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(71) Applicant (for all designated States except US): **THE UNIVERSITY OF LIVERPOOL** [GB/GB]; Foundation Building, 765 Brownlow Hill, Liverpool Merseyside L69 7ZX (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **SUCHOMEL, Matthew** [US/US]; Advanced Photo Source, 9700 South Cass Avenue, Bldg. 433/D006, Argonne National Laboratory, Argonne, Illinois 60439-4856 (US). **ROSSEIN-SKY, Matthew** [GB/GB]; 5 Birchway, Heswall Cheshire CH60 3SX (GB). **NIU, Hongjun** [CN/GB]; 40 Westhead Avenue, Kirby, Liverpool Merseyside L33 5XA (GB). **CHALKER, Paul** [GB/GB]; 8 Darmonds Green, West Kirby, Wirral Cheshire CH48 5DU (GB). **YAN, Lei** [CN/GB]; Flat 1, Botanic Road, Liverpool Merseyside L7 5PZ (GB).

(74) Agent: **STUTTARD, Garry**; Tower North Central, Mer-
rion Way, Leeds Yorkshire LS2 8PA (GB).

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(54) Title: PROCESS FOR PREPARING A DEVICE

(57) Abstract: The present invention relates to a process for preparing a functional device which comprises a substrate and an element composed of a strontium-hafnium- titanium oxide or strontium- zirconium- titanium oxide. The process involves exposing the substrate to discrete volatalised amounts of a strontium precursor, a hafnium or zirconium precursor an a titanium precursor in sequential steps.



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PROCESS FOR PREPARING A DEVICE

The present invention relates to a process for preparing a functional device which comprises a substrate and an element composed of a strontium-hafnium-titanium oxide or strontium-zirconium-titanium oxide.

The silicon dioxide (SiO_2) gate layer in a MOS (metal-oxide-semiconductor) field effect transistor device may be substituted by an oxide material with a higher dielectric constant (high-k). However there are few oxide materials which satisfy the requirements of dielectric constant, thermal stability and band gap, whilst providing an interface suitable for integration by silicon processing (see J Robertson, J. Appl. Phys. 104, 7 (2008)). These oxides include ZrO_2 (see M N S Miyazaki *et al*, Microelectronic Engineering 59, 6 (2001) and R N Wen-Jie Qi *et al*, Appl. Phys. Lett. 77, 3 (2000)), HfO_2 (see T M R C Smith *et al*, Adv. Mater. Opt. Electron. 10, 10 (2000); E C E P Gusev *et al*, Microelectronic Engineering 59, 9 (2001); and R H D C Gilmer *et al*, Appl. Phys. Lett. 81, 3 (2002)), Al_2O_3 (see E C M Copel *et al*, Appl. Phys. Lett. 78, 3 (2001) and C P E Ghiraldelli *et al*, Thin Solid Films 517, 3 (2008)) and LaAlO_3 (see S K Seung-Gu Lim *et al*, J. Appl. Phys. 91, 6 (2002); H B L L Yan, *et al*, Appl. Phys. A 77, 4 (2003); and H L Wenfeng Xiang *et al*, J. Appl. Phys. 93, 4 (2003)). SrHfO_3 is attracting increasing interest as a candidate for a high-k material (B M C Rossel *et al*, Appl. Phys. Lett. 89, 3 (2006); G K G. Lupina *et al*, Appl. Phys. Lett. 93, 3 (2008) and C R M Sousa *et al*, J. Appl. Phys. 102, 6 (2007)). SrTiO_3 and $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3$ are attractive candidates for a gate dielectric because of their large permittivity.

Thus it is generally desirable to identify techniques for growing specific mixed oxides such as strontium-titanium mixed oxides on a substrate for use as a functional device.

The present invention seeks to improve the preparation of a strontium-hafnium-titanium or strontium-zirconium-titanium oxide-based functional device by exploiting saturating surface reactions which control the growth of oxide films with improved properties such as conformality.

Viewed from a first aspect the present invention provides a process for preparing a functional device comprising a substrate and an element composed of a mixed metal oxide of formula $\text{SrM}_{1-x}\text{Ti}_x\text{O}_3$ (wherein x is $0 < x < 1$ and M is Hf or Zr), wherein the process comprises:

exposing discrete volatilised amounts of a strontium precursor, of a hafnium or zirconium precursor and of a titanium precursor to the substrate in sequential exposure steps in a contained environment.

Preferably each discrete volatilised amount is fed to the contained environment in a pulse. The pulse length may be in the range 1ms to 30s.

The process may further comprise: feeding an oxidising agent to the contained environment during one or more (preferably each) of the exposure steps or in one or more of the intervals between the exposure steps. The oxidising agent may be fed into the contained environment continuously or in a pulse during the exposure step.

Preferably the process further comprises: feeding the oxidising agent into the contained environment in a pulse during each exposure step.

The oxidising agent may be selected from the group consisting of oxygen (*eg* oxygen plasma), water vapor, hydrogen peroxide (or an aqueous solution thereof), ozone, an oxide of nitrogen (such as N_2O , NO or NO_2), a halide-oxygen compound (for example chlorine dioxide or perchloric acid), a peracid (for example perbenzoic acid or peracetic acid), an alcohol (such as methanol or ethanol) and radicals (such as oxygen radicals and hydroxyl radicals).

A preferred oxidising agent is oxygen plasma.

The process may further comprise: purging the contained environment during one or more (preferably each) of the exposure steps or in one or more of the intervals between the exposure steps. Purging may be carried out by an inert gas flow. The inert gas flow may be fed into the contained environment in a pulse during the exposure step.

Preferably the process further comprises: purging the contained environment with an inert gas flow in a pulse during each exposure step.

Preferably the sequential exposure steps are cyclical. The number and order of each of the steps of exposing discrete volatilised amounts of a strontium precursor, a hafnium or zirconium precursor and a titanium precursor to the substrate in the sequential exposure steps may be empirically determined to achieve a desired stoichiometry and incorporation rate. The number of cycles is determined generally by the desired oxide thickness. Typically the sequential exposure steps are cycled 2 to 100 times.

Preferably the process of the invention comprises a cycle of sequential exposure steps (A), (B) and (C), wherein

step (A) comprises: feeding the discrete volatilised amount of strontium precursor into the contained environment and purging the strontium precursor from the contained environment,

step (B) comprises: feeding the discrete volatilised amount of hafnium or zirconium precursor into the contained environment and purging the hafnium or zirconium precursor from the contained environment,

step (C) comprises: feeding the discrete volatilised amount of a titanium precursor into the contained environment and purging the titanium precursor from the contained environment.

Particularly preferably step (A) comprises: feeding the discrete volatilised amount of strontium precursor into the contained environment, purging the strontium precursor from the contained environment and feeding an oxidising agent into the contained environment and purging the contained environment.

Particularly preferably step (B) comprises: feeding the discrete volatilised amount of hafnium or zirconium precursor into the contained environment, purging the hafnium or zirconium precursor from the contained environment, feeding an oxidising agent into the contained environment and purging the contained environment.

Particularly preferably step (C) comprises: feeding the discrete volatilised amount of a titanium precursor into the contained environment, purging the titanium precursor from the contained environment and feeding an oxidising agent into the contained environment and purging the contained environment.

Each of steps (A), (B) and (C) may be independently cyclical. Preferably the ratio of the number of cycles of step (B) to the number of cycles of step (C) is in the range 3:1 to 1:3 (eg 3:1, 2:1, 1:1, 1:2 or 1:3). Particularly preferably the ratio of the number of cycles of step (B) to the number of cycles of step (C) is in the range 1:1 to 1:3.

Alternatively preferably the process of the invention comprises a cycle of sequential exposure steps (A'), (B'), (A'') and (C'), wherein

each of steps (A') and (A'') comprises: feeding the discrete volatilised amount of strontium precursor into the contained environment, purging the strontium precursor from the contained environment, feeding an oxidising agent into the contained environment and purging the contained environment,

step (B') comprises: feeding the discrete volatilised amount of hafnium or zirconium precursor into the contained environment, purging the hafnium or zirconium precursor from the contained environment, feeding an oxidising agent into the contained environment and purging the contained environment,

step (C') comprises: feeding the discrete volatilised amount of a titanium precursor into the contained environment, purging the titanium precursor from the contained

environment, feeding an oxidising agent into the contained environment and purging the contained environment.

Each of steps (A'), (B'), (A'') and (C') may be independently cyclical. Preferably the ratio of the number of cycles of step (A') to the number of cycles of step (B') is 3:1. Preferably the ratio of the number of cycles of step (A'') to the number of cycles of step (C') is 3:1.

Preferably the ratio of the number of cycles of step (B') to the number of cycles of step (C') is in the range 3:1 to 1:3 (*eg* 3:1, 2:1, 1:1, 1:2 or 1:3). Particularly preferably the ratio of the number of cycles of step (B') to the number of cycles of step (C') is in the range 1:1 to 1:3.

The contained environment is typically a reaction chamber.

Each precursor may be a volatile liquid or solid, a solid dissolvable or suspendable in a solvent medium for flash vaporization or a sublimable solid. Volatilisation of the precursor may be heat-assisted or photo-assisted. Each discrete volatilised amount may be fed into the contained environment in the gaseous phase (*eg* as a vapour). The contained environment may be at a temperature in the range 100 to 700°C, preferably 150 to 500°C.

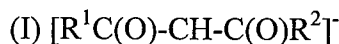
The process may further comprise: pre-treating (*eg* pre-heating) the substrate.

The process may further comprise: a post-treatment step. The post-treatment step may be a post-annealing (*eg* rapid thermal post-annealing) step, oxidizing step or reducing step. The step of post-annealing is typically carried out at a temperature in excess of the temperature at which the sequential steps are carried out in the contained environment. For example, post-annealing may be carried out at a temperature in the range 500°C to 900°C for an annealing period of a few seconds to 60 minutes in an air flow.

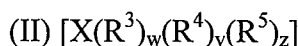
Each precursor may be a complex featuring one or more bonds between the metal and each of one or more organic ligands (*eg* coordination bonds between the metal and a heteroatom such as oxygen or nitrogen or bonds between the metal and carbon). The precursor may be a metal organic or an organometallic complex.

The titanium precursor may be a titanium (III) or titanium (IV) precursor. Preferably the titanium precursor is a titanium halide, titanium β -diketonate, titanium alkoxide (such as *iso*-propoxide or *tert*-butoxide), dialkylamino titanium complex, alkylamino titanium complex, silylamido titanium complex, cyclopentadienyl titanium complex, titanium dialkyldithiocarbamate or titanium nitrate.

The titanium of the titanium precursor may have one or more (for example four) organic ligands which may be the same or different selected from the group of organic ligands defined by formulae (I) to (IV) (preferably one of formulae (I) to (IV)) as follows:



(wherein each of R^1 and R^2 which may be the same or different is an optionally fluorinated, linear or branched C_{1-12} alkyl group);



(wherein X is a heteroatom;

R^3 is H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups or a $Si(R^6)_2$ or $Si(R^6)_3$ group;

R^4 is H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups or a $Si(R^7)_2$ or $Si(R^7)_3$ group;

R^5 is H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups or a $Si(R^8)_2$ or $Si(R^8)_3$ group;

each of R^6 , R^7 and R^8 is independently H or a linear or branched C_{1-12} alkyl, C_{6-12} aryl, C_{3-12} allyl or C_{3-12} vinyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups;

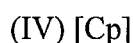
w is an integer of 1 or 2;

y is an integer of 0 or 1; and

z is an integer of 0 or 1);



(wherein each of R^9 and R^{10} is independently an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups);



(wherein Cp denotes a single or fused cyclopentadiene moiety optionally ring-substituted partially or fully by one or more of the group consisting of an optionally substituted, acyclic

or cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, aralkyl or alkoxy group or a thio, amino, cyano or silyl group).

Preferably the titanium of the titanium precursor has four organic ligands selected from the group of organic ligands defined by formulae (I) to (IV) (preferably one of formulae (I) to (IV)).

Preferably the ligand of formula (I) is an optionally methylated and/or optionally fluorinated (*eg* optionally tri- or hexa-fluorinated) acetylacetonato, heptanedionato or octanedionato ligand. For example, the ligand of formula (I) may be a 1,1,1-trifluoropentane-2,4-dionato, 1,1,1,5,5,5-hexafluoropentane-2,4-dionato or 2,2,6,6-tetramethyl-3,5-heptanedionato ligand.

Preferably either or both of R^1 and R^2 are trifluorinated or hexafluorinated.

Preferably R^1 is a C_{1-6} perfluoroalkyl. Preferably R^2 is a C_{1-6} perfluoroalkyl.

Preferably X is O. Particularly preferably X is O, y is 0, z is 0, w is 1 and R^3 is an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups. For example, the ligand of formula (II) may be a hexafluoroisopropoxy, 2-dimethylaminoethanolate, 2-methoxyethanolate or 1-methoxy-2-methyl-2-propanolate ligand.

Preferably X is N. Particularly preferably X is N, y is 1, w is 1, z is 1 and each of R^3 , R^4 and R^5 is independently H, an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups.

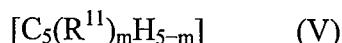
Alternatively particularly preferably, X is N, y is 1, w is 1, z is 1, R^3 is $Si(R^6)_2$ or $Si(R^6)_3$, R^4 is $Si(R^7)_2$ or $Si(R^7)_3$ and R^5 is $Si(R^8)_2$ or $Si(R^8)_3$, wherein each of R^6 , R^7 and R^8 is independently methyl, propyl or butyl.

Preferably each of R^3 , R^4 and R^5 is independently methyl, ethyl, propyl, butyl or pentyl, particularly preferably methyl, propyl or butyl, more preferably *n*-butyl, *tert*-butyl, *iso*-propyl or ethyl.

Preferably the titanium of the titanium precursor has two ligands of formula (IV). The cyclopentadiene moieties of the two ligands of formula (IV) may be bridged. The bridge may be a substituted or unsubstituted C_{1-6} -alkylene group which is optionally interrupted by a heteroatom (such as O, Si, N, P, Se or S).

Preferably the ligand of formula (IV) is a cyclopentadienyl, indenyl, fluorenyl, pentamethylcyclopentadienyl, *tert*-butylcyclopentadienyl or triisopropylcyclopentadienyl ligand.

Preferably in a titanium precursor the (or each) ligand of formula (IV) is a cyclopentadienyl ligand of formula (V)



(wherein m is an integer in the range 0 to 5 and

each R^{11} which may be the same or different is selected from the group consisting of a C_{1-12} alkyl, C_{1-12} alkylamino, C_{1-12} dialkylamino, C_{1-12} alkoxy, C_{3-10} cycloalkyl, C_{2-12} alkenyl, C_{7-12} aralkyl, C_{7-12} alkylaryl, C_{6-12} aryl, C_{5-12} heteroaryl, C_{1-10} perfluoroalkyl, silyl, alkylsilyl, perfluoroalkylsilyl, triarylsilyl and alkylsilylsilyl group).

Preferably the (or each) R^{11} group is methyl, ethyl, propyl (*eg* isopropyl) or butyl (*eg tert*-butyl).

The titanium precursor may be $Ti(OC_2H_5)_4$, $Ti(O^iPr)_4$, $Ti(O^tBu)_4$, $Ti(O^nBu)_4$ or $Ti(OCH_2(C_2H_5)CHC_4H_9)_4$.

The titanium precursor may be titanium nitrate.

The titanium precursor may be *di(iso-propoxy)bis*(2,2,6,6-tetramethyl-3,5-heptanedionato) titanium or *tris*(2,2,6,6-tetramethyl-3,5-heptanedionato) titanium or adducts or hydrates thereof.

The titanium precursor may be *tetrakis*(diethylamido) titanium, *tetrakis*(dimethylamido) titanium, *tetrakis*(ethylmethyldiamido) titanium, *tetrakis*(isopropylmethyldiamido) titanium, *bis*(diethylamido)*bis*(dimethylamido) titanium, *bis*(cyclopentadienyl)*bis*(dimethylamido) titanium, *tris*(dimethylamido)(*N,N,N'*-trimethylethyldiamido) titanium or *tert*-butyl*tris*(dimethylamido) titanium or adducts or hydrates thereof.

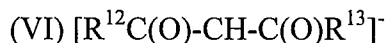
The titanium precursor may be titanium $(\eta^5-C_5H_5)_2$, titanium $(\eta^5-C_5H_5)(\eta^7-C_7H_7)$, $(\eta^5-C_5H_5)$ titanium Z_2 (wherein Z is alkyl (*eg* methyl), benzyl or carbonyl), *bis*(*tert*-butylcyclopentadienyl) titanium dichloride, *bis*(pentamethylcyclopentadienyl) titanium dichloride or $(C_5H_5)_2$ titanium $(CO)_2$ or adducts or hydrates thereof.

The titanium precursor may be a titaniumdialkyldithiocarbamate.

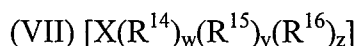
The titanium precursor may be $TiCl_4$, $TiCl_3$, $TiBr_3$, TiI_4 or TiI_3 .

The hafnium precursor may be a hafnium (IV) precursor. Preferably the hafnium precursor is a hafnium β -diketonate, hafnium alkoxide, dialkylamino hafnium complex, alkylamino hafnium complex or cyclopentadienyl hafnium complex.

The hafnium of the hafnium precursor may have one or more (for example four) organic ligands which may be the same or different selected from the group of organic ligands defined by formulae (VI) to (VIII) (preferably one of formulae (VI) to (VIII)) as follows:



(wherein each of R^{12} and R^{13} which may be the same or different is an optionally fluorinated, linear or branched C_{1-12} alkyl group);



(wherein X is a heteroatom;

R^{14} is H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups or a $(SiR^{17})_2$ or $(SiR^{17})_3$ group;

R^{15} is H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups or a $(SiR^{18})_2$ or $(SiR^{18})_3$ group;

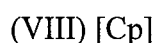
R^{16} is H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups or a $(SiR^{19})_2$ or $(SiR^{19})_3$ group;

each of R^{17} , R^{18} and R^{19} is independently H or a linear or branched C_{1-12} alkyl, C_{6-12} aryl, C_{3-12} allyl or C_{3-12} vinyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups;

w is an integer of 1 or 2;

y is an integer of 0 or 1; and

z is an integer of 0 or 1);



(wherein Cp denotes a single or fused cyclopentadiene moiety optionally ring-substituted partially or fully by one or more of the group consisting of an optionally substituted, acyclic

or cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, aralkyl or alkoxy group or a thio, amino, cyano or silyl group).

Preferably the hafnium of the hafnium precursor has four organic ligands selected from the group of organic ligands defined by formulae (VI) to (VIII) (preferably one of formulae (VI) to (VIII)).

Preferably the ligand of formula (VI) is an optionally methylated and/or optionally fluorinated (eg optionally tri- or hexa-fluorinated) acetylacetonato, heptanedionato or octanedionato ligand. For example, the ligand of formula (VI) may be a 1,1,1-trifluoropentane-2,4-dionato, 1,1,1,5,5,5-hexafluoropentane-2,4-dionato or 2,2,6,6-tetramethyl-3,5-heptanedionato ligand.

Preferably either or both of R^{12} and R^{13} are trifluorinated or hexafluorinated.

Preferably R^{12} is a C_{1-6} perfluoroalkyl. Preferably R^{13} is a C_{1-6} perfluoroalkyl.

Preferably X is O. Particularly preferably X is O, y is 0, w is 1, z is 0 and R^{14} is an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups. For example, the ligand of formula (VII) may be an isopropoxy, 2-dimethylaminoethanolate, 2-methoxyethanolate or 1-methoxy-2-methyl-2-propanolate ligand.

Preferably X is N. Particularly preferably X is N, y is 1, w is 1, z is 1 and each of R^{14} , R^{15} and R^{16} is independently H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups.

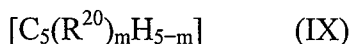
Preferably each of R^{14} , R^{15} and R^{16} is independently methyl, ethyl, propyl, butyl or pentyl, particularly preferably methyl, propyl or butyl, more preferably *n*-butyl, *tert*-butyl, *isopropyl* or ethyl.

The hafnium of the hafnium precursor may have one or two ligands of formula (VIII).

Preferably the hafnium of the hafnium precursor has two ligands of formula (VIII). The cyclopentadiene moieties of the two ligands of formula (VIII) may be bridged. The bridge may be a substituted or unsubstituted C_{1-6} -alkylene group which is optionally interrupted by a heteroatom (such as O, Si, N, P, Se or S).

Preferably the ligand of formula (VIII) is a cyclopentadienyl, indenyl, fluorenyl, methylcyclopentadienyl, pentamethylcyclopentadienyl or triisopropylcyclopentadienyl ligand.

Preferably in a hafnium precursor the (or each) ligand of formula (VIII) is a cyclopentadienyl ligand of formula (IX)



(wherein m is an integer in the range 0 to 5 and

each R^{20} which may be the same or different is selected from the group consisting of a C_{1-12} alkyl, C_{1-12} alkylamino, C_{1-12} dialkylamino, C_{1-12} alkoxy, C_{3-10} cycloalkyl, C_{2-12} alkenyl, C_{7-12} aralkyl, C_{7-12} alkylaryl, C_{6-12} aryl, C_{5-12} heteroaryl, C_{1-10} perfluoroalkyl, silyl, alkylsilyl, perfluoroalkylsilyl, triarylsilyl and alkylsilylsilyl group).

Preferably the (or each) R^{20} group is methyl, ethyl, propyl (eg *isopropyl*) or butyl (eg *tert*-butyl), particularly preferably methyl.

The hafnium precursor may be *di(isopropoxy)bis(2,2,6,6-tetramethyl-3,5-heptanedionato)* hafnium.

The hafnium precursor may be *bis(methylcyclopentadienyl)* dimethylhafnium, *bis(methylcyclopentadienyl)* methoxymethylhafnium or methylcyclopentadienyl hafnium *tris(dimethylamido)* or adducts or hydrates thereof.

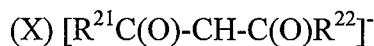
The hafnium precursor may be *tetrakis(dimethylamido)* hafnium, *tetrakis(diethylamido)* hafnium or *tetrakis(ethylmethylanido)* hafnium or adducts or hydrates thereof.

The hafnium precursor may be hafnium (IV) *iso*-propoxide, hafnium (IV) *tert*-butoxide, *tetrakis(2-methyl-2-methoxypropoxy)* hafnium, *bis(isopropoxy)bis(2-methyl-2-methoxypropoxy)* hafnium or *bis(tert-butoxy)bis(2-methyl-2-methoxypropoxy)* hafnium or adducts or hydrates thereof.

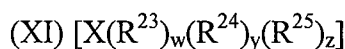
The hafnium precursor may be $HfCl_4$.

The zirconium precursor may be a zirconium (IV) precursor. Preferably the zirconium precursor is a zirconium β -diketonate, zirconium alkoxide, dialkylamino zirconium complex, alkylamino zirconium complex or cyclopentadienyl zirconium complex.

The zirconium of the zirconium precursor may have one or more (for example four) organic ligands which may be the same or different selected from the group of organic ligands defined by formulae (X) to (XII) (preferably one of formulae (X) to (XII)) as follows:



(wherein each of R^{21} and R^{22} which may be the same or different is an optionally fluorinated, linear or branched C_{1-12} alkyl group);



(wherein X is a heteroatom;

R^{23} is H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups or a $(SiR^{26})_2$ or $(SiR^{26})_3$ group;

R^{24} is H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups or a $(SiR^{27})_2$ or $(SiR^{27})_3$ group;

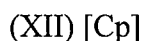
R^{25} is H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups or a $(SiR^{28})_2$ or $(SiR^{28})_3$ group;

each of R^{26} , R^{27} and R^{28} is independently H or a linear or branched C_{1-12} alkyl, C_{6-12} aryl, C_{3-12} allyl or C_{3-12} vinyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups;

w is an integer of 1 or 2;

y is an integer of 0 or 1; and

z is an integer of 0 or 1);



(wherein Cp denotes a single or fused cyclopentadiene moiety optionally ring-substituted partially or fully by one or more of the group consisting of an optionally substituted, acyclic or cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, aralkyl or alkoxy group or a thio, amino, cyano or silyl group).

Preferably the zirconium of the zirconium precursor has four organic ligands selected from the group of organic ligands defined by formulae (X) to (XII) (preferably one of formulae (X) to (XII)).

Preferably the ligand of formula (X) is an optionally methylated and/or optionally fluorinated (*eg* optionally tri- or hexa-fluorinated) acetylacetonato, heptanedionato or octanedionato ligand. For example, the ligand of formula (X) may be a 1,1,1-trifluoropentane-2,4-dionato, 1,1,1,5,5,5-hexafluoropentane-2,4-dionato or 2,2,6,6-tetramethyl-3,5-heptanedionato ligand.

Preferably either or both of R^{21} and R^{22} are trifluorinated or hexafluorinated.

Preferably R^{21} is a C_{1-6} perfluoroalkyl. Preferably R^{22} is a C_{1-6} perfluoroalkyl.

Preferably X is O. Particularly preferably X is O, z is 0, y is 0, w is 1 and R^{23} is an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups. For example, the ligand of formula (XI) may be a isopropoxy, 2-dimethylaminoethanolate, 2-methoxyethanolate or 1-methoxy-2-methyl-2-propanolate ligand.

Preferably X is N. Particularly preferably X is N, y is 1, w is 1, z is 1 and each of R^{23} , R^{24} and R^{25} is independently H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups.

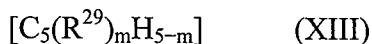
Preferably each of R^{23} , R^{24} and R^{25} is independently methyl, ethyl, propyl, butyl or pentyl, particularly preferably methyl, propyl or butyl, more preferably *n*-butyl, *tert*-butyl, isopropyl or ethyl.

The zirconium of the zirconium precursor may have one or two ligands of formula (XII).

Preferably the zirconium of the zirconium precursor has two ligands of formula (XII). The cyclopentadiene moieties of the two ligands of formula (XII) may be bridged. The bridge may be a substituted or unsubstituted C_{1-6} -alkylene group which is optionally interrupted by a heteroatom (such as O, Si, N, P, Se or S).

Preferably the ligand of formula (XII) is a cyclopentadienyl, indenyl, fluorenyl, pentamethylcyclopentadienyl or triisopropylcyclopentadienyl ligand.

Preferably in a zirconium precursor the (or each) ligand of formula (XII) is a cyclopentadienyl ligand of formula (XIII)



(wherein m is an integer in the range 0 to 5 and

each R^{29} which may be the same or different is selected from the group consisting of a C_{1-12} alkyl, C_{1-12} alkylamino, C_{1-12} dialkylamino, C_{1-12} alkoxy, C_{3-10} cycloalkyl, C_{2-12} alkenyl, C_{7-12} aralkyl, C_{7-12} alkylaryl, C_{6-12} aryl, C_{5-12} heteroaryl, C_{1-10} perfluoroalkyl, silyl, alkylsilyl, perfluoroalkylsilyl, triarylsilyl and alkylsilylsilyl group).

Preferably the (or each) R^{29} group is methyl, ethyl, propyl (*eg isopropyl*) or butyl (*eg tert-butyl*), particularly preferably methyl.

The zirconium precursor may be *di(isopropoxy)bis(2,2,6,6-tetramethyl-3,5-heptanedionato)* zirconium.

The zirconium precursor may be *bis(methylcyclopentadienyl)* dimethylzirconium, *bis(methylcyclopentadienyl)* methoxymethylzirconium or methylcyclopentadienyl zirconium *tris(dimethylamido)* or adducts or hydrates thereof.

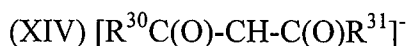
The zirconium precursor may be *tetrakis(dimethylamido)* zirconium, *tetrakis(diethylamido)* zirconium or *tetrakis(ethylmethylamido)* zirconium or adducts or hydrates thereof.

The zirconium precursor may be zirconium (IV) *iso*-propoxide, zirconium (IV) *tert*-butoxide, *tetrakis(2-methyl-2-methoxypropoxy)* zirconium, *bis(iso-propoxy)bis(2-methyl-2-methoxypropoxy)* zirconium or *bis(tert-butoxy)bis(2-methyl-2-methoxypropoxy)* zirconium or adducts or hydrates thereof.

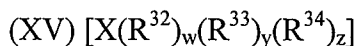
The zirconium precursor may be $ZrCl_4$ or $ZrBr_4$.

The strontium precursor may be a strontium (II) precursor. Preferably the strontium precursor is a strontium halide, strontium β -diketonate, strontium alkoxide (such as *iso*-propoxide or *tert*-butoxide), dialkylamino strontium complex, alkylamino strontium complex, silylamido strontium complex, cyclopentadienyl strontium complex or strontium nitrate.

The strontium of the strontium precursor may have one or more (for example four) organic ligands which may be the same or different selected from the group of organic ligands defined by formulae (XIV) to (XVI) (preferably one of formulae (XIV) to (XVI)) as follows:



(wherein each of R^{30} and R^{31} which may be the same or different is an optionally fluorinated, linear or branched C_{1-12} alkyl group);



(wherein X is a heteroatom;

R^{32} is H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups or a $(SiR^{35})_2$ or $(SiR^{35})_3$ group;

R^{33} is H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups or a $(SiR^{36})_2$ or $(SiR^{36})_3$ group;

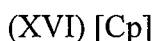
R^{34} is H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups or a $(SiR^{37})_2$ or $(SiR^{37})_3$ group;

each of R^{35} , R^{36} and R^{37} is independently H or a linear or branched C_{1-12} alkyl, C_{6-12} aryl, C_{3-12} allyl or C_{3-12} vinyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups;

w is an integer of 1 or 2;

z is an integer of 0 or 1; and

y is an integer of 0 or 1);



(wherein Cp denotes a single or fused cyclopentadiene moiety optionally ring-substituted partially or fully by one or more of the group consisting of an optionally substituted, acyclic or cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, aralkyl or alkoxy group or a thio, amino, cyano or silyl group).

Preferably the strontium of the strontium precursor has two organic ligands selected from the group of organic ligands defined by formulae (XIV) to (XVI) (preferably one of formulae (XIV) to (XVI)).

Preferably the ligand of formula (XIV) is an optionally methylated and/or optionally fluorinated (eg optionally tri- or hexa-fluorinated) acetylacetonato, heptanedionato or

octanedionato ligand. For example, the ligand of formula (XIV) may be a 1,1,1,5,5,5-hexafluoropentane-2,4-dionato, 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato or 2,2,6,6-tetramethyl-3,5-heptanedionato ligand.

Preferably either or both of R^{30} and R^{31} are trifluorinated or hexafluorinated.

Preferably R^{30} is a C_{1-6} perfluoroalkyl. Preferably R^{31} is a C_{1-6} perfluoroalkyl.

Preferably X is O. Particularly preferably X is O, y is 0, z is 0, w is 1 and R^{32} is an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups. For example, the ligand of formula (XV) may be a hexafluoroisopropoxy, 2-dimethylaminoethanolate, 2-methoxyethanolate or 1-methoxy-2-methyl-2-propanolate ligand.

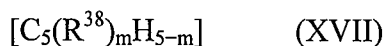
Preferably X is N. Particularly preferably X is N, y is 1, w is 1, z is 1 and each of R^{32} , R^{33} and R^{34} is independently H or an optionally fluorinated, linear or branched C_{1-12} alkyl group optionally substituted by one or more alkoxy, amino, alkylamino or dialkylamino groups.

Preferably each of R^{32} , R^{33} and R^{34} is independently methyl, ethyl, propyl, butyl or pentyl, particularly preferably methyl, propyl or butyl, more preferably *n*-butyl, *tert*-butyl, *isopropyl* or ethyl.

Preferably the ligand of formula (XVI) is a cyclopentadienyl, indenyl, fluorenyl, pentamethylcyclopentadienyl or triisopropylcyclopentadienyl ligand, particularly preferably a cyclopentadienyl or indenyl ligand.

The strontium of the strontium precursor may have one or two ligands of formula (XVI). Preferably the strontium of the strontium precursor has two ligands of formula (XVI). The cyclopentadiene moieties of the two ligands of formula (XVI) may be bridged. The bridge may be a substituted or unsubstituted C_{1-6} -alkylene group which is optionally interrupted by a heteroatom (such as O, Si, N, P, Se or S). The cyclopentadiene moieties of the two ligands of formula (XVI) may be the same or different. Preferably each of the cyclopentadiene moieties of the two ligands of formula (XVI) is cyclopentadienyl or indenyl. Preferably the cyclopentadiene moieties of the two ligands of formula (XVI) are cyclopentadienyl and indenyl respectively.

Preferably in a strontium precursor the (or each) ligand of formula (XVI) is a cyclopentadienyl ligand of formula (XVII)



(wherein m is an integer in the range 0 to 5 and

each R^{38} which may be the same or different is selected from the group consisting of a C_{1-12} alkyl, C_{1-12} alkylamino, C_{1-12} dialkylamino, C_{1-12} alkoxy, C_{3-10} cycloalkyl, C_{2-12} alkenyl, C_{7-12} aralkyl, C_{7-12} alkylaryl, C_{6-12} aryl, C_{5-12} heteroaryl, C_{1-10} perfluoroalkyl, silyl, alkylsilyl, perfluoroalkylsilyl, triarylsilyl and alkylsilylsilyl group).

Preferably the (or each) R^{38} group is methyl, ethyl, propyl (*eg isopropyl*) or butyl (*eg tert-butyl*). Particularly preferably each R^{38} group is methyl.

The strontium precursor may be strontium nitrate.

The strontium precursor may be *bis*(1,1,1-trifluoropentane-2,4-dionato) strontium, *bis*(1,1,1,5,5,5-hexafluoropentane-2,4-dionato) strontium, *bis*(2,2,6,6-tetramethyl-3,5-heptanedionato) strontium or *bis*(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) strontium or adducts or hydrates thereof.

The strontium precursor may be strontium $(C_5(CH_3)_5)_2$, *bis*((*tert*-Bu)₃cyclopentadienyl) strontium or *bis*(*n*-propyltetramethylcyclopentadienyl) strontium or adducts or hydrates thereof.

The strontium precursor may be *bis*[N,N,N',N',N''-pentamethyldiethylenetriamine] strontium, [tetramethyl-*n*-propylcyclopentadienyl] [N,N,N',N',N''-pentamethyldiethylenetriamine] strontium or [O*isopropyl*][indenyl] strontium or adducts or hydrates thereof.

In addition to one or more of the ligands mentioned hereinbefore, the metal in a precursor may have one or more additional ligands selected from anionic ligands, neutral monodentate or multidentate adduct ligands and Lewis base ligands. The metal may have 1 to 4 (*eg* two) additional ligands. For example, the (or each) additional ligand may be a β -diketonate (or a sulfur or nitrogen analogue thereof), halide, amide, alkoxide, carboxylate, substituted or unsubstituted C_{1-6} -alkyl group (which is optionally interrupted by a heteroatom such as O, Si, N, P, Se or S), benzyl, carbonyl, aliphatic ether, thioether, polyether, C_{1-12} alkylamino, C_{3-10} cycloalkyl, C_{2-12} alkenyl, C_{7-12} aralkyl, C_{7-12} alkylaryl, C_{6-12} aryl, C_{5-12} heteroaryl, C_{1-10} perfluoroalkyl, silyl, alkylsilyl, perfluoroalkylsilyl, triarylsilyl, alkylsilylsilyl, glyme (such as dimethoxyethane, diglyme, triglyme or tetraglyme), cycloalkenyl, cyclo dienyl, cyclooctatetraenyl, alkynyl, substituted alkynyl, diamine, triamine, tetraamine, phosphinyl, carbonyl, dialkyl sulfide, vinyltrimethylsilane, allyltrimethylsilane,

arylamine, primary amine, secondary amine, tertiary amine, polyamine, cyclic ether or pyridine aryl group. The additional ligand may be pyridine, toluene, tetrahydrofuran, bipyridine, a nitrogen-containing multidentate ligand (such as N,N,N',N',N"-pentamethyldiethylenetriamine (PMDETA) or N,N,N',N'-tetramethylethylenediamine) or a Schiff base. The neutral monodentate or multidentate adduct ligand may be derived from a solvent (*eg* tetrahydrofuran).

Preferred adduct ligands are dimethoxyethane, tetrahydrofuran, tetrahydropyran, diethylether, dimethoxymethane, diethoxymethane, dipropoxymethane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 1,2-dipropoxyethane, 1,3-dimethoxypropane, 1,3-dipropoxypropane, 1,2-dimethoxybenzene, 1,2-diethoxybenzene and 1,2-dipropoxybenzene.

The precursor may be dissolved, dispersed or suspended in a solvent such as an aliphatic hydrocarbon or aromatic hydrocarbon (*eg* xylene, toluene, benzene, 1,4-tertbutyltoluene, 1,3-diisopropylbenzene, tetralin or dimethyltetralin) optionally together with a stabilizing agent (*eg* a Lewis-base ligand), an amine (*eg* octylamine, NN-dimethyldodecylamine or dimethylaminopropylamine), an aliphatic or cyclic ether (*eg* tetrahydrofuran), a glyme (*eg* diglyme, triglyme, tetraglyme), a C₃₋₁₂ alkane (*eg* hexane, octane, decane, heptane or nonane) and a tertiary amine.

Unless specified otherwise, the term alkyl used herein may be a linear or branched, acyclic or cyclic, C₁₋₁₂ alkyl and includes methyl, ethyl, propyl, isopropyl, n-butyl, *tert*-butyl, pentyl, *isopentyl*, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl. Preferably each group C₁₋₁₂ alkyl mentioned herein is preferably C₁₋₈ alkyl, particularly preferably C₁₋₆ alkyl.

Unless specified otherwise, the term aryl used herein may be a substituted, monocyclic or polycyclic C₆₋₁₂ aryl and includes optionally substituted phenyl, naphthyl, xylene and phenylethane.

In a preferred embodiment, M is Hf.

In a preferred embodiment, M is Zr.

Preferably $0.01 < x < 0.99$, particularly preferably $0.05 \leq x \leq 0.95$, more particularly preferably $0.2 \leq x \leq 0.8$, yet more particularly preferably $0.3 \leq x \leq 0.7$, even more preferably $0.4 \leq x \leq 0.6$, yet even more preferably $0.45 \leq x \leq 0.55$. In a preferred embodiment, x is about 0.5.

In a preferred embodiment, the mixed metal oxide (in the form of a bulk material) exhibits a dielectric constant (typically at 10kHz) of greater than 35, preferably a dielectric

constant in the range 36 to 200, particularly preferably in the range 45 to 125, more preferably in the range 60 to 100.

In a preferred embodiment, the mixed metal oxide (in the form of a bulk material) exhibits a band gap of 3.10eV or more, preferably a band gap in the range 3.10 to 6.10eV, particularly preferably in the range 3.24 to 3.80eV, more preferably in the range 3.40 to 3.50eV.

The functional device may be an electrical, electronic, magnetic, mechanical, optical or thermal device. For example, the element may be a gate dielectric in a field effect transistor device (*eg* a MOSFET device) or in a high frequency dielectric application. For example, the element may be a capacitor (*eg* in a memory device such as DRAM or RAM), a voltage regulator, an electronic signal filter, a microelectromechanical device, a sensor, an actuator, a display (*eg* a TFT or OLED), a solar cell, a charged couple device, a particle and radiation detector, a printed circuit board, a CMOS device, an optical fibre or an optical waveguide. For example, the element may be an optical fibre or in an optical waveguide.

The mixed metal oxide may be present in the element in a multiphase composition. Preferably the mixed metal oxide is substantially monophasic.

The substrate may be a semiconductor such as an oxide semiconductor, an organic semiconductor, a III-V semiconductor (*eg* GaAs, InGaAs, GaN or InGaN), a II-VI semiconductor (*eg* ZnSe or CdTe) or a transparent conducting oxide (*eg* Al:ZnO, indium tin oxide or fluoride-doped tin oxide).

The substrate may be (or contain) silicon, doped silicon, silicon nitride or silicon dioxide. Typically the substrate is silicon.

The substrate may be composed of material selected from the group consisting of germanium, silicon, silicon dioxide, doped silicon, GaAs, InGaAs, GaN, InGaN, ZnSe, CdTe, TiN, ZnO, Al:ZnO, indium tin oxide, fluoride-doped tin oxide, platinum, RuO₂, IrO₂, SrRuO₃, LaSrCoO₃, IrO₂/Ir and RuO₂/Pt.

The substrate may be an electronic substrate which may comprise one or more electronic parts, devices or structures (*eg* a printed circuit board).

The substrate may be conductive. For example, the substrate may be a conductive mixed metal oxide such as a metal-doped metal oxide (*eg* Nb doped SrTiO₃).

An electrode may be placed on or applied to (*eg* deposited on) the element. The electrode may be composed of an elemental metal or metal alloy. For example, the electrode may be (or contain) tantalum, titanium, gold or platinum.

In a preferred embodiment, the functional device is a field effect transistor device wherein the substrate is a substrate layer and the element is a gate dielectric fabricated on the substrate layer, wherein the field effect transistor further comprises: a gate on the gate dielectric.

Preferably the field effect transistor device is a MOSFET device. The field effect transistor device may be present in a CPU or GPU.

The gate dielectric is typically a gate dielectric layer. The thickness of the gate dielectric layer may be 3.0nm or more. The gate dielectric layer may be deposited on the substrate layer. For example, the gate dielectric layer may be deposited epitaxially on the substrate layer.

The present invention will now be described in a non-limitative sense with reference to Examples and the following Figures in which:

Figure 1: X-ray diffraction pattern of a SrHfO_3 film grown from a 3:1 Sr:Hf deposition ratio annealed in air at 600°C for 30 minutes;

Figure 2: Atomic force micrographs: left - as deposited SrHfO_3 film; right – film after annealing in air at 600°C for 30 minutes; and

Figure 3: Capacitance dispersion of a SrHfO_3 MOS capacitor as a function of frequency.

Example 1: Process for Preparing $\text{Sr}(\text{Hf}_{1-x}\text{Ti}_x)\text{O}_3$

A film of the mixed oxide $\text{Sr}(\text{Hf}_{1-x}\text{Ti}_x)\text{O}_3$ is prepared on a substrate in a reactor (Oxford Instruments Opal Reactor) using the following precursors:

Precursor P1: *bis*(2,2,6,6-tetramethylheptane-3,5-dionato) strontium (source temperature 170°C)

Precursor P2: *bis*(methyl- η^5 -cyclopentadienyl)methoxymethyl hafnium (source temperature 80°C)

Precursor P3: Titanium (IV) isopropoxide (source temperature 50°C).

The reactor is maintained at a pressure of 1-2 mbar and the temperature of the substrate is 300°C. The purge gas is argon at a flow rate of 200sccm.

The duration of the steps in each deposition cycle for n cycles is as follows:

{[P1, 2s / purge 2s / H₂O, 0.5s / purge 3.5s], [P2, 2s / purge 2s / H₂O, 0.5s / purge 3.5s]_x, [P3, 2s / purge 2s / H₂O, 0.5s / purge 3.5s]_y]_n (x:y ~ 1:1 to 1:3)

Example 2: Process for Preparing Sr(Zr_{1-x}Ti_x)O₃

A film of the mixed oxide Sr(Zr_{1-x}Ti_x)O₃ is prepared on a substrate in a reactor (Oxford Instruments Opal Reactor) using the following precursors:

Precursor P1: *bis*(2,2,6,6-tetramethylheptane-3,5-dionato) strontium (source temperature 170°C)

Precursor P2: *bis*(methyl-η⁵-cyclopentadienyl) methoxymethyl zirconium (source temperature 70°C)

Precursor P3: Titanium (IV) isopropoxide (source temperature 50°C).

The reactor is maintained at a pressure of 2 mbar and the temperature of the substrate is 325°C. The purge gas is argon at a flow rate of 300sccm.

The duration of the steps in each deposition cycle for n cycles is as follows:

{[P1, 2s / purge 2s / H₂O, 0.5s / purge 3.5s], [P2, 2s / purge 2s / H₂O, 0.5s / purge 3.5s]_x, [P3, 2s / purge 2s / H₂O, 0.5s / purge 3.5s]_y]_n (x:y ~ 1:1 to 1:3)

Example 3: Process for Preparing Sr(Hf_{1-x}Ti_x)O₃

A film of the mixed oxide Sr(Hf_{1-x}Ti_x)O₃ is prepared on a substrate in a reactor (Oxford Instruments Opal Reactor) using the following precursors:

Precursor P1: Sr(*t*-Bu₃Cp)₂

Precursor P2: $\text{Hf}(\text{HNEtMe})_4$

Precursor P3: $\text{Ti}(\text{OMe}_3)_4$

The reactor is maintained at a pressure of 1-2 mbar and the temperature of the substrate is 275°C. The purge gas is argon at a flow rate of 200sccm.

The duration of the steps in each deposition cycle for n cycles is as follows:

$\{[\text{P1}, 1\text{s} / \text{purge } 2\text{s} / \text{H}_2\text{O}, 0.5\text{s} / \text{purge } 5\text{s}], [\text{P2}, 1\text{s} / \text{purge } 2\text{s} / \text{H}_2\text{O}, 0.5\text{s} / \text{purge } 5\text{s}]_x, [\text{P3}, 1\text{s} / \text{purge } 2\text{s} / \text{H}_2\text{O}, 0.5\text{s} / \text{purge } 5\text{s}]_y\}_n$ ($x:y \sim 1:1$ to $1:3$).

Example 4: Process for Preparing $\text{Sr}(\text{Hf}_{1-x}\text{Ti}_x)\text{O}_3$

Precursor P1: $\text{Sr}(t\text{-Bu}_3\text{Cp})_2$ (source temperature 120°C)

Precursor P2: *bis*(methyl- η^5 -cyclopentadienyl)methoxymethylhafnium (source temperature 80°C)

Precursor P3: Titanium(IV) isopropoxide (source temperature 50°C).

The reactor is maintained at a pressure of 150 - 200mbar and the temperature of the substrate is 250°C. The purge gas is argon at a flow rate of 200sccm.

Oxygen plasma is generated using a 300W power source, 60sccm of O_2 and 10sccm of Ar.

The duration of the steps in each deposition cycle for n cycles is as follows:

$\{[3[\text{P1}, 10\text{s} / \text{purge } 5\text{s} / \text{O}_2 \text{ plasma}, 3\text{s} / \text{purge } 5\text{s}], [\text{P2}, 3\text{s} / \text{purge } 2\text{s} / \text{H}_2\text{O}, 0.5\text{s} / \text{purge } 3.5\text{s}]]_x, 3[[\text{P1}, 10\text{s} / \text{purge } 5\text{s} / \text{O}_2 \text{ plasma}, 3\text{s} / \text{purge } 5\text{s}], [[\text{P3}, 3\text{s} / \text{purge } 5\text{s} / \text{O}_2 \text{ plasma}, 3\text{s} / \text{purge } 5\text{s}]]_y]\}_n$
 ($x:y \sim 3:1, 2:1, 1:1, 1:2$ or $1:3$).

Example 5: SrHfO_3 Films Grown on Si(100) Substrates

Examples 5 relates to an investigation of a half cycle of the sequential exposure steps of an embodiment of the process of the invention which lead to the deposition of a SrHfO_3 film on Si(100) substrates.

The deposition of SrHfO_3 was investigated at a substrate temperature of 250°C using an Oxford Instruments Opal Reactor to explore the relationship between its crystalline phase and permittivity. A growth temperature of 250°C was chosen as the optimum for matching the deposition rates of SrO and HfO_2 . The metal precursors used were $\text{Sr}(\text{isoPr}_3\text{Cp})_2$ and $(\text{MeCp})_2\text{Hf}(\text{OMe})\text{Me}$ with an oxygen plasma as the oxidant. The plasma was generated using a 300W power source, a frequency of 13.56MHz, 60sccm of O_2 and 10sccm of Ar. The Sr and Hf sources were evaporated at 120°C and 100°C respectively. An argon carrier gas flow rate of $200\text{ cm}^3\text{ min}^{-1}$ was used with a reactor pressure of 5 mbar. The number of cycles was in the range of 50–150, yielding film thicknesses of 15–57 nm. The [precursor /purge/oxidant/purge/-] pulse sequences were $n[\text{Sr}10\text{s}/5\text{s}/0.02\text{s}/5\text{s}]$ and $m[\text{Hf}3\text{s}/5\text{s}/0.02\text{s}/5\text{s}]$ (where n and m varied depending on the desired Sr:Hf ratio). The different precursor ratios used were: 3:1, 3:2, 5:2 and 7:2. Samples were prepared as thin sections so that energy-dispersive X-ray analysis could be carried out. This showed that for films deposited with a 3:1 (Sr:Hf) cycle ratio a Sr:Hf composition of 1:1 was observed. The need for a 3:1 ratio is attributed to the growth rate of HfO_2 using $(\text{MeCp})_2\text{Hf}(\text{OMe})\text{Me}$ being faster than the growth rate of SrO using $\text{Sr}(\text{iPr}_3\text{Cp})_2$.

Films deposited using the 3:1 Sr:Hf ratio were selected for subsequent physico-chemical and electrical characterisation. X-ray diffraction analysis of a film grown at 250°C did not reveal any diffraction features indicating that it was essentially amorphous as deposited. Figure 1 shows that (after annealing in air at 600°C for 30 min) the film showed diffraction features that correspond to either the cubic or orthorhombic phase of SrHfO_3 . These phases are indistinguishable for the thin films investigated using XRD. The c-lattice constant of the SrHfO_3 films determined by XRD was $4.06\text{ \AA}$. This is in agreement with structural parameters for bulk SrHfO_3 (cubic, $\text{Pm}3\text{m}$ $a=4.08\text{ \AA}$).

Atomic force microscopy (figure 2) showed that (after annealing in air) the SrHfO_3 films are smooth with a root mean square (rms) roughness of $7.0\text{ \AA}$ over a $5\times5\text{ }\mu\text{m}^2$ area. The darker areas of contrast that appear after annealing accompany the crystallisation process but represent a roughening of approximately only $1\text{ \AA}$ peak-to-valley for a film thickness of 57nm.

The retention of a smooth morphology is a significant advantage for dielectrics used in MOS gate-stack applications. Metal-oxide-semiconductor (MOS) capacitors were

fabricated to assess the dielectric properties of the SrHfO_3 films after air annealing at 600 °C. The performance of MOS field effect transistors can be significantly impaired by dielectric relaxation effects. This is a potential issue for most crystalline, high-k dielectrics compared with SiO_2 . Capacitance-frequency (C-f) data from a typical MOS capacitor [Au/ SrHfO_3 /Si/Al] is shown in Figure 3. The SrHfO_3 film thickness of 57 nm was chosen to minimise the contribution from a SiO_2 interlayer. The C-f data shows a shallow frequency dispersion without any low-frequency (<1kHz) 'sheath-like' grain boundary contributions. A relative permittivity (κ) of 21 was extracted from the accumulation capacitance at 100 kHz. This was derived after accounting for the presence of a 3.2 nm SiO_2 interlayer as quantified by X-ray reflectivity and ellipsometry. The thickness of the interlayer is attributed to the effects of annealing in air. This permittivity value is in close agreement with SrHfO_3 films deposited on Si by alternative deposition techniques such as MBE.

In summary, stoichiometric strontium hafnate thin films have successfully been deposited by employing a plasma-assisted cyclical deposition process. The film composition can be controlled by altering the Sr:Hf ratio by varying the relative numbers of cycles of strontium and hafnium deposition. Perovskite structure SrHfO_3 films crystallized after annealing at 600°C. The crystalline SrHfO_3 dielectric has a high relative permittivity (κ) of 21 measured at a 100 kHz bias voltage.

CLAIMS

1. A process for preparing a functional device comprising a substrate and an element composed of a mixed metal oxide of formula $\text{SrM}_{1-x}\text{Ti}_x\text{O}_3$ wherein x is $0 < x < 1$ and M is Hf or Zr, wherein the process comprises:

exposing discrete volatilised amounts of a strontium precursor, of a hafnium or zirconium precursor and of a titanium precursor to the substrate in sequential exposure steps in a contained environment.

2. A process as claimed in claim 1 wherein each discrete volatilised amount is fed to the contained environment in a pulse.

3. A process as claimed in claim 1 or 2 further comprising:
feeding an oxidising agent into the contained environment in a pulse during each exposure step.

4. A process as claimed in claim 3 wherein the oxidising agent is oxygen plasma.

5. A process as claimed in any preceding claim further comprising:
purging the contained environment with an inert gas flow in a pulse during each exposure step.

6. A process as claimed in any preceding claim wherein the sequential exposure steps are cyclical.

7. A process as claimed in any preceding claim comprising a cycle of sequential exposure steps (A), (B) and (C), wherein

step (A) comprises: feeding the discrete volatilised amount of strontium precursor into the contained environment, purging the strontium precursor from the contained environment and feeding an oxidising agent into the contained environment and purging the contained environment.

step (B) comprises: feeding the discrete volatilised amount of hafnium or zirconium precursor into the contained environment, purging the hafnium or zirconium precursor from

the contained environment, feeding an oxidising agent into the contained environment and purging the contained environment.

step (C) comprises: feeding the discrete volatilised amount of a titanium precursor into the contained environment, purging the titanium precursor from the contained environment and feeding an oxidising agent into the contained environment and purging the contained environment.

8. A process as claimed in claim 7 wherein each of steps (B) and (C) is cyclical and the ratio of the number of cycles of step (B) to the number of cycles of step (C) is in the range 3:1 to 1:3.

9. A process as claimed in any of claims 1 to 6 comprising a cycle of sequential exposure steps (A'), (B'), (A'') and (C'), wherein

each of steps (A') and (A'') comprises: feeding the discrete volatilised amount of strontium precursor into the contained environment, purging the strontium precursor from the contained environment, feeding an oxidising agent into the contained environment and purging the contained environment,

step (B') comprises: feeding the discrete volatilised amount of hafnium or zirconium precursor into the contained environment, purging the hafnium or zirconium precursor from the contained environment, feeding an oxidising agent into the contained environment and purging the contained environment,

step (C') comprises: feeding the discrete volatilised amount of a titanium precursor into the contained environment, purging the titanium precursor from the contained environment, feeding an oxidising agent into the contained environment and purging the contained environment.

10. A process as claimed in claim 9 wherein each of steps (A') and (B') is cyclical and the ratio of the number of cycles of step (A') to the number of cycles of step (B') is 3:1.

11. A process as claimed in claim 9 or 10 wherein each of steps (A'') and (C') is cyclical and the ratio of the number of cycles of step (A'') to the number of cycles of step (C') is 3:1.

12. A process as claimed in claim 9, 10 or 11 wherein each of steps (B') and (C') is cyclical and the ratio of the number of cycles of step (B') to the number of cycles of step (C') is in the range 3:1 to 1:3.

13. A process as claimed in any preceding claim wherein the titanium precursor is a titanium halide, titanium β -diketonate, titanium alkoxide, dialkylamino titanium complex, alkylamino titanium complex, silylamido titanium complex, cyclopentadienyl titanium complex, titanium dialkyldithiocarbamate or titanium nitrate.

14. A process as claimed in any preceding claim wherein the hafnium precursor is a hafnium β -diketonate, hafnium alkoxide, dialkylamino hafnium complex, alkylamino hafnium complex or cyclopentadienyl hafnium complex or the zirconium precursor is a zirconium β -diketonate, zirconium alkoxide, dialkylamino zirconium complex, alkylamino zirconium complex or cyclopentadienyl zirconium complex.

15. A process as claimed in any preceding claim wherein the strontium precursor is a strontium halide, strontium β -diketonate, strontium alkoxide, dialkylamino strontium complex, alkylamino strontium complex, silylamido strontium complex, cyclopentadienyl strontium complex or strontium nitrate.

1/1
Figure 1

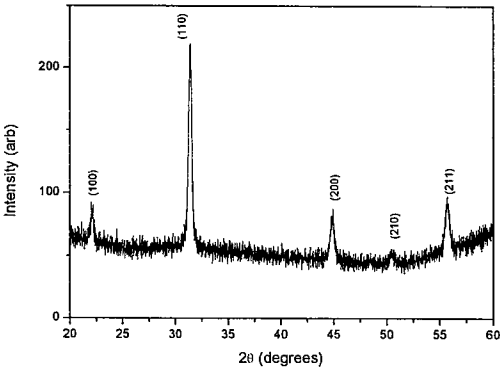


Figure 2

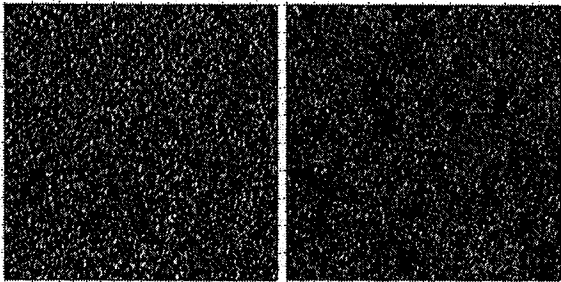
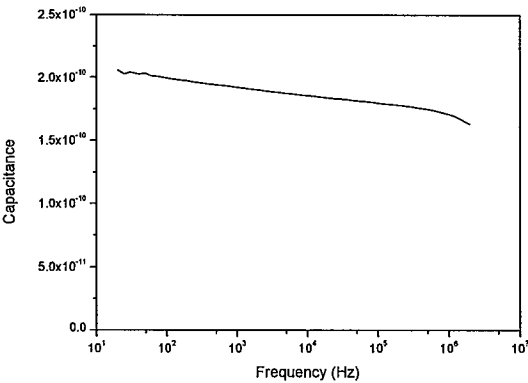


Figure 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/050679

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C16/40 C23C16/455
ADD.

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

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)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/012841 A2 (MOTOROLA INC [US]) 13 February 2003 (2003-02-13) claims 18,30,50,51; example 7 -----	1-15
Y	YAN L ET AL: "High permittivity SrHf0.5Ti0.5O3 films grown by pulsed laser deposition", APPLIED PHYSICS LETTERS, AIP, AMERICAN INSTITUTE OF PHYSICS, MELVILLE, NY, US, vol. 94, no. 23, 8 June 2009 (2009-06-08), pages 232903/1-232903/3, XP002591138, ISSN: 0003-6951, DOI: DOI:10.1063/1.3151815 [retrieved on 2009-06-11] page 232902-1, paragraphs 1 and 2; abstract; pages 232903-1, paragraph 1 - paragraph 2 ----- -/--	1-15

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

☒ See patent family annex.

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"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

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26 July 2011

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Patterson, Anthony

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/050679

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/032424 A1 (AHN KIE Y [US] ET AL) 7 February 2008 (2008-02-07) claims	1-15
X,P	----- WO 2010/116184 A1 (ULIVE ENTPR LTD [GB]; SUCHOMEL MATTHEW [US]; ROSSEINSKY MATTHEW [GB];) 14 October 2010 (2010-10-14) claim 14; examples -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2011/050679

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