Process for the Generation of Metallic Films

Description

The present invention is in the field of processes for the generation of thin inorganic films on substrates, in particular atomic layer deposition processes.

With the ongoing miniaturization, e.g. in the semiconductor industry, the need for thin inorganic films on substrates increases while the requirements of the quality of such films become stricter. Thin metal films serve different purposes such as barrier layers, conducting features, or capping layers. Several methods for the generation of metal films are known. One of them is the deposition of film forming compounds from the gaseous state on a substrate. In order to bring metal atoms into the gaseous state at moderate temperatures, it is necessary to provide volatile precursors, e.g. by complexation of the metals with suitable ligands. In order to convert deposited metal complexes to metal films, it is usually necessary to expose the deposited metal complex to a reducing agent.

Typically, hydrogen gas is used to convert deposited metal complexes to metal films. While hydrogen works reasonably well as reducing agent for relatively noble metals like copper or silver, it does not yield satisfactory results for less noble metals such as titanium or aluminum.

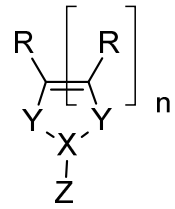
WO 2015 / 0 004 315 A1 discloses a reducing agents with a quinoid structure. However, these reducing agents leave a significant amount of impurities in the metal film which is unfavorable for some applications, for example microchip production.

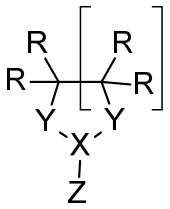
Dey et al. disclose in Theoretical Chemistry Accounts, volume 133 (2013), page 1 to 7 copper(I) carbene hydride complexes acting as reducing agent in atomic layer deposition. However, for high purity metal films copper traces can be detrimental to device performance.

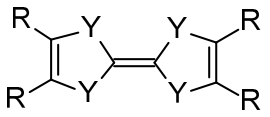
It was therefore an object of the embodiments disclosed herein to provide reducing agents, which are capable of reducing surface-bound metal atoms to the metallic state leaving less impurity in the metal film. The reducing agents should be easy to handle; in particular, it should be possible to vaporize them with as little decomposition as possible. Furthermore, the reducing agent should be versatile, so it can be applied to a broad range of different metals including electropositive metals.

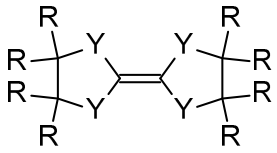
There is provided a process for preparing metal films comprising
(a) depositing a metal-containing compound from the gaseous state onto a solid substrate and
(b) bringing the solid substrate with the deposited metal-containing compound in contact with a reducing agent in the gaseous state or in solution,
wherein the reducing agent is or at least partially forms at the surface of the solid substrate a carbene, a silylene or a phosphor radical,

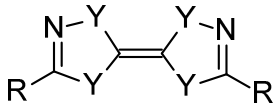
wherein the carbene is a compound of general formula (I), (II), (IVa), (IVb), (Va) or (Vb)

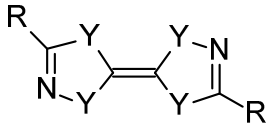

(I)


(II)


(IVa)


(IVb)

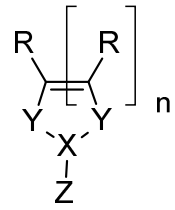

(Va)

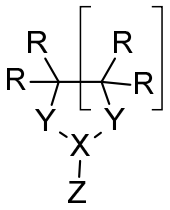

(Vb)

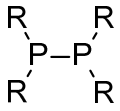
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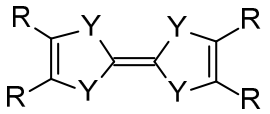
wherein R is hydrogen, an alkyl, alkenyl, aryl, or silyl group
X is C, Si, or P,
Y is S, NR, or CR_2,
Z is nothing, H, alkyl, halogen, an amine, PR_2 or a boron species, and
n is 0, 1 or 2.

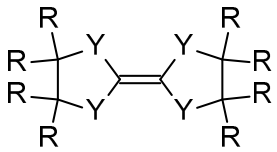
In an aspect, there is provided a process for preparing metal films comprising
(a) depositing a metal-containing compound from the gaseous state onto a solid substrate and
(b) bringing the solid substrate with the deposited metal-containing compound in contact with a reducing agent in the gaseous state or in solution,
wherein the reducing agent is a silylene or a compound of general formula (I), (II), (III), (IVa), (IVb), (Va) or (Vb)

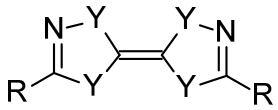

(I)

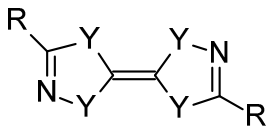

(II)


(III)


(IVa)


(IVb)

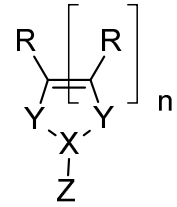

(Va)

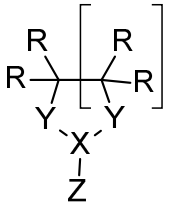

(Vb)

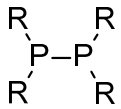
wherein R is hydrogen, an alkyl, alkenyl, aryl, or silyl group
X is C, Si, or P,
Y is S, NR, or CR_2,
Z is nothing, H, alkyl, halogen, an amine, PR_2 or a boron species, and
n is 0, 1 or 2.

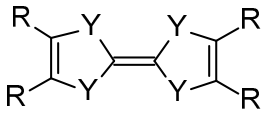
There is provided the use of a carbene, silylene, or phosphor radical as reducing agent in an atomic layer deposition process, wherein the carbene is a compound of general formula (I), (II), (IVa), (IVb), (Va) or (Vb).

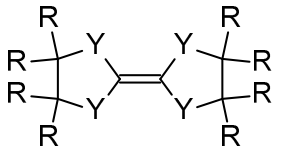
In another aspect, there is provided the use of a silylene, or a compound of general formula (I), (II), (III), (IVa), (IVb), (Va) or (Vb):

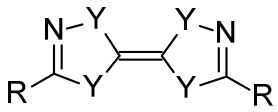

(I)

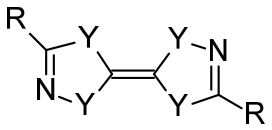

(II)


(III)


(IVa)


(IVb)


(Va)


(Vb)

as reducing agent in an atomic layer deposition process.

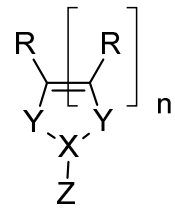
Preferred embodiments of the present disclosure can be found in the description and the claims. Combinations of different embodiments fall within the scope of the present disclosure.

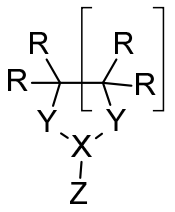
The process according to the present disclosure is for preparing metal films. Metal films in the context of the present disclosure are as generally used in the art metal-containing films with high electrical conductivity, usually at least 10^4 S/m, preferably at least 10^5 S/m, in particular at least 10^6 S/m.

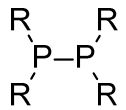
The process according to the present disclosure includes depositing a metal-containing compound from the gaseous state onto a solid substrate. The metal-containing compound contains at least one metal atom. Metals include Li, Be, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os Ir, Pt, Au, Hg, Tl, Bi. Preferably, the metal-containing compound contains a metal which is more electropositive than Cu, more preferably more electropositive than Ni. In particular, the metal-containing compound contains Ti, Ta, Mn, Mo, W, or Al. It is possible that more than one metal-containing compound is deposited

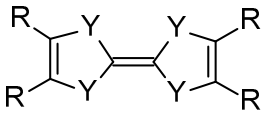
Claims

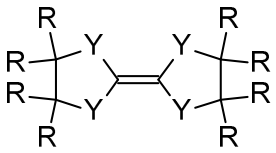
1. Process for preparing metal films comprising
(a) depositing a metal-containing compound from the gaseous state onto a solid substrate and
(b) bringing the solid substrate with the deposited metal-containing compound in contact with a reducing agent in the gaseous state or in solution,
wherein the reducing agent is a silylene or a compound of general formula (I), (II), (III), (IVa), (IVb), (Va) or (Vb)

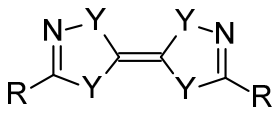

(I)

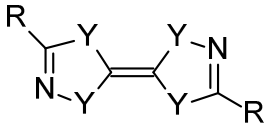

(II)


(III)


(IVa)


(IVb)

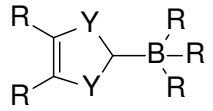

(Va)

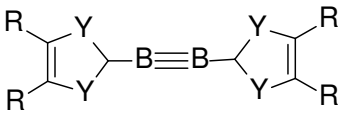

(Vb)

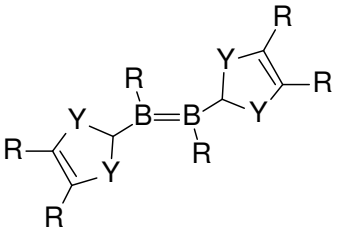
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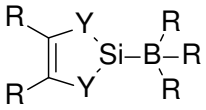
wherein R is hydrogen, an alkyl, alkenyl, aryl, or silyl group
X is C, Si, or P,
Y is S, NR, or CR_2,
Z is nothing, H, alkyl, halogen, an amine, PR_2 or a boron species, and
n is 0, 1 or 2.

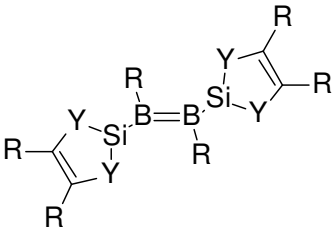
2. The process according to claim 1, wherein the reducing agent is a compound of general formula (Ia), (Ib), (Ic), (Id), (Ie), or (If).

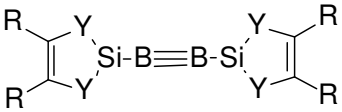

(Ia)


(Ib)

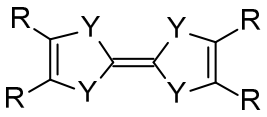

(Ic)

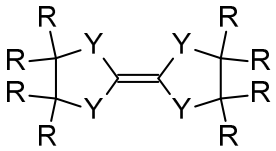

(Id)


(Ie)

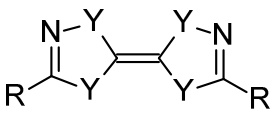

(If)

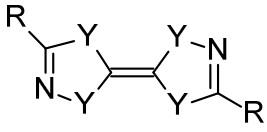
3. The process according to claim 1, wherein the reducing agent is a compound of general formula (IVa) or compounds of general formula (IVb)


(IVa)


(IVb)

4. The process according to claim 1, wherein the reducing agent is a compound of general formula (Va) or a compound of general formula (Vb)


(Va)


(Vb)

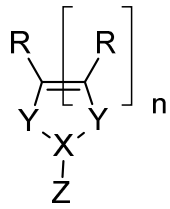
5. The process according to any of the claims 1 to 4, wherein the reducing agent has a vapor pressure of at least 0.1 mbar at 200 °C.

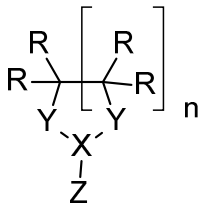
6. The process according to any of the claims 1 to 5, wherein (a) and (b) are successively performed at least twice.

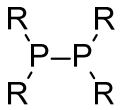
7. The process according to any of the claims 1 to 6, wherein the metal-containing compound contains Ti, Ta, Mn, Mo, W, or Al.

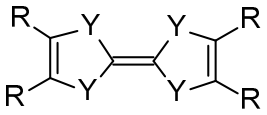
8. The process according to any of the claims 1 to 7, wherein the temperature does not exceed 350 °C.

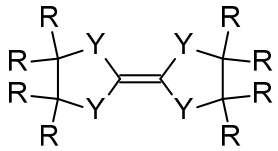
9. Use of a silylene, or a compound of general formula (I), (II), (III), (IVa), (IVb), (Va) or (Vb):

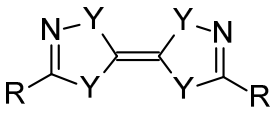

(I)

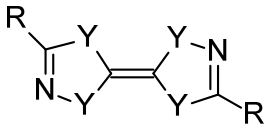

(II)


(III)


(IVa)


(IVb)


(Va)


(Vb)

as reducing agent in an atomic layer deposition process.