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**Dicopper(I) oxalate complexes as precursor for
metallic copper deposition**

Dicopper(I) oxalate complexes as precursor for metallic copper deposition

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The invention relates to dicopper(I) oxalate complexes stabilised by neutral Lewis bases, such as alkenes or alkynes, and to the use of dicopper(I) oxalate complexes as precursor for the deposition of metallic copper, in which the neutral Lewis bases used are alkynes, alkenes, triarylphosphines, CO or isonitriles.

1. Prior art and object of the invention

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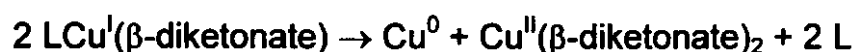
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Many organocopper precursors are now known for the deposition of thin copper films on substrates. Highly promising substances have proven to be copper compounds in oxidation state +1 which contain a β -diketonate ligand and a neutral Lewis base L, such as, for example, an alkene or an alkyne. Complexes of this type and the use thereof as precursors in the CVD (chemical vapour deposition) process are described, for example, in US 5,220,044, WO 00/71550, WO 00/17278, US 6,130,345 or in Chem. Mater. **2001**, 13, 3993; Inorg. Chem. **2001**, 40, 6167; Chem. Mater. **1992**, 4, 365; Organometallics **2001**, 20, 4001. Preference is given to the use of fluorine-containing β -diketonate ligands, such as, for example, hexafluoroacetyl acetate, since the corresponding copper(I) complexes have much higher thermal stability and higher volatility than their fluorine-free analogues. Fluorine-free copper(I) β -diketonate complexes, such as, for example, alkyne-stabilised copper(I) acetylacetonates, are extremely sensitive to oxygen, decompose even at 0°C (Chem. Ber. **1995**, 128, 525) and are thus not suitable as precursors for the CVD process. The copper layer is deposited in a thermally induced disproportionation reaction in accordance with the following equation:

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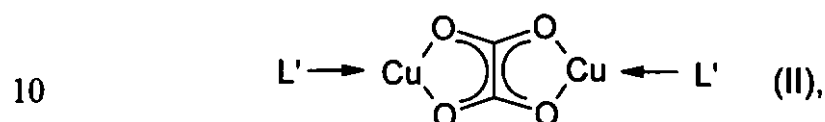
The resultant $\text{Cu}^{\text{II}}(\beta\text{-diketonate})_2$ and the Lewis base L are volatile under the conditions used in the CVD process and can thus be removed from the system. Ideally, a high-purity copper film remains. However, only 50% of the copper(I) precursor employed can be converted into copper(0) in this reaction; the remaining 50% end up in the corresponding $\text{Cu}^{\text{II}}(\beta\text{-diketonate})_2$. The same result is obtained on use of β -keto esters instead of β -diketones, as described, for example, in WO 00/08225 or in US 5,441,766. However, it has proven disadvantageous on use of fluorine-containing copper(I) precursors that the adhesion of the copper films to various substrate surfaces is not optimal, which can probably be attributed to the van der Waals forces of the fluorine atoms in the precursor molecule and thus to repulsive interactions. In addition, there is a risk of contamination of the wafer in microelectronics, especially of the silicon with fluorine, which results in the wafer being unusable.

Complete conversion of the copper is achieved with Lewis base-stabilised copper(I) alkoxides of the formula $\text{LCu}^{\text{I}}\text{OR}$ (EP 0468396) and with Lewis base-stabilised cyclopentadienylcopper(I) compounds of the formula $\text{LCu}^{\text{I}}(\eta^5\text{-C}_5\text{R}_5)$, described in EP 0297348 and DE 4124686. Some of the examples in the cited patents are even fluorine-free and stable at 25°C. However, since the thermal decomposition reactions do not proceed in a defined way in these cases, free-radical species are formed in the decomposition reactions, unfortunately resulting in contaminated copper films (oxygen about 5%, carbon about 1%) (MRS Bulletin/August 1994, 41; Chem.Mater. 1992, 4, 577).

The object of the present invention was therefore to provide fluorine-free copper(I) precursors for the deposition of metallic copper which are simple and inexpensive to prepare, are thermally and if possible air-stable, and can be converted fully into metallic copper films in a defined thermal decomposition reaction in the temperature range of about 50-400°C with formation of defined molecular, copper-free, non-toxic and if possible gaseous by-products. Further objects of the present invention consist in providing a process for the preparation of the precursor substances according to the invention which is simple and inexpensive to carry out and a suitable process for the production of thin high-purity

copper films or layers with the aid of these precursors and thus improved high-purity thin copper layers.

5 In accordance with the invention, the compounds of the general formula (II) are used for the production of high-purity thin copper-metal layers



in which copper is in oxidation state +1, and

15 L' is an unsaturated hydrocarbon containing at least one olefinic or acetylenic group or CO, $P(\text{aryl})_3$ or isonitrile $RN \equiv C$,

where

R is A, aryl or alkylaryl

and

20 A is straight-chain or branched C1-C30-alkyl, C3-C30-cycloalkyl, straight-chain or branched C2-C30-alkenyl, or straight-chain or branched C3-C30-cycloalkenyl,

aryl is C6-C10-aryl,

25 alkylaryl is C7-C18-alkylaryl.

Good results are obtained using the compounds of the general formula (II) in which

30 L' is an unsaturated hydrocarbon from the series consisting of open-chain C2-C30-alkenes and cyclic C4-C30-alkenes, open-chain C2-C30-alkynes and cyclic C10-C30-alkynes, CO, $P(\text{aryl})_3$ and $RN \equiv C$,

where

35 R is A,

aryl is phenyl

- 4 -

and

A is straight-chain or branched C1-C30-alkyl or C3-C30-cycloalkyl.

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Particularly good results are achieved using the compounds of the general formula (II) in which

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L' is an unsaturated hydrocarbon from the series consisting of open-chain C2-C15-alkenes and cyclic C4-C15-alkenes, open-chain C2-C15-alkynes and cyclic C10-C15-alkynes, CO, $P(C_6H_5)_3$ and $RN\equiv C$,

where

R is A and

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A is straight-chain or branched C1-C8-alkyl or C3-C10-cycloalkyl.

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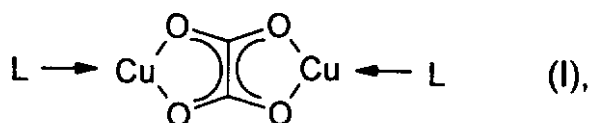
From this group, very particular preference is given to compounds in which open-chain C2-C15-alkene is ethene, propene, the isomers of butene, pentene, hexene, heptene, octene, nonene or decene, and/or cyclic C4-C15-alkene is cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclopentadiene, cyclohexadiene, cyclo-octadiene, norbornene or norbornadiene, which may be substituted by a hydrocarbon, and/or open-chain C2-C15-alkyne is acetylene, propyne, the isomers of butyne, pentyne, hexyne, heptyne, octyne, nonyne, decyne or diphenylacetylene, and/or cyclic C10-C15-alkyne is cyclodecyne, cyclodecadiyne, cyclododecyne or cyclododecadiyne, which may be substituted by a hydrocarbon. Equally preferred are compounds in which L' is one of the isonitriles cyclohexyl isonitrile or phenyl isonitrile.

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The object according to the invention is preferably achieved by compounds of the general formula (I)



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in which copper is in oxidation state +1, and

L is a hydrocarbon from the series consisting of open-chain alkyne of the formula $R-C\equiv C-R'$ and cyclic C10-C20-alkyne and open-chain internal alkene of the formula $R''HC=CHR'''$ and cyclic C4-C20-alkene,

10

where

R and R' are H, A, alkylaryl or alkynyl,

15

R'' and R''' are A, aryl, alkylaryl or alkynyl,

where L, R, R', R'' and R''' may each, independently of one another, adopt identical or different meanings in different positions of the molecule,

and

20

A is straight-chain or branched C1-C30-alkyl, C3-C30-cycloalkyl, straight-chain or branched C2-C30-alkenyl, or straight-chain or branched C3-C30-cycloalkenyl,

aryl is C6-C10-aryl,

25

alkylaryl is C7-C18-alkylaryl,

alkynyl is straight-chain or branched C2-C30-alkynyl.

30

These novel compounds are a further subject-matter of the present invention.

Compounds according to the invention are preferably also compounds of the general formula (I) in which

35

A is straight-chain or branched C1-C9-alkyl, straight-chain or branched C3-C9-cycloalkyl, straight-chain or branched C2-

C9-alkenyl, or straight-chain or branched C3-C9-cyclo-alkenyl,

aryl is phenyl or naphthyl,

5 alkylaryl is tolyl or mesityl,

alkynyl is straight-chain or branched C2-C9-alkynyl,

and L, R, R', R'' and R''' may each, independently of one another, adopt identical or different meanings in different positions of the molecule.

10 Further preferred sub-groups are formed by compounds of the general formula (I) in which

I.

A is straight-chain or branched C1-C4-alkyl from the group consisting of methyl, ethyl, n- and i-propyl and n-, i- and
15 tert-butyl, C3-C6-cycloalkyl from the group consisting of cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl, straight-chain or branched C2-C6-alkenyl from the group consisting of vinyl, propenyl, butenyl, pentenyl and hexenyl, or C3-C6-cycloalkenyl from the group consisting of cyclopropenyl,
20 cyclobutenyl, cyclopentenyl, cyclopentadienyl and methyl-cyclopentadienyl,

aryl is phenyl or naphthyl,

alkylaryl is tolyl or mesityl,

25 alkynyl is straight-chain or branched C2-C6-alkynyl from the group consisting of ethynyl, propynyl, butynyl, pentynyl and hexynyl,

and R, R', R'' and R''' may each, independently of one another, adopt identical or different meanings in different positions of the molecule,

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or

II.

in which L is an open-chain alkyne selected from the group consisting of
35 Me-C $\equiv$ C-Me, Et-C $\equiv$ C-Et, Pr-C $\equiv$ C-Pr and Bu-C $\equiv$ C-Bu

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or

III.

5 in which L is a cyclic alkyne selected from the group consisting of cyclodecyne, cyclodecadiyne, cyclododecyne and cyclododecadiyne

or

IV.

10 in which L is an open-chain internal alkene selected from the group consisting of $\text{HR}''\text{C}=\text{CHR}'''$, in which R'' and R''' are, independently of one another, CH_3 , C_2H_5 , C_3H_7 or C_4H_9 ,

or

15 V.

in which L is a cyclic alkene selected from the group consisting of cyclobutene, cyclopentene, cyclopentadiene, cyclohexene, cyclohexadiene, cycloheptene, cycloheptadiene, cyclooctene, cyclooctadiene, norbornene and norbornadiene.

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The object of the present invention is particularly preferably achieved by the novel compounds of the general formula (I)

25 di[(3-hexyne)copper(I)] oxalate and
di[(norbornene)copper(I)] oxalate.

The compounds according to the invention or compounds which can be used in accordance with the invention can be obtained by a process in
30 which Cu_2O is reacted with oxalic acid and a Lewis base L in an inert solvent, and the resultant product is isolated. This process is likewise a subject-matter of the present invention.

High-purity thin copper-metal layers are produced by a process in which
35 compounds of the general formula (II) are heated, causing the elimination of the Lewis base L' and deposition of metallic copper by

decarboxylation. This production process is also a subject-matter of the present invention.

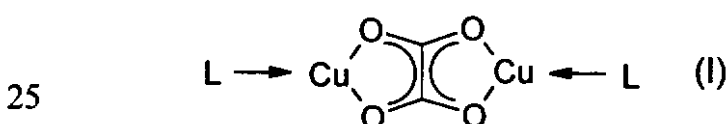
5 The elimination of the Lewis base L' is preferably carried out in a temperature range of from about 50 to about 200°C. The decarboxylation with formation of metallic copper and carbon dioxide which takes place as the second reaction is preferably completed in a temperature range of from about 150 to 350°C.

10 The eliminated Lewis base L' is preferably recycled, re-employed in a process for the preparation of the compounds of the general formula (II) and used for the production of high-purity thin metallic copper layers.

15 The object according to the invention is thus achieved, in particular, by high-purity thin metallic copper layers having improved properties produced using a compound of the general formula (II) in the process according to the invention.

20 2. Detailed description of the invention

The present invention provides compounds of the general formula (I)



in which, in each case independently of the position in the complex and independently of one another,

30 L is an open-chain alkyne $R-C\equiv C-R'$ or a cyclic alkyne, or an open-chain alkene $R''HC=CHR'''$ or a cyclic alkene. The oxidation state of the copper is +1.

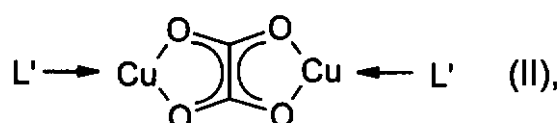
35 R and R' may, independently of one another, be H or a hydrocarbon from the series consisting of alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkylaryl and alkynyl.

R'' and R''' may, independently of one another, be a hydrocarbon from the series consisting of alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkylaryl and alkynyl.

5 The compound of the general formula (I) is prepared by reaction of Cu₂O, oxalic acid and the neutral ligand L or the two different neutral ligands in an inert aprotic organic solvent. The compounds of the general formula (I) can be isolated in pure form as temperature-stable substances. In addition, the substances obtained are distinguished by
10 surprisingly and unusually high oxidation stability and can be handled in air without problems, which enormously simplifies subsequent use of the substances as precursors for the deposition of metallic copper.

Heating of the compounds of the general formula (II)

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in which copper is in oxidation state +1, and

L' is an unsaturated hydrocarbon containing at least one olefinic or acetylenic group or CO, P(aryl)₃ or isonitrile RN≡C,

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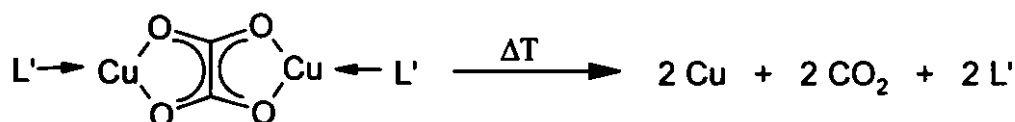
where

R is alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkylaryl or alkynyl,

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leaves a high-purity copper mirror; all by-products are volatile and can thus be removed very simply from the reaction site. The thermal decomposition proceeds in accordance with the following equation:

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Besides metallic copper, the only reaction products formed are carbon dioxide and the Lewis base L', which can be regenerated and re-used.

5 The compounds of the general formula (II) can be used as precursors for the deposition of metallic copper. The deposition can be carried out from the gas phase or from a solution of the precursor and a suitable solvent or from the solid state of the precursor by contact of the precursor with a heated substrate. Compared with the prior art, it is
10 advantageous firstly that copper(I) precursors are accessible with which metallic copper can be deposited, preferably quantitatively, in a defined decomposition reaction with no free radicals with formation of high-purity copper films. The yield of deposited metallic copper can thus be increased from 50 to 100% compared with the prior art. The high
15 stability and insensitivity of the compounds, in particular the high oxidation stability, enormously simplify handling of the compounds in the process for the deposition of metallic copper and thus reduce the costs of the deposition process.

20 The advantages of the compounds of the general formula (II) compared with the substance used in accordance with the prior art (CupraSelect®) are thus: better physical properties, such as higher thermal stability, better chemical properties, such as higher oxidation stability, simpler handling, less expensive synthesis owing to the much less expensive
25 starting material oxalic acid compared with hexafluoroacetylacetone, twice the yield of metallic copper in the deposition process, copper-free and non-toxic by-products, fewer by-products and thus lower environmental pollution. In addition, the compounds contain no fluorine atoms which can result in fluorine contamination and thus in wafers
30 being unusable.

Overall, the synthesis of the copper(I) precursors according to the invention is thus simpler and less expensive than that of the commercially available copper(I) precursor CupraSelect®, which is
35 (trimethylvinylsilane)copper(I) hexafluoroacetylacetonate. At the same time, the precursors according to the invention enable both the quality of

the copper coatings to be increased and the process to be carried out in a more environmentally friendly manner.

5 Compounds of the general formula (I) according to the invention contain an oxalate dianion, two copper centres in oxidation state +1 and at least two neutral ligands L, where the oxalate dianion is bonded to the two copper(I) centres as a bridge in μ -1,2,3,4 mode. The dicopper(I) oxalate unit $\text{CuO}_2\text{C}_2\text{O}_2\text{Cu}$ is stabilised by coordination of at least two neutral ligands L to the two copper(I) centres, preferably of two identical ligands L, so that the two copper(I) centres have at least a pseudotrigonal-planar, possibly also a tetrahedral environment. The copper atoms present in the complex can be bonded to two different ligands L. For simplification, the following text refers generally to the ligand or the Lewis base L although this may also be taken to mean two different ligands or Lewis bases L.

15 L is an open-chain alkyne $\text{R}-\text{C}\equiv\text{C}-\text{R}'$ or cyclic C10-C20-alkyne or an open-chain alkene $\text{R}''\text{HC}=\text{CHR}'''$ or cyclic C4-C20-alkene. R and R' may in turn, independently of one another, be H, alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkylaryl or alkynyl. R'' and R''' may, independently of one another, be alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkylaryl or alkynyl.

20 Cyclic C10-C20-alkyne may be straight-chain or branched C10-C20-cycloalkyne, preferably straight-chain or branched C10-C15-cycloalkyne, particularly preferably C10-C12-cycloalkyne from the series consisting of cyclodecyne, cyclodecadiyne, cyclododecyne and cyclododecadiyne.

25 Cyclic C4-C20-alkene may be straight-chain or branched C4-C20-cycloalkene, preferably straight-chain or branched C4-C15-cycloalkene, particularly preferably C4-C8-cycloalkene from the series consisting of cyclobutene, cyclopentene, cyclopentadiene, cyclohexene, cyclohexadiene, cycloheptene, cycloheptadiene, cyclooctene, cyclooctadiene, norbornene and norbornadiene.

35 Alkyl groups may be straight-chain or branched C1-C30-alkyl, preferably straight-chain or branched C1-C9-alkyl, particularly preferably straight-

chain or branched C1-C4-alkyl from the group consisting of methyl, ethyl, n- and i-propyl and n-, i- and tert-butyl. Cycloalkyl groups may be straight-chain or branched C3-C30-cycloalkyl, preferably C3-C9-cycloalkyl, particularly preferably C3-C6-cycloalkyl from the group consisting of cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

Alkenyl groups may be straight-chain or branched C2-C30-alkenyl, preferably straight-chain or branched C2-C9-alkenyl, particularly preferably straight-chain or branched C2-C6-alkenyl from the group consisting of vinyl, propenyl, butenyl, pentenyl and hexenyl. Cycloalkenyl groups may be straight-chain or branched C3-C30-cycloalkenyl, preferably C3-C9-cycloalkenyl, particularly preferably C3-C6-cycloalkenyl from the group consisting of cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclopentadienyl and methylcyclopentadienyl.

Aryl groups may be C6-C10-aryl, preferably phenyl or naphthyl. Alkylaryl may be C7-C18-alkylaryl, preferably tolyl or mesityl.

Alkynyl groups may be straight-chain or branched C2-C30-alkynyl, preferably straight-chain or branched C2-C9-alkynyl, particularly preferably straight-chain or branched C2-C6-alkynyl from the group consisting of ethynyl, propynyl, butynyl, pentynyl and hexynyl.

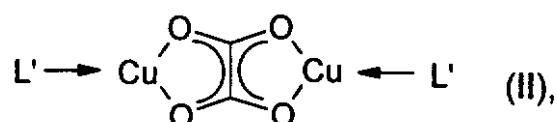
Particularly suitable neutral Lewis bases are open-chain alkynes of the formula $R-C\equiv C-R'$, cyclic alkynes, open-chain alkenes of the formula $R''HC=CHR'''$ and cyclic alkenes. Preference is given to the use of open-chain alkynes from the group consisting of $R-C\equiv C-R'$, and particularly good results are obtained with the alkynes $R-C\equiv C-R'$ (R and $R' = CH_3, C_2H_5, C_3H_7$ or C_4H_9). Preference is given to the use of open-chain alkenes from the group consisting of $R''HC=CHR'''$ (R'' and $R''' = CH_3, C_2H_5, C_3H_7$ or C_4H_9) and cyclic alkenes, and particularly good properties are obtained with the cyclic alkenes cyclohexene and norbornene. Particularly good results are obtained with the alkyne $Et-C\equiv C-Et$ and the alkene norbornene.

The compound of the general formula (I) is preferably prepared by reaction of Cu_2O , oxalic acid and the Lewis base L under a protective-

gas atmosphere in an inert aprotic organic solvent. For this purpose, two different Lewis bases L in an equimolar ratio can be employed as Lewis base L. The sequence of addition of the components can be selected as desired. If the Lewis base L employed is to be a mixture of two corresponding compounds, the two compounds are preferably added simultaneously to the reaction mixture or mixed with one another before the addition. The starting compounds can be pre-dissolved or suspended in a suitable solvent or added as a solid or liquid without a solvent. Suitable solvents for carrying out the reaction are inert aprotic solvents, such as open-chain or cyclic aliphatic and aromatic hydrocarbons, which may be partially halogenated, or ethers and cyclic ethers. Particular preference is given to the use of pentane, hexane, heptane, cyclohexane, toluene, methylene chloride, trichloromethane, chlorobenzene, diethyl ether or tetrahydrofuran. The protective-gas atmosphere used can be nitrogen or argon. The stoichiometric ratio of the starting materials Cu_2O , oxalic acid and the Lewis base L is between 1:1:2 and 1:1:4, preferably between 1:1:2 and 1:1:3 and is particularly preferably 1:1:2. The Lewis base L should not be added in less than the stoichiometric amount with respect to oxalic acid and Cu_2O . The reaction can be carried out in a temperature range of from -30 to +100°C, preferably from 0 to 50°C and very preferably between 20 and 40°C. The highest yields are obtained at room temperature. The reaction time is between 1 and 24 hours, preferably between 2 and 8 hours and very preferably between 3 and 6 hours. The reaction solution changes from a red suspension to a colourless or brownish solution or suspension, depending on the nature of the complex formed. The insoluble constituents are separated off. This can be carried out by filtration, centrifugation or other methods known to the person skilled in the art. A clear colourless, yellow or red solution is obtained, depending on the type of Lewis base L employed. The compounds of the general formula (I) are subsequently isolated. This can be carried out by methods known to the person skilled in the art after removal of the solvent. Further purification is carried out if necessary. Instead of mechanical removal of the solids from the reaction mixture by filtration or other methods, an extraction can also be carried out for removal of the product formed. The compounds of the general formula (I) are, as

already described above, surprisingly temperature-stable and can therefore be isolated well as pure substances and subsequently characterised analytically and spectroscopically.

5 Compounds of the general formula (II) according to the invention



10 can be used for the production of high-purity thin copper-metal layers.

L' is an open-chain alkyne $R-C\equiv C-R'$, cyclic alkyne, open-chain alkene $RHC=CHR'$, cyclic alkene, CO, $P(\text{aryl})_3$ or isonitrile $RN\equiv C$. R and R' may in turn, independently of one another, be H, alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkylaryl or alkynyl.

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The meanings of alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, alkylaryl or alkynyl correspond to the meanings in the compounds of the general formula (I).

20 Cycloalkyne may be straight-chain or branched C10-C20-cycloalkyne, preferably straight-chain or branched C10-C15-cycloalkyne, particularly preferably C10-C12-cycloalkyne from the series consisting of cyclodecyne, cyclodecadiyne, cycloundecyne, cycloundecadiyne, cyclododecyne and cyclododecadiyne.

25 Cycloalkene may be straight-chain or branched C4-C20-cycloalkene, preferably straight-chain or branched C4-C15-cycloalkene, particularly preferably C4-C8-cycloalkene from the series consisting of cyclobutene, cyclopentene, cyclopentadiene, cyclohexene, cyclohexadiene, cycloheptene, cycloheptadiene, cyclooctene, cyclooctadiene, norbornene and norbornadiene.

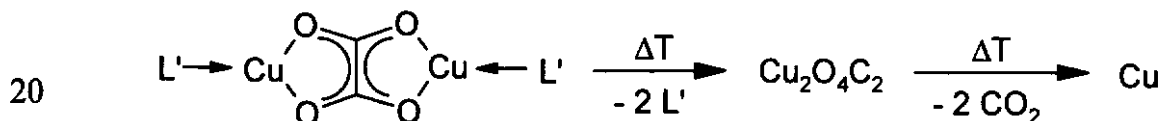
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Particularly suitable neutral Lewis bases L' are open-chain alkynes of the formula $R-C\equiv C-R'$, cyclic alkynes, open-chain alkenes of the formula $RHC=CHR'$, cyclic alkenes, CO, $P(\text{aryl})_3$ and $RN\equiv C$. Preference is given to the use of open-chain alkynes from the group consisting of $R-C\equiv C-R'$, open-chain alkenes of the formula $RHC=CHR'$, cyclic alkenes, CO and

35

RN $\equiv$ C. Particularly good results are obtained with the alkynes R-C $\equiv$ C-R' (R and R' = CH₃, C₂H₅, C₃H₇ or C₄H₉), with the open-chain alkenes RHC=CHR' (R and R' = CH₃, C₂H₅, C₃H₇ or C₄H₉), with the cyclic alkenes cyclohexene and norbornene, with CO and RN $\equiv$ C (R = C₄H₉, C₆H₁₁ or C₆H₅). Preference is given to the use of open-chain alkenes from the group consisting of RHC=CHR' (R and R' = CH₃, C₂H₅, C₃H₇ or C₄H₉), the cyclic alkenes cyclohexene and norbornene, CO and C₆H₁₁N $\equiv$ C, and particularly good properties are obtained with the open-chain alkyne Et-C $\equiv$ C-Et, the cyclic alkene norbornene, CO and C₆H₁₁N $\equiv$ C. Particularly good results are obtained with the alkyne Et-C $\equiv$ C-Et and the alkene norbornene.

The thermal behaviour of the compounds can be investigated by TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry). Investigations carried out have shown that the decomposition of the compounds according to the invention takes place in two main steps:



Firstly, the Lewis base L' is eliminated from the copper(I) complex. This elimination can also take place in steps, depending on the compound, and can be detected by TGA. In the second step, decarboxylation takes place through an internal redox reaction of the remaining fragment CuO₂C₂O₂Cu, with formation of metallic copper and carbon dioxide. The first step takes place, depending on the precursor, in a temperature range of from about 50 to about 200°C, and the second from about 150°C and is complete at about 350°C. However, it is perfectly possible for the elimination of the Lewis bases and the decarboxylation reaction to proceed in parallel at the transition to higher temperatures. The residual content corresponds precisely to the copper content in the corresponding copper(I) precursor, so that the yield of metallic copper is 100% with the compounds of the general formula (II) and is thus twice as high as that in the prior art.

5 This efficient decomposition reaction causes the formation of fewer by-products with the compounds of the general formula (II) compared with the prior art. The free Lewis base L' re-forms in the deposition process and can be collected by appropriate equipment, such as, for example, cold traps in the exhaust air, and re-used; the second by-product formed is carbon dioxide. The by-products are thus copper-free, non-toxic and thus less hazardous compared with the prior art, in which copper(II) hexafluoroacetylacetonate and the Lewis base trimethylvinylsilane are formed as by-products. The environmental pollution is thus considerably lower than on use of the compounds from the prior art.

10 (Norbornene)₂Cu₂O₄C₂ has proven to be a thermally stable and very oxidation-insensitive compound. The compound is stable up to 100°C and can be handled in air over an extended period. This is an enormous advance compared with the prior art, since CupraSelect® decomposes slowly even from about 50°C, and the compound is also oxidised rapidly in air to give copper(II). This enables very much simpler handling, not only in the synthesis, but also in the deposition process.

20 The compounds of the general formula (II) can be used as precursors for the deposition of metallic copper. The deposition of metallic copper films can be carried out from the gas phase or from a solution of the precursor and a suitable solvent or from the solid state of the precursor by contact of the precursor with a heated substrate.

25 Examples are given below for illustration and for better understanding of the present invention. However, these are not suitable, owing to the general validity of the inventive principle described, for reducing the scope of protection of the present application merely to these examples. Furthermore, the contents of the cited patent applications are to be regarded as part of the disclosure content of the present invention, which is based on the description.

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3. Examples

Example 1

Di[(3-hexyne)copper(I)] oxalate

3 ml of $\text{EtC}\equiv\text{CEt}$ and 1.1 g of oxalic acid are added to a suspension of 1.8 g of Cu_2O in 30 ml of methylene chloride under an inert-gas atmosphere, and the mixture is stirred at room temperature for 4 hours. In order to remove insoluble residues, the solution is passed through a frit with silica gel, and the residue is washed twice on the frit with methylene chloride. The colourless solution is evaporated, and colourless crystals of $(\text{EtC}\equiv\text{CEt})_2\text{Cu}_2\text{O}_4\text{C}_2$ are obtained at -30°C .

$\text{C}_{14}\text{H}_{20}\text{Cu}_2\text{O}_4$ (379.40 g/mol). Analysis [%]: calculated: C 44.3, H 5.3, found: C 44.7, H 4.9. IR (KBr) [cm^{-1}]: $\nu_{\text{C}\equiv\text{C}}$ 2053, 2020 (w), ν_{CO_2} 1645 (vs), 1355 (w), 1314 (m). ^1H -NMR (CDCl_3): δ 1.22 (t, 12 H, $^3J = 7.3$ Hz, CH_3), 2.49 (q, 8 H, $^3J = 7.4$ Hz, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 14.4 (CH_3), 15.5 (CH_2), 87.6 ($\text{C}\equiv\text{C}$), 171.4 (COO). MS (m/e (%)): 525 (7) [$\text{M} + \text{Cu}(\text{EtC}\equiv\text{CEt})^+$], 443 (7) [$\text{M} + \text{Cu}]^+$, 227 (100) [$\text{M} - \text{CuO}_4\text{C}_2]^+$, 145 (96) [$\text{M} - (\text{EtC}\equiv\text{CEt})\text{CuO}_4\text{C}_2]^+$. TG (30–1000°C, $5^\circ\text{C}/\text{min}$) three-stage decomposition, 1st stage temperature range 60–120°C weight reduction 22% ($\text{EtC}\equiv\text{CEt}$), 2nd stage temperature range 120–150°C weight reduction 19% ($\text{EtC}\equiv\text{CEt}$), 3rd stage temperature range 200–310°C, weight reduction 24% (2 CO_2), residual content 35% (2 Cu).

Fig. 1 shows the decomposition of the prepared di[(3-hexyne)copper(I)] oxalate as a function of the temperature with deposition of a thin copper layer on a substrate.

Example 2

5 *Di[(norbornene)copper(I)] oxalate*

2.4 g of norbornene and 1.1 g of oxalic acid are added to a suspension of 1.8 g of Cu₂O in 50 ml of methylene chloride under an inert-gas atmosphere, and the mixture is stirred at room temperature for 5 hours. In order to remove insoluble residues, the solution is passed through a frit with silica gel, and the residue is washed twice on the frit with methylene chloride. The colourless solution is evaporated, and colourless crystals of (norbornene)₂Cu₂O₄C₂ are obtained at -30°C.

15 C₁₆H₂₀Cu₂O₄ (403.43 g/mol). IR (KBr) [cm⁻¹]: ν_{C=C} 1473 (w); ν_{CO₂} 1644 (m), 1362 (m), 1303 (vs). ¹H-NMR (CDCl₃) [ppm]: 1.00 (d, ²J = 7.8 Hz, 2 H, H_{endo}), 1.03 (d, ²J = 9.5 Hz, 1 H, H_{anti}), 1.28 (d, ²J = 9.6 Hz, 1 H, H_{syn}), 1.59 (d, ²J = 7.7 Hz, 2 H, H_{exo}), 3.08 (s, 2 H, CH), 5.25 (s, 2 H, =CH). ¹³C{¹H}NMR (CDCl₃) [ppm]: 24.4 (CH₂CH₂), 42.7 (CHCH₂), 45.7 (CHCH₂CH), 109.2 (=CH), 171.4 (COO). TG (30–1000°C, 5°C/min) two-stage decomposition, 1st stage temperature range 100-150°C weight reduction 46% (2 norbornene), 2nd stage temperature range 200-300°C, weight reduction 23% (2 CO₂), residual content 31% (2 Cu).

25 Fig. 2 shows the decomposition of the prepared di[(norbornene)-copper(I)] oxalate as a function of the temperature with deposition of a thin copper layer on a substrate.

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List of figures:

5 Fig. 1 shows the decomposition of the di[(3-hexyne)copper(I)] oxalate prepared as described in Example 1 as a function of the temperature with deposition of a thin copper layer on a substrate (TGA measurement).

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15 Fig. 2 shows the decomposition of the di[(norbornene)copper(I)] oxalate prepared as described in Example 2 as a function of the temperature with deposition of a thin copper layer on a substrate (TGA measurement).

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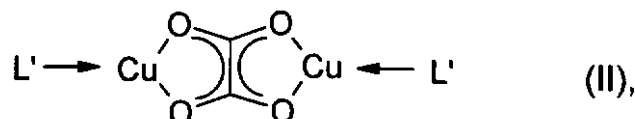
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PATENT CLAIMS

1. Use of compounds of the general formula (II) for the production of high-purity thin copper-metal layers

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in which copper is in oxidation state +1, and

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L' is an unsaturated hydrocarbon containing at least one olefinic or acetylenic group or CO, $P(\text{aryl})_3$ or isonitrile $RN \equiv C$,

where

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R is A, aryl or alkylaryl

and

A is straight-chain or branched C1-C30-alkyl, C3-C30-cycloalkyl, straight-chain or branched C2-C30-alkenyl, or straight-chain or branched C3-C30-cycloalkenyl,

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aryl is C6-C10-aryl,

alkylaryl is C7-C18-alkylaryl.

25

2. Use according to Claim 1 of compounds of the general formula (II) in which

L' is an unsaturated hydrocarbon from the series consisting of open-chain C2-C30-alkenes and cyclic C4-C30-alkenes, open-chain C2-C30-alkynes and cyclic C10-C30-alkynes, CO, $P(\text{aryl})_3$ and $RN \equiv C$,

30

where

R is A,

aryl is phenyl

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and

A is straight-chain or branched C1-C30-alkyl or C3-C30-cycloalkyl.

3. Use according to Claim 1 of compounds of the general formula (II) in which

L' is an unsaturated hydrocarbon from the series consisting of open-chain C2-C15-alkenes and cyclic C4-C15-alkenes, open-chain C2-C15-alkynes and cyclic C10-C15-alkynes, CO, $P(C_6H_5)_3$ and $RN \equiv C$,

where

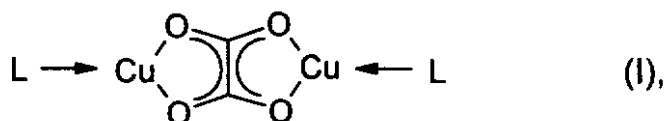
R is A and

A is straight-chain or branched C1-C8-alkyl or C3-C10-cycloalkyl.

4. Use according to Claim 1 of compounds of the general formula (II) in which open-chain C2-C15-alkene is selected from ethene, propene, the isomers of butene, pentene, hexene, heptene, octene, nonene or decene, and/or cyclic C4-C15-alkene is selected from cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclopentadiene, cyclohexadiene, cyclooctadiene, norbornene or norbornadiene, which may be substituted by a hydrocarbon, and/or open-chain C2-C15-alkyne is selected from acetylene, propyne, the isomers of butyne, pentyne, hexyne, heptyne, octyne, nonyne, decyne or diphenylacetylene, and/or cyclic C10-C15-alkyne is selected from cyclodecyne, cyclodecadiyne, cyclododecyne or cyclododecadiyne, which may be substituted by a hydrocarbon, and/or L' is one of the isonitriles cyclohexyl isonitrile or phenyl isonitrile.

5. Use according to Claim 1 of compounds of the general formula (I)

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in which copper is in oxidation state +1, and

L is a hydrocarbon from the series consisting of open-chain alkyne of the formula $R-C\equiv C-R'$ and cyclic C10-C20-alkyne and open-chain internal alkene of the formula $R''HC=CHR'''$ and cyclic C4-C20-alkene,

where

R and R' are H, A, alkylaryl or alkynyl,

R'' and R''' are A, aryl, alkylaryl or alkynyl,

where L, R, R', R'' and R''' may each, independently of one another, adopt identical or different meanings in different positions of the molecule,

and

A is straight-chain or branched C1-C30-alkyl, C3-C30-cycloalkyl, straight-chain or branched C2-C30-alkenyl or straight-chain or branched C3-C30-cycloalkenyl,

aryl is C6-C10-aryl,

alkylaryl is C7-C18-alkylaryl,

alkynyl is straight-chain or branched C2-C30-alkynyl.

6. Process for the production of high-purity thin copper-metal layers, characterised in that compounds of the general formula (II) according to at least one of Claims 1 to 6 are heated, causing the elimination of the Lewis base L' and deposition of metallic copper.

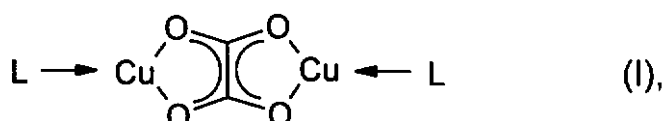
7. Process according to Claim 6, characterised in that the elimination of the Lewis base L' is carried out in a temperature range of from 50 to about 200°C, and the decarboxylation with formation of metallic copper is completed in a temperature range of from 150 to 350°C.

8. Process according to at least one of Claims 6 and 7, characterised in that the eliminated Lewis base L' is recycled, re-employed in a process according to Claim 6 or 7 and used for the production of high-purity thin metallic copper layers.

9. High-purity thin metallic copper layer produced using a compound of the general formula (II) according to at least one of Claims 1 to 5.

10. Compounds of the general formula (I)

5



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in which copper is in oxidation state +1, and

L is a hydrocarbon from the series consisting of open-chain alkyne of the formula $R-C\equiv C-R'$ and cyclic C10-C20-alkyne and open-chain internal alkene of the formula $R''HC=CHR'''$ and cyclic C4-C20-alkene,

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where

R and R' are H, A, alkylaryl or alkynyl,

R'' and R''' are A, aryl, alkylaryl or alkynyl,

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where L, R, R', R'' and R''' may each, independently of one another, adopt identical or different meanings in different positions of the molecule,

and

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A is straight-chain or branched C1-C30-alkyl, C3-C30-cycloalkyl, straight-chain or branched C2-C30-alkenyl, or straight-chain or branched C3-C30-cycloalkenyl,

aryl is C6-C10-aryl,

alkylaryl is C7-C18-alkylaryl,

alkynyl is straight-chain or branched C2-C30-alkynyl.

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11. Compounds of the general formula (I) according to Claim 10, in which

A is straight-chain or branched C1-C9-alkyl, straight-chain or branched C3-C9-cycloalkyl, straight-chain or branched C2-C9-alkenyl, or straight-chain or branched C3-C9-cycloalkenyl,

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aryl is phenyl or naphthyl,
alkylaryl is tolyl or mesityl,
alkynyl is straight-chain or branched C2-C9-alkynyl,
and L, R, R', R'' and R''' may each, independently of one another,
5 adopt identical or different meanings in different positions of the molecule.

12. Compounds of the general formula (I) according to Claim 10, in which

10 A is straight-chain or branched C1-C4-alkyl from the group consisting of methyl, ethyl, n- and i-propyl and n-, i- and tert-butyl, C3-C6-cycloalkyl from the group consisting of cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl, straight-chain or branched C2-C6-alkenyl
15 from the group consisting of vinyl, propenyl, butenyl, pentenyl and hexenyl, or C3-C6-cycloalkenyl from the group consisting of cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclopentadienyl and methylcyclopentadienyl,
20 aryl is phenyl or naphthyl,
alkylaryl is tolyl or mesityl,
alkynyl is straight-chain or branched C2-C6-alkynyl from the group consisting of ethynyl, propynyl, butynyl, pentynyl and hexynyl,
25 and R, R', R'' and R''' may each, independently of one another, adopt identical or different meanings in different positions of the molecule.

30 13. Compounds of the general formula (I) according to Claim 10, in which L is an open-chain alkyne selected from the group consisting of Me-C $\equiv$ C-Me, Et-C $\equiv$ C-Et, Pr-C $\equiv$ C-Pr and Bu-C $\equiv$ C-Bu.

35 14. Compounds of the general formula (I) according to Claim 10, in which L is a cyclic alkyne selected from the group consisting of cyclodecyne, cyclodecadiyne, cyclododecyne and cyclododecadiyne.

15. Compounds of the general formula (I) according to Claim 10, in which L is an open-chain internal alkene selected from the group consisting of $\text{HR}''\text{C}=\text{CHR}'''$, in which R'' and R''' are, independently of one another, CH_3 , C_2H_5 , C_3H_7 or C_4H_9 .
- 5 16. Compounds of the general formula (I) according to Claim 10, in which L is a cyclic alkene selected from the group consisting of cyclobutene, cyclopentene, cyclopentadiene, cyclohexene, cyclohexadiene, cycloheptene, cycloheptadiene, cyclooctene, cyclooctadiene, norbornene and norbornadiene.
- 10 17. Compounds of the general formula (I) according to Claim 10, characterised in that they are di[(3-hexyne)copper(I)] oxalate and/or di[(norbornene)copper(I)] oxalate.
- 15 18. Process for the preparation of the compounds of the general formula (I) according to at least one of Claims 10 to 17, characterised in that Cu_2O is reacted with oxalic acid and a Lewis base L in an inert solvent, and the resultant product is isolated.
- 20 19. Process according to Claim 18, characterised in that an inert aprotic organic solvent is used which is an open-chain or cyclic aliphatic or aromatic hydrocarbon, a halogenated aliphatic or halogenated aromatic hydrocarbon or a linear or cyclic ether or a mixture of these hydrocarbons, where the solvent is preferably selected from the group consisting of pentane, hexane, heptane, cyclohexane, 25 toluene, methylene chloride, trichloromethane, chlorobenzene, diethyl ether and tetrahydrofuran.
- 30 20. Process according to Claim 18, characterised in that it is carried out under a protective-gas atmosphere, where the protective gas employed is preferably nitrogen or argon.
- 35 21. Process according to Claim 18, characterised in that the Lewis base L is employed in excess relative to the stoichiometric ratio of the starting materials Cu_2O and oxalic acid, but at least in twice the stoichiometric ratio.

22. Process according to at least one of Claims 18 to 21, characterised in that the starting materials Cu_2O , oxalic acid and Lewis base L are employed in a stoichiometric ratio of from 1:1:2 to 1:1:4.
- 5 23. Process according to one or more of Claims 18-21, characterised in that two different Lewis bases L are employed in the same molar amounts.
- 10 24. Process according to one or more of Claims 18 – 23, characterised in that the reaction is carried out within a reaction time of from 1 to 24 hours in a temperature range of from -30 to +100°C, preferably at room temperature.
- 15 25. Process according to one or more of Claims 18 to 24, characterised in that, when the reaction is complete, insoluble constituents are separated off, preferably by extraction, and the reaction product is isolated from the solution, and, if necessary, purified, or in that the reaction product is separated off from the reaction mixture by extraction, isolated and, if necessary, purified.

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