PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : **H01L 21/285, C23C 16/02** | **A3**

(11) International Publication Number: **WO 00/03420**

(43) International Publication Date: 20 January 2000 (20.01.00)

(21) International Application Number: PCT/US99/15583

(22) International Filing Date: 9 July 1999 (09.07.99)

(30) Priority Data:
09/113,852 10 July 1998 (10.07.98) US

(71) Applicant: CVC, INC. [US/US]; 525 Lee Road, Rochester, NY 14603 (US).

(72) Inventors: PARANJPE, Ajit, P.; 355 North Wolfe Road #336, Sunnyvale, CA 94086 (US). MOSLEHI, Mehrdad, M.; 956 Stanley Avenue, Los Altos, CA 94024 (US). VELO, Lino, A.; P.O. Box 2690, San Ramon, CA 94583 (US). OMSTEAD, Thomas, R.; 4201 Bowstring Cove, Austin, TX 78735 (US). CAMPBELL, David, R., Sr.; 33 Littlewood Lane, West, Rochester, NY 14625 (US). LIU, Zeming; 13408 Caballero Cove, Austin, TX 78727 (US). SHANG, Guihua; 825 East Evelyn Avenue #620, Sunnyvale, CA 94086 (US).

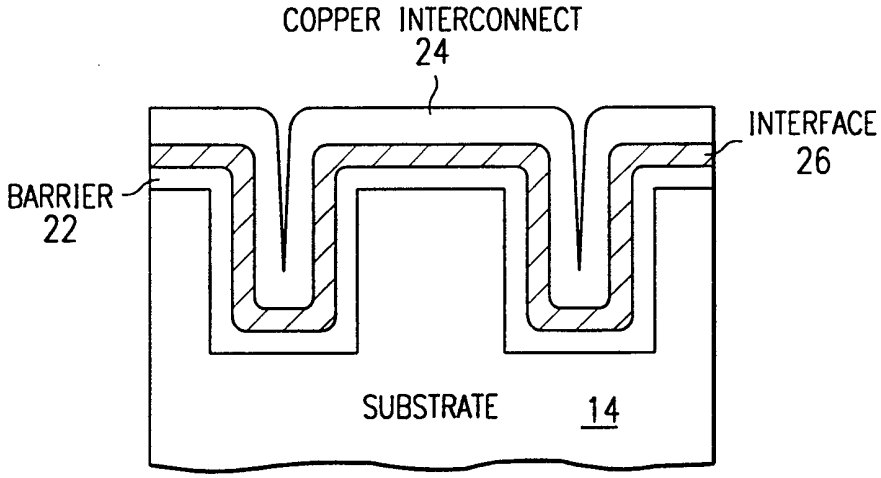
(74) Agent: HOLLAND, Robert, W.; Baker & Botts, L.L.P., 2001 Ross Avenue, Dallas, TX 75201-2980 (US).

(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(88) Date of publication of the international search report:
29 June 2000 (29.06.00)

(54) Title: METHOD FOR FORMING A COPPER FILM ON A SUBSTRATE



(57) Abstract

Adhesion of a copper film, such as a copper interconnect (24), to a substrate underlayer, such as a substrate diffusion barrier, is enhanced with adhesion promotion techniques. The adhesion promotion techniques can repair the interface (26) of the copper film and the substrate to enhance adhesion of the copper film for high-yield formation of inlaid copper metal lines and plugs. For instance, thermal annealing of a seed layer, including a copper seed layer, an alloy seed layer or a reactant seed layer, can repair contamination at the interface of the seed layer and the substrate. Alternatively, the adhesion promotion techniques can avoid contamination of the interface by depositing an inert seed layer, such as a noble (e.g., platinum) or passivated metal seed layer, or by depositing the seed layer under predetermined conditions that minimize contamination of the interface, and then depositing a bulk coper layer under predetermined conditions that maximize throughput. Alternatively, the adhesion promotion techniques can avoid the formation of an interface by graduated deposition of a first material and copper.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/15583

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01L21/285 C23C16/02

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 7 H01L 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	STUMM T H ET AL: "Selectivity in low pressure chemical vapor deposition of copper from hexafluoroacetylacetonate-copper(I)-trimethylvinylsilane in the presence of water" MATERIALS SCIENCE & ENGINEERING B (SOLID-STATE MATERIALS FOR ADVANCED TECHNOLOGY), FEB. 1994, SWITZERLAND, vol. B23, no. 1, pages 48-53, XP002121804 ISSN: 0921-5107	1-3,69, 71
Y	page 49, left-hand column, paragraph 2 -page 51, right-hand column, paragraph 2; figures 1,3	4-6,70

X	US 5 763 953 A (IIJIMA TADASHI ET AL) 9 June 1998 (1998-06-09) column 14, line 30 -column 15, line 18; figures 30A-G	1,2,4

	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in 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	Date of mailing of the international search report
7 April 2000	17.04.00

Name and mailing address of the ISA	Authorized officer
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	Micke, K

2

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/15583

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 354 712 A (HO YU Q ET AL) 11 October 1994 (1994-10-11) column 6, line 22 - line 43	1,11,16
X	EP 0 297 348 A (IBM) 4 January 1989 (1989-01-04) column 11, line 40 -column 12, line 15	1,11,12
Y	US 5 723 028 A (PORIS JAIME) 3 March 1998 (1998-03-03) column 6, line 53 -column 7, line 30; figure 3	4,5
Y	US 5 674 787 A (ZHAO BIN ET AL) 7 October 1997 (1997-10-07) column 5, line 9 -column 7, line 24 column 9, line 30 -column 10, line 18; figures 4,5,10-12	6
Y	EP 0 698 918 A (TEXAS INSTRUMENTS INC ;CALIFORNIA INST OF TECHN (US)) 28 February 1996 (1996-02-28) page 6, line 1 - line 3	70
Y	US 5 112 448 A (CHAKRAVORTY KISHORE K) 12 May 1992 (1992-05-12) column 3, line 37 -column 5, line 43; figures 13A,14	6
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 09, 31 July 1998 (1998-07-31) & JP 10 092977 A (INTERNATL BUSINESS MACH CORP <IBM>), 10 April 1998 (1998-04-10) abstract -& US 5 866 237 A (ANGELOPOULOS ANASTASIOS PETER ET AL) 2 February 1999 (1999-02-02) column 2, line 24 - line 32	1,11,13
A	EP 0 725 439 A (TOKYO SHIBAURA ELECTRIC CO) 7 August 1996 (1996-08-07) page 3, line 25 - line 50 page 4, line 44 - line 52	1,15
P,X	EP 0 881 673 A (IBM) 2 December 1998 (1998-12-02) column 9, line 27 -column 10, line 28 column 11, line 19 - line 32; figures 3,4	1,11,13

2

INTERNATIONAL SEARCH REPORT

Ir. ıational application No.
PCT/US 99/15583

Box I Observations where certain claims were found unsearchable (Continuation of item 1 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 II Observations where unity of invention is lacking (Continuation of item 2 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.:

1-6,11-16, 69-71

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: 1-6,69-71

   Before depositing a bulk copper film, depositing a seed layer consisting of a noble metal.

2. Claims: 7-10

   Before depositing a bulk copper film, depositing a passivated metal (TaN,TiN,TaOxNy,TiOxNy) as a seed layer.

3. Claims: 11-16

   Before depositing a bulk copper film, depositing a catalytic material (Cr,Sn,Zn,Ti,W) as a seed layer.

4. Claims: 17-21

   Before depositing a bulk copper film, depositing a seed layer of a reactant material (Si,Ge).

5. Claims: 22-24

   Before depositing a bulk copper film, depositing a copper seed layer.

6. Claims: 25-30

   Before depositing a bulk copper film, depositing a seed layer by CVD from a precursor with firmly bonded hfac ligands.

7. Claims: 31-38

   Before depositing a bulk copper film, depositing a seed layer by CVD from a precursor that has no hfac-ligands.

8. Claims: 39-52

   Before depositing a bulk copper film, depositing a seed layer on a barrier layer and performing thermal annealing.

9. Claims: 53-68

   Before depositing a bulk copper film, depositing a first

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

material at a first deposition rate and grading the first material with copper, slowly reducing the first deposition rate to zero.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/15583

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5763953 A	09-06-1998	JP 6204218 A	22-07-1994
		JP 6326102 A	25-11-1994
		US 5529954 A	25-06-1996
		DE 4400200 A	07-07-1994
US 5354712 A	11-10-1994	CA 2082771 A,C	13-05-1994
EP 0297348 A	04-01-1989	AU 609493 B	02-05-1991
		AU 1850388 A	05-01-1989
		CA 1332036 A	20-09-1994
		DE 3868724 A	09-04-1992
		JP 1011975 A	17-01-1989
		JP 1902412 C	08-02-1995
		JP 6027327 B	13-04-1994
		US 4948623 A	14-08-1990
US 5723028 A	03-03-1998	US 5368711 A	29-11-1994
		US 5256274 A	26-10-1993
US 5674787 A	07-10-1997	NONE	
EP 0698918 A	28-02-1996	US 5622893 A	22-04-1997
		JP 8191137 A	23-07-1996
		US 5729054 A	17-03-1998
		US 5696018 A	09-12-1997
US 5112448 A	12-05-1992	NONE	
JP 10092977 A	10-04-1998	US 5866237 A	02-02-1999
EP 0725439 A	07-08-1996	DE 69322233 D	07-01-1999
		DE 69322233 T	08-07-1999
		EP 0594286 A	27-04-1994
		JP 6326103 A	25-11-1994
		KR 132402 B	15-04-1998
		US 5709958 A	20-01-1998
		US 6001461 A	14-12-1999
EP 0881673 A	02-12-1998	JP 11045887 A	16-02-1999