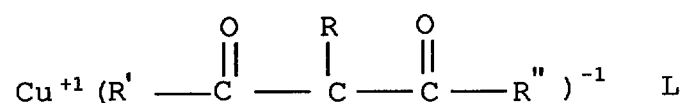


**NOVEL COPPER (I) PRECURSORS FOR CHEMICAL DEPOSIT IN GAS
PHASE OF METALLIC COPPER**

The present invention relates to the chemical deposit method in gas phase of pure metals such as copper and silver, in the electronics industry, for the production of integrated circuits. This method, called
 5 CVD for "Chemical Vapor Deposition" is widely used to produce, from precursors of said metals in oxidised form (+1), the interconnections and metallisation of integrated circuits measuring 0.25 μm or less.

Numerous copper precursors are known in the
 10 prior art for the fabrication of films made up of said pure metal. The most promising precursors are complex compounds of oxidised copper (+1) stabilised by a ligand in which the copper is compounded with a β -diketonate having the following general formula :

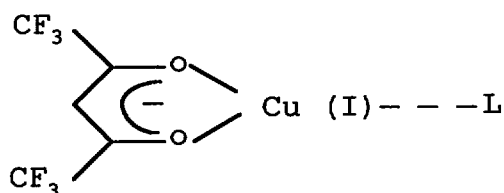
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in which R, R' and R'', identical or different, are chosen from among a hydrogen atom, a halogen atom such as fluorine, a lower alkyl optionally substituted by one or more fluorine atoms.

Preferred complexes are those in which R is a hydrogen atom and R' and R'' are perfluorine alkyls, advantageously -CF₃ groups meeting the following structural formula :

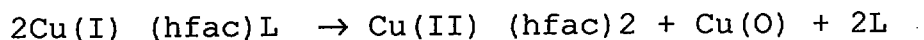
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Such complexes and the way they are used in the CVD method are, for example, described in US Patents n° 5 085 731, 5 096 737, 5 098 516, 5 144 049, 5 187 300 whose teaching on the CVD method is incorporated herein by reference.

The work conducted on these precursors demonstrates that their molecular structure is decisive for the reproducible production of films of good quality (P. Doppelt and T.H. Baum, MRS Bull. XIX(8) 41, 1994). However, the electronics industry does not have available an ideal precursor for the reproducible fabrication of electronic circuits containing thin copper films to enable defect-free filling of vertical lines and interconnections that offers low resistivity and good long term thermal stability.

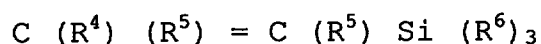
As reported in the above-mentioned patents, the formation of metallic copper results from the dismutation of two copper molecules (I) on a surface heated to a temperature close to 200°C in accordance with the following reaction :



The nature of the Lewis base L, also called hereafter the ligand, only slightly influences the nature of the copper films obtained by CVD. Copper films are generally very pure, free of carbon or oxygen atoms (less than 1%), and resistivity in the region of 1.8 $\mu\Omega$ is frequently found in copper films obtained by CVD ; this value is very close to the one found in solid copper (1.67 $\mu\Omega$.cm). On the other hand, the nature of ligand L determines the volatility of the complex and consequently the rate of deposit of the copper obtained.

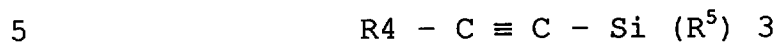
In the prior art, more than 80 copper complexes (I) (hfac) are known which have been tested for the CVD of copper, such as for example :

- carbon monoxide, isonitrile, unsaturated hydrocarbon ligands, comprising at least one non-aromatic insaturation cited in US Patent n° 5 098 516 ;
- alkynes and acetylene derivatives, dienes, olefins and phosphines, cited in US Patent 5 096 737 ;
- the compounds cited in US Patent 5 144 049 meeting the formula :



in which R^4 , R^5 and R^6 are hydrogen atoms or lower alkyls at C_1 to C_8 .

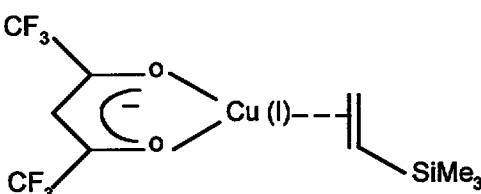
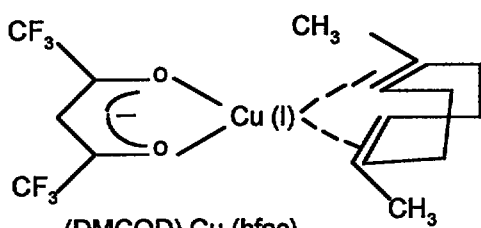
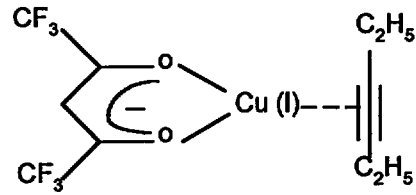
- the compounds cited in US Patent 5 187 300 meeting the formula :



in which R^4 and R^5 are lower alkyls at C_1 to C_8 .

The three copper precursors for CVD, liquid at ambient temperature, given in Table I below have been
10 the subject of particular study :

Table I

Precursors	Volatility
 (VTMS) Cu (hfac)	Very volatile up to 200 nm/min (H₂O)
 (DMCOD) Cu (hfac)	Scarcely volatile : 140 nm/min
 (3-hexyne) Cu (hfac)	Very volatile up to 400 nm/min. Formation of a less volatile secondary product

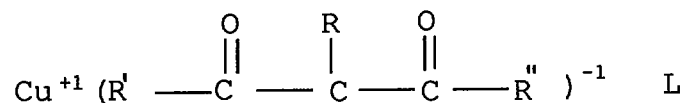
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Among the latter, the (3-hexyne) Cu(hfac) complex is the one which gives the highest growth rate. On the other hand, it has recently been shown that it leads to the formation of dinuclear complexes which form a major obstacle to its use (P. Doppelt and T.H. Baum, Journal of Organometallic Chemistry 517, 53-62, 1996).

In order to remedy this disadvantage, the inventors have examined electronic phenomena related to the formation of dinuclear complexes during the use of a copper complex for CVD stabilised by a ligand made up of an alkyne whether substituted or not. Research work conducted has been able to demonstrate that the formation of these dinuclear species is helped when the alkyne carries electron-donor groups, such as for example the Si(R)_3 group described in US Patent 5 187 300.

The present invention sets out precisely to provide a solution to the problem raised by the formation of dinuclear complexes during the use of a copper complex stabilised by a ligand of triple bond carrying type, while maintaining the potentialities of the precursor for CVD. This objective is reached by using ligands in which the triple bond is partially deactivated by one or two groups slightly attracting electrons, such as a double bond or one or two alkoxy groups with the formula $-\text{O}-(\text{CH}_2)_n-\text{CH}_3$ in which n is 0 up to the order of 8 and is advantageously a methoxy group ($-\text{O}-\text{CH}_3$).

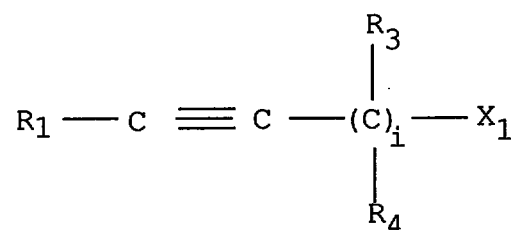
The invention therefore relates to organometallic complexes that are liquid volatile or solid with low melting point, also called hereafter copper precursors (I) for gas phase chemical deposit having the general formula (I) :



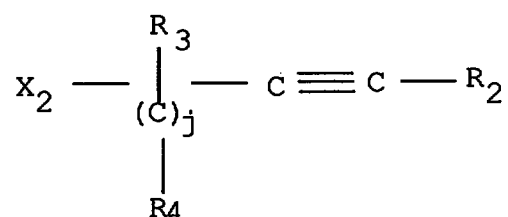
in which R' and R'', identical or different, are a lower alkyl optionally substituted by one or more halogen atoms such as fluorine, R is chosen from among
 5 a hydrogen atom, a halogen atom such as fluorine, a lower alkyl optionally substituted by one or more halogen atoms such as fluorine, and L represents the stabilising ligand of said complex characterized in that L is an alkyne whose triple bond is partially
 10 deactivated by one or two groups slightly attracting the electrons carried by said alkyne.

When L is an alkyne of which the triple bond is partially deactivated by two slightly electron-attracting groups, it is preferred that the latter be
 15 arranged either side of said triple bond.

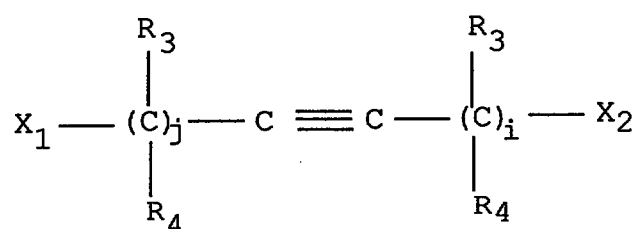
One ligand of the invention meets the following formula (II) :



or the following formula (III) :

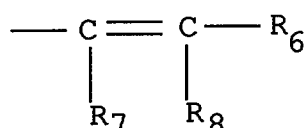


5 or the following formula (IV) :

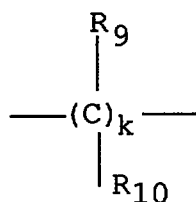


in which R_1 , R_2 , R_3 and R_4 , identical or different, are chosen from among a hydrogen atom, a lower alkyl substituted by one or more fluorine atoms,
 10 a $-\text{Si}(\text{R}_5)_3$ group in which R_5 is a lower alkyl, i and j are 0 to 3 and X_1 and X_2 , identical or different, represent a group that is slightly electron-attracting.

One first group of preferred ligands of the invention are alkene-ynes, that is to say compounds comprising one or two double bonds and one triple bond. These ligands are those with the formula (II), (III) or
 5 (IV) in which X_1 and X_2 identical or different are radicals with the following formula (V) :

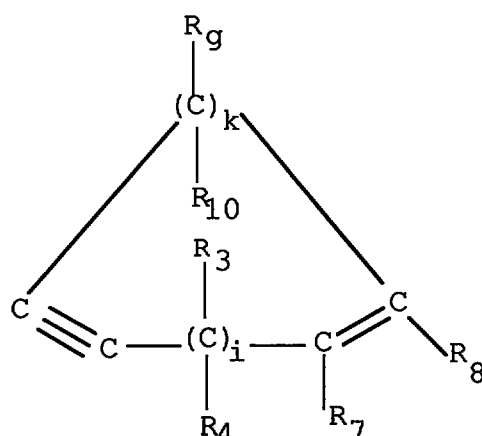


in which R_6 , R_7 and R_8 are chosen from among a hydrogen atom, a lower alkyl substituted by one or more fluorine atoms, a $\text{Si}(\text{R}_5)_3$ group in which R_5 is a lower alkyl, or
 10 in which R_6 and R_2 together or R_6 and R_1 together, or two R_6 radicals together, form a group having the formula (VI) :



15

in which R_9 and R_{10} are chosen from among a hydrogen atom, a lower alkyl substituted by one or more fluorine atoms, a $\text{Si}(\text{R}_5)_3$ group in which R_5 is a lower alkyl, and k is 1 to 3, such as to form ligands with
 20 cyclical formulas, such as for example :

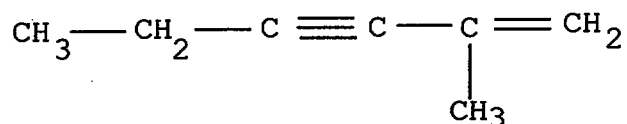


in which R_3 , R_4 , R_6 , R_7 , R_8 , R_9 , R_{10} , i and k have the same denotation as in formulas (II), (V) and (VI).

Among the formula (IV) compounds in which X_1 and X_2 are of formula (V), preference is given to those in which i or j is different from 0, such as to avoid combining of the double bonds and the triple bond.

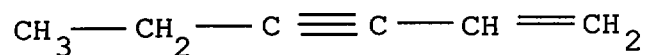
Among the compounds of formulas (II) or (III), particular preference is given to :

- 2-methyl-1-hexen-3-yne with the formula :



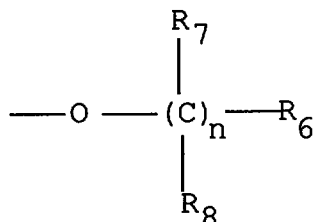
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- 1-hexene-3-yne with the formula :



A second group of preferred ligands of the invention are those with formulas (II), (III) or (IV) in which X_1 and X_2 , identical or different, are radicals with the following formula (VII) :

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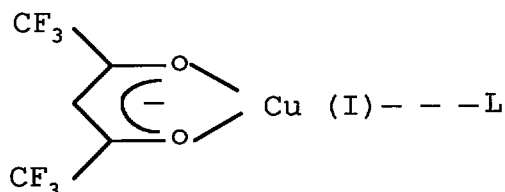


in which R_6 , R_7 , R_8 have the same denotation as
 in formula (V) and n is 0 to 8 such that $(\text{C})_n\text{---R}_6$
 5 remains a lower alkyl.

A third group of ligands of the invention are
 those comprising both an alkoxy group and a group
 comprising a double bond each placed either side of the
 double bond, these ligands meeting formula (IV) in
 10 which X_1 has the formula (V) and X_2 has the formula
 (VII) or the reverse.

In the above formulas, by lower alkyl is meant
 more particularly the alkyls at C_1 to C_8 , linear or
 branched, such as ---CH_3 or $\text{---C}_2\text{H}_5$. These may be
 15 substituted by one or more fluorine atoms such as the
 radicals : ---CF_3 , $\text{---C}_2\text{F}_5$, $\text{---CH}_2\text{CF}_3$, $\text{---CF}_2\text{CH}_3$).

Other advantages and characteristics of the
 invention will become apparent in the following
 examples relating to the preparation and analysis of
 20 copper complexes with the formula :



in which L is 2-methyl-1-hexen-3-yne or 1-hexene-3-yne
 which are compounds whose preparation has already been
 described in the prior art and which are known in
 5 particular as polymerization agents.

Example 1 :

The ligand used in this example is 2-methyl-1-hexen-3-yne that is commercially available. The copper complex was synthesized using a method described in the
 10 prior art (P. Doppelt, T. H. Baum and L. Ricard, Inorg. Chem. 35, 1286, 1996). Its characteristics are as follows : Anal. Calculated for $\text{CuC}_{12}\text{H}_{11}\text{F}_6\text{O}_2$: C, 39.6 ; H, 3.05 ; F, 31.32 ; Cu, 17.3. Found : C, 40.0 ; H, 3.10 ; Cu 17.0. m.p. = 15°C. IR (liquid between two NaCl
 15 discs) : 2983 (f), 2016.3 (f. $\text{C}\equiv\text{C}$), 1671 (m), 1556 (m), 1531 (m), 1490 (s), 1348 (f), 1258 (F), 1203 (F), 1147 (F), 1104 (f), 917 (f), 800 (m), 673 (m), 665 (m), 581 (m), cm^{-1} . ^1H NMR (Bruker, 300 Mhz, CDCl_3 , 20°C) : δ 1.34 (t, 9 Hz, CH_3), 2.07 (s, CH_3), 2.71 (q, 9 Hz, CH_2),
 20 5.33 (s = CH), 5.58 (s, = CH), 6.18 (s, C-H hfac), ^{13}C NMR : δ 13.74 (s, CH_3), 16.24 (s, CH_3), 23.73 (s, CH_2), 87.68 (s, C-H), 89.90 (s, $\text{C}\equiv\text{C}$), 95.76 (s, $\text{C}\equiv\text{C}$), 117.82 (q, 315 MHz, CF_3), 121.54 (s, $\text{C}\equiv\text{C}$), 178.12 (q, 32 Hz, $\text{C}=\text{O}$).

25

Example 2 :

The ligand used in this example is 1-hexene-3-yne which is not commercially available but whose characteristics are known. This compound was prepared by adapting a method described in the prior art (G. Eglinton and M. C. Whiting, J. Org. Chem. 3650 (1950). The copper complex was synthesized as in example 1, and its characteristics are the following : m.p. = 18°C. IR (liquid between two NaCl discs) : 2986 (f), 2944 (f), 2885 (rf), 2016.4 (f, C≡C), 1641 (m), 1556 (m), 1531 (m), 1472 (s), 1409 (m), 1348 (f), 1257 (F), 1202 (F), 1147 (F), 1102 (f), 967 (f), 800 (m), 673 (m), 589 (m), cm⁻¹. ¹H NMR (Bruker, 300 MHz, CDCl₃, 20°C) : δ 1.37 (t, 7.3 Hz, CH₃), 2.67 (qd, 1.5 and 7.5 Hz, CH₂), 5.47 (dd, 1.5 and 10.7 Hz, =CHH), 5.8 (dd, 1.5 and 16.9 Hz, =CHH), 6.05 (ddt, 16.9, 1.5 and 10.7 Hz, =CH, 6.15 (s, C-H, hfac), ¹³C NMR ; δ 13.49 (s, CH₃), 16.05 (s, CH₂), 83.72 (s, C≡C), 89.77 (s, C-H), 96.15 (s, C≡C), 112.5 (s, =CH), 117.8 (q, 315 Hz, CF₃), 121.91 (s, C=C), 178.27 (q, 32 Hz, C=O).

Example 3 : analysis of the complexes in examples 1 and 2

With the NMR spectrum of the proton it is possible to determine the stoichiometry of the complexes by comparing the peak integration of the ligand and of H methine of hexafluoroacetylacetonate ; this ratio is definitely 1 which confirms the structure of the complexes given in examples 1 and 2.

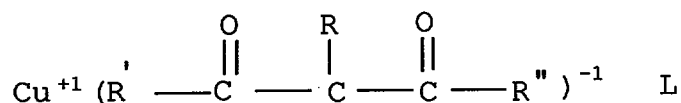
The NMR spectra of ¹³C lead to asserting that the copper is bound to the triple bond by comparing the peaks of the free ligand and of the chelated ligand. The new complexes of the invention are much more stable

than the corresponding complex in which the ligand is 3-hexyne ; in the latter case it has been shown that the triple bond is capable of chelating (hfac)Cu⁺ ions to yield a much less stable complex. With the complexes
5 of the invention, however, the triple bond is sufficiently deactivated owing to the combining of two insaturations to prevent the formation of binuclear complexes.

The complexes of examples 1 and 2 are both
10 yellow liquids at ambient temperature. They have been successfully used as precursors to deposit films of metallic copper by CVD. They offer both good volatility, and consequent rapid growth of the copper film, and great stability at evaporation temperature.
15 By way of comparison, for the complex in example 1, the temperature of the bubbler was maintained at 65°C with no detectable degradation after two periods of 12 hours.

CLAIMS

1 Complex compound of oxidised copper (+1) stabilised by a ligand for the gas phase chemical deposit of copper having the general formula (I) :



5

in which R' and R'', identical or different, are a lower alkyl, optionally substituted by one or more halogen atoms such as fluorine, R is chosen from among
 10 a hydrogen atom, a halogen atom such as fluorine, a lower alkyl optionally substituted by one more halogen atoms such as fluorine, and L represents the ligand stabilising said complex, characterized in that L is an alkyne of which the triple bond is partially
 15 deactivated by one or two groups slightly attracting the electrons carried by said alkyne.

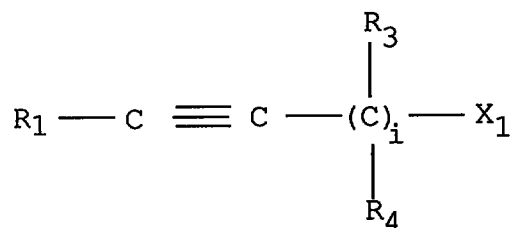
2. Complex according to claim 1, characterized in that L is an alkyne of which the triple bond is partially deactivated by two groups slightly attracting
 20 electrons arranged either side of said triple bond.

3. Complex compound of oxidised copper (+1) stabilised by a ligand for the gas phase chemical deposit of copper, characterized in that said ligand L meets the following formula (II) :

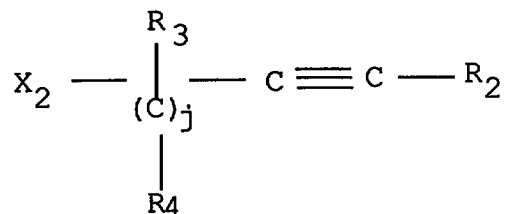
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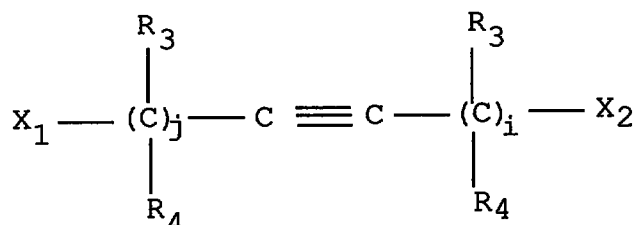


or formula (III) as follows :



or formula (IV) as follows :

5



in which R_1 , R_2 , R_3 and R_4 , identical or different, are chosen from among a hydrogen atom, a lower alkyl substituted by one or more fluorine atoms, a $-\text{Si}(\text{R}_5)_3$ group in which R_5 is a lower alkyl, i and j are 0 to 3 and X_1 and X_2 , identical or different, represent a group that is slightly electron-attracting.

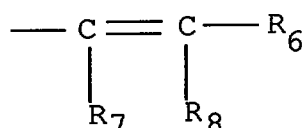
4. Complex compound of oxidised copper (+1) stabilised by a ligand for the gas phase chemical deposit of copper according to claim 3, characterized

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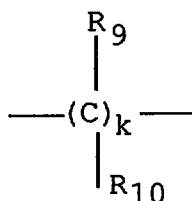
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in that said ligand meets one of formulas (II), (III) or (IV) in which X_1 and X_2 , identical or different, are radicals with formula (V) as follows:



5

in which R_6 , R_7 and R_8 are chosen from among a hydrogen atom, a lower alkyl substituted by one or more fluorine atoms, a $\text{Si}(\text{R}_5)_3$ group in which R_5 is a lower alkyl, or in which R_6 and R_2 together or R_6 and R_1 together, or two R_6 radicals together form a group having the following formula (VI) :



in which R_9 and R_{10} are chosen from among a hydrogen atom, a lower alkyl substituted by one or more fluorine atoms, a $\text{Si}(\text{R}_5)_3$ group in which R_5 is a lower alkyl, and k is 1 to 3 such as to form ligands having cyclical formulas.

5. Complex according to claim 4, characterized in that it meets formula (IV) in which X_1 and X_2 are of formula (V) and i or j is different from 0.

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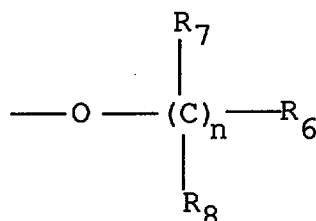
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6. Complex according to claim 4, characterized in that L is 2-methyl-1-hexen-3-yne.

7. Complex according to claim 4, characterized in that L is 1-hexene-3-yne.

5 8. Complex compound of oxidised copper (+1) stabilised by a ligand for the gas phase chemical deposit of copper according to claim 3, characterized in that said ligand meets one of formulas (II), (III) or (IV) in which X_1 and X_2 , identical or different, are
10 radicals of formula (VII) as follows :



in which R_6 , R_7 , R_8 have the same denotation as in claim 4, and n is 0 to 8.

9. Complex compound of oxidised copper (+1)
15 stabilised by a ligand for the gas phase chemical despoit of copper according to claim 3, characterized in that said ligand meets formula (IV) in which X_1 and X_2 of formulas (V) or (VII) are different.

10. Complex according to any one of claims 3
20 to 9, characterized in that in formulas (II), (III), (IV), (V), (VI) and (VII) the lower alkyls are chosen from among alkyls at C_1 to C_8 either linear or branched optionally substituted by one or fluorine atoms.

11. Method for the gas phase chemical
25 deposit of a metallic copper film on a substrate by

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contact of said substrate with an organometallic copper precursor volatile in gas phase, characterized in that a complex according to any of claims 1 to 10 is used as said precursor.

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