

Process for the Generation of Aluminum Oxide Films

Description

- 5 The present invention is in the field of processes for preparing an aluminum oxide film on a substrate, 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 on the quality of such films become stricter. Thin aluminum oxide films serve
10 different purposes such as barrier layers or dielectrics. Several methods for the generation of aluminum oxide 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 or semimetal atoms into the gaseous state at moderate temperatures, it is necessary to provide volatile precursors, e.g. by complexation of the metals or semimetals with suitable ligands. These precursors need to be sufficiently stable for evaporation, but on the other hand they need to be reactive enough to react with the surface
15 of deposition.

Corsino et al. disclose in Journal of Physics D: Applied Physics volume 53 (2020), page 165103 a process for the generation of aluminum oxide films using dimethyl aluminum hydride precursors. Plasma-enhanced decomposition is required to convert the deposited precursor into an aluminum oxide film. Such harsh conditions are not suitable for all
20 applications. Also, films of very high quality are difficult to obtain.

EP 1 788 116 A1 discloses a process for depositing aluminum films from dialkyl amido dihydro aluminum precursors. However, films other than aluminum films are not accessible with this method.

- 25 S. Buttera et al. disclose in Inorganic Chemistry volume 60 (2021), page 11025–11031 the use of $[\text{AlH}_2(\text{NMe}_2)]_3$ for producing aluminum nitride films. A nitrogen plasma was used to obtain the films. Such harsh conditions are not suitable for all applications. Also, no aluminum oxide films are mentioned.

US 2023 / 0 019 365 discloses a method of preparing an aluminum-containing film using an aluminum-containing
30 film-forming precursor. However, the deposition requires plasma-enhanced decomposition which can be undesirable for sensitive substrates.

S. Potts et al. disclose in the Journal of Vacuum Science and Technology A, volume 30 (2012), page 021505-1 to 021505-12 dimethyl aluminum isopropoxide (DMAI) as aluminum precursor. However, the deposition requires
35 plasma-enhanced decomposition which can be undesirable for sensitive substrates.

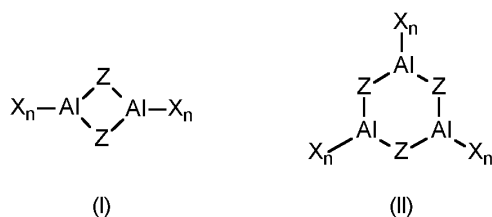
It was therefore an object of the present invention to provide a process for preparing an aluminum oxide film of high quality under mild conditions. An efficient preparation process was targeted, in particular involving high growth rates

per cycle. The process materials should be easy to handle; in particular, it should be possible to vaporize them with as little decomposition as possible. Further, the process material should not decompose at the deposition surface under process conditions but at the same time it should have enough reactivity to participate in the surface reaction. Furthermore, the process should be versatile, so it can be applied to a variety of different substrates.

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These objects were achieved by a process for preparing an aluminum oxide film comprising

- a) depositing a compound of general formula (I) or (II) on a substrate



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wherein Z is NR₂, PR₂, OR, SR, CR₂, SiR₂,

X is H or NR'₂,

n is 1 or 2, and

R and R' is an alkyl group, an alkenyl group, an aryl group, or a silyl group,

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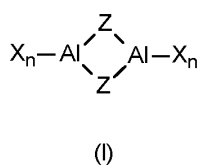
wherein the temperature of the substrate is 20 to 250 °C and

- b) bringing the deposited compound of general formula (I) or (II) in contact with an oxygen-containing decomposition compound.

In another aspect the invention relates to a process for preparing an aluminum oxide film comprising

20

- a) depositing a compound of general formula (I) on a substrate



wherein Z is NR₂, PR₂, OR, SR, CR₂, SiR₂,

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X is H, R' or NR'₂,

n is 1 or 2, and

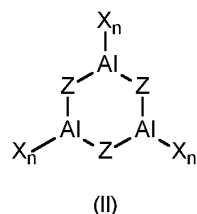
R and R' is an alkyl group, an alkenyl group, an aryl group, or a silyl group, and

- b) bringing the deposited compound of general formula (I) or (II) in contact with an oxygen-containing decomposition compound.

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In another aspect the invention relates to a process for preparing an aluminum oxide film comprising

- a) depositing a compound of general formula (II) on a substrate



5 wherein Z is NR_2 , PR_2 , OR , SR , CR_2 , SiR_2 ,

X is H, R' or NR'_2 ,

n is 1 or 2, and

R and R' is an alkyl group, an alkenyl group, an aryl group, or a silyl group, and

- b) bringing the deposited compound of general formula (I) or (II) in contact with an oxygen-containing
10 decomposition compound.

The invention further relates to the use of a compound of general formula (I) or (II) for preparing an aluminum oxide film.

- 15 The invention further relates to the use of a compound of general formula (I) or (II) for preparing an aluminum oxide film on a substrate, wherein the temperature of the substrate is 20 to 250 °C during deposition.

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

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- The process according to the present invention is suitable for preparing an aluminum oxide film. Aluminum oxide films are inorganic films which contain aluminum and oxygen. Inorganic in the context of the present invention refers to materials which contain at least 5 wt.-% of at least one metal or semimetal, preferably at least 10 wt.-%, more preferably at least 20 wt.-%, in particular at least 30 wt.-%. Inorganic films typically contain carbon only in the form of a carbide phase including mixed carbide phases such as nitride carbide phases. The carbon content of carbon which is not part of a carbide phase in an inorganic film is preferably less than 5 wt.-%, more preferable less than 1 wt.-%, in particular less than 0.2 wt.-%.
- 25

- The aluminum oxide film can contain Al_2O_3 , but it can also contain other forms, for example hydrated forms of aluminum oxide such as $\text{AlO}(\text{OH})$ or $\text{Al}(\text{OH})_3$. The aluminum oxide can be amorphous, partially crystalline or crystalline, preferably it is amorphous. The aluminum oxide film preferably contains at least 30 wt.-% aluminum, more preferably at least 40 wt.-% aluminum, in particular at least 45 wt.-% aluminum. The aluminum oxide film preferably contains at least 35 wt.-% oxygen, more preferably at least 45 wt.-% oxygen, in particular at least 50 wt.-% oxygen.
- 30

The substrate can be any solid material. These include for example metals, semimetals, oxides, nitrides, and polymers. It is also possible that the substrate is a mixture of different materials. Examples for metals are aluminum, steel, and copper. Examples for semimetals are silicon, germanium, and gallium arsenide. Examples for oxides are silicon dioxide, and titanium dioxide. Examples for nitrides are silicon nitride, aluminum nitride, titanium nitride, and gallium nitride. Examples for polymers are polyethylene terephthalate (PET), polyethylene naphthalene-dicarboxylic acid (PEN), and polyamides.

The substrate can have any shape. These include sheet plates, films, fibers, particles of various sizes, and substrates with trenches or other indentations. The substrate can be of any size. If the substrate has a particle shape, the size of particles can range from below 100 nm to several centimeters, preferably from 1 μm to 1 mm. In order to avoid particles or fibers to stick to each other while the metal- or semimetal-containing compound is deposited onto them, it is preferably to keep them in motion. This can, for example, be achieved by stirring, by rotating drums, or by fluidized bed techniques.

In the compound of general formula (I) or (II) Z is NR_2 , PR_2 , OR, SR, CR_2 , SiR_2 , preferably NR_2 , PR_2 , OR, SR, in particular NR_2 or PR_2 . The Z can all be the same or different to each other, preferably they are the same. X may be H, R' or NR'_2 , or X may be H or NR'_2 , preferably at least one X is H, more preferably at least one X for each Al atom is H, in particular all X are H, or one X for each Al atom is H and the other X is NR'_2 or R' . In the context of the present invention, H includes all isotopes of hydrogen, in particular ^1H and ^2H . The latter is also referred to as deuterium D.

The index n can be 1 or 2 depending on Z. Typically, if Z is NR_2 , PR_2 , OR, SR n is 2 and if Z is CR_2 , SiR_2 n is 1.

R and R' in the compound of general formula (I) or (II) is an alkyl group, an alkenyl group, an aryl group, or a silyl group, preferably an alkyl group or silyl group, in particular methyl, ethyl, iso-propyl, sec-butyl, tert-butyl, trimethylsilyl. The R and R' can be the same or different from each other. In many cases it has been observed that if R and/or R' are different to each other, the melting point and/or the boiling point of the compound of general formula (I) or (II) is lower which facilitates bringing them into the gaseous state. Therefore, it is preferable that the compound of general formula (I) or (II) has at least two R which are different to each other or at least two R' which are different to each other. It is possible that two R together form a ring, preferably a three to eight-membered ring, in particular a five- or six-membered ring.

An alkyl group can be linear or branched. Examples for a linear alkyl group are methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl. Examples for a branched alkyl group are iso-propyl, iso-butyl, sec-butyl, tert-butyl, 2-methyl-pentyl, neo-pentyl, 2-ethyl-hexyl, cyclopropyl, cyclohexyl, indanyl, norbornyl. Preferably, the alkyl group is a C_1 to C_8 alkyl group, more preferably a C_1 to C_6 alkyl group, in particular a C_1 to C_4 alkyl group, such as methyl, ethyl, iso-propyl or tert-butyl.

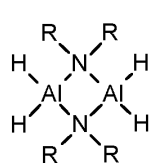
An alkenyl group contains at least one carbon-carbon double bond. The double bond can include the carbon atom with which R or R' is bound to the rest of the molecule, or it can be placed further away from the place where R or R'

is bound to the rest of the molecule. Alkenyl groups can be linear or branched. Examples for linear alkenyl groups in which the double bond includes the carbon atom with which R or R' is bound to the rest of the molecule include 1-ethenyl, 1-propenyl, 1-n-butenyl, 1-n-pentenyl, 1-n-hexenyl, 1-n-heptenyl, 1-n-octenyl. Examples for linear alkenyl groups in which the double bond is placed further away from the place where R or R' is bound to the rest of the molecule include 1-n-propen-3-yl, 2-buten-1-yl, 1-buten-3-yl, 1-buten-4-yl, 1-hexen-6-yl. Examples for branched alkenyl groups in which the double bond includes the carbon atom with which R or R' is bound to the rest of the molecule include 1-propen-2-yl, 1-n-buten-2-yl, 2-buten-2-yl, cyclopenten-1-yl, cyclohexen-1-yl. Examples for branched alkenyl groups in which the double bond is placed further away from the place where R' is bound to the rest of the molecule include 2-methyl-1-buten-4-yl, cyclopenten-3-yl, cyclohexene-3-yl. Examples for an alkenyl group with more than one double bond include 1,3-butadien-1-yl, 1,3-butadien-2-yl, cyclopentadien-5-yl.

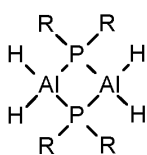
Aryl groups include aromatic hydrocarbons such as phenyl, naphthalyl, anthracenyl, phenanthrenyl groups and heteroaromatic groups such as pyrrolyl, furanyl, thienyl, pyridinyl, quinoyl, benzofuryl, benzothiophenyl, thienothieryl. Several of these groups or combinations of these groups are also possible like biphenyl, thienophenyl or furanylthienyl. Aryl groups can be substituted for example by halogens like fluoride, chloride, bromide, iodide; by pseudohalogens like cyanide, cyanate, thiocyanate; by alcohols; alkyl chains or alkoxy chains. Aromatic hydrocarbons are preferred, phenyl is more preferred.

A silyl group is a silicon atom with typically three substituents. Preferably a silyl group has the formula SiE_3 , wherein E is independent of each other hydrogen, an alkyl group, an aryl group or a silyl group. It is possible that all three E are the same or that two E are the same and the remaining E is different or that all three E are different from each other, preferably all E are the same. Alkyl and aryl groups are as described above. Examples for silyl groups include SiH_3 , methylsilyl, trimethylsilyl, triethylsilyl, tri-n-propylsilyl, tri-iso-propylsilyl, tricyclohexylsilyl, dimethyl-tert-butylsilyl, dimethylcyclohexylsilyl, methyl-di-iso-propylsilyl, triphenylsilyl, phenylsilyl, dimethylphenylsilyl, pentamethyldisilyl.

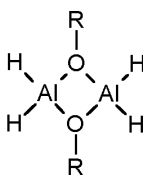
Preferably, the compound of general formula (I) is one of the following general formulae.



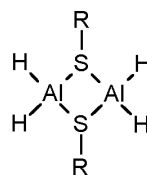
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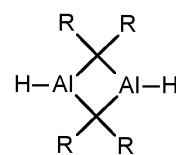
(Ib)



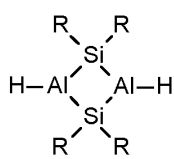
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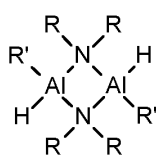
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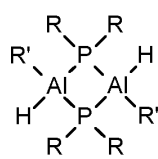
(Ie)



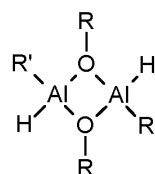
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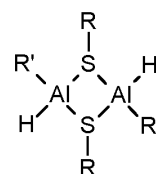
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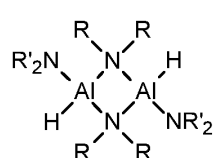
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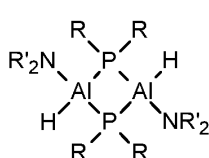
(Ii)



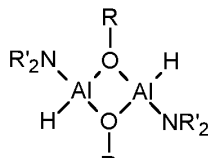
(Ij)



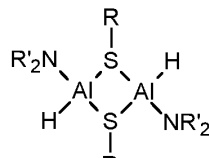
(Ik)



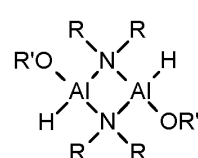
(Im)



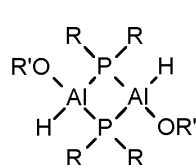
(In)



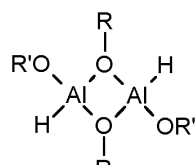
(Io)



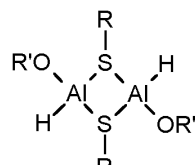
(Ip)



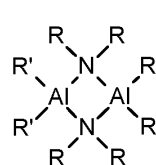
(Iq)



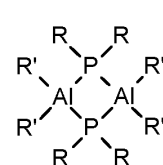
(Ir)



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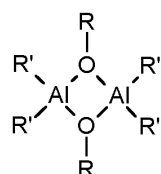


(It)

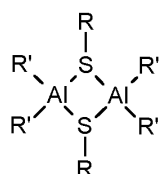


(Iu)

5



(Iv)



(Iw)

10 Preferred examples for the compound of general formula (I) with reference to these general formulae are given in the following table.

No.	Formula	R	R'
Ia-1	Ia	Me	-
Ia-2	Ia	Et	-
Ia-3	Ia	Me, Et	-
Ia-4	Ia	Et, n-Bu	-
Ia-5	Ia	-(CH ₂) ₂ -	-
Ia-6	Ia	-(CH ₂) ₄ -	-
Ib-1	Ib	Me	-

lb-2	lb	Et	-
lb-3	lb	-(CH ₂) ₂ -	-
lb-4	lb	-(CH ₂) ₄ -	-
lc-1	lc	Me	-
lc-2	lc	Et	-
lc-3	lc	-(CH ₂) ₂ -	-
lc-4	lc	-(CH ₂) ₄ -	-
ld-1	ld	Me	-
ld-2	ld	Et	-
ld-3	ld	-(CH ₂) ₂ -	-
ld-4	ld	-(CH ₂) ₄ -	-
le-1	le	Me	-
le-2	le	Et	-
le-3	le	-(CH ₂) ₂ -	-
le-4	le	-(CH ₂) ₄ -	-
lf-1	lf	Me	-
lf-2	lf	Et	-
lf-3	lf	-(CH ₂) ₂ -	-
lf-4	lf	-(CH ₂) ₄ -	-
lg-1	lg	Me	Me
lg-2	lg	Et	Me
lg-3	lg	Me	Et
lg-4	lg	Et	Et
lg-5	lg	-(CH ₂) ₂ -	Me
lg-6	lg	-(CH ₂) ₂ -	Et
lg-7	lg	-(CH ₂) ₄ -	Me
lg-8	lg	-(CH ₂) ₄ -	Et
lh-1	lh	Me	Me
lh-2	lh	Et	Me
lh-3	lh	Me	Et
lh-4	lh	Et	Et
lh-5	lh	-(CH ₂) ₂ -	Me
lh-6	lh	-(CH ₂) ₂ -	Et
lh-7	lh	-(CH ₂) ₄ -	Me
lh-8	lh	-(CH ₂) ₄ -	Et
li-1	li	Me	Me
li-2	li	Et	Me

li-3	li	Me	Et
li-4	li	Et	Et
li-5	li	-(CH ₂) ₂ -	Me
li-6	li	-(CH ₂) ₂ -	Et
li-7	li	-(CH ₂) ₄ -	Me
li-8	li	-(CH ₂) ₄ -	Et
lj-1	lj	Me	Me
lj-2	lj	Et	Me
lj-3	lj	Me	Et
lj-4	lj	Et	Et
lj-5	lj	-(CH ₂) ₂ -	Me
lj-6	lj	-(CH ₂) ₂ -	Et
lj-7	lj	-(CH ₂) ₄ -	Me
lj-8	lj	-(CH ₂) ₄ -	Et
lk-1	lk	Me	Me
lk-2	lk	Et	Me
lk-3	lk	Me	Et
lk-4	lk	Et	Et
lk-5	lk	-(CH ₂) ₂ -	Me
lk-6	lk	-(CH ₂) ₂ -	Et
lk-7	lk	-(CH ₂) ₄ -	Me
lk-8	lk	-(CH ₂) ₄ -	Et
lm-1	lm	Me	Me
lm-2	lm	Et	Me
lm-3	lm	Me	Et
lm-4	lm	Et	Et
lm-5	lm	-(CH ₂) ₂ -	Me
lm-6	lm	-(CH ₂) ₂ -	Et
lm-7	lm	-(CH ₂) ₄ -	Me
lm-8	lm	-(CH ₂) ₄ -	Et
ln-1	ln	Me	Me
ln-2	ln	Et	Me
ln-3	ln	Me	Et
ln-4	ln	Et	Et
ln-5	ln	-(CH ₂) ₂ -	Me
ln-6	ln	-(CH ₂) ₂ -	Et
ln-7	ln	-(CH ₂) ₄ -	Me

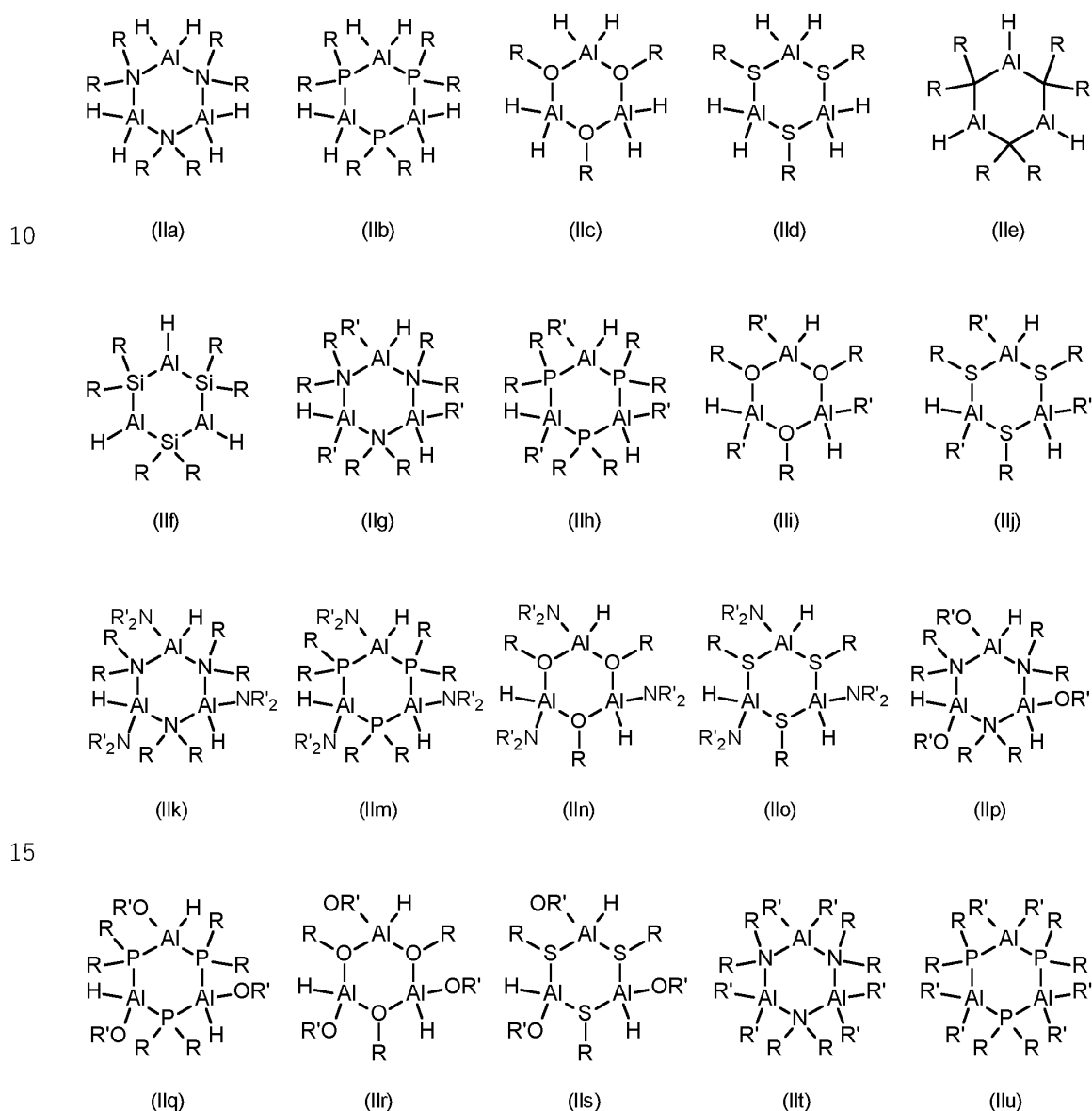
ln-8	ln	-(CH ₂) ₄ -	Et
lo-1	lo	Me	Me
lo-2	lo	Et	Me
lo-3	lo	Me	Et
lo-4	lo	Et	Et
lo-5	lo	-(CH ₂) ₂ -	Me
lo-6	lo	-(CH ₂) ₂ -	Et
lo-7	lo	-(CH ₂) ₄ -	Me
lo-8	lo	-(CH ₂) ₄ -	Et
lp-1	lp	Me	Me
lp-2	lp	Et	Me
lp-3	lp	Me	Et
lp-4	lp	Et	Et
lp-5	lp	-(CH ₂) ₂ -	Me
lp-6	lp	-(CH ₂) ₂ -	Et
lp-7	lp	-(CH ₂) ₄ -	Me
lp-8	lp	-(CH ₂) ₄ -	Et
lq-1	lq	Me	Me
lq-2	lq	Et	Me
lq-3	lq	Me	Et
lq-4	lq	Et	Et
lq-5	lq	-(CH ₂) ₂ -	Me
lq-6	lq	-(CH ₂) ₂ -	Et
lq-7	lq	-(CH ₂) ₄ -	Me
lq-8	lq	-(CH ₂) ₄ -	Et
lr-1	lr	Me	Me
lr-2	lr	Et	Me
lr-3	lr	Me	Et
lr-4	lr	Et	Et
lr-5	lr	-(CH ₂) ₂ -	Me
lr-6	lr	-(CH ₂) ₂ -	Et
lr-7	lr	-(CH ₂) ₄ -	Me
lr-8	lr	-(CH ₂) ₄ -	Et
ls-1	ls	Me	Me
ls-2	ls	Et	Me
ls-3	ls	Me	Et
ls-4	ls	Et	Et

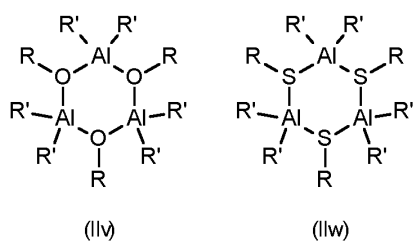
ls-5	ls	-(CH ₂) ₂ -	Me
ls-6	ls	-(CH ₂) ₂ -	Et
ls-7	ls	-(CH ₂) ₄ -	Me
ls-8	ls	-(CH ₂) ₄ -	Et
lt-1	lt	Me	Me
lt-2	lt	Et	Me
lt-3	lt	Me	Et
lt-4	lt	Et	Et
lt-5	lt	-(CH ₂) ₂ -	Me
lt-6	lt	-(CH ₂) ₂ -	Et
lt-7	lt	-(CH ₂) ₄ -	Me
lt-8	lt	-(CH ₂) ₄ -	Et
lu-1	lu	Me	Me
lu-2	lu	Et	Me
lu-3	lu	Me	Et
lu-4	lu	Et	Et
lu-5	lu	-(CH ₂) ₂ -	Me
lu-6	lu	-(CH ₂) ₂ -	Et
lu-7	lu	-(CH ₂) ₄ -	Me
lu-8	lu	-(CH ₂) ₄ -	Et
lv-1	lv	Me	Me
lv-2	lv	Et	Me
lv-3	lv	Me	Et
lv-4	lv	Et	Et
lv-5	lv	-(CH ₂) ₂ -	Me
lv-6	lv	-(CH ₂) ₂ -	Et
lv-7	lv	-(CH ₂) ₄ -	Me
lv-8	lv	-(CH ₂) ₄ -	Et
lw-1	lw	Me	Me
lw-2	lw	Et	Me
lw-3	lw	Me	Et
lw-4	lw	Et	Et
lw-5	lw	-(CH ₂) ₂ -	Me
lw-6	lw	-(CH ₂) ₂ -	Et
lw-7	lw	-(CH ₂) ₄ -	Me
lw-8	lw	-(CH ₂) ₄ -	Et

Me stands for methyl, Et for ethyl, n-Bu for n-butyl, $-(CH_2)_2-$ for an ethylene group which is formed by two R, $-(CH_2)_4-$ for a butylene group which is formed by two R.

- The synthesis for some of the compounds of general formula (I) is described for example by E. Ashby et al in
 5 Inorganic Chemistry, volume 10 (1971), pages 893-899 or by I. Krossing et al. in Zeitschrift für Naturforschung B, volume 63 (2008), pages 1045-1051.

Preferably, the compound of general formula (II) is one of the following general formulae.





Preferred examples for the compound of general formula (II) with reference to these general formulae are given in the following table.

5

No.	Formula	R	R'
IIa-1	IIa	Me	-
IIa-2	IIa	Et	-
IIa-3	IIa	Me, Et	-
IIa-4	IIa	Et, n-Bu	-
IIa-5	IIa	-(CH ₂) ₂ -	-
IIa-6	IIa	-(CH ₂) ₄ -	-
IIb-1	IIb	Me	-
IIb-2	IIb	Et	-
IIb-3	IIb	-(CH ₂) ₂ -	-
IIb-4	IIb	-(CH ₂) ₄ -	-
IIc-1	IIc	Me	-
IIc-2	IIc	Et	-
IIc-3	IIc	-(CH ₂) ₂ -	-
IIc-4	IIc	-(CH ₂) ₄ -	-
IId-1	IId	Me	-
IId-2	IId	Et	-
IId-3	IId	-(CH ₂) ₂ -	-
IId-4	IId	-(CH ₂) ₄ -	-
IIe-1	IIe	Me	-
IIe-2	IIe	Et	-
IIe-3	IIe	-(CH ₂) ₂ -	-
IIe-4	IIe	-(CH ₂) ₄ -	-
IIf-1	IIf	Me	-
IIf-2	IIf	Et	-
IIf-3	IIf	-(CH ₂) ₂ -	-
IIf-4	IIf	-(CH ₂) ₄ -	-

IIg-1	IIg	Me	Me
IIg-2	IIg	Et	Me
IIg-3	IIg	Me	Et
IIg-4	IIg	Et	Et
IIg-5	IIg	-(CH ₂) ₂ -	Me
IIg-6	IIg	-(CH ₂) ₂ -	Et
IIg-7	IIg	-(CH ₂) ₄ -	Me
IIg-8	IIg	-(CH ₂) ₄ -	Et
IIh-1	IIh	Me	Me
IIh-2	IIh	Et	Me
IIh-3	IIh	Me	Et
IIh-4	IIh	Et	Et
IIh-5	IIh	-(CH ₂) ₂ -	Me
IIh-6	IIh	-(CH ₂) ₂ -	Et
IIh-7	IIh	-(CH ₂) ₄ -	Me
IIh-8	IIh	-(CH ₂) ₄ -	Et
IIII-1	IIII	Me	Me
IIII-2	IIII	Et	Me
IIII-3	IIII	Me	Et
IIII-4	IIII	Et	Et
IIII-5	IIII	-(CH ₂) ₂ -	Me
IIII-6	IIII	-(CH ₂) ₂ -	Et
IIII-7	IIII	-(CH ₂) ₄ -	Me
IIII-8	IIII	-(CH ₂) ₄ -	Et
IIj-1	IIj	Me	Me
IIj-2	IIj	Et	Me
IIj-3	IIj	Me	Et
IIj-4	IIj	Et	Et
IIj-5	IIj	-(CH ₂) ₂ -	Me
IIj-6	IIj	-(CH ₂) ₂ -	Et
IIj-7	IIj	-(CH ₂) ₄ -	Me
IIj-8	IIj	-(CH ₂) ₄ -	Et
IIk-1	IIk	Me	Me
IIk-2	IIk	Et	Me
IIk-3	IIk	Me	Et
IIk-4	IIk	Et	Et
IIk-5	IIk	-(CH ₂) ₂ -	Me

IIk-6	IIk	-(CH ₂) ₂ -	Et
IIk-7	IIk	-(CH ₂) ₄ -	Me
IIk-8	IIk	-(CH ₂) ₄ -	Et
IIl-m-1	IIl-m	Me	Me
IIl-m-2	IIl-m	Et	Me
IIl-m-3	IIl-m	Me	Et
IIl-m-4	IIl-m	Et	Et
IIl-m-5	IIl-m	-(CH ₂) ₂ -	Me
IIl-m-6	IIl-m	-(CH ₂) ₂ -	Et
IIl-m-7	IIl-m	-(CH ₂) ₄ -	Me
IIl-m-8	IIl-m	-(CH ₂) ₄ -	Et
IIl-n-1	IIl-n	Me	Me
IIl-n-2	IIl-n	Et	Me
IIl-n-3	IIl-n	Me	Et
IIl-n-4	IIl-n	Et	Et
IIl-n-5	IIl-n	-(CH ₂) ₂ -	Me
IIl-n-6	IIl-n	-(CH ₂) ₂ -	Et
IIl-n-7	IIl-n	-(CH ₂) ₄ -	Me
IIl-n-8	IIl-n	-(CH ₂) ₄ -	Et
IIl-o-1	IIl-o	Me	Me
IIl-o-2	IIl-o	Et	Me
IIl-o-3	IIl-o	Me	Et
IIl-o-4	IIl-o	Et	Et
IIl-o-5	IIl-o	-(CH ₂) ₂ -	Me
IIl-o-6	IIl-o	-(CH ₂) ₂ -	Et
IIl-o-7	IIl-o	-(CH ₂) ₄ -	Me
IIl-o-8	IIl-o	-(CH ₂) ₄ -	Et
IIl-p-1	IIl-p	Me	Me
IIl-p-2	IIl-p	Et	Me
IIl-p-3	IIl-p	Me	Et
IIl-p-4	IIl-p	Et	Et
IIl-p-5	IIl-p	-(CH ₂) ₂ -	Me
IIl-p-6	IIl-p	-(CH ₂) ₂ -	Et
IIl-p-7	IIl-p	-(CH ₂) ₄ -	Me
IIl-p-8	IIl-p	-(CH ₂) ₄ -	Et
IIl-q-1	IIl-q	Me	Me
IIl-q-2	IIl-q	Et	Me

IIq-3	IIq	Me	Et
IIq-4	IIq	Et	Et
IIq-5	IIq	-(CH ₂) ₂ -	Me
IIq-6	IIq	-(CH ₂) ₂ -	Et
IIq-7	IIq	-(CH ₂) ₄ -	Me
IIq-8	IIq	-(CH ₂) ₄ -	Et
IIr-1	IIr	Me	Me
IIr-2	IIr	Et	Me
IIr-3	IIr	Me	Et
IIr-4	IIr	Et	Et
IIr-5	IIr	-(CH ₂) ₂ -	Me
IIr-6	IIr	-(CH ₂) ₂ -	Et
IIr-7	IIr	-(CH ₂) ₄ -	Me
IIr-8	IIr	-(CH ₂) ₄ -	Et
IIs-1	IIs	Me	Me
IIs-2	IIs	Et	Me
IIs-3	IIs	Me	Et
IIs-4	IIs	Et	Et
IIs-5	IIs	-(CH ₂) ₂ -	Me
IIs-6	IIs	-(CH ₂) ₂ -	Et
IIs-7	IIs	-(CH ₂) ₄ -	Me
IIs-8	IIs	-(CH ₂) ₄ -	Et
IIt-1	IIt	Me	Me
IIt-2	IIt	Et	Me
IIt-3	IIt	Me	Et
IIt-4	IIt	Et	Et
IIt-5	IIt	-(CH ₂) ₂ -	Me
IIt-6	IIt	-(CH ₂) ₂ -	Et
IIt-7	IIt	-(CH ₂) ₄ -	Me
IIt-8	IIt	-(CH ₂) ₄ -	Et
IIu-1	IIu	Me	Me
IIu-2	IIu	Et	Me
IIu-3	IIu	Me	Et
IIu-4	IIu	Et	Et
IIu-5	IIu	-(CH ₂) ₂ -	Me
IIu-6	IIu	-(CH ₂) ₂ -	Et
IIu-7	IIu	-(CH ₂) ₄ -	Me

IIu-8	IIu	-(CH ₂) ₄ -	Et
IIv-1	IIv	Me	Me
IIv-2	IIv	Et	Me
IIv-3	IIv	Me	Et
IIv-4	IIv	Et	Et
IIv-5	IIv	-(CH ₂) ₂ -	Me
IIv-6	IIv	-(CH ₂) ₂ -	Et
IIv-7	IIv	-(CH ₂) ₄ -	Me
IIv-8	IIv	-(CH ₂) ₄ -	Et
IIw-1	IIw	Me	Me
IIw-2	IIw	Et	Me
IIw-3	IIw	Me	Et
IIw-4	IIw	Et	Et
IIw-5	IIw	-(CH ₂) ₂ -	Me
IIw-6	IIw	-(CH ₂) ₂ -	Et
IIw-7	IIw	-(CH ₂) ₄ -	Me
IIw-8	IIw	-(CH ₂) ₄ -	Et

Me stands for methyl, Et for ethyl, n-Bu for n-butyl, -(CH₂)₂- for an ethylene group which is formed by two R, -(CH₂)₄- for a butylene group which is formed by two R.

- 5 The synthesis for some of the compounds of general formula (II) is described for example by K. Ouzounis et al. in Zeitschrift fuer Anorganische und Allgemeine Chemie, volume 504 (1983) pages 67-76 or by A. Storr et al. in Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999), 1972, pages 326-330.

- 10 Preferably, R bears no hydrogen atom in the 1-position, i.e. R bears no hydrogen atom which is bonded to the atom which is bonded to the nitrogen or oxygen atom, which is thus in the beta-position with regard to the aluminum atom. Also preferably, R' bears no hydrogen atom in the 1-position. More preferably, both R and R' bear no hydrogen in the 1-position. Examples are alkyl group bearing two alkyl side groups in the 1-position, i.e. 1,1-dialkylalkyl, such as tert-butyl, 1,1-dimethylpropyl; alkyl groups with two halogens in the 1-position such as trifluoromethyl, trichloromethyl, 1,1-difluoroethyl; trialkylsilyl groups such as trimethylsilyl, triethylsilyl, dimethyl-tert-butylsilyl; aryl groups, in particular
- 15 phenyl or alkyl-substituted phenyl such as 2,6-diisopropylphenyl, 2,4,6-triisopropylphenyl. Alkyl groups bearing no hydrogen atom in the 1-position are particularly preferred.

- The compound of general formula (I) or (II) preferably has a molecular weight of not more than 1000 g/mol, more preferably not more than 800 g/mol, even more preferably not more than 600 g/mol, in particular not more than 500
- 20 g/mol.

Preferably, the compound of general formula (I) or (II) has a melting point ranging from -80 to 125 °C, preferably from -60 to 80 °C, even more preferably from -40 to 50 °C, in particular from -20 to 20 °C. It is advantageous if the compound of general formula (I) or (II) melts to give a clear liquid which remains unchanged until a decomposition temperature.

5

Preferably, the compound of general formula (I) or (II) has a decomposition temperature of at least 80 °C, more preferably at least 100 °C, in particular at least 120 °C, such as at least 150 °C. Often, the decomposition temperature is not more than 250 °C. The compound of general formula (I) or (II) has a high vapor pressure.

Preferably, the vapor pressure is at least 1 mbar at a temperature of 200 °C, more preferably at 150 °C, even more preferably at 120 °C, in particular at 100 °C, such as at 70 °C. Usually, the temperature at which the vapor pressure is 1 mbar is at least 20 °C such as 50 °C.

The compound of general formula (I) or (II) used in the process according to the present invention are used at high purity to achieve the best results. High purity means that the substance used contains at least 90 wt.-% metal- or semimetal-containing compound or compound of general formula (I) or (II), preferably at least 95 wt.-%, more preferably at least 98 wt.-%, in particular at least 99 wt.-%. The purity can be determined by elemental analysis according to DIN 51721 (Prüfung fester Brennstoffe - Bestimmung des Gehaltes an Kohlenstoff und Wasserstoff - Verfahren nach Radmacher-Hoverath, August 2001).

The compound of general formula (I) or (II) is brought in contact with the substrate from the gaseous state. It can be brought into the gaseous state for example by heating it to elevated temperatures. In any case a temperature below the decomposition temperature of the compound of general formula (I) or (II) has to be chosen. The decomposition temperature is the temperature at which the pristine compound of general formula (I) or (II) begins changing its chemical structure and composition. Preferably, the heating temperature ranges from 0 °C to 300 °C, more preferably from 10 °C to 250 °C, even more preferably from 20 °C to 200 °C, in particular from 30 °C to 150 °C.

Another way of bringing the compound of general formula (I) or (II) into the gaseous state is direct liquid injection (DLI) as described for example in US 2009 / 0 226 612 A1. In this method the compound of general formula (I) or (II) is typically dissolved in a solvent and sprayed in a carrier gas or vacuum. If the vapor pressure of the compound of general formula (I) or (II) and the temperature are sufficiently high and the pressure is sufficiently low the compound of general formula (I) or (II) is brought into the gaseous state. Various solvents can be used provided that the compound of general formula (I) or (II) shows sufficient solubility in that solvent such as at least 1 g/l, preferably at least 10 g/l, more preferably at least 100 g/l. Examples for these solvents are coordinating solvents such as tetrahydrofuran, dioxane, diethoxyethane, pyridine or non-coordinating solvents such as hexane, heptane, benzene, toluene, or xylene. Solvent mixtures are also suitable.

Alternatively, the compound of general formula (I) or (II) can be brought into the gaseous state by direct liquid evaporation (DLE) as described for example by J. Yang et al. (Journal of Materials Chemistry, 2015). In this method,

the compound of general formula (I) or (II) is mixed with a solvent, for example a hydrocarbon such as tetradecane, and heated below the boiling point of the solvent. By evaporation of the solvent, the compound of general formula (I) or (II) is brought into the gaseous state. This method has the advantage that no particulate contaminants are formed on the surface.

5

It is preferred to bring the compound of general formula (I) or (II) into the gaseous state at decreased pressure. In this way, the process can usually be performed at lower heating temperatures leading to decreased decomposition of the compound of general formula (I) or (II). It is also possible to use increased pressure to push the compound of general formula (I) or (II) in the gaseous state towards the substrate. Often, an inert gas, such as nitrogen or argon, is used as carrier gas for this purpose. Preferably, the pressure is 10 bar to 10^{-7} mbar, more preferably 1 bar to 10^{-3} mbar, in particular 1 to 0.01 mbar, such as 0.1 mbar.

10

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The exposure of the substrate with the compound of general formula (I) or (II) can take from milliseconds to several minutes, preferably from 0.1 second to 1 minute, in particular from 1 to 10 seconds. The longer the substrate at a temperature below the decomposition temperature of the compound of general formula (I) or (II) is exposed to the compound of general formula (I) or (II) the more regular films are formed with less defects.

20

According to the present invention the deposited compound of general formula (I) or (II) is brought in contact with an oxygen-containing decomposition compound. Suitable oxygen-containing decomposition compounds are capable of reacting with the compound of general formula (I) or (II) to form aluminum oxide. The oxygen-containing decomposition compound may be water, oxygen ozone. The oxygen-containing decomposition compound may be applied as is or as a plasma, for example an oxygen plasma. Preferably, the deposited compound of general formula (I) or (II) is brought in contact with an oxygen-containing decomposition compound in unmodified form, i.e. no plasma is applied, such that the reaction is thermally initiated.

25

The oxygen-containing decomposition compound can be brought into the gaseous state as described for the compound of general formula (I) or (II) above. The oxygen-containing decomposition compound may be brought in contact with the deposited compound of general formula (I) or (II) at a partial pressure of 10 bar to 10^{-7} mbar, preferably 1 bar to 10^{-3} mbar, in particular 1 to 0.01 mbar, such as 0.1 mbar. The oxygen-containing decomposition compound may be brought in contact with the deposited compound of general formula (I) or (II) as pristine compound or as a mixture with an inert gas such as nitrogen or argon.

30

Depositing the compound of general formula (I) or (II) and bringing the deposited compound of general formula (I) or (II) in contact with an oxygen-containing decomposition compound can be performed at the same or at different temperatures, preferably at the same.

35

The deposited compound of general formula (I) or (II) may be brought in contact with an oxygen-containing decomposition compound for a period of milliseconds to several minutes, preferably from 0.1 second to 1 minute, in particular from 1 to 10 seconds.

- 5 The process of the present invention may be an atomic layer deposition (ALD) process. Preferably, the sequence comprising (a) and (b) is performed at least twice, more preferably at least five times, even more preferably at least 10 times, in particular at least 50 times. Often, the sequence comprising (a) and (b) is performed not more than 1000 times.
- 10 Generally, it is preferred to purge the substrate and its surrounding apparatus with an inert gas each time the substrate is exposed to the compound of general formula (I) or (II) or the oxygen-containing decomposition compound in the gaseous state. Preferred examples for inert gases are nitrogen and argon. Purging can take 1 s to 1 min, preferably 5 to 30 s, more preferably from 10 to 25 s, in particular 15 to 20 s.
- 15 Preferably, the temperature of the substrate is 5 °C to 40 °C higher than the place where the compound of general formula (I) or (II) or the oxygen-containing decomposition compound is brought into the gaseous state, for example 20 °C. Preferably, the temperature of the substrate is from room temperature or 20 °C to 400 °C, more preferably from 100 to 300 °C, such as 120 to 250 °C or 150 to 220 °C.
- 20 The process according to the present invention yields an aluminum oxide film. A film can be only one monolayer or be thicker such as 0.1 nm to 1 µm, preferably 0.5 to 50 nm. A film can contain defects like holes. These defects, however, generally constitute less than half of the surface area covered by the film. The film preferably has a very uniform film thickness which means that the film thickness at different places on the substrate varies very little, usually less than 10 %, preferably less than 5 %. Furthermore, the film is preferably a conformal film on the surface
- 25 of the substrate. Suitable methods to determine the film thickness and uniformity are XPS or ellipsometry.

The film obtained by the process according to the present invention can be used in an electronic element. Electronic elements can have structural features of various sizes, for example from 1 nm to 100 µm, for example 10 nm, 14 nm or 22 nm. The process for forming the films for the electronic elements is particularly well suited for very fine

30 structures. Therefore, electronic elements with sizes below 1 µm are preferred. Examples for electronic elements are field-effect transistors (FET), charge-trap memory cells, solar cells, light emitting diodes, sensors, or capacitors. In optical devices such as light emitting diodes or light sensors the film obtained by the process according to the present invention serves to increase the refractive index of the layer which reflects light.

35 Examples

Example 1

In an ALD reactor (Plasma Electronic GmbH) a Si wafer coupon with a native SiO_x layer was heated to 180 °C. The substrate was brought in contact with compound IIa-1 vapor, purged for 12 s with argon, then brought in contact to water vapor followed by a 12 s purge with argon. This sequence was performed 100 times. A film was obtained with a thickness of 22 nm as determined by ellipsometry. The bulk composition of this film was 40.8 at% Al, and 59.2 at% O according to XPS profiling.

Example 2

The procedure of example 2 was repeated using a reactor temperature of 200 °C. A film was obtained with a thickness of 21 nm as determined by ellipsometry. The bulk composition of this film was 40.8 at% Al, and 59.2 at% O according to XPS profiling.

Example 3

The procedure of example 1 was repeated using compound Ia-2 instead of compound IIa-1. A film was obtained with a thickness of 16 nm and a roughness of 1.4 nm as determined by ellipsometry. The bulk composition of this film was 40 at% Al, and 60 at% O according to XPS profiling.

Example 4

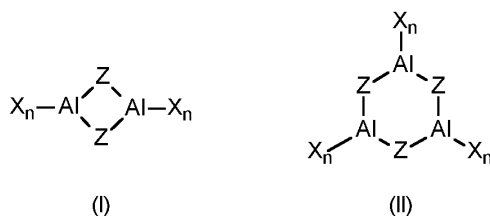
The procedure of example 3 was repeated using a reactor temperature of 200 °C. A film was obtained with a thickness of 17 nm as determined by ellipsometry. The bulk composition of this film was 40 at% Al, and 60 at% O according to XPS profiling.

25

Claims

1. Process for preparing an aluminum oxide film comprising
- a) depositing a compound of general formula (I) or (II) from the gaseous state onto a substrate

5



wherein Z is NR_2 , PR_2 , OR , SR , CR_2 , SiR_2 ,

X is H or NR'_2 ,

n is 1 or 2, and

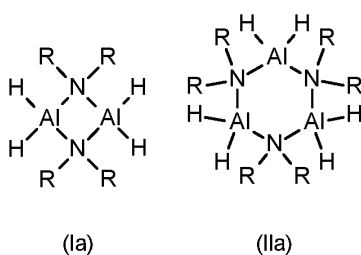
R and R' is an alkyl group, an alkenyl group, an aryl group, or a silyl group,

wherein the temperature of the substrate is 20 to 250 °C and

- b) bringing the deposited compound of general formula (I) or (II) in contact with an oxygen-containing decomposition compound in the gaseous state.

15

2. The process according to claim 1, wherein Z is NR_2 , PR_2 , OR , or SR .
3. The process according to claim 1 or 2, wherein at least one X for each Al atom is H.
4. The process according to claim 1, wherein the compound of general formula (I) or (II) is a compound of general formula (Ia) or (IIa)

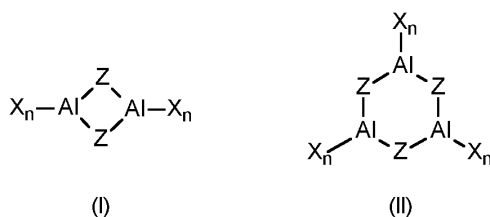


and wherein R is an alkyl group, an alkenyl group, an aryl group, or a silyl group.

5. The process according to any of the claims 1 to 4, wherein R is methyl, ethyl, iso-propyl, sec-butyl, tert-butyl, trimethylsilyl.

25

6. The process according to any of the claims 1 to 5, wherein the oxygen-containing decomposition compound water, oxygen or ozone.
7. The process according to any of the claims 1 to 6, wherein the sequence containing (a) and (b) is performed at least twice.
8. The process according to any of the claims 1 to 7, wherein the compound of general formula (I) or (II) has a molecular weight of not more than 600 g/mol.
9. The process according to any of the claims 1 to 8, wherein the compound of general formula (I) or (II) has a vapor pressure at least 1 mbar at a temperature of 70 °C.
10. The process according to any of the claims 1 to 9, wherein the aluminum oxide film contains at least 40 wt.-% aluminum and at least 45 wt.-% oxygen.
11. The process according to any of the claims 1 to 10, wherein the aluminum oxide film is amorphous.
12. Use of a compound of general formula (I) or (II) for preparing an aluminum oxide film,



wherein Z is NR₂, PR₂, OR, SR, CR₂, SiR₂,

X is H or NR'₂,

n is 1 or 2, and

R and R' is an alkyl group, an alkenyl group, an aryl group, or a silyl group.

13. Use according to claim 12, wherein the aluminum oxide film is amorphous.
14. Use according to claim 12 or 13, wherein the aluminum oxide film has a thickness of 0.5 to 50 nm.
15. Use according to any of the claims 12 to 14, wherein the aluminum oxide film is prepared by atomic layer deposition.