

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 February 2007 (15.02.2007)

PCT

(10) International Publication Number
WO 2007/019436 A3

(51) International Patent Classification:
C23C 16/455 (2006.01)

(21) International Application Number:
PCT/US2006/030711

(22) International Filing Date: 7 August 2006 (07.08.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/706,490 8 August 2005 (08.08.2005) US

(71) Applicant (for all designated States except US): **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, Delaware 19898 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **THOMPSON, Jeffrey, Scott** [US/US]; 1508 Skiles Boulevard, West Chester, Pennsylvania 19382 (US). **RADZEWICH, Catherine, E.** [US/US]; 1313 Prospect Drive, Wilmington, Delaware 19809 (US).

(74) Agent: **DALICKAS, Gail, A.**; E. I. du Pont de Nemours and Company, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

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

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, 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, 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).

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

(88) Date of publication of the international search report:
12 April 2007

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 2007/019436 A3

(54) Title: ATOMIC LAYER DEPOSITION OF TANTALUM-CONTAINING FILMS USING SURFACE-ACTIVATING AGENTS AND NOVEL TANTALUM COMPLEXES

(57) Abstract: Atomic layer deposition processes for the formation of tantalum-containing films on surfaces are provided. Also provided are novel tantalum complexes that can be used as tantalum precursors in the disclosed deposition processes.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/030711

A. CLASSIFICATION OF SUBJECT MATTER INV. C23C16/455				
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) C23C				
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, COMPENDEX, INSPEC, WPI Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	US 2005/059240 A1 (CHOI KYUNG-IN [KR] ET AL) 17 March 2005 (2005-03-17) paragraphs [0034], [0051] - [0058]	1,3,8,9		
X	US 2004/187304 A1 (CHEN LING [US] ET AL) 30 September 2004 (2004-09-30) paragraphs [0036], [0039], [0040]	1,8,9,15		
Y	-----	2,3,5,14		
X	WO 03/102265 A (APPLIED MATERIALS INC [US]) 11 December 2003 (2003-12-11) paragraphs [0029] - [0055]; figures 1,2 -----	1,4,5,15		
-/--				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. </td> <td style="width: 50%; border: none;"> <input checked="" type="checkbox"/> See patent family annex. </td> </tr> </table>			<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.			
* Special categories of cited documents :				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> *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 </td> <td style="width: 50%; border: none; vertical-align: top;"> *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 </td> </tr> </table>			*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
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	Date of mailing of the international search report			
12 February 2007	01/03/2007			
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 Schuhmacher, Jörg			

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/030711

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KIM H ET AL: "Plasma-enhanced atomic layer deposition of tantalum thin films: the growth and film properties" PREPARATION AND CHARACTERIZATION, ELSEVIER SEQUOIA, NL, vol. 441, no. 1-2, 22 September 2003 (2003-09-22), pages 311-316, XP004450871 ISSN: 0040-6090 page 312 - page 314	1-3,8
Y	LEMONDS A M ET AL: "Surface science investigations of atomic layer deposition half-reactions using TaF5 and Si2H6" SURFACE SCIENCE ELSEVIER NETHERLANDS, vol. 538, no. 3, 20 July 2003 (2003-07-20), pages 191-203, XP002409965 ISSN: 0039-6028 pages 193,194,, column 202	2,3,5
Y	LEHN JEAN-SEBASTIEN M ET AL: "A new precursor for the chemical vapor deposition of tantalum nitride films" J. MATER. CHEM.; JOURNAL OF MATERIALS CHEMISTRY NOV 7 2004, vol. 14, no. 21, 7 November 2004 (2004-11-07), pages 3239-3245, XP002409855 cited in the application page 3239 - page 3240	14
A	SUNKWON LIM ET AL: "A study on the development of chemical vapor deposition precursors. 4. Syntheses and characterization of new n-alkoxo-[beta]-ketoiminate complexes of niobium and tantalum" CHEMISTRY OF MATERIALS AMERICAN CHEM. SOC USA, vol. 14, no. 4, April 2002 (2002-04), pages 1548-1554, XP002409966 ISSN: 0897-4756 page 1549	11-13
A	GUERIN F ET AL: "CONFORMATIONALLY RIGID DIAMIDE COMPLEXES: SYNTHESIS AND STRUCTURE OF TANTALUM(3) ALKYNE DERIVATIVES" ORGANOMETALLICS, WASHINGTON, DC, US, vol. 14, July 1995 (1995-07), pages 3154-3156, XP000957606 ISSN: 0276-7333 page 3155	16
	----- -/--	

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2006/030711

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>OSHIKI TOSHIYUKI ET AL: "Catalytic performance of tantalum-eta<2>-alkyne complexes [TaCl₃ (R<1>C EQUIV. CR<2>L₂) for alkyne cyclotrimerization" BULL. CHEM. SOC. JPN.; BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN 2004, vol. 77, no. 5, 2004, pages 1009-1011, XP002419654 Scheme 1</p>	16
Y	<p>FRANCESCHINI PIER LUIGI ET AL: "VOLATILE BETA-KETOIMINATO- AND BETA-DIKETIMINATO-BASED ZIRCONIUM COMPLEXES AS POTENTIAL MOCVD PRECURSORS" INORGANIC CHEMISTRY, AMERICAN CHEMICAL SOCIETY. EASTON, US, vol. 42, no. 22, November 2003 (2003-11), pages 7273-7282, XP009077525 ISSN: 0020-1669 figure 6</p>	17-19
Y	<p>US 6 527 848 B2 (HINTERMAIER FRANK [DE] ET AL HINTERMAIER FRANK [DE] ET AL) 4 March 2003 (2003-03-04) column 1, line 59 - column 2, line 9</p>	17-19
A	<p>US 6 511 936 B1 (THEOPOLD KLAUS H [US] ET AL) 28 January 2003 (2003-01-28) abstract</p>	17-19

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2006/030711

Box 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 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 additional 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 an additional fee, this Authority did not invite payment of any additional fee.

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.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-15

A process for depositing a tantalum containing film on a surface comprising steps a), b), and c) as indicated in independent claim 1

2. claim: 16

A tantalum complex with an alkyne ligand as indicated in independent claim 16

3. claims: 17-19

A tantalum complex with a 1,3 diminate ligand as indicated in independent claims 17-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2006/030711

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2005059240	A1	17-03-2005	NONE	
US 2004187304	A1	30-09-2004	NONE	
WO 03102265	A	11-12-2003	US 2004077183 A1	22-04-2004
US 6527848	B2	04-03-2003	CN 1328562 A WO 0032608 A1 EP 1133499 A1 JP 3566211 B2 JP 2002531692 T US 2002000175 A1	26-12-2001 08-06-2000 19-09-2001 15-09-2004 24-09-2002 03-01-2002
US 6511936	B1	28-01-2003	AU 2566399 A CA 2321419 A1 EP 1053260 A1 JP 2002503733 T WO 9941290 A1	30-08-1999 19-08-1999 22-11-2000 05-02-2002 19-08-1999