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(57) Abstract: Methods are provided to form and stabilize high- $\kappa$  dielectric films by vapor deposition processes using metal-source precursors and cerium-based precursors according to Formula I:  $\text{Ce}(\text{L})_x$  (Formula I) wherein L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; or L is alkoxy;  $\text{R}_1$  and  $\text{R}_2$  are independently hydrogen or alkyl; and x is 3 or 4. Further provided are methods of improving high- $\kappa$  gate property of semiconductor devices by using cerium precursors according to Formula I. High- $\kappa$  dielectric film-forming lattices are also provided comprising cerium precursors according to Formula I.



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## **HIGH-K DIELECTRIC FILMS AND METHODS OF PRODUCING USING CERIUM-BASED PRECURSORS**

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

**[0001]** This patent claims the benefit of U.S. provisional application Serial No. 61/055,620, filed on 23 May 2008, the disclosure of which is incorporated herein by reference in its entirety. Disclosure of copending U.S. provisional application Serial No. 61/055,646, filed on 23 May 2008; copending U.S. provisional application Serial No. 61/055,594, filed on 23 May 2008; copending U.S. provisional application Serial No. 61/105,594, filed on 15 October 2008; and copending U.S. provisional application Serial No. 61/055,695, filed on 23 May 2008, are each incorporated herein by reference in their entirety without admission that such disclosures constitute prior art to the present invention.

### **FIELD OF THE INVENTION**

**[0002]** The present invention relates to methods of forming high- $\kappa$  dielectric thin metallic films, improving such films, and a lattice capable of forming such films.

### **BACKGROUND OF THE INVENTION**

**[0003]** Various organometallic precursors are used to form high- $\kappa$  dielectric thin metal films for use in the semiconductor industry. Various deposition processes are used to form the metal films, such as chemical vapor deposition ("CVD") or atomic layer deposition ("ALD"), also known as atomic layer epitaxy.

**[0004]** CVD is a chemical process whereby precursors are deposited on a substrate to form a solid thin film. In a typical CVD process, the precursors are passed over a substrate (wafer) within a low pressure or ambient pressure reaction chamber. The precursors react and/or decompose on the substrate surface creating a thin film of deposited material. Volatile by-products are removed by gas flow through the reaction chamber. The deposited film thickness can be difficult to control because it depends on coordination of many parameters such as temperature, pressure, gas flow volumes and uniformity, chemical depletion effects and time.

**[0005]** ALD is a chemical process which separates the precursors during the reaction. The first precursor is passed over the substrate producing a monolayer on the substrate. Any excess unreacted precursor is pumped out of the reaction chamber. A second

precursor is then passed over the substrate and reacts with the first precursor, forming a second monolayer of film over the first-formed film on the substrate surface. This cycle is repeated to create a film of desired thickness. ALD film growth is self-limited and based on surface reactions, creating uniform depositions that can be controlled at the nanometer-thickness scale.

[0006] Yashima M., *et. al.* report zirconia-ceria solid solutions and lattice in an abstract presented at the Fall Meeting of the Ceramic Society of Japan, Kanazawa, Japan, September 26-28 1990 (Paper No. 6-3A07), and at the 108<sup>th</sup> Annual Meeting of the Japan Institute of Metals, Tokyo, Japan, April 2-4, 1991 (Paper No. 508).

[0007] Scott, H.G. reports metastable and equilibrium phase relationships in zirconia-yttria system. ["Phase Relationships in the zirconia-yttria system," J. Mat. Science. 1975. 10:1527-1535].

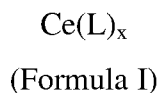
[0008] International Publication No. WO 02/27063 reports vapor deposition processes using metal oxides, silicates and phosphates, and silicon dioxide.

[0009] Zirconia, hafnia and TiO<sub>2</sub> have been used to create dielectric films, generally to replace silicon dioxide gates for use in the semiconductor industry. Replacing silicon dioxide with a high- $\kappa$  dielectric material allows increased gate capacitance without concomitant leakage effects.

[0010] Therefore, methods are needed to create and improve high- $\kappa$  dielectric films by either increasing the dielectric constant, or stabilizing the film to maintain a high dielectric constant, or both.

#### SUMMARY OF THE INVENTION

[0011] There is now provided a method to form a high- $\kappa$  dielectric film by a vapor deposition process. The method comprises delivering at least one metal-source precursor and at least one cerium precursor to a substrate, wherein the at least one cerium precursor corresponds in structure to Formula I:



wherein:

L is a cyclopentadienyl ring optionally substituted with one or more substituents selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; or L is alkoxy;

$\text{R}_1$  and  $\text{R}_2$  are independently hydrogen or alkyl; and

x is 3 or 4.

**[0012]** There is further provided a method to improve high- $\kappa$  gate property of a semiconductor device. The method comprises using at least one cerium precursor to form a high- $\kappa$  dielectric film for use in the semiconductor device, wherein the at least one cerium precursor corresponds in structure to Formula I.

**[0013]** There is further provided a method to stabilize a high- $\kappa$  dielectric material. The method comprises adding at least one cerium precursor to the high- $\kappa$  dielectric material wherein the at least one cerium precursor corresponds in structure to Formula I.

**[0014]** There is further provided a high- $\kappa$  dielectric film-forming lattice, wherein the lattice is comprised of hafnium oxide, titanium oxide or mixtures thereof and the lattice contains cerium atoms.

**[0015]** Other embodiments, including particular aspects of the embodiments summarized above, will be evident from the detailed description that follows.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0016]** In various aspects of the invention, methods are provided that utilize cerium (III) and/or cerium (IV) precursors as dopants to form high- $\kappa$  dielectric thin films. The methods of the invention are used to create or grow thin films with an improved high- $\kappa$  gate property, and thus are able to maintain high dielectric constants. In other aspects of the invention a lattice is provided capable of forming a high- $\kappa$  gate film.

**[0017]** As used herein, the term “high- $\kappa$  dielectric” refers to a material, such as a metal-containing film, with a higher dielectric constant ( $\kappa$ ) when compared to silicon dioxide (which has a dielectric constant of about 3.7). Typically, a high- $\kappa$  dielectric film is used in semiconductor manufacturing processes to replace the silicon dioxide gate dielectric. A high- $\kappa$  dielectric film may be referred to as having a “high- $\kappa$  gate property” when the dielectric film is used as a gate material and has at least a higher dielectric constant than silicon dioxide.

**[0018]** As used herein, the term “relative permittivity” is synonymous with dielectric constant ( $\kappa$ ).

**[0019]** As used herein, the term “vapor deposition process” is used to refer to any type of vapor deposition technique such as CVD or ALD. In various embodiments of the invention, CVD may take the form of liquid injection CVD. In other embodiments, ALD may be either photo-assisted ALD or liquid injection ALD.

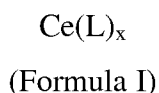
**[0020]** As used herein, the term “precursor” refers to an organometallic molecule, complex and/or compound which is deposited or delivered to a substrate to form a thin film by a vapor deposition process such as CVD or ALD.

**[0021]** As used herein, the term “alkyl” refers to a saturated hydrocarbon chain of 1 to 10 carbon atoms in length, such as, but not limited to, methyl, ethyl, propyl and butyl. The alkyl group may be straight-chain or branched-chain. For example, as used herein, propyl encompasses both *n*-propyl and *iso*-propyl; butyl encompasses *n*-butyl, *sec*-butyl, *iso*-butyl and *tert*-butyl.

**[0022]** As used herein, the term “alkoxy” (alone or in combination with another term(s)) refers to a substituent, *i.e.*, -O-alkyl. Examples of such a substituent include methoxy (-O-CH<sub>3</sub>), ethoxy, *etc.* The alkyl portion may be straight-chain or branched-chain. For example, as used herein, propoxy encompasses both *n*-propoxy and *iso*-propoxy; butoxy encompasses *n*-butoxy, *iso*-butoxy, *sec*-butoxy, and *tert*-butoxy.

**[0023]** As used herein, the term “cyclopentadienyl” or “Cp” (C<sub>5</sub>H<sub>5</sub>) refers to a 5-membered carbon ring which is bound to a transition metal. As used herein, all five carbon atoms of the Cp ligand are bound to the metal center in  $\eta^5$ -coordination by  $\pi$  bonding.

**[0024]** In a first embodiment, a method to form a high- $\kappa$  dielectric film by a vapor deposition process is provided. The method comprises delivering at least one metal-source precursor and at least one cerium precursor to a substrate, wherein the at least one cerium precursor corresponds in structure to Formula I:



wherein:

L is a cyclopentadienyl ring optionally substituted with one or more substituents selected from the group consisting of alkyl, alkoxy and NR<sub>1</sub>R<sub>2</sub>; or L is alkoxy;

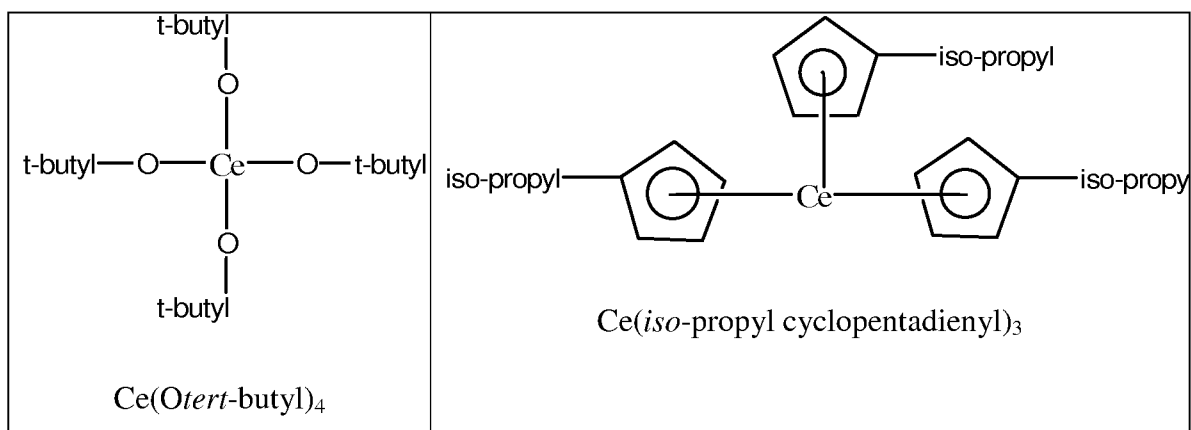
R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or alkyl; and

x is 3 or 4.

**[0025]** In one embodiment, L is a cyclopentadienyl ring optionally substituted with one or more substituents such as alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ . In a particular embodiment, the cyclopentadienyl ring is substituted with one or more substituents such as alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ . In a further particular embodiment, L is a cyclopentadienyl ring and x is 3, therefore in this embodiment there are three cyclopentadienyl rings attached to cerium.

**[0026]** In another embodiment, L is alkoxy group such as methoxy, ethoxy, propoxy, butoxy or pentoxy. In a particular embodiment, L is alkoxy and x is 4, therefore in this embodiment there are four alkoxy groups attached to cerium.

**[0027]** Examples of the at least one cerium precursor include, without limitation:



**[0028]** Any metal-source precursor suitable for forming a film may be used according to the invention. In a particular embodiment, the at least one metal-source precursor is compatible with the at least one cerium precursor. For example, without limitation, the at least one metal-source precursor may be compatible with the at least one cerium precursor for purposes of depositing a metal oxide film with the composition  $\text{Ce}_x\text{M}_{1-x}\text{O}_y$  where M is either Hf, Zr or Ti; x has a value between about zero and about 0.5; and y has a value less than about 2.

**[0029]** Examples of the at least one metal-source precursor include, without limitation:

a metal amide, such as Hafnium dimethylamide, Zirconium dimethylamide, Titanium dimethylamide, Hafnium ethylmethylamide, Zirconium

ethylmethanamide, Titanium ethylmethanamide, Hafnium diethylamide, Zirconium diethylamide and Titanium diethylamide;

a metal alkoxide, such as Hafnium t-butoxide, Zirconium t-butoxide, Titanium t-butoxide, Hafnium i-propoxide, Zirconium i-propoxide, Titanium i-propoxide, Hafnium bis t-butoxy bis 2-methyl-2-methoxy propoxide, Zirconium bis t-butoxy bis 2-methyl-2-methoxy propoxide, Titanium bis t-butoxy bis 2-methyl-2-methoxy propoxide, Zirconium bis i-propoxy bis 2-methyl-2-methoxy propoxide, Titanium bis i-propoxy bis 2-methyl-2-methoxy propoxide, Hafnium 2-methyl-2-methoxy propoxide, Zirconium 2-methyl-2-methoxy propoxide and Titanium 2-methyl-2-methoxy propoxide;

a metal  $\beta$ -diketonate, such as Hafnium 2,2,6,6-tetramethyl-3,5-heptanedionate, Zirconium 2,2,6,6-tetramethyl-3,5-heptanedionate, Titanium 2,2,6,6-tetramethyl-3,5-heptanedionate, Zirconium bis i-propoxy bis 2,2,6,6-tetramethyl-3,5-heptanedionate and Titanium bis i-propoxy 2,2,6,6-tetramethyl-3,5-heptanedionate;

a metal cyclopentadienyl, such as bis methylcyclopentadienyl Hafnium dimethyl, bis methylcyclopentadienyl Zirconium dimethyl, bis methylcyclopentadienyl Hafnium methyl methoxide, bis methylcyclopentadienyl Zirconium methyl methoxide, methylcyclopentadienyl Hafnium tris dimethylamide, methylcyclopentadienyl Zirconium tris dimethylamide and methylcyclopentadienyl Titanium tris dimethylamide.

**[0030]** Therefore, in one embodiment, the high- $\kappa$  dielectric film formed by a method of the invention may comprise:

- (1) hafnium oxide and cerium,
- (2) zirconium oxide and cerium,
- (3) titanium oxide and cerium, or
- (4) mixtures of hafnium, zirconium and/or titanium oxide and cerium.

**[0031]** In a particular embodiment, at least one cerium precursor is used in a vapor deposition process with at least one hafnium precursor to create a cerium-doped hafnium oxide film.

**[0032]** In another particular embodiment, at least one cerium precursor is used in a

vapor deposition process with at least one zirconium precursor to create a cerium-doped zirconium oxide film.

**[0033]** In another particular embodiment, at least one cerium precursor is used in a vapor deposition process with at least one titanium precursor to create a cerium-doped titanium oxide film.

**[0034]** In another particular embodiment, at least one cerium precursor is used in a vapor deposition process with at least one hafnium precursor, zirconium precursor and/or titanium precursor to create a cerium doped “mixed” metal oxide film. Therefore, a “mixed” metal oxide film, as used herein, refers to a metal oxide film comprising cerium and one or more of the following: hafnium oxide, zirconium oxide and titanium oxide.

**[0035]** In one embodiment, the method of the invention creates either hafnium oxide, zirconium oxide, titanium oxide or a mixed metal oxide dielectric film that contains from about 0.5 to about 35 atomic metal % cerium. In a particular embodiment the metal oxide or mixed metal oxide film contains from about 5 to about 20 atomic metal % cerium. In a further particular embodiment, the metal oxide or mixed metal oxide film contains from about 8 to about 12 atomic metal % cerium.

**[0036]** In one embodiment, the at least one metal source precursor and/or the at least one cerium precursor may be dissolved in an appropriate hydrocarbon or amine solvent. Appropriate hydrocarbon solvents include, but are not limited to aliphatic hydrocarbons, such as hexane, heptane and nonane; aromatic hydrocarbons, such as toluene and xylene; aliphatic and cyclic ethers, such as diglyme, triglyme and tetraglyme. Examples of appropriate amine solvents include, without limitation, octylamine and N,N-dimethyldodecylamine. For example, a precursor may be dissolved in toluene to yield a 0.05 to 1M solution.

**[0037]** In a particular embodiment, the at least one cerium precursor is dissolved in an organic solvent, such as toluene, heptane, octane, nonane or tetrahydrofuran (THF).

**[0038]** The cerium-doped films of the invention can be formed by chemical vapor deposition. In a particular embodiment, the chemical vapor deposition is liquid injection chemical vapor deposition.

**[0039]** Alternatively, the cerium-doped films of the invention can be formed by atomic layer deposition. In a particular embodiment, the atomic layer deposition is



photo-assisted atomic layer deposition. And in another particular embodiment, the atomic layer deposition is liquid injection atomic layer deposition.

**[0040]** In the methods of the invention, each precursor is deposited and/or delivered onto a substrate in pulses alternating with pulses of an oxygen source. Any suitable oxygen source may be used, for example, H<sub>2</sub>O, O<sub>2</sub> or ozone.

**[0041]** In a particular embodiment, each precursor is deposited onto a substrate in pulses with a continuous supply of the oxygen source such as H<sub>2</sub>O, O<sub>2</sub> or ozone.

**[0042]** In one embodiment of the invention, the cerium-doped high- $\kappa$  dielectric film has a relative permittivity of about 20 to about 100, particularly from about 40 to about 70. Further, the high- $\kappa$  dielectric film is capable of maintaining a relative permittivity of about 20 to about 100 at frequencies of about 1KHz to about 1GHz.

**[0043]** A variety of substrates can be used in the methods of the present invention. For example, the precursors according to Formula I may be deposited on substrates such as, but not limited to, silicon, silicon oxide, silicon nitride, tantalum, tantalum nitride, or copper.

**[0044]** In another embodiment of the invention, a method is provided to improve the high- $\kappa$  gate property of a semiconductor device. The method comprises using at least one cerium precursor to form a high- $\kappa$  dielectric film for use in the semiconductor device, wherein the at least one cerium precursor corresponds in structure to Formula I above.

**[0045]** Including at least one cerium precursor according to Formula I in a metal oxide film improves the high- $\kappa$  gate property by either increasing the dielectric constant, allowing longer maintenance of a high dielectric constant or both, when compared to the particular metal oxide film without the at least one cerium precursor. This improves the high- $\kappa$  gate property of the semiconductor device by increasing gate capacitance and improving permittivity for faster transistors and smaller devices.

**[0046]** For example, the dielectric constant can be increased about 20 to about 50 units by using at least one cerium precursor according to Formula I; or a high dielectric constant can be maintained at about 1KHz to about 1GHz, when compared to not using at least one cerium precursor according to Formula I.

**[0047]** In another embodiment of the invention, a method is provided to stabilize a high- $\kappa$  dielectric material. The method comprises adding at least one cerium precursor to

the high- $\kappa$  dielectric material wherein the at least one cerium precursor corresponds in structure to Formula (I) above. The term “stabilize” refers generally to altering the high- $\kappa$  dielectric material such that the high- $\kappa$  dielectric material is able to maintain a high dielectric constant at frequencies of about 1KHz to about 1GHz.

**[0048]** Therefore, in one embodiment of the invention, the cerium-doped high- $\kappa$  dielectric film has a relative permittivity of about 20 to about 100, particularly from about 40 to about 70. Further, the high- $\kappa$  dielectric film is capable of maintaining a relative permittivity of about 20 to about 100 at frequencies of about 1KHz to about 1GHz.

**[0049]** The high- $\kappa$  dielectric material may be any material wherein stabilization is needed to improve or maintain a high dielectric constant. For example, the high- $\kappa$  dielectric material may be provided by a film composed of one or more of hafnium oxide, zirconium oxide, titanium oxide or a “mixed” metal oxide, for example, a hafnium, zirconium and/or titanium oxide mixture. Additionally, if three metals are present, then a “ternary” mixed metal oxide film can be stabilized.

**[0050]** Without being bound by theory, it is believed that doping hafnium, zirconium, or titanium with a +3-oxidation-state rare earth element causes or permits ‘dielectric relaxation’ in the film-forming materials or film thereby formed. High frequencies cause the dielectric constant (or relative permittivity) of the material to decrease, which is known as dielectric relaxation. It is hypothesized that dielectric relaxation occurs because substitution of hafnium, zirconium or titanium with the +3 element in the lattice causes an oxygen vacancy in order to maintain balanced charge. In order to improve the dielectric constant and/or maintain the dielectric constant at high frequencies, a hafnium oxide, zirconium oxide, titanium oxide or mixed oxide film can be created using a precursor as disclosed herein such that cerium (IV) is incorporated into the lattice.

**[0051]** Thus in one embodiment of the invention, the high- $\kappa$  dielectric material is stabilized by stabilizing the metastable phase of the metal used. For example, and without being bound by theory, pure zirconium oxide and hafnium oxide exhibit a stable monoclinic crystalline phase with dielectric constant typically in the range of about 18 to about 22. The metastable phases, such as tetragonal and cubic crystal structures of these materials, have high permittivities. Therefore, it is hypothesized that in order to stabilize the metastable phases, some of the Group IV metal may be replaced with one or more

cerium precursors of Formula I which can adopt a +4 charge and may obviate the formation of charged oxygen ion vacancies.

**[0052]** Further, the use of cerium precursor(s) to stabilize different phases also has implications for radiation hardness, as the resistance to radiation can be increased which is very useful for space applications where resistance to degradation by various forms of radiation is key to device lifetimes and efficiencies. Therefore, these stabilized high- $\kappa$  dielectric materials are useful in semiconductor devices and are useful for computer memory and logic applications, such as dynamic random access memory (DRAM) and complementary metal oxide semi-conductor (CMOS) circuitry.

**[0053]** In another embodiment of the invention, a high- $\kappa$  dielectric film-forming lattice is provided. The lattice, which is an array of points repeating periodically in three dimensions, is comprised of hafnium oxide, titanium oxide, or mixtures thereof; and the lattice contains cerium atoms. The atoms are arranged upon the points of the lattice. The points form unit cells that fill the space of the lattice.

**[0054]** In addition to phase stabilization discussed above, without being bound by theory, the cerium may also have an effect on the polarizability of the unit cell, *i.e.* the relative tendency of a charge distribution, like the electron cloud of an atom or molecule, to be distorted from its normal shape by an external electric field, which may be caused by the presence of a nearby ion or dipole. With cerium present it is hypothesized that this polarizability is enhanced which may impact the dielectric constant value beneficially by increasing or maintaining the dielectric constant longer. Polarizability of the unit cell coupled with stabilization of the highest dielectric constant phase of each metal oxide may ensure that the maximum dielectric constant value can be obtained from the particular material system in use.

**[0055]** The cerium atoms for the lattice are provided from at least one cerium precursor corresponding in structure to Formula I.

**[0056]** The cerium may be substitutional on the Group IV atomic sites or located interstitially, as interstitial inclusions.

**[0057]** The lattice is capable of forming a high- $\kappa$  dielectric film by a vapor deposition process, such as CVD or ALD.

**[0058]** In one embodiment, the film formed by the lattice has a thickness from about

0.2 nm to about 500 nm; and contains from about 0.5 to about 35 atomic metal % cerium. In a particular embodiment the metal oxide or mixed metal oxide film contains from about 5 to about 20 atomic metal % cerium. In a further particular embodiment, the metal oxide or mixed metal oxide film contains from about 8 to about 12 atomic metal % cerium.

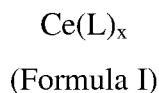
**[0059]** In another embodiment, the film formed by the lattice has a relative permittivity of about 20 to about 100, particularly from about 40 to about 70. Further, the film formed is capable of maintaining a relative permittivity of about 20 to about 100 at frequencies of about 1KHz to about 1GHz.

**[0060]** All patents and publications cited herein are incorporated by reference into this application in their entirety.

**[0061]** The words “comprise”, “comprises”, and “comprising” are to be interpreted inclusively rather than exclusively.

## WHAT IS CLAIMED IS:

1. A method to form a high- $\kappa$  dielectric film by a vapor deposition process, the method comprising delivering at least one metal-source precursor and at least one cerium precursor to a substrate, wherein the at least one cerium precursor corresponds in structure to Formula I:



wherein:

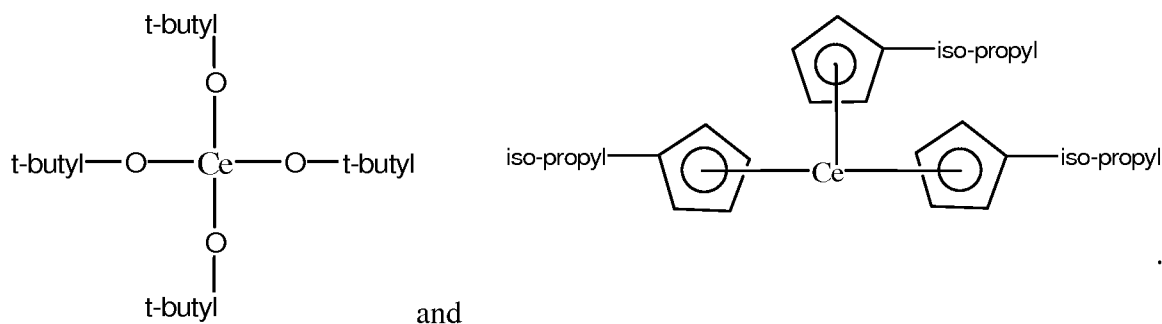
L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; or

L is alkoxy;

$\text{R}_1$  and  $\text{R}_2$  are independently hydrogen or alkyl; and

x is 3 or 4.

2. The method of Claim 1, wherein  
L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ .
3. The method of Claim 2, wherein the cyclopentadienyl ring is substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; and  
x is 3.
4. The method of Claim 1, wherein  
L is independently selected from the group consisting of methoxy, ethoxy, propoxy, butoxy and pentoxy; and  
x is 4.
5. The method of Claim 1, wherein the at least one cerium precursor is selected from the group consisting of



6. The method of Claim 1, wherein the high- $\kappa$  dielectric film comprises hafnium oxide and cerium; or zirconium oxide and cerium; or titanium oxide and cerium; or mixtures of hafnium oxide, zirconium oxide and/or titanium oxide and cerium.
7. The method of Claim 6, wherein the hafnium oxide, zirconium oxide, titanium oxide or mixture thereof contains from about 0.5 to about 35 atomic metal % cerium.
8. The method of Claim 7, wherein the hafnium oxide, zirconium oxide, titanium oxide or mixture thereof contains from about 5 to about 20 atomic metal % cerium.
9. The method of Claim 7, wherein the hafnium oxide, zirconium oxide, titanium oxide or mixture thereof contains from about 8 to about 12 atomic metal % cerium.
10. The method of Claim 1, wherein the vapor deposition process is chemical vapor deposition.
11. The method of Claim 10, wherein the chemical vapor deposition is liquid injection chemical vapor deposition.

12. The method of Claim 1, wherein the vapor deposition process is atomic layer deposition.
13. The method of Claim 12, wherein the atomic layer deposition is photo-assisted atomic layer deposition.
14. The method of Claim 12, wherein the atomic layer deposition is liquid injection atomic layer deposition.
15. The method of Claim 1, wherein the at least one cerium precursor is dissolved in an organic solvent.
16. The method of Claim 15, wherein the organic solvent is selected from the group consisting of toluene, heptane, octane, nonane and tetrahydrofuran.
17. The method of Claim 1, wherein each precursor is deposited onto the substrate in pulses alternating with pulses of an oxygen source.
18. The method of Claim 17, wherein the oxygen source is H<sub>2</sub>O, O<sub>2</sub> or ozone.
19. The method of Claim 1, wherein each precursor is deposited onto the substrate in pulses with a continuous supply of the oxygen source.
20. The method of Claim 19, wherein the oxygen source is H<sub>2</sub>O, O<sub>2</sub> or ozone.
21. The method of Claim 1, wherein the at least one metal-source precursor is compatible with the cerium precursor.
22. The method of Claim 1, wherein the at least one metal-source precursor is selected from the group consisting of
  - a metal amide selected from the group consisting of Hafnium dimethylamide, Zirconium dimethylamide, Titanium dimethylamide, Hafnium ethylmethanamide, Zirconium ethylmethanamide, Titanium ethylmethanamide, Hafnium diethylamide, Zirconium diethylamide and Titanium diethylamide;

a metal alkoxide selected from the group consisting of Hafnium t-butoxide, Zirconium t-butoxide, Titanium t-butoxide, Hafnium i-propoxide, Zirconium i-propoxide, Titanium i-propoxide, Hafnium bis t-butoxy bis 2-methyl-2-methoxy propoxide, Zirconium bis t-butoxy bis 2-methyl-2-methoxy propoxide, Titanium bis t-butoxy bis 2-methyl-2-methoxy propoxide, Zirconium bis i-propoxy bis 2-methyl-2-methoxy propoxide, Titanium bis i-propoxy bis 2-methyl-2-methoxy propoxide, Hafnium 2-methyl-2-methoxy propoxide, Zirconium 2-methyl-2-methoxy propoxide and Titanium 2-methyl-2-methoxy propoxide;

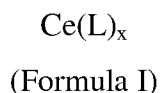
a metal  $\beta$ -diketonate selected from the group consisting of Hafnium 2,2,6,6-tetramethyl-3,5-heptanedionate, Zirconium 2,2,6,6-tetramethyl-3,5-heptanedionate, Titanium 2,2,6,6-tetramethyl-3,5-heptanedionate, Zirconium bis i-propoxy bis 2,2,6,6-tetramethyl-3,5-heptanedionate and Titanium bis i-propoxy 2,2,6,6-tetramethyl-3,5-heptanedionate;

a metal cyclopentadienyl selected from the group consisting of bis methylcyclopentadienyl Hafnium dimethyl, bis methylcyclopentadienyl Zirconium dimethyl, bis methylcyclopentadienyl Hafnium methyl methoxide, bis methylcyclopentadienyl Zirconium methyl methoxide, methylcyclopentadienyl Hafnium tris dimethylamide, methylcyclopentadienyl Zirconium tris dimethylamide and methylcyclopentadienyl Titanium tris dimethylamide.

23. The method of Claim 1, wherein the high- $\kappa$  dielectric film has a relative permittivity of about 20 to about 100.
24. The method of Claim 1, wherein the high- $\kappa$  dielectric film can maintain a relative permittivity of about 20 to about 100 at frequencies of about 1KHz to about 1GHz.
25. The method of Claim 1, wherein the high- $\kappa$  dielectric film is used for memory and logic applications in silicon chips.
26. A method to improve high- $\kappa$  gate property of a semiconductor device, the method comprising using at least one cerium precursor to form a high- $\kappa$  dielectric film for



use in the semiconductor device, wherein the at least one cerium precursor corresponds in structure to Formula I:



wherein:

L is a cyclopentadienyl ring optionally substituted with one or more substituents selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; or L is alkoxy;  
 $\text{R}_1$  and  $\text{R}_2$  are independently hydrogen or alkyl; and  
x is 3 or 4.

27. The method of Claim 26, wherein

L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ .

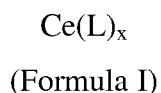
28. The method of Claim 26, wherein the cyclopentadienyl ring is substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; and x is 3.

29. The method of Claim 26, wherein

L is independently selected from the group consisting of methoxy, ethoxy, propoxy, butoxy and pentoxy; and  
x is 4.

30. The method of Claim 26, wherein the high- $\kappa$  dielectric film comprises hafnium oxide containing cerium; zirconium oxide containing cerium; titanium oxide containing cerium; or mixtures of hafnium oxide, zirconium oxide and/or titanium oxide containing cerium.

31. The method of Claim 26, wherein the high- $\kappa$  dielectric film has a relative permittivity of about 20 to about 100.
32. The method of Claim 26, wherein the high- $\kappa$  dielectric film can maintain a relative permittivity of about 20 to about 100 at frequencies of about 1KHz to about 1GHz.
33. The method of Claim 26, wherein the high- $\kappa$  dielectric film is formed by chemical vapor deposition or atomic layer deposition.
34. A method to stabilize a high- $\kappa$  dielectric material, the method comprising adding at least one cerium precursor to the high- $\kappa$  dielectric material wherein the at least one cerium precursor corresponds in structure to Formula I:



wherein:

L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; or

L is alkoxy;

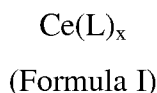
$\text{R}_1$  and  $\text{R}_2$  are independently hydrogen or alkyl; and

x is 3 or 4.

35. The method of Claim 34, wherein L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ .
36. The method of Claim 34, wherein the cyclopentadienyl ring is substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; and  
x is 3.

37. The method of Claim 34, wherein  
L is independently selected from the group consisting of methoxy, ethoxy, propoxy, butoxy and pentoxy; and  
x is 4.
38. The method of Claim 34, wherein the high- $\kappa$  dielectric material is hafnium oxide, zirconium oxide, titanium oxide or a mixture of hafnium oxide, zirconium oxide and/or titanium oxide.
39. The method of Claim 38, wherein to stabilize the high- $\kappa$  dielectric material a hafnium, zirconium or titanium oxide metastable phase is maintained.
40. The method of Claim 38, wherein stabilization of a hafnium oxide, zirconium oxide or titanium oxide results in a relative permittivity of about 20 to about 100.
41. The method of Claim 38, wherein stabilization of a hafnium oxide, zirconium oxide or titanium oxide results in a relative permittivity of about 25 to about 100 at frequencies of about 1KHz to about 1GHz.
42. The method of Claim 34, wherein the stabilized high- $\kappa$  dielectric material is used in a semiconductor device.
43. A high- $\kappa$  dielectric film-forming lattice, wherein the lattice is comprised of hafnium oxide, titanium oxide or mixture thereof and the lattice contains cerium atoms.
44. The high- $\kappa$  dielectric film-forming lattice of Claim 43, wherein the cerium is substitutionally part of the lattice or the cerium is part of the lattice as interstitial inclusions.

45. The high- $\kappa$  dielectric film-forming lattice of Claim 43, wherein the cerium atoms are provided from at least one cerium precursor corresponding in structure to Formula I:



wherein:

L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; or

L is alkoxy;

$\text{R}_1$  and  $\text{R}_2$  are independently hydrogen or alkyl; and

x is 3 or 4.

46. The high- $\kappa$  dielectric film-forming lattice of Claim 45, wherein

L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ .

47. The high- $\kappa$  dielectric film-forming lattice of Claim 45, wherein the

cyclopentadienyl ring is substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; and

x is 3.

48. The high- $\kappa$  dielectric film-forming lattice of Claim 45, wherein

L is independently selected from the group consisting of methoxy, ethoxy, propoxy, butoxy and pentoxy; and

x is 4.

49. The high- $\kappa$  dielectric film-forming lattice of Claim 43, wherein the film formed has a thickness from about 0.2nm to about 500nm.

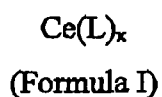
50. The high- $\kappa$  dielectric film forming lattice of Claim 43, wherein the film formed has a relative permittivity of about 20 to about 100.

51. The high- $\kappa$  dielectric film forming lattice of Claim 43, wherein the film formed has a relative permittivity of about 20 to about 100 at frequencies of about 1KHz to about 1GHz.

## AMENDED CLAIMS

received by the International Bureau on 30 September 2009 (30.09.2009)

1. A method to form a cerium-doped high- $\kappa$  dielectric film by a vapor deposition process, the method comprising delivering at least one metal-source precursor and at least one cerium precursor to a substrate, wherein the at least one cerium precursor corresponds in structure to Formula I:



wherein:

L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; or

L is alkoxy;

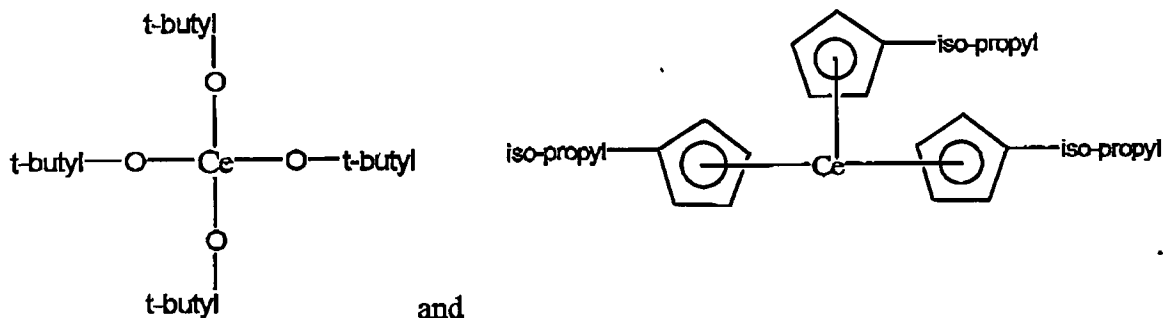
$\text{R}_1$  and  $\text{R}_2$  are independently hydrogen or alkyl; and

x is 3 or 4;

wherein the high- $\kappa$  dielectric film is selected from the group consisting of hafnium oxide; zirconium oxide; titanium oxide; and two or more of hafnium oxide, zirconium oxide and titanium oxide.

2. The method of Claim 1, wherein  
L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ .
3. The method of Claim 2, wherein the cyclopentadienyl ring is substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; and x is 3.
4. The method of Claim 1, wherein  
L is independently selected from the group consisting of methoxy, ethoxy, propoxy, butoxy and pentoxy; and x is 4.

5. The method of Claim 1, wherein the at least one cerium precursor is selected from the group consisting of



6. [Cancelled]
7. The method of Claim 1, wherein the hafnium oxide, zirconium oxide, titanium oxide or two or more thereof contains from about 0.5 to about 35 atomic metal % cerium.
8. The method of Claim 7, wherein the hafnium oxide, zirconium oxide, titanium oxide or two or more thereof contains from about 5 to about 20 atomic metal % cerium.
9. The method of Claim 7, wherein the hafnium oxide, zirconium oxide, titanium oxide or two or more thereof contains from about 8 to about 12 atomic metal % cerium.
10. The method of Claim 1, wherein the vapor deposition process is chemical vapor deposition.
11. The method of Claim 10, wherein the chemical vapor deposition is liquid injection chemical vapor deposition.

12. The method of Claim 1, wherein the vapor deposition process is atomic layer deposition.
13. The method of Claim 12, wherein the atomic layer deposition is photo-assisted atomic layer deposition.
14. The method of Claim 12, wherein the atomic layer deposition is liquid injection atomic layer deposition.
15. The method of Claim 1, wherein the at least one cerium precursor is dissolved in an organic solvent.
16. The method of Claim 15, wherein the organic solvent is selected from the group consisting of toluene, heptane, octane, nonane and tetrahydrofuran.
17. The method of Claim 1, wherein each precursor is deposited onto the substrate in pulses alternating with pulses of an oxygen source.
18. The method of Claim 17, wherein the oxygen source is H<sub>2</sub>O, O<sub>2</sub> or ozone.
19. The method of Claim 1, wherein each precursor is deposited onto the substrate in pulses with a continuous supply of the oxygen source.
20. The method of Claim 19, wherein the oxygen source is H<sub>2</sub>O, O<sub>2</sub> or ozone.
21. The method of Claim 1, wherein the at least one metal-source precursor is compatible with the cerium precursor.
22. The method of Claim 1, wherein the at least one metal-source precursor is selected from the group consisting of  
a metal amide selected from the group consisting of Hafnium dimethylamide, Zirconium dimethylamide, Titanium dimethylamide, Hafnium ethylmethylanide, Zirconium ethylmethylanide, Titanium ethylmethylanide, Hafnium diethylamide, Zirconium diethylamide and Titanium diethylamide;



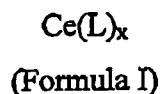
a metal alkoxide selected from the group consisting of Hafnium t-butoxide, Zirconium t-butoxide, Titanium t-butoxide, Hafnium i-propoxide, Zirconium i-propoxide, Titanium i-propoxide, Hafnium bis t-butoxy bis 2-methyl-2-methoxy propoxide, Zirconium bis t-butoxy bis 2-methyl-2-methoxy propoxide, Titanium bis t-butoxy bis 2-methyl-2-methoxy propoxide, Zirconium bis i-propoxy bis 2-methyl-2-methoxy propoxide, Titanium bis i-propoxy bis 2-methyl-2-methoxy propoxide, Hafnium 2-methyl-2-methoxy propoxide, Zirconium 2-methyl-2-methoxy propoxide and Titanium 2-methyl-2-methoxy propoxide;

a metal  $\beta$ -diketonate selected from the group consisting of Hafnium 2,2,6,6-tetramethyl-3,5-heptanedionate, Zirconium 2,2,6,6-tetramethyl-3,5-heptanedionate, Titanium 2,2,6,6-tetramethyl-3,5-heptanedionate, Zirconium bis i-propoxy bis 2,2,6,6-tetramethyl-3,5-heptanedionate and Titanium bis i-propoxy 2,2,6,6-tetramethyl-3,5-heptanedionate;

a metal cyclopentadienyl selected from the group consisting of bis methylcyclopentadienyl Hafnium dimethyl, bis methylcyclopentadienyl Zirconium dimethyl, bis methylcyclopentadienyl Hafnium methyl methoxide, bis methylcyclopentadienyl Zirconium methyl methoxide, methylcyclopentadienyl Hafnium tris dimethylamide, methylcyclopentadienyl Zirconium tris dimethylamide and methylcyclopentadienyl Titanium tris dimethylamide.

23. The method of Claim 1, wherein the high- $\kappa$  dielectric film has a relative permittivity of about 20 to about 100.
24. The method of Claim 1, wherein the high- $\kappa$  dielectric film can maintain a relative permittivity of about 20 to about 100 at frequencies of about 1KHz to about 1GHz.
25. The method of Claim 1, wherein the high- $\kappa$  dielectric film is used for memory and logic applications in silicon chips.
26. A method to improve high- $\kappa$  gate property of a semiconductor device, the method comprising using at least one cerium precursor to form a high- $\kappa$  dielectric film for

use in the semiconductor device, wherein the at least one cerium precursor corresponds in structure to Formula I:



wherein:

L is a cyclopentadienyl ring optionally substituted with one or more substituents selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; or L is alkoxy;  $\text{R}_1$  and  $\text{R}_2$  are independently hydrogen or alkyl; and x is 3 or 4.

27. The method of Claim 26, wherein

L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ .

28. The method of Claim 26, wherein the cyclopentadienyl ring is substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; and x is 3.

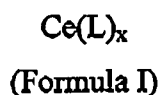
29. The method of Claim 26, wherein

L is independently selected from the group consisting of methoxy, ethoxy, propoxy, butoxy and pentoxy; and x is 4.

30. The method of Claim 26, wherein the high- $\kappa$  dielectric film is selected from the group consisting of hafnium oxide containing cerium; zirconium oxide containing cerium; titanium oxide containing cerium; and two or more of hafnium oxide, zirconium oxide and titanium oxide containing cerium.

31. The method of Claim 26, wherein the high- $\kappa$  dielectric film has a relative permittivity of about 20 to about 100.

32. The method of Claim 26, wherein the high- $\kappa$  dielectric film can maintain a relative permittivity of about 20 to about 100 at frequencies of about 1KHz to about 1GHz.
33. The method of Claim 26, wherein the high- $\kappa$  dielectric film is formed by chemical vapor deposition or atomic layer deposition.
34. A method to stabilize a high- $\kappa$  dielectric material, the method comprising adding at least one cerium precursor to the high- $\kappa$  dielectric material wherein the at least one cerium precursor corresponds in structure to Formula I:



wherein:

L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; or

L is alkoxy;

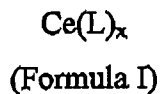
$\text{R}_1$  and  $\text{R}_2$  are independently hydrogen or alkyl; and

x is 3 or 4;

wherein the high- $\kappa$  dielectric material is selected from the group consisting of hafnium oxide; zirconium oxide; titanium oxide; and two or more of hafnium oxide, zirconium oxide and titanium oxide.

35. The method of Claim 34, wherein L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ .
36. The method of Claim 34, wherein the cyclopentadienyl ring is substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; and x is 3.

37. The method of Claim 34, wherein  
L is independently selected from the group consisting of methoxy, ethoxy, propoxy, butoxy and pentoxy; and x is 4.
38. [Cancelled]
39. The method of Claim 34, wherein to stabilize the high- $\kappa$  dielectric material a hafnium, zirconium or titanium oxide metastable phase is maintained.
40. The method of Claim 34, wherein stabilization of a hafnium oxide, zirconium oxide or titanium oxide results in a relative permittivity of about 20 to about 100.
41. The method of Claim 34, wherein stabilization of a hafnium oxide, zirconium oxide or titanium oxide results in a relative permittivity of about 25 to about 100 at frequencies of about 1KHz to about 1GHz.
42. The method of Claim 34, wherein the stabilized high- $\kappa$  dielectric material is used in a semiconductor device.
43. A high- $\kappa$  dielectric film-forming lattice, wherein the lattice is comprised of hafnium oxide, titanium oxide or mixture thereof and the lattice contains cerium atoms.
44. The high- $\kappa$  dielectric film-forming lattice of Claim 43, wherein the cerium is substitutionally part of the lattice or the cerium is part of the lattice as interstitial inclusions.
45. The high- $\kappa$  dielectric film-forming lattice of Claim 43, wherein the cerium atoms are provided from at least one cerium precursor corresponding in structure to Formula I:



wherein:

L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; or

L is alkoxy;

$\text{R}_1$  and  $\text{R}_2$  are independently hydrogen or alkyl; and

x is 3 or 4.

46. The high- $\kappa$  dielectric film-forming lattice of Claim 45, wherein

L is a cyclopentadienyl ring optionally substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ .

47. The high- $\kappa$  dielectric film-forming lattice of Claim 45, wherein the

cyclopentadienyl ring is substituted with one or more substituents independently selected from the group consisting of alkyl, alkoxy and  $\text{NR}_1\text{R}_2$ ; and  
x is 3.

48. The high- $\kappa$  dielectric film-forming lattice of Claim 45, wherein

L is independently selected from the group consisting of methoxy, ethoxy, propoxy, butoxy and pentoxy; and  
x is 4.

49. The high- $\kappa$  dielectric film-forming lattice of Claim 43, wherein the film formed has a thickness from about 0.2nm to about 500nm.

50. The high- $\kappa$  dielectric film forming lattice of Claim 43, wherein the film formed has a relative permittivity of about 20 to about 100.

51. The high- $\kappa$  dielectric film forming lattice of Claim 43, wherein the film formed has a relative permittivity of about 20 to about 100 at frequencies of about 1KHz to about 1GHz.

60595316.1

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2009/045024

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C16/40 C07F5/00 H01L21/316

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C C07F H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, COMPENDEX, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 248 605 B1 (HÄRKÖNEN GITTE [FI] ET AL) 19 June 2001 (2001-06-19)  example 1	1-3, 10, 12, 26-28, 34-36
X	US 2005/112874 A1 (SKARP JARMO [FI] ET AL) 26 May 2005 (2005-05-26)	1-3, 6, 10, 12, 17, 18, 21-27, 30-35, 38, 40-42
Y	paragraphs [0014], [0023] - [0025], [0031], [0036] - [0040], [0049], [0051]  ----- -/--	4, 5, 7-9, 11, 13-16, 19, 20, 29, 37, 39

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \* & \* document member of the same patent family

Date of the actual completion of the international search

16 July 2009

Date of mailing of the international search report

30/07/2009

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
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Fax: (+31-70) 340-3016

Authorized officer

Hoyer, Wolfgang

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2009/045024

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 11 2005 000134 T5 (ADEKA CORP [JP]) 15 February 2007 (2007-02-15)  paragraphs [0002], [0019] - [0023], [0030], [0038], [0039], [0041] - [0044] -----	11, 13-16, 19,20, 29,37
Y	ASPINALL H C: "Requirements of precursors for MOCVD and ALD of rare earth oxides" RARE EARTH OXIDE THIN FILMS, 2006, pages 53-72, XP009120065 SPRINGER BERLIN [DE] ISSN: 1437-0859 ISBN: 978-3-540-35796-4 the whole document -----	4,5
Y	TCHÉLIEBOU F ET AL: "Electrical behaviour of thin ZrO <sub>2</sub> films containing some ceramic oxides" MATERIALS SCIENCE AND ENGINEERING B, vol. 38, no. 1, 1 March 1996 (1996-03-01), pages 90-95, XP004017433 ELSEVIER SEQUOIA, LAUSANNE [CH] ISSN: 0921-5107 figure 11 -----	7-9,39
Y	MARDARE D ET AL: "Comparison of the dielectric properties for doped and undoped TiO <sub>2</sub> thin films" JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, vol. 6, no. 1, March 2004 (2004-03), pages 333-336, XP002537286 National Institute of Optoelectronics, Bucharest [RO] ISSN: 1841-7132 table 1 -----	7
A	GASKELL J M ET AL: "Deposition of lanthanum zirconium oxide high-k films by liquid injection ALD and MOCVD" CHEMICAL VAPOR DEPOSITION, vol. 13, no. 12, December 2007 (2007-12), pages 684-690, XP002537287 WILEY-VCH VERLAG [DE] the whole document -----	11,14-16



## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 43-51

In present claim 43, "a high-kappa dielectric film forming lattice comprised of hafnium oxide, titanium oxide or mixture thereof and the lattice contains cerium atoms" is claimed, followed by dependent claims 44 - 51. The claims are directed to a "lattice" per se. A "lattice" is not a product but a structural information presenting the crystallographic relations of atom positions in a compound. A claim directed to an information, however, is excluded from International Search and International Preliminary Examination (see Rule 67.1 (v) PCT and PCT International Search and Preliminary Examination Guidelines, ch. 9.11). Hence, no search is carried out for claims 43 - 51.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2)PCT declaration be overcome.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US2009/045024

### Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 43-51  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

### Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search reportcovers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

#### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2009/045024

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