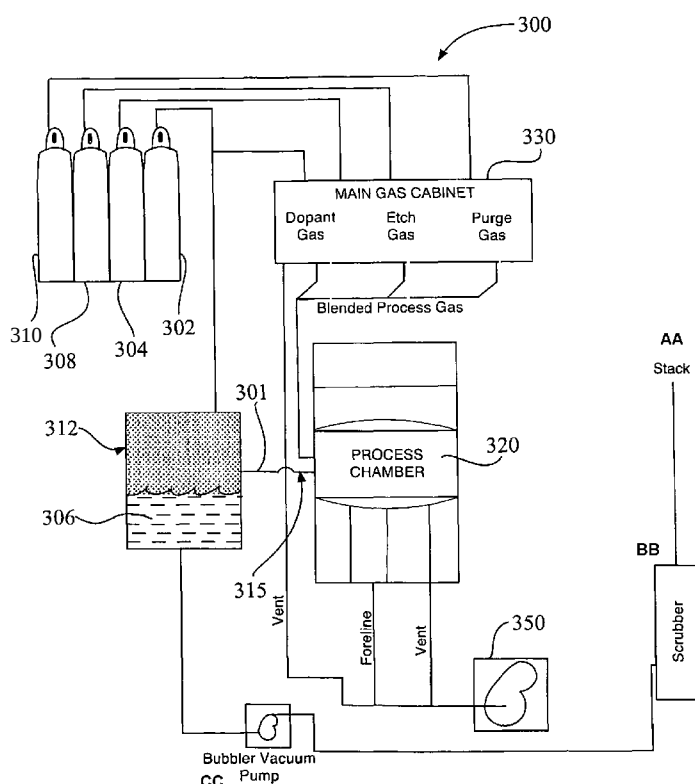


FIGURE 3

(57) Abstract: Cyclohexasilane is used in chemical vapor deposition methods to deposit epitaxial silicon-containing films over substrates. Such methods are useful in semiconductor manufacturing to provide a variety of advantages, including uniform deposition over heterogeneous surfaces, high deposition rates, and higher manufacturing productivity. Furthermore, the crystalline Si may be *in situ* doped to contain relatively high levels of substitutional carbon by carrying out the deposition at a relatively high flow rate using cyclohexasilane as a silicon source and a carbon-containing gas such as dodecylmethylcyclohexasilane or tetramethyldisilane under modified CVD conditions.

(84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(88) **Date of publication of the international search report:**

15 March 2012

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 11/01 117

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01L 21/469 (2012.01)

USPC - 438/787; 257/E21 .277

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)

IPC(8)- H01L 21/469 (201 1.01);

USPC- 438/787; 257/E21.277

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Patents and NPL (classification, keyword; search terms below)Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWest (US Pat, PgPub, EPO, JPO), GoogleScholar (PL, NPL), FreePatentsOnline (US Pat, PgPub, EPO, JPO, WIPO, NPL);
search terms: cyclohexasilane, Si6H12, deposit, CVD, PVD, epitaxy, epitaxial, silicon, Si, carbon, C, ratio, tetramethyldisilane, methylated

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,985,689 A (Gofuku et al.) 16 November 1999 (16.1 1.1999), col 2 to col 3; col 6 to col 7; col 19, ln 45-67; col 29, ln 16-24; col 34, ln 50-60; col 39 to col 40	1-14
Y	US 6,846,51 3 B2 (FURUSAWA et al.) 25 January 2005 (25.01 .2005), col 3, ln 6-1 1; col 5, ln 3-14	1-14
Y	US 2009/0104791 A1 (NEMANI et al.) 23 April 2009 (23.04.2009), Fig. 1; para [0006], [0008], [0018], [0022], [0031], [0032], [0034], [0056], [0065]	6, 13, 14
Y	US 2009/0242019 A1 (RAMAMOORTHY et al.) 01 October 2009 (01.10.2009), para [0006]-[0010], [0027]-[0062]	1-14
Y	US 5,686,734 A (HAMAKAWA et al.) 11 November 1997 (11.11.1997), col 3-5; col 7-18	1-14

☐ Further documents are listed in the continuation of Box C. 1

• Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"G" document member of the same patent family
"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	

Date of the actual completion of the international search

09 January 2012 (09.01.2012)

Date of mailing of the international search report

19 JAN 2012

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 11/01 117

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
-See Extra Sheet-

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

-Continued from Box No. III:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: claims 1-14 directed to a method for depositing a thin film, comprising:
introducing a process gas comprising cyclohexasilane to a chamber, wherein said chamber contains a substrate;
establishing cyclohexasilane chemical vapor deposition conditions in said chamber;
initiating decomposition of said cyclohexasilane; and
depositing an epitaxial Si-containing film onto said substrate.

Group II: claims 15-19 directed to a method for blanket depositing a silicon containing material on a substrate, comprising:
positioning a substrate containing a crystalline surface and at least one feature surface within a process chamber, wherein said feature surface comprises a material selected from the group consisting of an oxide material, a nitride material, poly silicon, photoresist or combinations thereof;
heating the substrate to a predetermined temperature of about 550°C or less; and
exposing the substrate to a process gas containing cyclohexasilane to deposit a silicon-containing blanket layer across the crystalline surface and the feature surfaces wherein said process carrier gas flows at a rate of about 150 to 250 times greater than said cyclohexasilane.

Group III: claim 20 directed to an apparatus for forming an epitaxial film on a substrate in a chemical vapor deposition system, comprising:
a decomposition chamber having an inlet and an outlet;
a deposition chamber having chamber dimensions and opposite ends operatively connected to said deposition chamber;
high-speed pump means connected to one of the ends of the chamber and operative to maintain the deposition pressure in the chamber at or below 200 Torr;
a gas inlet adjacent the other of the ends of the chamber for introducing gas into the chamber so that the gas flows generally in a direction from the gas inlet to the pump means;
substrate support means for supporting the substrate within the chamber; and
high speed pump evacuates a carrier gas out of said chamber at a speed sufficient to maintain the pressure less than 200 Torr.

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because under PCT Rule 13.2 they lack the same or corresponding technical features for the following reasons:

Group III does not include the cyclohexasilane of groups I and II.

Groups I and II do not include the chamber dimensions, gas pump and pressure nor the inlet and outlet features of group III.

Groups I and III do not include the gas flow rates nor the temperature parameters of group II.

Groups II and III do not include the decomposition of cyclohexasilane of group I.

The common feature of groups I, II and III of a chemical vapor deposition chamber used to deposit a film on a substrate is taught by US 2009/0104791 A1 to Nemani et al. (hereinafter 'Nemani') (Abstract; fig. 1; para [0006]). The common feature of groups I and II of cyclohexasilane as the silicon source is taught by Nemani (para [0034]). The common feature of carrier gas of groups II and III is taught by Nemani (para [0035]).

The common features of groups I and III of growing an epitaxial film in a chemical vapor deposition chamber on a substrate is taught by US 6,846,513 B2 to Furusawa et al. (col 3, ln 6-11; col 5, ln 3-14); therefore the common feature is not an improvement over the prior art.

None of these technical features are common to the other groups, nor do they correspond to a special technical feature in the other groups. Therefore, unity of invention is lacking.