



- (51) International Patent Classification:
H01L 21/31 (2006.01) *H01L 21/8238* (2006.01)
- (21) International Application Number:
PCT/US2012/032902
- (22) International Filing Date:
10 April 2012 (10.04.2012)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
61/477,422 20 April 2011 (20.04.2011) US
13/437,305 2 April 2012 (02.04.2012) US
- (71) Applicant (for all designated States except US): **APPLIED MATERIALS, INC.** [US/US]; 3050 Bowers Avenue, Santa Clara, California 95054 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **KIM, Hyungjun** [KR/KR]; B-107 Jinju APT, Yeoido-dong, Yeongdeungpo-Gu, Seoul 150-895 (KR). **KIM, Woo-Hee** [KR/KR]; 1036-26, Sinjeong 1-dong, Yangcheon-gu, Seoul 158-862 (KR). **KIM, Min-Kyu** [KR/KR]; Jaan apt. 104-703, Galsan 1-dong, Bupyeong-gu, Incheon 403-081 (KR). **HUNG, Steven** [—/US]; 915 Mango Avenue, Sunnyvale, California 94087 (US). **NOORI, Atif** [US/US]; 13443 Ward

Way, Saratoga, California 95070 (US). **THOMPSON, David** [CA/US]; 2590 New Jersey Avenue, San Jose, California 95124 (US). **ANTHIS, Jeffrey W.** [US/US]; 1008 Empey Way, San Jose, California 95128 (US).

- (74) Agent: **BLANKMAN, Jeffrey I.**; Diehl Servilla LLC, 33 Wood Avenue South, Second Floor, Suite 210, Iselin, New Jersey 08830 (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, QA, RO, RS, RU, RW, 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.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, 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,

[Continued on next page]

(54) Title: METHODS FOR MANUFACTURING HIGH DIELECTRIC CONSTANT FILMS

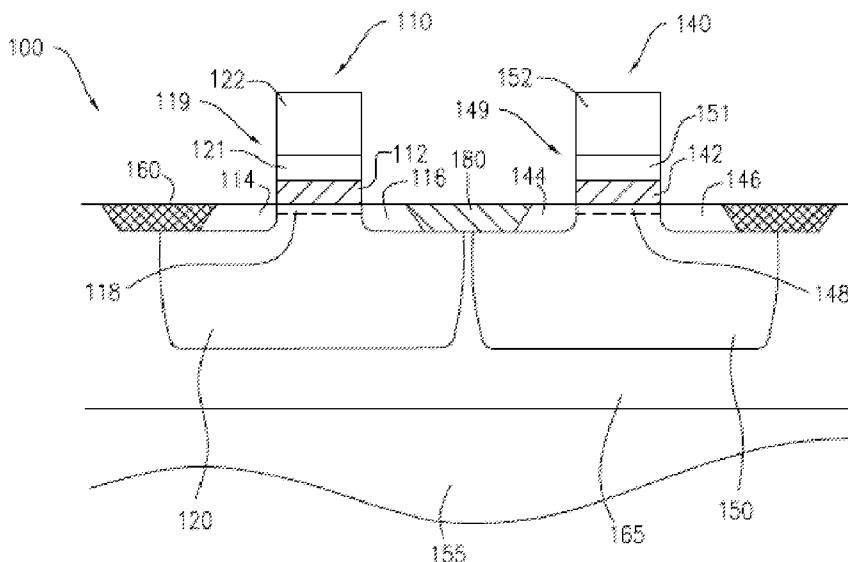


FIG. 1

(57) Abstract: Provided are methods for depositing a cerium doped hafnium containing high-k dielectric film on a substrate. The reagents of specific methods include hafnium tetrachloride, an organometallic complex of cerium and water.





SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

— 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))

Published:

— with international search report (Art. 21(3))

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

3 January 2013

A. CLASSIFICATION OF SUBJECT MATTER**H01L 21/31(2006.01)i, H01L 21/8238(2006.01)i**

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)

H01L 21/31; H01L 2358; C23C 16/40; H01L 29/76; C23C 16/455; H01L 31/00

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: high-k, dielectric, hafnium, cerium, precursor, oxidant, oxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| Y | WO 2009-143456 A1 (SIGMA-ALDRICH CO. et al.) 26 November 2009 See abstract; paragraphs [0049]-[0075]; and figure 1. | 1-5 |
| Y | US 2011-0039419 A1 (LUCIEN DATE et al.) 17 February 2011 See claim 8. | 1-5 |
| A | US 2007-0158702 A1 (MARK L. DOCZY et al.) 12 July 2007 See abstract; figures 3A-4C; and paragraphs [0027]-[0042]. | 1-5 |
| A | US 6849925 B1 (ARVIND HALLIYAL et al.) 01 February 2005 See abstract; figures 2-10; and column 11 line 34 - column 14 line 19. | 1-5 |

 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 application or patent 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 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

30 OCTOBER 2012 (30.10.2012)

Date of mailing of the international search report

31 OCTOBER 2012 (31.10.2012)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan
City, 302-701, Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

CHOI, SANGWON

Telephone No. 82-42-481-5695



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/032902

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|--|------------------|---|--|
| WO 2009-143456 A1 | 26.11.2009 | CN 102137952 A EP 2297379 A1 IL 209378 D0 JP 2011-525699 A KR 10-2012-0007949 A TW 200951242 A US 2011-0165401 A1 | 27.07.2011 23.03.2011 31.01.2011 22.09.2011 25.01.2012 16.12.2009 07.07.2011 |
| US 2011-0039419 A1 | 17.02.2011 | WO 2011-008925 A2 WO 2011-008925 A3 WO 2011-008925 A3 | 20.01.2011 07.04.2011 20.01.2011 |
| US 2007-0158702 A1 | 12.07.2007 | None | |
| US 6849925 B1 | 01.02.2005 | US 6645882 B1 | 11.11.2003 |