(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
18 September 2014 (18.09.2014)

WIPO | PCT

(10) International Publication Number
WO 2014/140672 A1

(51) International Patent Classification:
H01L 21/205 (2006.01) *H01L 21/318* (2006.01)

(21) International Application Number:
PCT/IB2013/001038

(22) International Filing Date:
15 March 2013 (15.03.2013)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant: **L'AIR LIQUIDE, SOCIETE ANONYME POUR I'ETUDE ET I'EXPLOITATION DES PROCEDES GEORGES CLAUDE** [FR/FR]; 75, Quai D'orsay, F-75007 Paris (FR).

(72) Inventors; and
(71) Applicants : **GATINEAU, Julien** [FR/JP]; 1-5-24 Nishinenishi, Tsuchiura, Ibaraki 300-0848 (JP). **KO, Changhee** [KR/JP]; Ninomiya 1-6-2, Ninomiya House, Tsukuba, Ibaraki 5208 HO (JP). **YOKOTA, Jiro** [JP/JP]; Prendre 205, D51-5, KenkyuuGakuen, Tsukuba, Ibaraki 305-0817 (JP). **LANSALOT-MATRAS, Clement** [FR/KR]; A501 Picasso Villa, 79-5 Banpo-dong, Seocho-gu, Seoul 137-040 (KR).

(74) Agents: **CONAN, Philippe** et al.; L'Air Liquide, Société Anonyme pour I'Etude et I'Exploitation des Procédés Georges Claude, Direction de la Propriete Intellectuelle, 75 Quai d'Orsay, F-75321 PARIS CEDEX 07 (FR).

(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, BN, 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, PA, 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, 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))*

(54) **Title**: BIS(ALKYLIMIDO)-BIS(ALKYLAMIDO)MOLYBDENUM MOLECULES FOR DEPOSITION OF MOLYBDENUM-CONTAINING FILMS

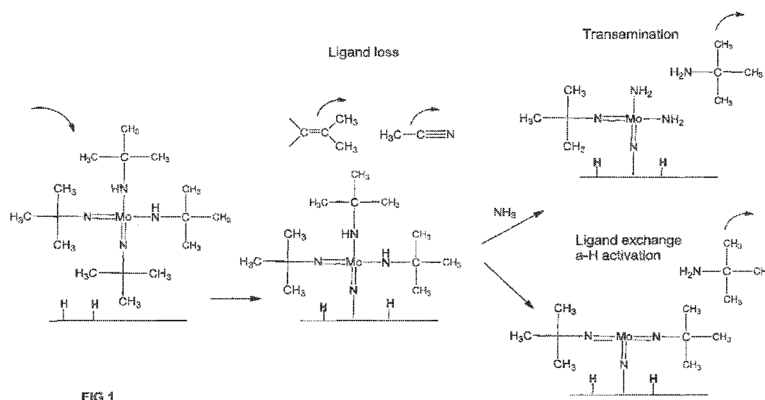


FIG 1

(57) **Abstract**: Bis(alkylimido)-bis(alkylamido)molybdenum compounds, their synthesis, and their use for the deposition of molybdenum-containing films are disclosed.

WO 2014/140672 A1

BIS(ALKYLIMIDO)-BIS(ALKYLAMIDO)MOLYBDENUM MOLECULES FOR DEPOSITION OF MOLYBDENUM-CONTAINING FILMS

Technical Field

5 Bis(alkylimido)-bis(alkylamido)molybdenum compounds, their synthesis, and their use for the deposition of Mo-containing films are disclosed.

Background Art

One of the goals for many semiconductor teams around the world is to be 10 able to deposit MoN films with low resistivity. Hiltunen et al. deposited molybdenum nitride films at 500°C with $MoCl_5$ and NH_3 as precursors in Thin Solid Films (166 (1988) 149-154). The same $MoCl_5$-NH_3 process was later studied at 400°C and 500°C in J. Electrochem. Soc. (Juppo et al., 147 (2000) 3377-3381). The results obtained by Juppo et al. at 500°C were fairly similar to 15 those obtained in the earlier study by Hiltunen et al. The deposited films had very low resistivity (100μΩ cm) and chlorine content (1 at. %). Moreover, the films deposited at 400°C were of poor quality, the deposition rate was only 0.02 Å/cycle, the chlorine content was 10 at.%, and the sheet resistance could not be measured. With these halide-ammonia systems, reactive hydrogen halides are 20 released as by-products.

Halide-free imido-amido metal-organic precursors having the general formula $Mo(NR)_2(NR'_2)_2$ have been introduced for molybdenum nitride or carbonitride depositions. Chiu et al., J. Mat. Res. 9 (7), 1994, 1622-1624; U.S. Pat. No. 6,114,242 to Sun et al.; Crane et al., J. Phys. Chem. B 2001, 105, 3549-25 3556; Miikkulainen et al., Chem Mater. (2007), 19, 263-269; Miikkulainen et al., Chem. Vap. Deposition (2008) 14, 71-77.

Miikkulainen et al. disclose ALD deposition using $Mo(NR)_2(NR'_2)_2$ precursors. Id. at Chem. Mater. (2007) and Chem. Vap. Deposition (2008). ALD saturation mode was observed at lower temperatures than the case of $MoCl_5$ and 30 the emission of corrosive by-products was avoided. *Id.* Miikkulainen et al. reported that the isopropyl derivative (i.e. $Mo(NtBu)_2(NiPr_2)_2$) is thermally unstable. Id. Miikkulainen et al. reported that the ethyl derivates was applicable as an ALD precursor with an ALD window of 285-300°C.

Chiu et al. disclose CVD deposition of MoN using $Mo(NtBu)_2(NHtBu)_2$. Id at J. Mat. Res.

Another goal is to be able to deposit MoO films having higher κ values and low leakage current.

5 A need remains for suitable molybdenum precursors for deposition of commercially suitable MoN or MoO films.

Notation and Nomenclature

Certain abbreviations, symbols, and terms are used throughout the
10 following description and claims, and include:

As used herein, the indefinite article "a" or "an" means one or more.

As used herein, the term "independently" when used in the context of describing R groups should be understood to denote that the subject R group is not only independently selected relative to other R groups bearing the same or
15 different subscripts or superscripts, but is also independently selected relative to any additional species of that same R group. For example in the formula $Mo(NR)_2(NHR')_2$, the two imido R groups may, but need not be identical to each other.

As used herein, the term "alkyl group" refers to saturated functional groups
20 containing exclusively carbon and hydrogen atoms. Further, the term "alkyl group" refers to linear, branched, or cyclic alkyl groups. Examples of linear alkyl groups include without limitation, methyl groups, ethyl groups, propyl groups, butyl groups, etc. Examples of branched alkyls groups include without limitation, t-butyl. Examples of cyclic alkyl groups include without limitation, cyclopropyl
25 groups, cyclopentyl groups, cyclohexyl groups, etc.
As used herein, the term "hydrocarbon" means a functional group containing exclusively hydrogen and carbon atoms. The functional group may be saturated (containing only single bonds) or unsaturated (containing double or triple bonds).

As used herein, the abbreviation "Me" refers to a methyl group; the
30 abbreviation "Et" refers to an ethyl group; the abbreviation "Pr" refers to a n-propyl group; the abbreviation "iPr" refers to an isopropyl group; the abbreviation "Bu" refers to a n-butyl group; the abbreviation "tBu" refers to a tert-butyl group; the abbreviation "sBu" refers to a sec-butyl group; the abbreviation "iBu" refers to an

iso-butyl group; and the abbreviation “tAmyl” refer to a tert-amyl group (also known as a pentyl group or C_5H_{11}).

The standard abbreviations of the elements from the periodic table of elements are used herein. It should be understood that elements may be referred
5 to by these abbreviations (e.g., Mo refers to molybdenum, N refers to nitrogen, H refers to hydrogen, etc.).

Please note that the Mo-containing films, such as MoN, MoCN, MoSi, MoSiN, and MoO, are listed throughout the specification and claims without reference to their proper stoichiometry. The molybdenum-containing layers
10 resulting from the processes may include pure molybdenum (Mo), molybdenum nitride (Mo_kN_l), molybdenum carbide (Mo_kC_l), molybdenum carbonitride ($Mo_kC_lN_m$), molybdenum silicide (Mo_nSi_m), or molybdenum oxide (Mo_nO_m) film, wherein k, l, m, and n inclusively range from 1 to 6. Preferably, molybdenum nitride and molybdenum carbide are Mo_kN_l or Mo_kC_l, where k and l each range
15 from 0.5 to 1.5. More preferably molybdenum nitride is Mo_1N_1 and molybdenum carbide is Mo_1C_1. Preferably molybdenum oxide and molybdenum silicide are Mo_nO_m and Mo_nSi_m, where n ranges from 0.5 to 1.5 and m ranges from 1.5 to 3.5. More preferably, molybdenum oxide is MoO_2 or MoO_3 and molybdenum silicide is $MoSi_2$.

20

Summary of Invention

Vapor deposition methods for forming molybdenum-containing films on a substrate are disclosed. A molybdenum-containing precursor is introduced into a vapor deposition chamber containing a substrate. Part or all of the molybdenum-
25 containing precursor is deposited on the substrate to form the molybdenum-containing film. The molybdenum-containing precursor has the formula $Mo(NR)_2(NHR')_2$, wherein R and R' are independently chosen from the group consisting of a C1-C4 alkyl group, a C1-C4 perfluoroalkyl group, and an alkylsilyl group. The disclosed methods may include one or more of the following aspects:
30
- the molybdenum-containing precursor being $Mo(NMe)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHPr)_2$;

- the molybdenum-containing precursor being $Mo(NMe)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHEt)_2$;

- the molybdenum-containing precursor being $Mo(NBu)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHiBu)_2$;
- 5 the molybdenum-containing precursor being $Mo(NBu)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHPr)_2$;
- 10 the molybdenum-containing precursor being $Mo(NiBu)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHtBu)_2$;
- 15 the molybdenum-containing precursor being $Mo(NsBu)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHBu)_2$;
- 20 the molybdenum-containing precursor being $Mo(NsBu)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHEt)_2$;
- 25 the molybdenum-containing precursor being $Mo(NtBu)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHsBu)_2$;
- 30 the molybdenum-containing precursor being $Mo(NtBu)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHMe)_2$;

- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHtBu)_2$; the molybdenum-containing precursor being $Mo(NCF_3)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)(NtAmyl)(NHtBu)_2$;
- the vapor deposition method being ALD;
- the vapor deposition method being PE-ALD;

- the vapor deposition method being spatial ALD;
- the vapor deposition method being CVD;
- the vapor deposition method being PE-CVD;
- at least part of the molybdenum-containing precursor being deposited on the substrate by plasma enhanced atomic layer deposition;
- a plasma power is between about 30 W and about 600 W;
- a plasma power is between about 100 W and about 500 W;
- reacting the molybdenum-containing precursor with a reducing agent;
- the reducing agent being selected from the group consisting of N_2, H_2, NH_3, N_2H_4 and any hydrazine based compounds, SiH_4, Si_2H_6, radical species thereof, and combinations thereof;
- reacting the at least part of the molybdenum-containing precursor with an oxidizing agent;
- the oxidizing agent being selected from the group consisting of O_2, H_2O, O_3, H_2O_2, N_2O, NO, acetic acid, the radical species thereof, and combinations thereof;
- performing the method at a pressure between about 0.01 Pa and about 1×10^5 Pa;
- performing the method at a pressure between about 0.1 Pa and about 1×10^4 Pa;
- performing the method at a temperature between about 20°C and about 500°C;
- performing the method at a temperature between about 330°C and about 500°C;
- the molybdenum-containing film being Mo;
- the molybdenum-containing film being MoO;
- the molybdenum-containing film being MoN;
- the molybdenum-containing film being MoSi;
- the molybdenum-containing film being MoSiN; and
- the molybdenum-containing film being MoCN.

Chemical vapor deposition methods for forming molybdenum oxide films on a substrate are also disclosed. A molybdenum-containing precursor is introduced

into a vapor deposition chamber containing a substrate. At least part of the molybdenum-containing precursor reacts with an oxidizing agent at the surface of the substrate to form the molybdenum oxide film. The molybdenum-containing precursor has the formula $Mo(NR)_2(NHR')_2$, wherein R and R' are independently chosen from the group consisting of a C1-C4 alkyl group, a C1-C4 perfluoroalkyl group, and an alkylsilyl group. The disclosed methods may include one or more of the following aspects:

- the molybdenum-containing precursor being $Mo(NMe)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHMe)_2$;

- the molybdenum-containing precursor being $Mo(NiPr)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHBu)_2$;
5
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHEt)_2$;
10
- the molybdenum-containing precursor being $Mo(NBu)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHsBu)_2$;
15
- the molybdenum-containing precursor being $Mo(NBu)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHiPr)_2$;
20
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHMe)_2$;
25
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHiBu)_2$;
30
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHtBu)_2$;

- the molybdenum-containing precursor being $Mo(NtBu)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHtBu)_2$; the molybdenum-containing precursor being $Mo(NCF_3)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHPr)_2$;

- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)(NtAmyl)(NHtBu)_2$;
- the chemical vapor deposition method being plasma enhanced chemical vapor deposition;
- a plasma power is between about 30 W and about 600 W;
- a plasma power is between about 100 W and about 500 W;
- the oxidizing agent being selected from the group consisting of O_2, H_2O, O_3, H_2O_2, N_2O, NO, acetic acid, the radical species thereof, and combinations thereof;
- performing the method at a pressure between about 0.01 Pa and about 1×10^5 Pa;
- performing the method at a pressure between about 0.1 Pa and about 1×10^4 Pa;
- performing the method at a temperature between about 20°C and about 500°C; and
- performing the method at a temperature between about 330°C and about 500°C.

Also disclosed are atomic layer deposition methods for forming molybdenum-containing films on a substrate. A molybdenum-containing precursor is introduced into a vapor deposition chamber containing a substrate. Part or all of the molybdenum-containing precursor is deposited on the substrate by atomic layer deposition to form the molybdenum-containing film. The molybdenum-containing precursor has the formula $Mo(NR)_2(NHR')_2$, wherein R and R' are independently chosen from the group consisting of a C1-C4 alkyl group, a C1-C4 perfluoroalkyl group, and an alkylsilyl group. The disclosed methods may include one or more of the following aspects:

- the molybdenum-containing precursor being $Mo(NMe)_2(NHMe)_2$;

- the molybdenum-containing precursor being $Mo(NMe)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHBu)_2$;
5
- the molybdenum-containing precursor being $Mo(NMe)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHEt)_2$;
10
- the molybdenum-containing precursor being $Mo(NEt)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHsBu)_2$;
15
- the molybdenum-containing precursor being $Mo(NEt)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHiPr)_2$;
20
- the molybdenum-containing precursor being $Mo(NPr)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NPr)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHMe)_2$;
25
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHiBu)_2$;
30
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NiPr)_2(NHtBu)_2$;

- the molybdenum-containing precursor being $Mo(NBu)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHiPr)_2$;
5 - the molybdenum-containing precursor being $Mo(NBu)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NBu)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHMe)_2$;
10 - the molybdenum-containing precursor being $Mo(NiBu)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHiBu)_2$;
15 - the molybdenum-containing precursor being $Mo(NiBu)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NiBu)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHPr)_2$;
20 - the molybdenum-containing precursor being $Mo(NsBu)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NsBu)_2(NHtBu)_2$;
25 - the molybdenum-containing precursor being $Mo(NtBu)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHBu)_2$;
30 - the molybdenum-containing precursor being $Mo(NtBu)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHsBu)_2$;

- the molybdenum-containing precursor being $Mo(NtBu)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHPr)_2$;
5
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NSiMe_3)_2(NHtBu)_2$; the
10 molybdenum-containing precursor being $Mo(NCF_3)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHPr)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHBu)_2$;
15
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NCF_3)_2(NHtBu)_2$;
- the molybdenum-containing precursor being $Mo(NMe)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NEt)_2(NHSiMe_3)_2$;
20
- the molybdenum-containing precursor being $Mo(NPr)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHMe)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHEt)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHPr)_2$;
25
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHiPr)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHBu)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHiBu)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHsBu)_2$;
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHtBu)_2$;
30
- the molybdenum-containing precursor being $Mo(NtAmyl)_2(NHSiMe_3)_2$;
- the molybdenum-containing precursor being $Mo(NtBu)(NtAmyl)(NHtBu)_2$;

- at least part of the molybdenum-containing precursor being deposited on the substrate by plasma enhanced atomic layer deposition;
- a plasma power is between about 30 W and about 600 W;
- a plasma power is between about 100 W and about 500 W;
- reacting the molybdenum-containing precursor with a reducing agent;
- the reducing agent being selected from the group consisting of N_2, H_2, NH_3, N_2H_4 and any hydrazine based compounds, SiH_4, Si_2H_6, radical species thereof, and combinations thereof;
- reacting the at least part of the molybdenum-containing precursor with an oxidizing agent;
- the oxidizing agent being selected from the group consisting of O_2, H_2O, O_3, H_2O_2, N_2O, NO, acetic acid, the radical species thereof, and combinations thereof;
- performing the method at a pressure between about 0.01 Pa and about 1 x 10^5 Pa;
- performing the method at a pressure between about 0.1 Pa and about 1 x 10^4 Pa;
- performing the method at a temperature between about 20°C and about 500°C;
- performing the method at a temperature between about 330°C and about 500°C;
- the molybdenum-containing film being Mo;
- the molybdenum-containing film being MoO;
- the molybdenum-containing film being MoN;
- the molybdenum-containing film being MoSi;
- the molybdenum-containing film being MoSiN; and
- the molybdenum-containing film being MoCN.

Brief Description of Drawings

For a further understanding of the nature and objects of the present invention, reference should be made to the following detailed description, taken in conjunction with the accompanying graphs, and wherein:

FIG 1 is a figure illustrating the benefit of including H in the NHR' amido ligand of the disclosed molybdenum compounds.

FIG 2 is a graph illustrating molybdenum nitride film growth per cycle as a function of deposition temperature on a SiO_2 substrate. The pulse lengths of molybdenum precursor and ammonia were fixed at 2sec and 5sec respectively.

FIG 3 is a graph illustrating molybdenum nitride film growth per cycle as a function of molybdenum precursor pulse time on a SiO_2 substrate. The pulse length of ammonia was fixed at 5sec.

FIG 4 is a graph illustrating Molybdenum nitride film thickness deposited at 400°C as a function of deposition cycles on a SiO_2 substrate. The pulse lengths of molybdenum precursor and ammonia were fixed at 2sec and 5sec respectively.

FIG 5 is a scanning electron microscope (SEM) cross section of a molybdenum nitride film deposited at 400°C on a TEOS patterned wafer. The pulse lengths of molybdenum precursor and ammonia were fixed at 2sec and 5sec respectively.

FIG 6 is a graph illustrating the X-ray Photoelectron Spectroscopy (XPS) depth profile of a molybdenum nitride film deposited at 400°C on a SiO_2 substrate

FIG 7 is a graph illustrating the molybdenum nitride film resistivity value as a function of deposition temperature on a SiO_2 substrate. The pulse lengths of molybdenum precursor and ammonia were fixed at 2sec and 5sec respectively.

FIG 8 is a graph illustrating molybdenum nitride film growth per cycle as a function of deposition temperature with plasma source on a SiO_2 substrate. The pulse lengths of molybdenum precursor and ammonia were fixed at 2sec and 5sec respectively.

FIG 9 is a graph illustrating the XPS depth profile of a molybdenum nitride film deposited at 400°C with plasma source on a SiO_2 substrate.

FIG 10 is a graph illustrating the molybdenum nitride film resistivity value as a function of deposition temperature with plasma source on a SiO_2 substrate. The pulse length of molybdenum precursor and ammonia were fixed at 2sec and 5sec respectively.

Description of Embodiments

Bis(alkylimido)-bis(alkylamido)molybdenum compounds are disclosed. The bis(alkylimido)-bis(alkylamido)molybdenum compounds have the formula $Mo(NR)_2(NHR')_2$, wherein R and R' are independently chosen from the group consisting of a C1-C4 alkyl group, a C1-C4 perfluoroalkyl group, and an alkylsilyl group.

Exemplary bis(alkylimido)-bis(alkylamido)molybdenum compounds include $Mo(NMe)_2(NHMe)_2$, $Mo(NMe)_2(NHEt)_2$, $Mo(NMe)_2(NHPr)_2$, $Mo(NMe)_2(NHiPr)_2$, $Mo(NMe)_2(NHBu)_2$, $Mo(NMe)_2(NHiBu)_2$, $Mo(NMe)_2(NHsBu)_2$, $Mo(NMe)_2(NHtBu)_2$, $Mo(NEt)_2(NHMe)_2$, $Mo(NEt)_2(NHEt)_2$, $Mo(NEt)_2(NHPr)_2$, $Mo(NEt)_2(NHiPr)_2$, $Mo(NEt)_2(NHBu)_2$, $Mo(NEt)_2(NHiBu)_2$, $Mo(NEt)_2(NHsBu)_2$, $Mo(NEt)_2(NHtBu)_2$, $Mo(NPr)_2(NHMe)_2$, $Mo(NPr)_2(NHEt)_2$, $Mo(NPr)_2(NHPr)_2$, $Mo(NPr)_2(NHiPr)_2$, $Mo(NPr)_2(NHBu)_2$, $Mo(NPr)_2(NHiBu)_2$, $Mo(NPr)_2(NHsBu)_2$,$Mo(NPr)_2(NHtBu)_2$, $Mo(NiPr)_2(NHMe)_2$, $Mo(NiPr)_2(NHEt)_2$, $Mo(NiPr)_2(NHPr)_2$, $Mo(NiPr)_2(NHiPr)_2$, $Mo(NiPr)_2(NHBu)_2$, $Mo(NiPr)_2(NHiBu)_2$, $Mo(NiPr)_2(NHsBu)_2$, $Mo(NiPr)_2(NHtBu)_2$, $Mo(NBu)_2(NHMe)_2$, $Mo(NBu)_2(NHEt)_2$, $Mo(NBu)_2(NHPr)_2$, $Mo(NBu)_2(NHiPr)_2$, $Mo(NBu)_2(NHBu)_2$, $Mo(NBu)_2(NHiBu)_2$, $Mo(NBu)_2(NHsBu)_2$, $Mo(NBu)_2(NHtBu)_2$, $Mo(NiBu)_2(NHMe)_2$, $Mo(NiBu)_2(NHEt)_2$, $Mo(NiBu)_2(NHPr)_2$, $Mo(NiBu)_2(NHiPr)_2$, $Mo(NiBu)_2(NHBu)_2$, $Mo(NiBu)_2(NHiBu)_2$, $Mo(NiBu)_2(NHsecBu)_2$, $Mo(NiBu)_2(NHtBu)_2$, $Mo(NsBu)_2(NHMe)_2$, $Mo(NsBu)_2(NHEt)_2$, $Mo(NsBu)_2(NHPr)_2$, $Mo(NsBu)_2(NHiPr)_2$, $Mo(NsBu)_2(NHBu)_2$, $Mo(NsBu)_2(NHiBu)_2$, $Mo(NsBu)_2(NHsBu)_2$, $Mo(NsBu)_2(NHtBu)_2$, $Mo(NtBu)_2(NHMe)_2$, $Mo(NtBu)_2(NHEt)_2$, $Mo(NtBu)_2(NHPr)_2$, $Mo(NtBu)_2(NHiPr)_2$, $Mo(NtBu)_2(NHBu)_2$, $Mo(NtBu)_2(NHiBu)_2$, $Mo(NtBu)_2(NHsBu)_2$, $Mo(NtBu)_2(NHtBu)_2$, $Mo(NSiMe_3)_2(NHMe)_2$, $Mo(NSiMe_3)_2(NHEt)_2$, $Mo(NSiMe_3)_2(NHPr)_2$, $Mo(NSiMe_3)_2(NHiPr)_2$, $Mo(NSiMe_3)_2(NHBu)_2$, $Mo(NSiMe_3)_2(NHiBu)_2$, $Mo(NSiMe_3)_2(NHsBu)_2$, $Mo(NSiMe_3)_2(NHtBu)_2$, $Mo(NCF_3)_2(NHMe)_2$, $Mo(NCF_3)_2(NHEt)_2$, $Mo(NCF_3)_2(NHPr)_2$, $Mo(NCF_3)_2(NHiPr)_2$, $Mo(NCF_3)_2(NHBu)_2$, $Mo(NCF_3)_2(NHiBu)_2$, $Mo(NCF_3)_2(NHsBu)_2$, $Mo(NCF_3)_2(NHtBu)_2$, $Mo(NMe)_2(NHSiMe_3)_2$, $Mo(NEt)_2(NHSiMe_3)_2$, $Mo(NPr)_2(NHSiMe_3)_2$, $Mo(NtBu)_2(NHSiMe_3)_2$, $Mo(NtAmyl)_2(NHMe)_2$, $Mo(NtAmyl)_2(NHEt)_2$, $Mo(NtAmyl)_2(NHPr)_2$, $Mo(NtAmyl)_2(NHiPr)_2$, $Mo(NtAmyl)_2(NHBu)_2$, $Mo(NtAmyl)_2(NHiBu)_2$, $Mo(NtAmyl)_2(NHsBu)_2$, $Mo(NtAmyl)_2(NHtBu)_2$, $Mo(NtAmyl)_2(NHSiMe_3)_2$, and $Mo(NtBu)(NtAmyl)(NHtBu)_2$, preferably

$Mo(NtBu)_2(NHiPr)_2$, $Mo(NtBu)_2(NHtBu)_2$, $Mo(NtAmyl)_2(NHiPr)_2$, or $Mo(NtAmyl)_2(NHtBu)_2$.

The Bis(alkylimido)-bis(alkylamido) molybdenum compounds may be synthesized by the method described by R.L. Harlow, Inorganic Chemistry, 1980,
5 19, 777, and W.A. Nugent, Inorganic Chemistry, 1983, 22, 965, with minor modifications obvious to one of ordinary skill in the art (e.g., $MoO_2Cl_2 \rightarrow$ adducted $Mo(NR)_2Cl_2 \rightarrow Mo(NR)_2(NHR')_2$). The final product may be prepared under reaction with an excess amount of LiNHR'. The perfluoroalkyl- and alkylsilyl-containing bis(alkylimido)-bis(alkylamido) molybdenum compounds may also be
10 prepared using the same synthesis routes.

Vapor deposition methods of depositing molybdenum-containing films from the bis(alkylimido)-bis(alkylamido)molybdenum compounds are also disclosed. The bis(alkylimido)-bis(alkylamido)molybdenum compound is introduced into a reactor having a substrate disposed therein. At least part of the
15 bis(alkylimido)-bis(alkylamido)molybdenum compound is deposited onto the substrate to form the molybdenum-containing film.

As partially illustrated in the Examples, Applicants have surprisingly found that inclusion of hydrogen in the amido group (i.e., NHR') provides a faster ALD growth rate, a higher ALD temperature window, and lower impurity concentrations
20 in the resulting films when compared to films deposited by analogous di-alkyl amido groups (i.e., NR_2). A faster growth rate is a key advantage because it allows higher throughput in the industrial deposition tools (e.g., processing more wafers per hour), provided the resulting layer has similar or better electrical performance.

25 The ALD temperature window and impurity concentrations are related to a certain extent. The higher thermal stability of the disclosed molecules allows deposition in ALD mode at higher temperatures when compared to the thermal stability and ALD temperature window of the analogous di-alkyl amido groups. Deposition at higher temperatures may increase the reactivity of the reducing
30 agent, resulting in better film density and lower C and O concentrations for MoN films and lower C and N concentrations for MoO films. The higher density of the MoN film will increase the barrier properties of the film. For deposition of MoO

films, the higher ALD temperature window allows for deposition of a better crystallographic phase, which provides higher κ values.

The resistivity of the MoN film is impacted by the concentration of any impurities in the film, such as C or O. Higher C concentrations may suggest decomposition of the bis(alkylimido)-bis(alkylamido)molybdenum compound (i.e., thermal instability of the compound). Resistivity and barrier properties of the MoN films have a direct impact on the chip efficiency (RC delay, electromigration, reliability). Higher C and N concentrations in the MoO films may increase leakage current of the film. As a result, Applicants have surprisingly discovered an improved ALD deposition process using the disclosed precursors for MoN films. More surprising are the significant improvements in the properties of the resulting film from the use of $Mo(NtBu)_2(NHtBu)_2$ as compared to the results obtained with the analogous dialkyl compounds. For the reasons described above, one of ordinary skill in the art would expect similar improved results using the disclosed precursors in the deposition of pure molybdenum, molybdenum silicide (MoSi), molybdenum silicide nitride (MoSiN) films, and molybdenum oxide (MoO) films.

Applicants believe that hydrogen in the amido group (i.e., NHR') is critical to the stability of the chemisorped species. Applicants further believe that the bulky tBu amido groups offer a great advantage by fully occupying the space around the metal in a symmetrical fashion with the tBu imido group. This may be a result of delocalization of the double bond in between the amido and imido groups. As reported by Correia-Anacleto et al., the ALD mechanism may take place through the imido group (i.e., NR) (8th Int'l Conference on Atomic Layer Deposition – ALD 2008, WedM2b-8). Applicants believe the inclusion of H in the amido group renders the amido ligand more acidic than the analogous dialkyl amido group. The acidity of the NHR' group may make the amido group more reactive to the reducing or oxidizing agent. The acidity of the NHR' group may further make the amido group less reactive to the substrate surface. As a result, the chemisorped Mo species remains in contact with the substrate for a longer time period, permitting the species to react through ligand exchange by α-H activation and either transamination with the reducing agent or oxidation with the oxidizing agent. See **FIG 1**. Applicants believe that both of these reactions produce faster ALD growth rate and a higher ALD temperature window. As a

result, ALD deposition using the class of disclosed molecules will provide better films compared to those of the analogous dialkyl compounds.

At least part of the disclosed bis(alkylimido)-bis(alkylamido) molybdenum compounds may deposited onto a substrate to form the molybdenum-containing films by chemical vapor deposition (CVD), atomic layer deposition (ALD), or other types of depositions that are related to vapor coating such as a plasma enhanced CVD (PECVD), plasma enhanced ALD (PEALD), pulsed CVD (PCVD), low pressure CVD (LPCVD), sub-atmospheric CVD (SACVD) or atmospheric pressure CVD (APCVD), hot-wire CVD (HWCVD, also known as cat-CVD, in which a hot wire serves as an energy source for the deposition process), spatial ALD, hot-wire ALD (HWALD), radicals incorporated deposition, and super critical fluid deposition or combinations thereof. The deposition method is preferably ALD, PE-ALD, or spatial ALD in order to provide suitable step coverage and film thickness control.

The disclosed methods may be useful in the manufacture of semiconductor, photovoltaic, LCD-TFT, or flat panel type devices. The method includes introducing the vapor of at least one bis(alkylimido)-bis(alkylamido)molybdenum compound disclosed above into a reactor having at least one substrate disposed therein and depositing at least part of the bis(alkylimido)-bis(alkylamido)molybdenum compound onto the at least one substrate to form a molybdenum-containing layer using a vapor deposition process. The temperature and the pressure within the reactor and the temperature of the substrate are held at conditions suitable for formation of the Mo-containing layer on at least one surface of the substrate. A reaction gas may also be used to help in formation of the Mo-containing layer.

The disclosed methods may also be used to form a two metal-containing layer on a substrate using a vapor deposition process and, more particularly, for deposition of $MoMO_x$ layers, wherein M is the second element and is selected from the group consisting of group 2, group 3, group 4, group 5, group 13, group 14, transition metal, lanthanides, and combinations thereof, and more preferably from Mg, Ca, Sr, Ba, Hf, Nb, Ta, Al, Si, Ge, Y, or lanthanides. The method includes: introducing at least one bis(alkylimido)-bis(alkylamido)molybdenum compound disclosed above into a reactor having at least one substrate disposed therein, introducing a second precursor into the reactor, and depositing at least

part of the bis(alkylimido)-bis(alkylamido)molybdenum compound and at least part of the second precursor onto the at least one substrate to form the two element-containing layer using a vapor deposition process.

5 The reactor may be any enclosure or chamber of a device in which deposition methods take place, such as, without limitation, a parallel-plate type reactor, a cold-wall type reactor, a hot-wall type reactor, a single-wafer reactor, a multi-wafer reactor, or other such types of deposition systems. All of these exemplary reactors are capable of serving as an ALD or CVD reactor. The reactor may be maintained at a pressure ranging from about 0.01 Pa to about 1×10^5 Pa, preferably from about 0.1 Pa to about 1×10^4 Pa. In addition, the temperature within the reactor may range from about room temperature (20°C) to about 500°C, preferably from about 330°C to about 500°C. One of ordinary skill in the art will recognize that the temperature may be optimized through mere experimentation to achieve the desired result.

15 The temperature of the reactor may be controlled by either controlling the temperature of the substrate holder (called a cold wall reactor) or controlling the temperature of the reactor wall (called a hot wall reactor) or a combination of both methods. Devices used to heat the substrate are known in the art.

20 The reactor wall may be heated to a sufficient temperature to obtain the desired film at a sufficient growth rate and with desired physical state and composition. A non-limiting exemplary temperature range to which the reactor wall may be heated includes from approximately 20°C to approximately 500°C. When a plasma deposition process is utilized, the deposition temperature may range from approximately 20°C to approximately 500°C. Alternatively, when a thermal process is performed, the deposition temperature may range from approximately 100°C to approximately 500°C.

Alternatively, the substrate may be heated to a sufficient temperature to obtain the desired molybdenum-containing layer at a sufficient growth rate and with desired physical state and composition. A non-limiting exemplary temperature range to which the substrate may be heated includes from 100°C to 500°C. Preferably, the temperature of the substrate remains less than or equal to 500°C.

The type of substrate upon which the molybdenum-containing layer will be deposited will vary depending on the final use intended. In some embodiments, the substrate may be chosen from oxides which are used as dielectric materials in MIM, DRAM, or FeRam technologies (for example, ZrO_2 based materials, HfO_2 based materials, TiO_2 based materials, rare earth oxide based materials, ternary oxide based materials, etc.) or from nitride-based layers (for example, TaN) that are used as an oxygen barrier between copper and the low-k layer. Other substrates may be used in the manufacture of semiconductors, photovoltaics, LCD-TFT, or flat panel devices. Examples of such substrates include, but are not limited to, solid substrates such as copper and copper based alloys like CuMn, metal nitride-containing substrates (for example, TaN, TiN, WN, TaCN, TiCN, TaSiN, and TiSiN); insulators (for example, SiO_2, Si_3N_4, SiON, HfO_2, Ta_2O_5, ZrO_2, TiO_2, Al_2O_3, and barium strontium titanate); or other substrates that include any number of combinations of these materials. The actual substrate utilized may also depend upon the specific compound embodiment utilized. In many instances though, the preferred substrate utilized will be selected from Si and SiO_2 substrates.

The disclosed bis(alkylimido)-bis(alkylamido)molybdenum compounds may be supplied either in neat form or in a blend with a suitable solvent, such as ethyl benzene, xylene, mesitylene, decane, dodecane, to form a precursor mixture. The disclosed compounds may be present in varying concentrations in the solvent.

One or more of the neat compounds or precursor mixtures are introduced into a reactor in vapor form by conventional means, such as tubing and/or flow meters. The vapor form of the neat compound or precursor mixture may be produced by vaporizing the neat compound or precursor mixture through a conventional vaporization step such as direct vaporization, distillation, by bubbling, or by using a sublimator such as the one disclosed in PCT Publication WO2009/087609 to Xu et al. The neat compound or precursor mixture may be fed in liquid state to a vaporizer where it is vaporized before it is introduced into the reactor. Alternatively, the neat compound or precursor mixture may be vaporized by passing a carrier gas into a container containing the neat compound or precursor mixture or by bubbling the carrier gas into the neat compound or

precursor mixture. The carrier gas may include, but is not limited to, Ar, He, N_2, and mixtures thereof. The carrier gas and compound are then introduced into the reactor as a vapor.

If necessary, the container of the neat compound or precursor mixture
5 may be heated to a temperature that permits the neat compound or precursor mixture to be in its liquid phase and to have a sufficient vapor pressure. The container may be maintained at temperatures in the range of, for example, approximately 0°C to approximately 200°C. Those skilled in the art recognize that the temperature of the container may be adjusted in a known manner to control
10 the amount of precursor vaporized.

In addition to the optional mixing of the bis(alkylimido)-bis(alkylamido) molybdenum compound with solvents, second precursors, and stabilizers prior to introduction into the reactor, the bis(alkylimido)-bis(alkylamido) molybdenum compound may be mixed with a reaction gas inside the reactor. Exemplary
15 reaction gases include, without limitation, second precursors such as transition metal-containing precursors (eg. Niobium), rare earth-containing precursors, strontium-containing precursors, barium-containing precursors, aluminum-containing precursors such as TMA, and any combination thereof. These or other second precursors may be incorporated into the resultant layer in small quantities,
20 as a dopant, or as a second or third metal in the resulting layer, such as $MoMO_x$.

The reaction gas may include a reducing agent which is selected from, but not limited to, N_2, H_2, NH_3, SiH_4 , Si_2H_6, Si_3H_8, $(Me)_2SiH_2$, $(C_2H_5)_2SiH_2$, $(CH_3)_3SiH$, $(C_2H_5)_3SiH$, $[N(C_2H_5)_2]_2SiH_2$, $N(CH_3)_3$, $N(C_2H_5)_3$, $(SiMe_3)_2NH$, $(CH_3)HNNH_2$, $(CH_3)_2NNH_2$, phenyl hydrazine, B_2H_6, $(SiH_3)_3N$, radical species of these reducing
25 agents, and mixtures of these reducing agents. Preferably, when an ALD process is performed, the reducing reagent is H_2.

When the desired molybdenum-containing layer also contains oxygen, such as, for example and without limitation, MoO_x and $MoMO_x$, the reaction gas may include an oxidizing agent which is selected from, but not limited to, O_2, O_3,
30 H_2O, H_2O_2, acetic acid, formalin, para-formaldehyde, radical species of these oxidizing agents, and mixtures of these oxidizing agents. Preferably, when an ALD process is performed, the oxidizing reagent is H_2O.

The reaction gas may be treated by plasma in order to decompose the reaction gas into its radical form. The plasma may be generated or present within the reaction chamber itself. Alternatively, the plasma may generally be at a location removed from the reaction chamber, for instance, in a remotely located plasma system. One of skill in the art will recognize methods and apparatus suitable for such plasma treatment.

For example, the reaction gas may be introduced into a direct plasma reactor, which generates plasma in the reaction chamber, to produce the plasma-treated reaction gas in the reaction chamber. Exemplary direct plasma reactors include the Titan™ PECVD System produced by Trion Technologies. The reaction gas may be introduced and held in the reaction chamber prior to plasma processing. Alternatively, the plasma processing may occur simultaneously with the introduction of the reaction gas. In-situ plasma is typically a 13.56 MHz RF capacitively coupled plasma that is generated between the showerhead and the substrate holder. The substrate or the showerhead may be the powered electrode depending on whether positive ion impact occurs. Typical applied powers in in-situ plasma generators are from approximately 30 W to approximately 1000 W. Preferably, powers from approximately 30 W to approximately 600 W are used in the disclosed methods. More preferably, the powers range from approximately 100 W to approximately 500 W. The disassociation of the reaction gas using in-situ plasma is typically less than achieved using a remote plasma source for the same power input and is therefore not as efficient in reaction gas disassociation as a remote plasma system, which may be beneficial for the deposition of molybdenum-containing films on substrates easily damaged by plasma.

Alternatively, the plasma-treated reaction gas may be produced outside of the reaction chamber. The MKS Instruments' ASTRONi® reactive gas generator may be used to treat the reaction gas prior to passage into the reaction chamber. Operated at 2.45 GHz, 7kW plasma power, and a pressure ranging from approximately 3 Torr to approximately 10 Torr, the reaction gas O_2 may be decomposed into two O^- radicals. Preferably, the remote plasma may be generated with a power ranging from about 1 kW to about 10 kW, more preferably from about 2.5 kW to about 7.5 kW.

When the desired molybdenum-containing layer also contains another element, such as, for example and without limitation, Nb, Sr, Ba, Al, Ta, Hf, Nb, Mg, Y, Ca, As, Sb, Bi, Sn, Pb, Mn, lanthanides (such as Er), or combinations thereof, the reaction gas may include a second precursor which is selected from, but not limited to, metal alkyls, such as $(Me)_3Al$, metal amines, such as $Nb(Cp)(NtBu)(NMe_2)_3$, and any combination thereof.

The bis(alkylimido)-bis(alkylamido)molybdenum compound and one or more reaction gases may be introduced into the reactor simultaneously (chemical vapor deposition), sequentially (atomic layer deposition), or in other combinations. For example, the bis(alkylimido)-bis(alkylamido)molybdenum compound may be introduced in one pulse and two additional precursors may be introduced together in a separate pulse [modified atomic layer deposition]. Alternatively, the reactor may already contain the reaction gas prior to introduction of the bis(alkylimido)-bis(alkylamido)molybdenum compound. Alternatively, the bis(alkylimido)-bis(alkylamido)molybdenum compound may be introduced to the reactor continuously while other reaction gases are introduced by pulse (pulsed-chemical vapor deposition). The reaction gas may be passed through a plasma system localized or remotely from the reactor, and decomposed to radicals. In each example, a pulse may be followed by a purge or evacuation step to remove excess amounts of the component introduced. In each example, the pulse may last for a time period ranging from about 0.01 s to about 30 s, alternatively from about 0.3 s to about 3 s, alternatively from about 0.5 s to about 2 s. In another alternative, the bis(alkylimido)-bis(alkylamido)molybdenum compound and one or more reaction gases may be simultaneously sprayed from a shower head under which a susceptor holding several wafers is spun (spatial ALD).

In one non-limiting exemplary atomic layer deposition type process, the vapor phase of a bis(alkylimido)-bis(alkylamido)molybdenum compound is introduced into the reactor, where it is contacted with a suitable substrate. Excess bis(alkylimido)-bis(alkylamido)molybdenum compound may then be removed from the reactor by purging and/or evacuating the reactor. An oxidizing reagent is introduced into the reactor where it reacts with the absorbed bis(alkylimido)-bis(alkylamido)molybdenum compound in a self-limiting manner. Any excess oxidizing reagent is removed from the reactor by purging and/or evacuating the

reactor. If the desired layer is a molybdenum oxide layer, this two-step process may provide the desired layer thickness or may be repeated until a layer having the necessary thickness has been obtained.

Alternatively, if the desired MoO layer contains a second element (i.e., $MoMO_x$), the two-step process above may be followed by introduction of the vapor of a second precursor into the reactor. The second precursor will be selected based on the nature of the $MoMO_x$ layer being deposited. After introduction into the reactor, the second precursor is contacted with the substrate. Any excess second precursor is removed from the reactor by purging and/or evacuating the reactor. Once again, an oxidizing reagent may be introduced into the reactor to react with the second precursor. Excess oxidizing reagent is removed from the reactor by purging and/or evacuating the reactor. If a desired layer thickness has been achieved, the process may be terminated. However, if a thicker layer is desired, the entire four-step process may be repeated. By alternating the provision of the bis(alkylimido)-bis(alkylamido) molybdenum compound, second precursor, and oxidizing reagent, a $MoMO_x$ layer of desired composition and thickness may be deposited.

Additionally, by varying the number of pulses, layers having a desired stoichiometric M:Mo ratio may be obtained. For example, a $MoMO_2$ layer may be obtained by having one pulse of the bis(alkylimido)-bis(alkylamido) molybdenum compound and one pulse of the second precursor, with each pulse being followed by pulses of the oxidizing reagent. However, one of ordinary skill in the art will recognize that the number of pulses required to obtain the desired layer may not be identical to the stoichiometric ratio of the resulting layer.

The molybdenum-containing layers resulting from the processes disclosed aabove may include pure molybdenum (Mo), molybdenum nitride (Mo_kN_l), molybdenum carbide (Mo_kC_l), molybdenum carbonitride ($Mo_kC_lN_m$), molybdenum silicide (Mo_nSi_m), or molybdenum oxide (Mo_nO_m) film, wherein k, l, m, and n inclusively range from 1 to 6. Preferably, molybdenum nitride and molybdenum carbide are Mo_kN_l or Mo_kC_l, where k and l each range from 0.5 to 1.5. More preferably molybdenum nitride is Mo_1N_1 and molybdenum carbide is Mo_1C_1. Preferably molybdenum oxide and molybdenum silicide are Mo_nO_m and Mo_nSi_m,

where n ranges from 0.5 to 1.5 and m ranges from 1.5 to 3.5. More preferably, molybdenum oxide is MoO_2 or MoO_3 and molybdenum silicide is $MoSi_2$.

One of ordinary skill in the art will recognize that by judicial selection of the appropriate bis(alkylimido)-bis(alkylamido) molybdenum compound and reaction gases, the desired Mo-containing layer composition may be obtained.

The Mo or MoN films will have a resistivity ranging from 50 to 5000 $\mu\Omega\cdot cm^{-1}$, preferably from 50 to 1000 $\mu\Omega\cdot cm^{-1}$. The C content in the Mo or MoN films will range from approximately 0.01 atomic% to approximately 10 atomic % for films deposited by thermal ALD and from approximately 0.01 atomic% to approximately 4 atomic % for films deposited by PEALD. The C content in the MoO films will range from approximately 0.01 atomic % to approximately 2 atomic %.

Upon obtaining a desired film thickness, the film may be subject to further processing, such as thermal annealing, furnace-annealing, rapid thermal annealing, UV or e-beam curing, and/or plasma gas exposure. Those skilled in the art recognize the systems and methods utilized to perform these additional processing steps. For example, the molybdenum-containing film may be exposed to a temperature ranging from approximately 200°C to approximately 1000°C for a time ranging from approximately 0.1 second to approximately 7200 seconds under an inert atmosphere, a H-containing atmosphere, a N-containing atmosphere, an O-containing atmosphere, or combinations thereof. Most preferably, the temperature is 400°C for 3600 seconds under a H-containing atmosphere. The resulting film may contain fewer impurities and therefore may have an improved density resulting in improved leakage current. The annealing step may be performed in the same reaction chamber in which the deposition process is performed. Alternatively, the substrate may be removed from the reaction chamber, with the annealing/flash annealing process being performed in a separate apparatus. Any of the above post-treatment methods, but especially thermal annealing, is expected to effectively reduce any carbon and nitrogen contamination of the molybdenum-containing film. This in turn is expected to improve the resistivity of the film. The resistivity of the MoN film after post-treatment may range from approximately 50 to approximately 1000 $\mu\Omega\cdot cm^{-1}$.

In another alternative, the disclosed bis(alkylimido)-bis(alkylamido) molybdenum compounds may be used as doping or implantation agents. Part of the disclosed bis(alkylimido)-bis(alkylamido) molybdenum compound may be deposited on top of the film to be doped, such as an indium oxide (In_2O_3) film, vanadium dioxide (VO_2) film, a titanium oxide film, a copper oxide film, or a tin dioxide (SnO_2) film. The molybdenum then diffuses into the film during an annealing step to form the molybdenum-doped films {(Mo)In_2O_3, (Mo)VO_2, (Mo)TiO, (Mo)CuO, or (Mo)SnO_2}. See, e.g., US2008/0241575 to Lavoie et al., the doping method of which is incorporated herein by reference in its entirety. Alternatively, high energy ion implantation using a variable energy radio frequency quadrupole implanter may be used to dope the molybdenum of the bis(alkylimido)-bis(alkylamido) molybdenum compound into a film. See, e.g., Kensuke et al., JVSTA 16(2) Mar/Apr 1998, the implantation method of which is incorporated herein by reference in its entirety. In another alternative, plasma doping, pulsed plasma doping or plasma immersion ion implantation may be performed using the disclosed bis(alkylimido)-bis(alkylamido) molybdenum compounds. See, e.g., Felch et al., Plasma doping for the fabrication of ultra-shallow junctions Surface Coatings Technology, 156 (1-3) 2002, pp. 229-236, the doping method of which is incorporated herein by reference in its entirety.

Examples

The following non-limiting examples are provided to further illustrate embodiments of the invention. However, the examples are not intended to be all inclusive and are not intended to limit the scope of the inventions described herein.

<u>EXAMPLE 1</u>: Deposition of MoN film using $Mo(NtBu)_2(NHtBu)_2$ and ammonia

$Mo(NtBu)_2(NHtBu)_2$ was used for deposition of MoN films in ALD mode using ammonia as a co-reactant. The molybdenum molecule is stored in a canister, heated at 80°C, and vapors are provided to the reaction furnace by N_2 or Ar bubbling method. The lines are heated at 100°C to prevent condensation of the reactants. The delivery set-up enables alternate introduction of the vapors of the molybdenum precursor and of ammonia. Molybdenum nitride films are obtained at

a deposition rate of ~1.3Å/cycle at 425°C (**FIG 2**). Above this temperature, the deposition rate increases drastically, which may evidence that $Mo(NtBu)_2(NHtBu)_2$ undergoes thermal self decomposition above this temperature.

The saturation mode characteristic of ALD was obtained at 350°C and 400°C, as the increase of the pulse time of the precursor did not impact the growth rate of the MoN film, which remained constant (**FIG 3**). At 400°C, good linearity (R^2=0.9998) of film growth was obtained as a function of number of cycles (**FIG 4**). Highly conformal film growth at 400°C was characterized by scanning electron microscopy (SEM), indicating that the high stability of the molecule is beneficial to good step coverage (**FIG 5**). The composition of the films was analyzed by XPS (**FIG 6**). The films are stoichiometric MoN. The concentration of C is approximately 10 at.%. The concentration of O is approximately 8 atomic%. These low concentrations indicate the good quality of the film. The good quality of the film was further confirmed by the low resistivity of the MoN films. The resistivity of the MoN films were measured through a large window of deposition temperature (**FIG 7**). It is observed that the higher the deposition temperature, the lower the resistivity of the films. This result proves the benefit of high temperature ALD process enabled by the use of the family of stable molecules described in this document.

<u>Counter Example from Literature</u>:

Miikkulainen et al. disclose results of MoN ALD depositions from NH_3 with $Mo(NtBu)_2(NMe_2)_2$ or $Mo(NtBu)_2(NEt_2)_2$ in Chem. Vap. Deposition ((2008) 14, 71-77). Miikkulainen et al. disclose that ALD is unsuitable with $Mo(NtBu)_2(NiPr_2)_2$ due to its thermal instability. Id. at 72. Miikkulainen et al. report that deposition test results for $Mo(NtBu)_2(NEt_2)_2$ were similar to those previously reported for $Mo(NtBu)_2(NMe_2)_2$, with both exhibiting a maximum growth temperature of 300°C and a growth rate of 0.5Å/cycle. Id. at 73. Additionally, MoN films produced by deposition of $Mo(NtBu)_2(NMe_2)_2$ and $Mo(NtBu)_2(NEt_2)_2$ have similar elemental composition: Mo, 37%; N, 41%; C, 8%; O, 14%. Id. at 74-75.

The ALD temperature window for the $Mo(NtBu)_2(NHtBu)_2$ compound described in Example 1 is approximately 100°C higher than that of $Mo(NtBu)_2(NMe_2)_2$ and $Mo(NtBu)_2(NEt_2)_2$. The growth rate using the

$Mo(NtBu)_2(NMe_2)_2$ and $Mo(NtBu)_2(NEt_2)_2$ is less than half the growth rate obtained with the $Mo(NtBu)_2(NHtBu)_2$ compound described in Example 1. The concentration of O in the MoN films produced by $Mo(NtBu)_2(NMe_2)_2$ and $Mo(NtBu)_2(NEt_2)_2$ is almost double the concentration in MoN films produced by the $Mo(NtBu)_2(NHtBu)_2$ compound of Example 1.

The process using $Mo(NtBu)_2(NHtBu)_2$ provides unexpectedly superior results to the process using $Mo(NtBu)_2(NMe_2)_2$ and $Mo(NtBu)_2(NEt_2)_2$ in terms of temperature window, growth rate, and O concentration.

EXAMPLE 2 (prophetic): MoO_3 deposition

The same precursor as in Example 1 will be used, but NH_3 will be replaced by ozone (O_3). The same ALD introduction scheme will be used. Saturation is expected to be obtained at 400°C. Composition analyses is expected to confirm that the obtained films are MoO_3 and that the carbon content in the films is low (0-2 atomic %).

EXAMPLE 3: PEALD MoN deposition

The same precursor as in Example 1 was used with NH_3 and provided to the reaction chamber in an ALD mode scheme. In this case, 200W of direct plasma source was switched on during the NH_3 pulse. Molybdenum Nitride films were obtained up to 450°C at a deposition rate of ~1.0A/cycle (**FIG 8**). The use of plasma source allowed decreasing the concentration of carbon and oxygen impurities to ~ < 2% (**FIG 9**). The resistivity of the MoN films were measured through a large window of deposition temperature (**FIG 10**) and as a result of low impurities in the films, resistivity is also lowered as 612 μΩ·cm.

While embodiments of this invention have been shown and described, modifications thereof can be made by one skilled in the art without departing from the spirit or teaching of this invention. The embodiments described herein are exemplary only and not limiting. Many variations and modifications of the composition and method are possible and within the scope of the invention. Accordingly the scope of protection is not limited to the embodiments described

herein, but is only limited by the claims which follow, the scope of which shall include all equivalents of the subject matter of the claims.

We claim:

1. An atomic layer deposition method for forming a molybdenum-containing film on a substrate, the method comprising:

5 introducing a molybdenum-containing precursor into a vapor deposition chamber containing a substrate, the molybdenum-containing precursor having the formula $Mo(NR)_2(NHR')_2$, wherein R and R' are independently chosen from the group consisting of a C1-C4 alkyl group, a C1-C4 perfluoroalkyl group, and an alkylsilyl group; and

10 depositing at least part of the molybdenum-containing precursor on the substrate by atomic layer deposition to form the molybdenum-containing film.

2. The atomic layer deposition method of claim 1, wherein the molybdenum-containing precursor is selected from the group consisting of $Mo(NMe)_2(NHMe)_2$,
15 $Mo(NMe)_2(NHEt)_2$, $Mo(NMe)_2(NHPr)_2$, $Mo(NMe)_2(NHiPr)_2$, $Mo(NMe)_2(NHBu)_2$, $Mo(NMe)_2(NHiBu)_2$, $Mo(NMe)_2(NHsBu)_2$, $Mo(NMe)_2(NHtBu)_2$, $Mo(NEt)_2(NHMe)_2$, $Mo(NEt)_2(NHEt)_2$, $Mo(NEt)_2(NHPr)_2$, $Mo(NEt)_2(NHiPr)_2$, $Mo(NEt)_2(NHBu)_2$, $Mo(NEt)_2(NHiBu)_2$, $Mo(NEt)_2(NHsBu)_2$, $Mo(NEt)_2(NHtBu)_2$, $Mo(NPr)_2(NHMe)_2$, $Mo(NPr)_2(NHEt)_2$, $Mo(NPr)_2(NHPr)_2$, $Mo(NPr)_2(NHiPr)_2$, $Mo(NPr)_2(NHBu)_2$,
20 $Mo(NPr)_2(NHiBu)_2$, $Mo(NPr)_2(NHsBu)_2$,$Mo(NPr)_2(NHtBu)_2$, $Mo(NiPr)_2(NHMe)_2$, $Mo(NiPr)_2(NHEt)_2$, $Mo(NiPr)_2(NHPr)_2$, $Mo(NiPr)_2(NHiPr)_2$, $Mo(NiPr)_2(NHBu)_2$, $Mo(NiPr)_2(NHiBu)_2$, $Mo(NiPr)_2(NHsBu)_2$, $Mo(NiPr)_2(NHtBu)_2$, $Mo(NBu)_2(NHMe)_2$, $Mo(NBu)_2(NHEt)_2$, $Mo(NBu)_2(NHPr)_2$, $Mo(NBu)_2(NHiPr)_2$, $Mo(NBu)_2(NHBu)_2$, $Mo(NBu)_2(NHiBu)_2$, $Mo(NBu)_2(NHsBu)_2$, $Mo(NBu)_2(NHtBu)_2$, $Mo(NiBu)_2(NHMe)_2$,
25 $Mo(NiBu)_2(NHEt)_2$, $Mo(NiBu)_2(NHPr)_2$, $Mo(NiBu)_2(NHiPr)_2$, $Mo(NiBu)_2(NHBu)_2$, $Mo(NiBu)_2(NHiBu)_2$, $Mo(NiBu)_2(NHsBu)_2$, $Mo(NiBu)_2(NHtBu)_2$, $Mo(NsBu)_2(NHMe)_2$, $Mo(NsBu)_2(NHEt)_2$, $Mo(NsBu)_2(NHPr)_2$, $Mo(NsBu)_2(NHiPr)_2$, $Mo(NsBu)_2(NHBu)_2$, $Mo(NsBu)_2(NHiBu)_2$, $Mo(NsBu)_2(NHsBu)_2$, $Mo(NsBu)_2(NHtBu)_2$, $Mo(NtBu)_2(NHMe)_2$, $Mo(NtBu)_2(NHEt)_2$, $Mo(NtBu)_2(NHPr)_2$,
30 $Mo(NtBu)_2(NHiPr)_2$, $Mo(NtBu)_2(NHBu)_2$, $Mo(NtBu)_2(NHiBu)_2$, $Mo(NtBu)_2(NHsBu)_2$, $Mo(NtBu)_2(NHtBu)_2$, $Mo(NSiMe_3)_2(NHMe)_2$, $Mo(NSiMe_3)_2(NHEt)_2$, $Mo(NSiMe_3)_2(NHPr)_2$, $Mo(NSiMe_3)_2(NHiPr)_2$, $Mo(NSiMe_3)_2(NHBu)_2$, $Mo(NSiMe_3)_2(NHiBu)_2$, $Mo(NSiMe_3)_2(NHsBu)_2$, $Mo(NSiMe_3)_2(NHtBu)_2$,

$Mo(NCF_3)_2(NHMe)_2$, $Mo(NCF_3)_2(NHEt)_2$, $Mo(NCF_3)_2(NHPr)_2$, $Mo(NCF_3)_2(NHiPr)_2$, $Mo(NCF_3)_2(NHBu)_2$, $Mo(NCF_3)_2(NHiBu)_2$, $Mo(NCF_3)_2(NHsBu)_2$, $Mo(NCF_3)_2(NHtBu)_2$, $Mo(NMe)_2(NHSiMe_3)_2$, $Mo(NEt)_2(NHSiMe_3)_2$, $Mo(NPr)_2(NHSiMe_3)_2$, $Mo(NtBu)_2(NHSiMe_3)_2$, $Mo(NtAmyl)_2(NHMe)_2$,
5 $Mo(NtAmyl)_2(NHEt)_2$, $Mo(NtAmyl)_2(NHPr)_2$, $Mo(NtAmyl)_2(NHiPr)_2$, $Mo(NtAmyl)_2(NHBu)_2$, $Mo(NtAmyl)_2(NHiBu)_2$, $Mo(NtAmyl)_2(NHsBu)_2$, $Mo(NtAmyl)_2(NHtBu)_2$, $Mo(NtAmyl)_2(NHSiMe_3)_2$, and $Mo(NtBu)(NtAmyl)(NHtBu)_2$, preferably $Mo(NtBu)_2(NHiPr)_2$, $Mo(NtBu)_2(NHtBu)_2$, $Mo(NtAmyl)_2(NHiPr)_2$, or $Mo(NtAmyl)_2(NHtBu)_2$

10

3. The atomic layer deposition method of claim 2, wherein the at least part of the molybdenum-containing precursor is deposited on the substrate by plasma enhanced atomic layer deposition.

15 4. The atomic layer deposition method of claim 3, wherein a plasma power is between about 30 W and about 600 W, preferably between about 100 W and about 500 W

5. The atomic layer deposition method of any one of claims 1 to 4, further
20 comprising reacting the at least part of the molybdenum-containing precursor with a reducing agent.

6. The atomic layer deposition method of claim 5, wherein the reducing agent is selected from the group consisting of N_2, H_2, NH_3, N_2H_4 and any hydrazine
25 based compounds, SiH_4, Si_2H_6, radical species thereof, and combinations thereof.

7. The atomic layer deposition method of any one of claims 1 to 4, further comprising reacting the at least part of the molybdenum-containing precursor with an oxidizing agent.

30

8. The atomic layer deposition method of claim 7, wherein the oxidizing agent is selected from the group consisting of O_2, H_2O, O_3, H_2O_2, N_2O, NO, acetic acid, the radical species thereof, and combinations thereof.

9. The atomic layer deposition method of any one of claims 1 to 4, wherein the method is performed at a pressure between about 0.01 Pa and about 1×10^5 Pa, preferably between about 0.1 Pa and about 1×10^4 Pa.

5 10. The atomic layer deposition method of any one of claim 1 to 4, wherein the method is performed at a temperature between about 20°C and about 500°C, preferably between about 330°C and about 500°C.

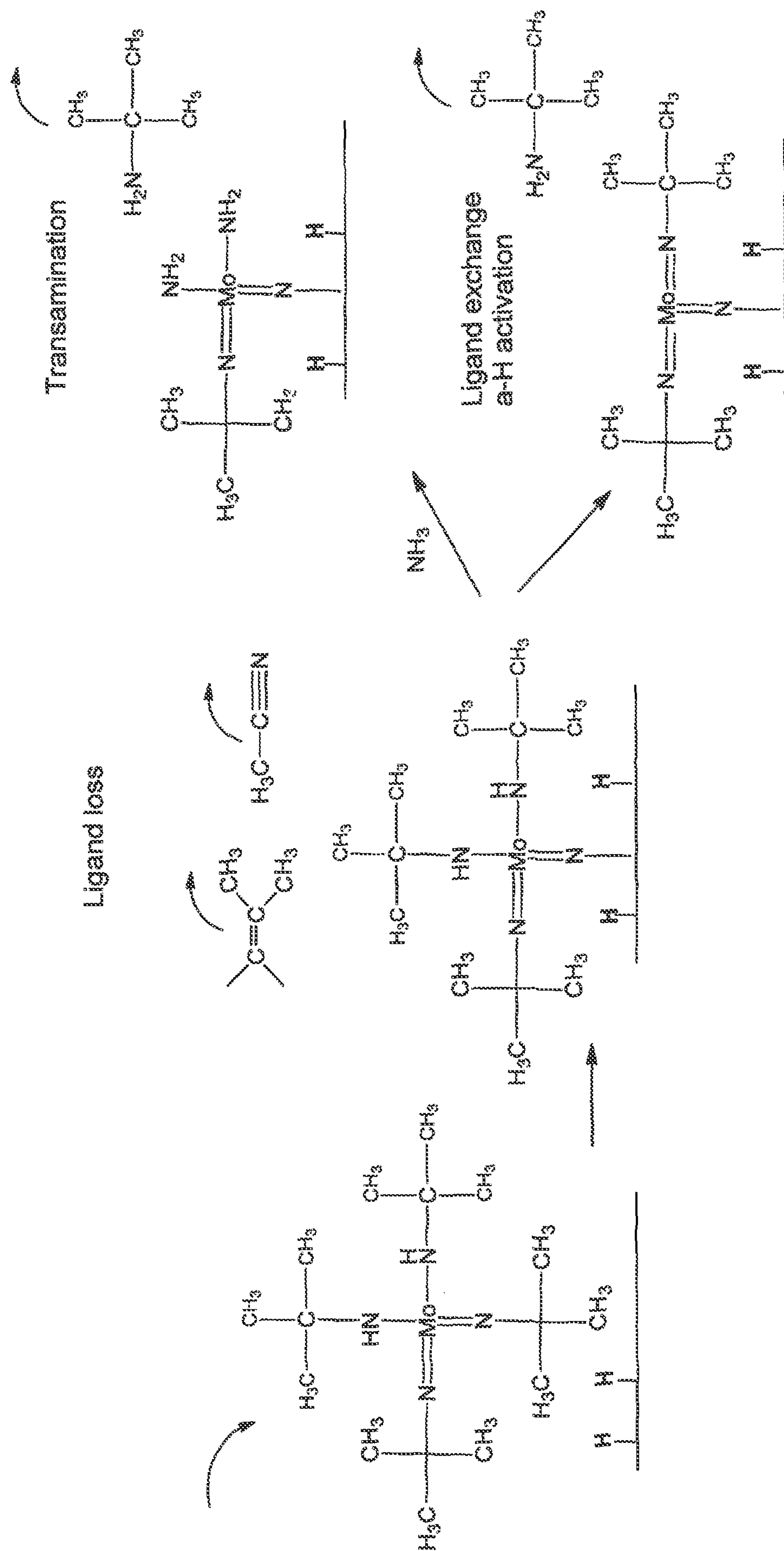


FIG 1

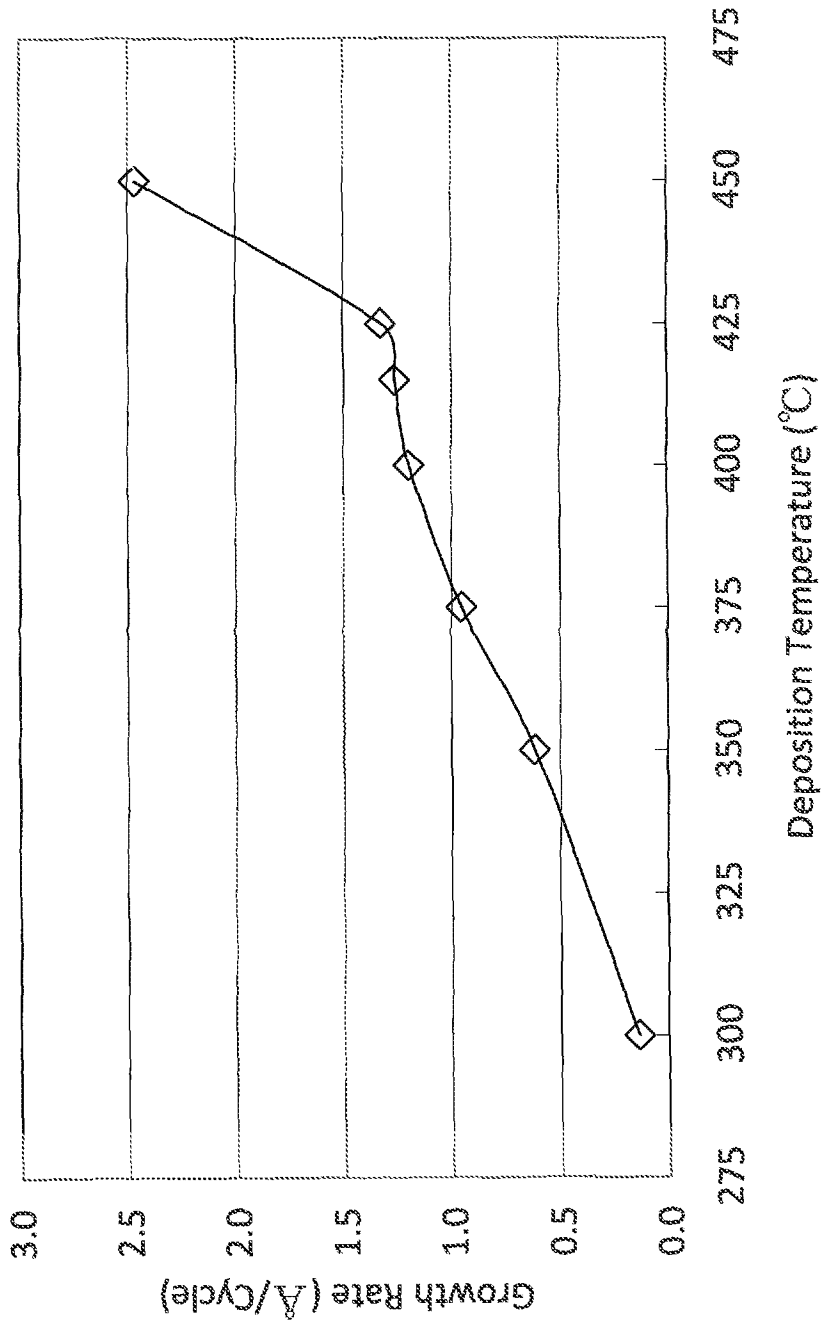


FIG 2

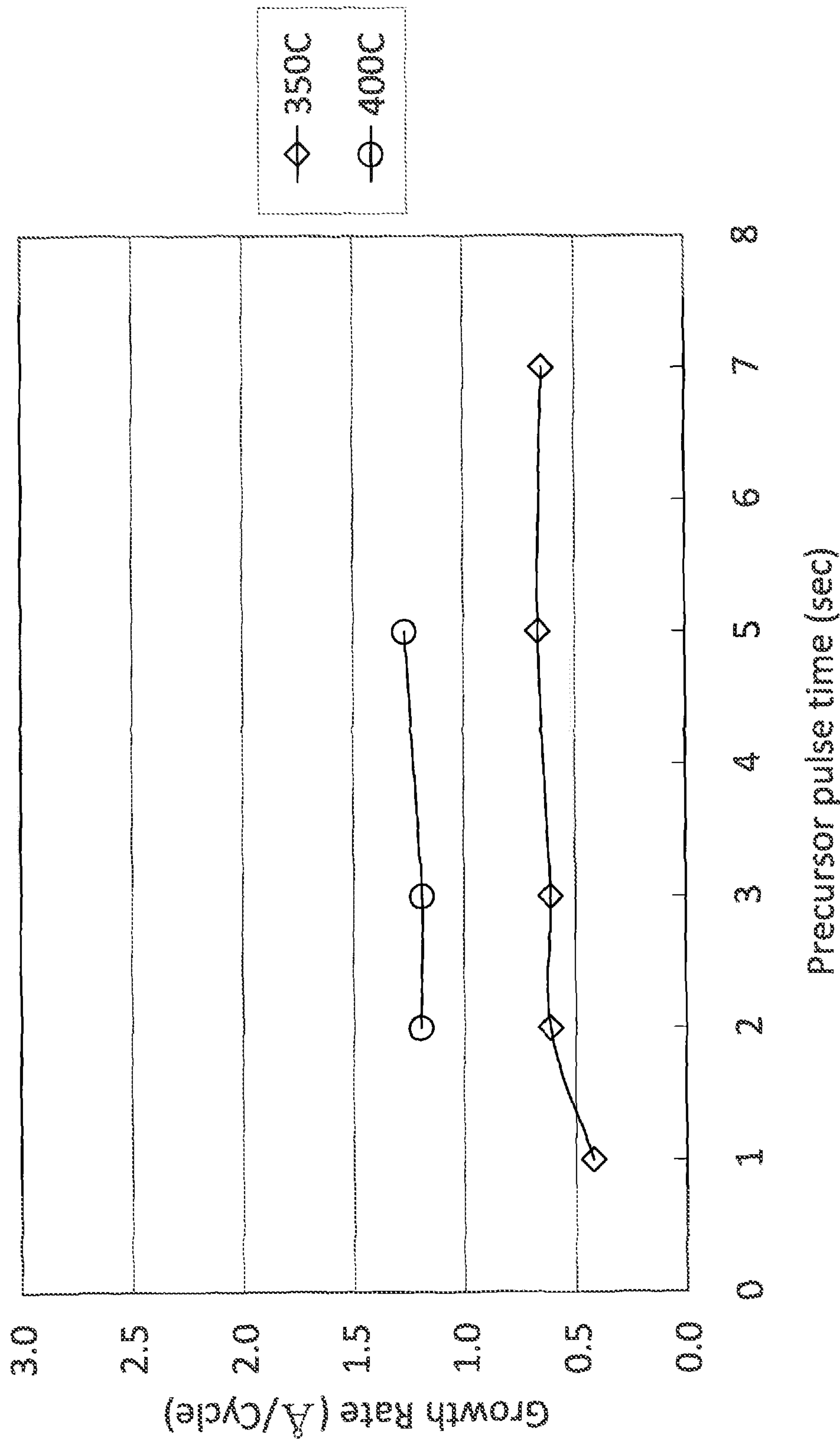


FIG 3

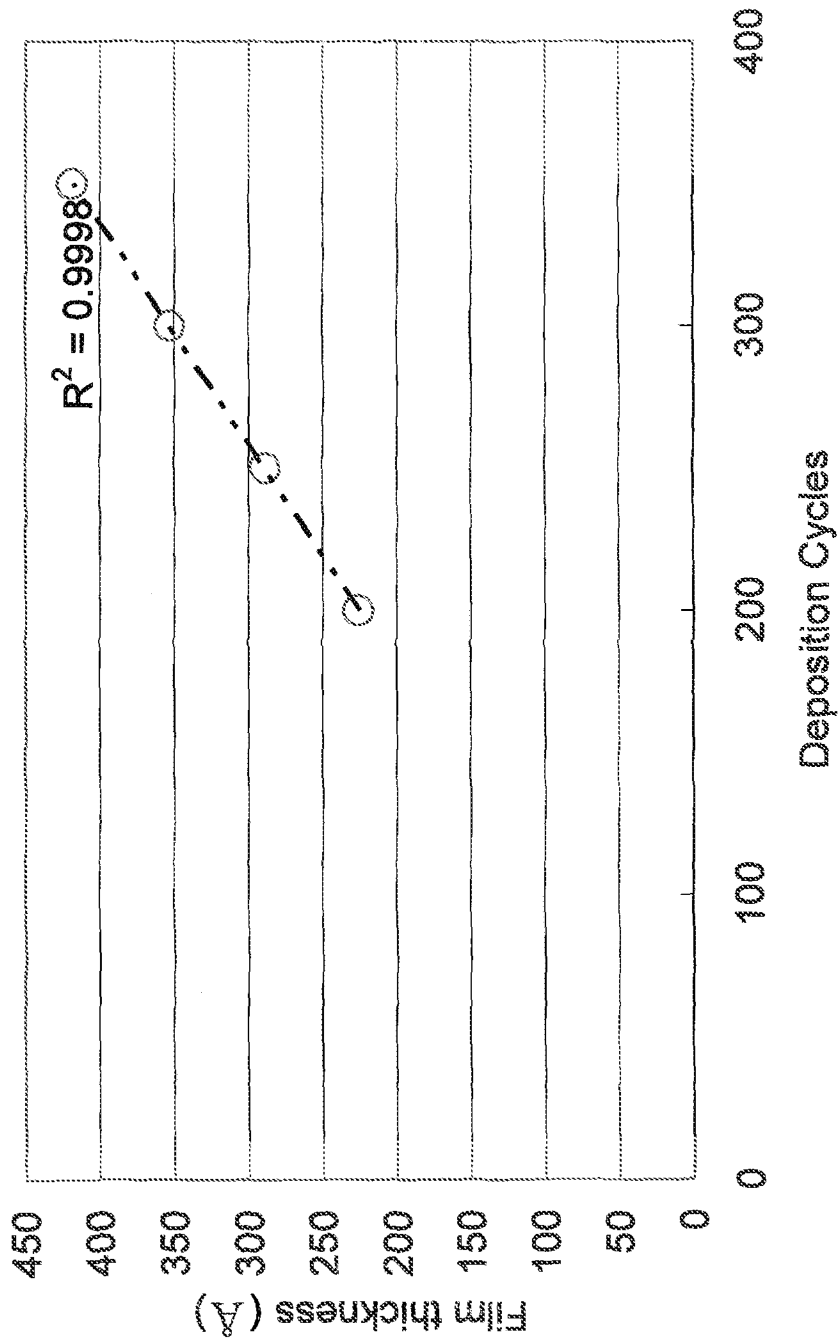


FIG 4

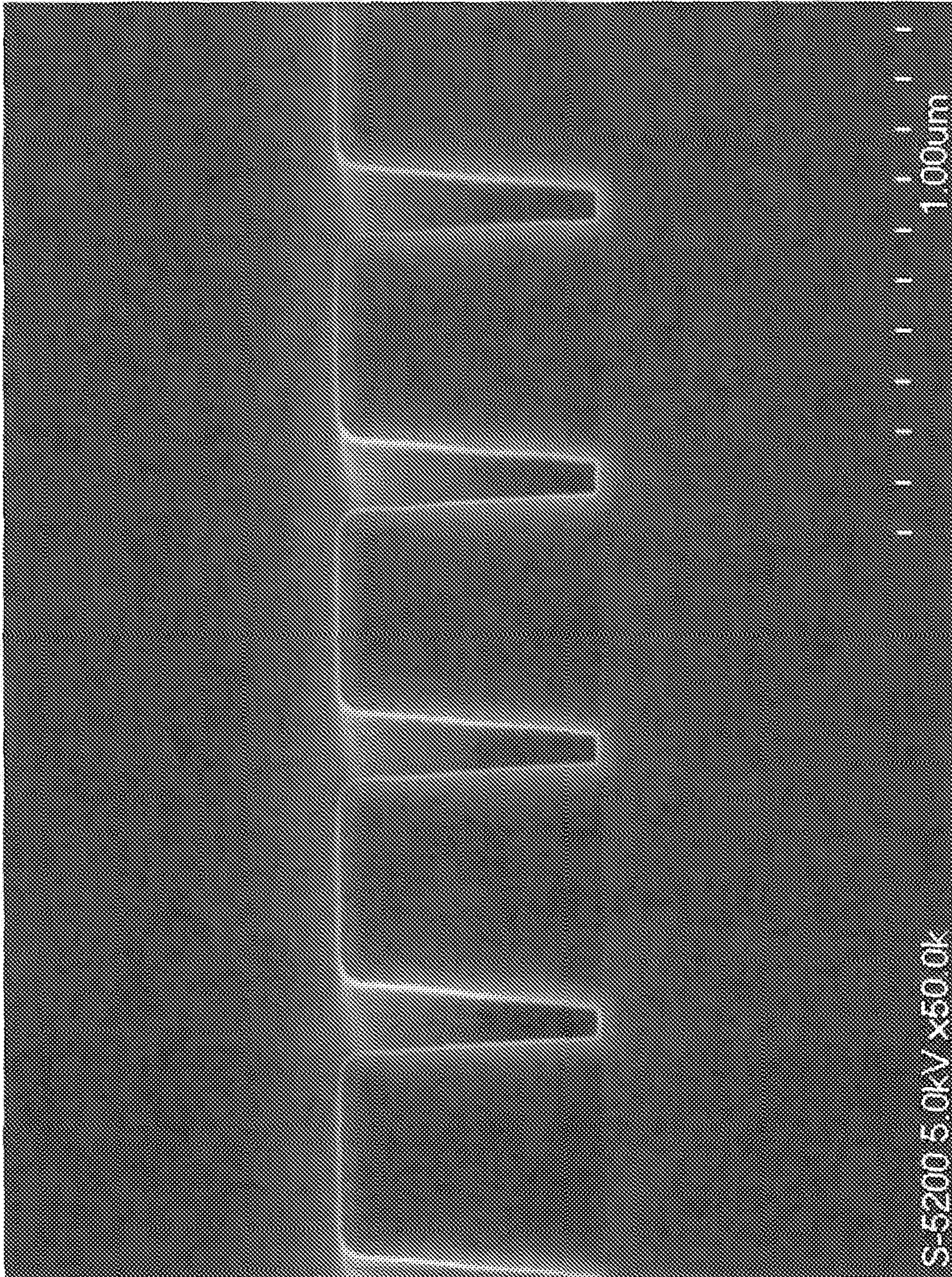


FIG 5

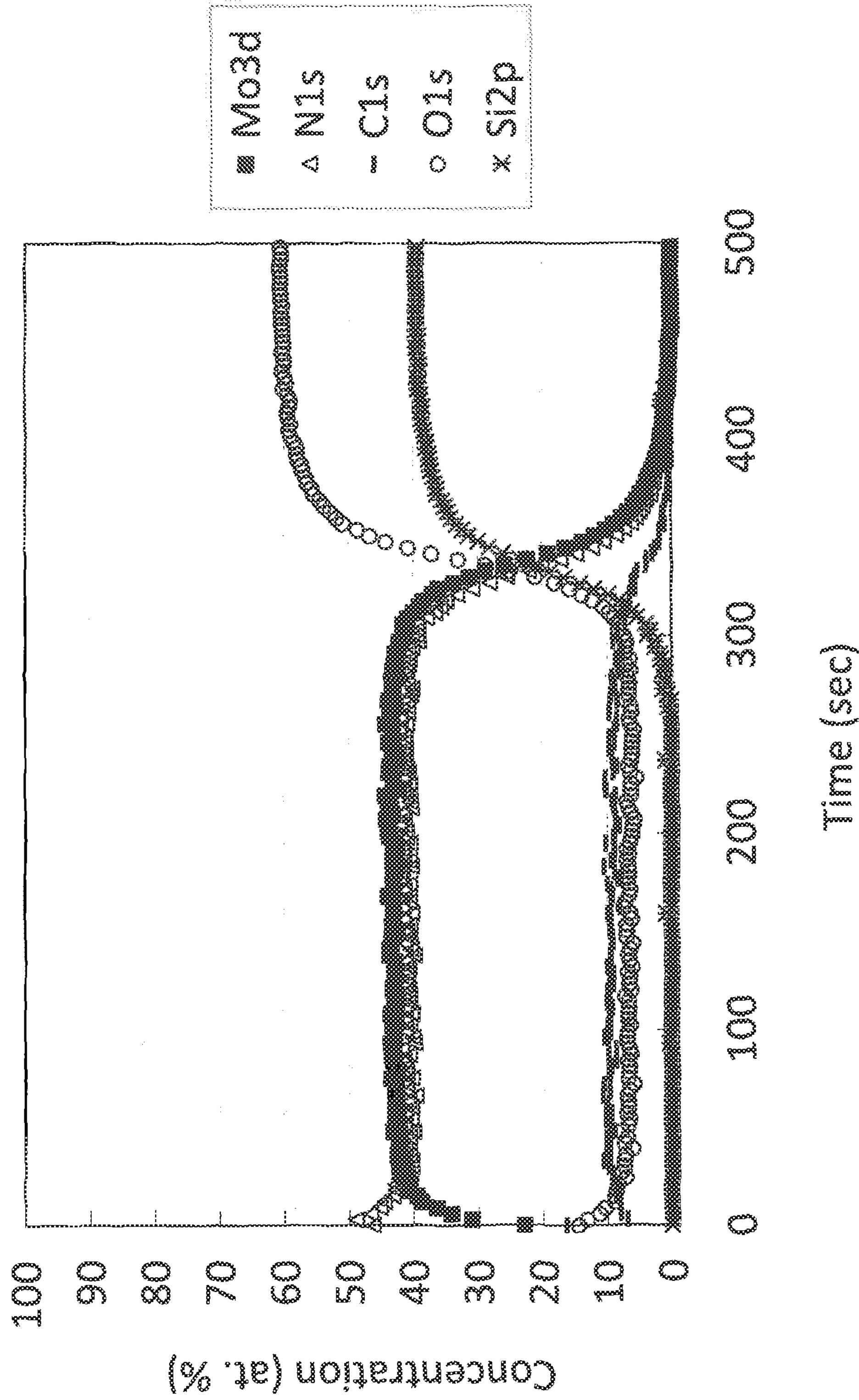


FIG 6

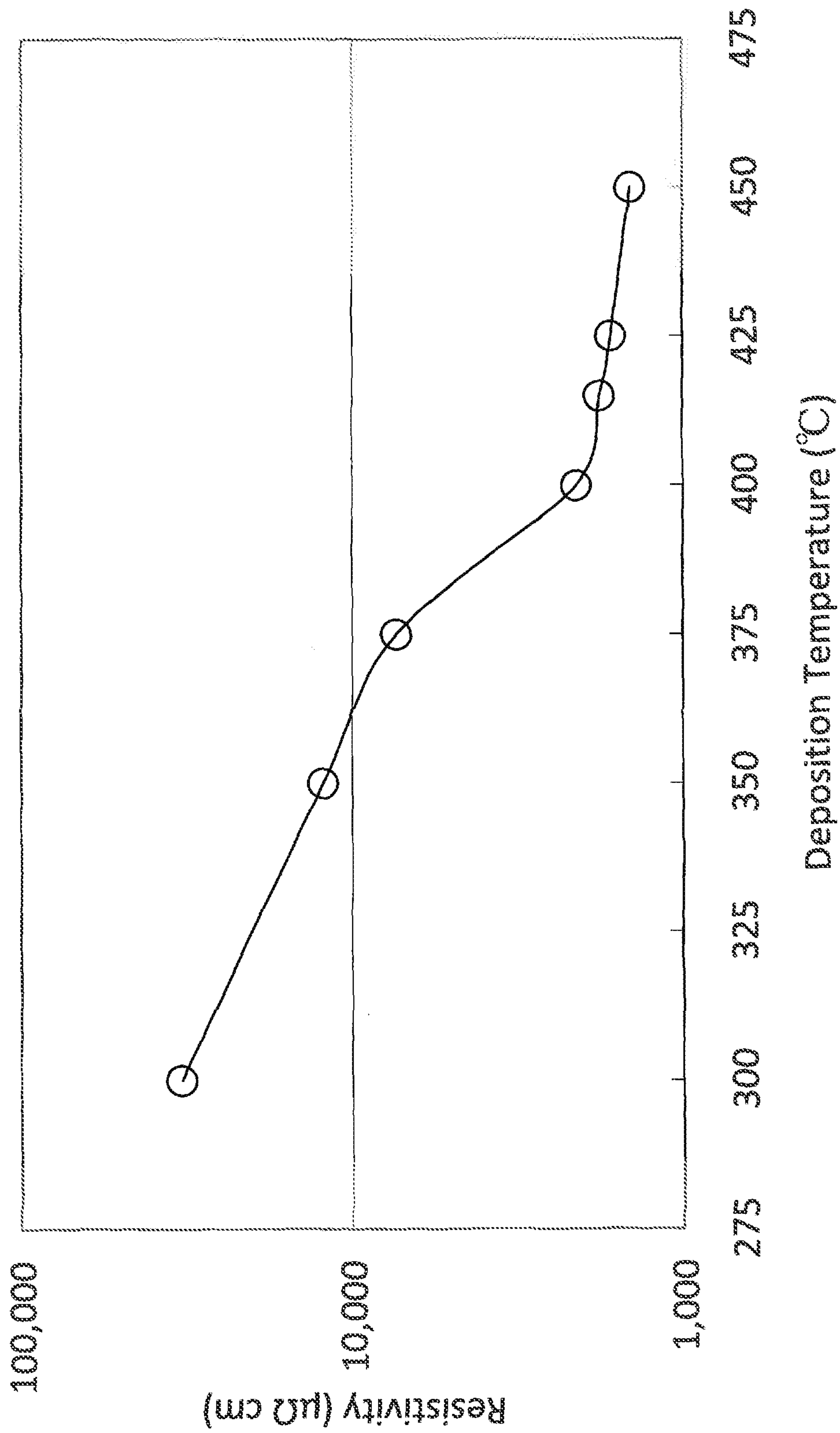


FIG 7

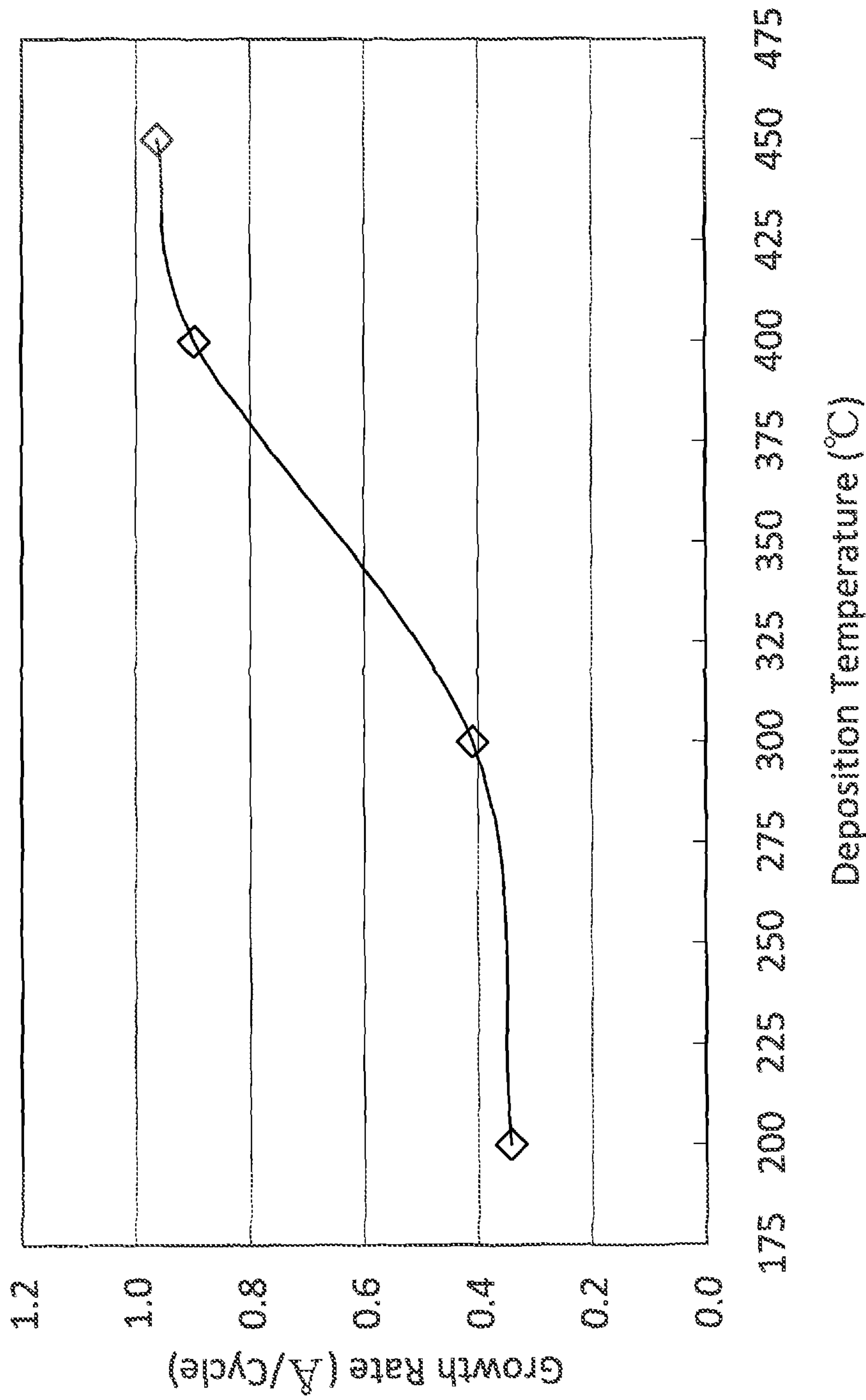


FIG 8

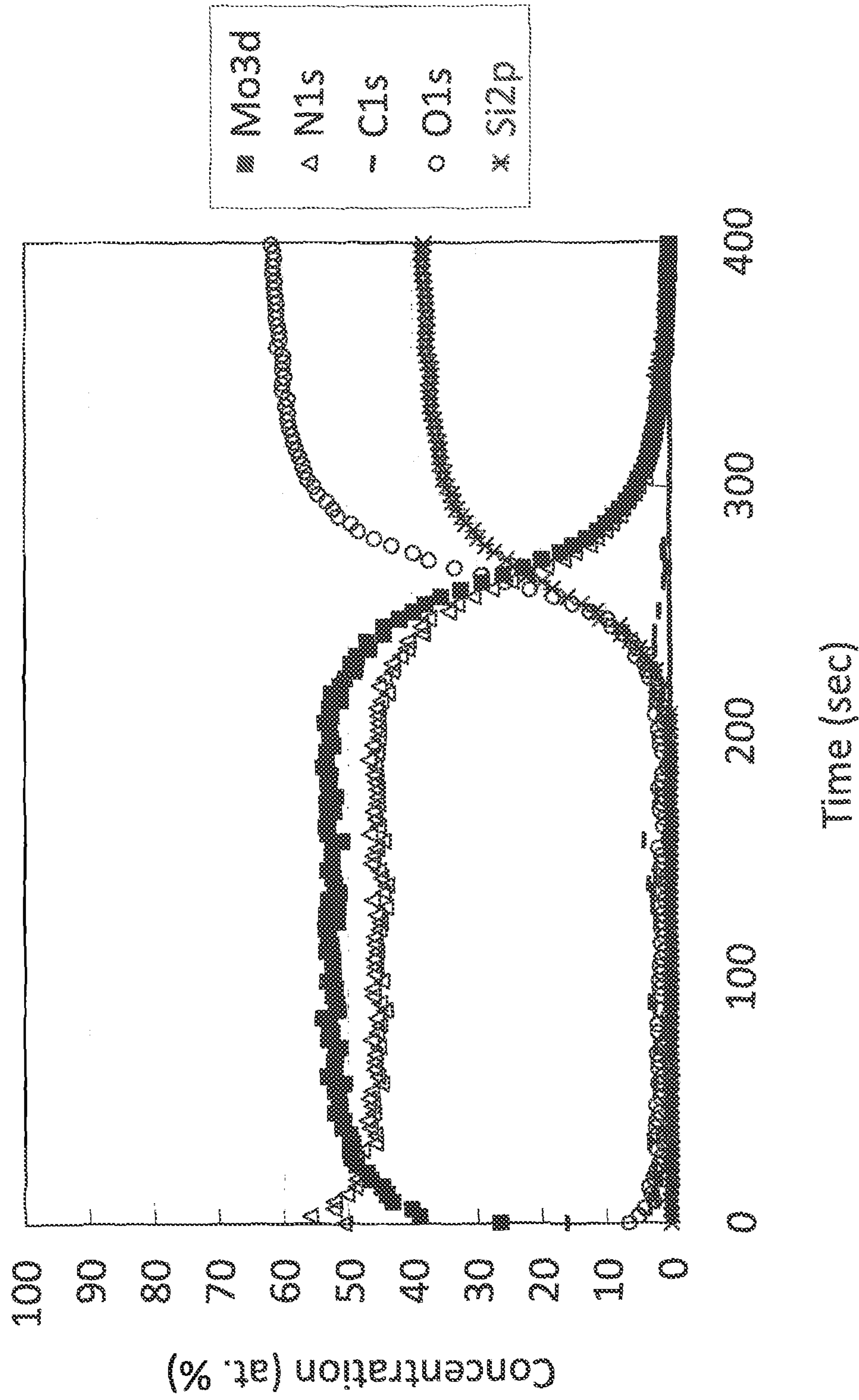


FIG 9

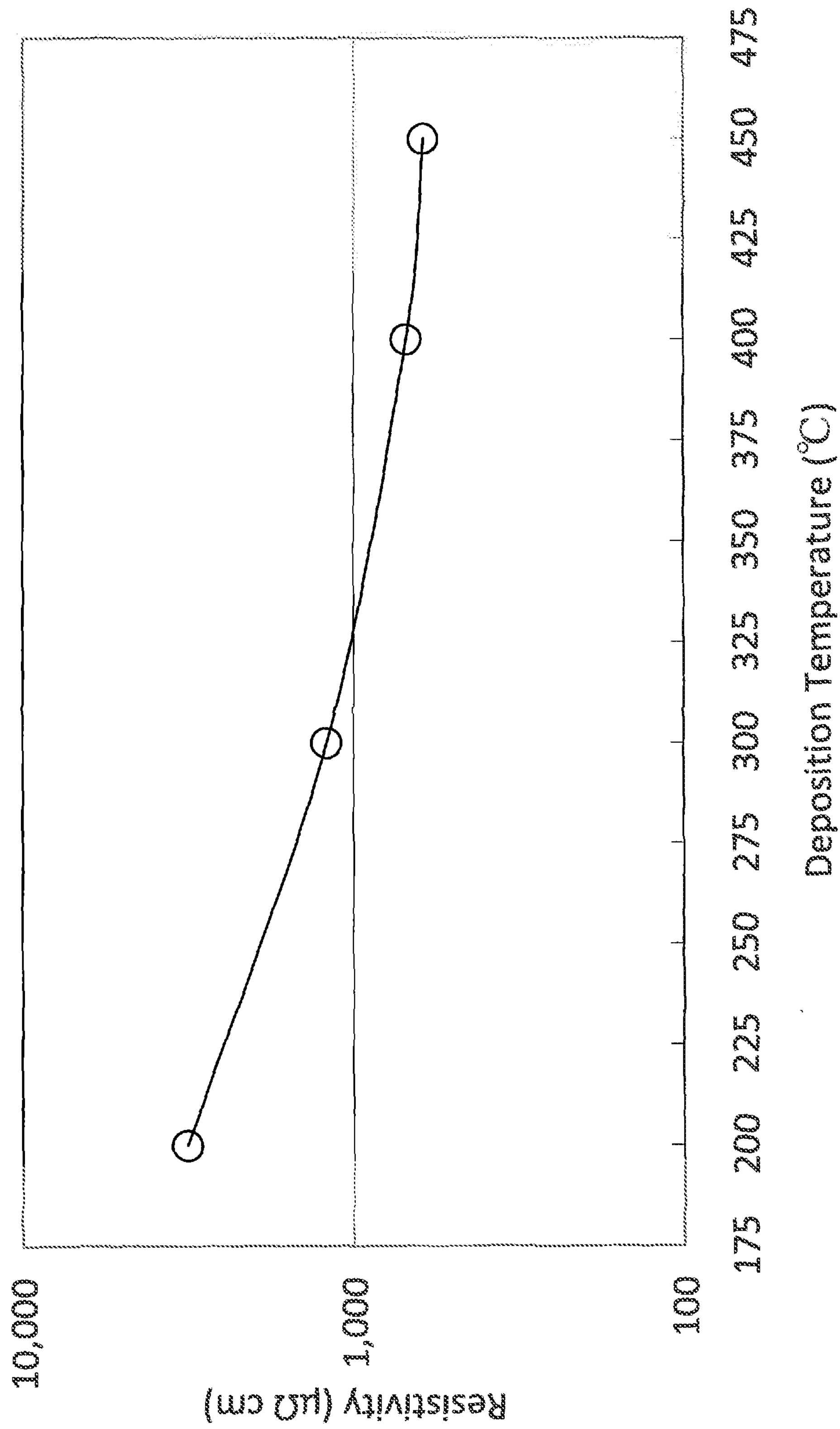


FIG 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2013/001038

A. CLASSIFICATION OF SUBJECT MATTER

H01L 21/205(2006.01)i, H01L 21/318(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 21/205; C07F 17/00; C07F 11/00; B01J 23/882; C23C 16/40; H01L 21/44; H01L 21/318

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: ALD, deposit, molybdenum, precursor and MoN

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012-027575 A1 (SIGMA-ALDRICH CO. LLC et al.) 01 March 2012 See abstract, paragraphs [0008]-[0040] and claims 1-21.	1-10
A	PETRA ALEN, "Atomic Layer Deposition of TaN, NbN, and MoN Films for Cu Metallizations" ACADEMIC DISSERTATION, Laboratory of Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Helsinki, 22 June 2005 See page 41, line 1 - page 43, line 6 and table VII.	1-10
A	TOBIAS B. THIEDE et al. "NOVEL PRECURSORS FOR THE MOCVD OF MOLYBDENUM NITRIDE" In: The Electrochemical Society, 216th ECS Meeting, Abstract #2512, 2009 See full text and figure 1.	1-10
A	WO 2010-114386 A1 (UNIVERSITETET I OSLO et al.) 07 October 2010 See abstract, page 3, line 4 - page 5, line 37 and claims 1-12.	1-10
A	US 6359160 B1 (SHI-CHUNG SUN et al.) 19 March 2002 See abstract, column 2, line 36 - column 3, line 40, claims 1-4 and figure 3.	1-10

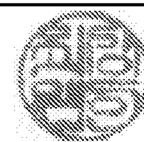
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* 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	Date of mailing of the international search report
24 December 2013 (24.12.2013)	**27 December 2013 (27.12.2013)**

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea
Facsimile No. +82-42-472-7140

Authorized officer
CHOI, Sang Won
Telephone No. +82-42-481-8291


INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/IB2013/001038

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2012-027575 A1	01/03/2012	CN 103097394 A	08/05/2013
		EP 2609102 A1	03/07/2013
		SG 187920 A1	28/03/2013
		TW 201219405 A	16/05/2012
		US 2013-0196065 A1	01/08/2013
WO 2010-114386 A1	07/10/2010	WO 2010-114386 A8	29/09/2011
US 6359160 B1	19/03/2002	TW 402741 A	21/08/2000
		US 6114242 A	05/09/2000