(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 December 2024 (19.12.2024)

WIPO | PCT

(10) International Publication Number
WO 2024/256745 A1

(51) International Patent Classification:
C23C 16/40 (2006.01) *H01L 21/02* (2006.01)
C23C 16/455 (2006.01) *C23C 16/44* (2006.01)

(21) International Application Number:
PCT/FI2024/050235

(22) International Filing Date:
16 May 2024 (16.05.2024)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20235660 13 June 2023 (13.06.2023) FI

(71) Applicant: **BENEQ OY** [FI/FI]; Olarinluoma 9, 02200 Espoo (FI).

(72) Inventor: **LEPPILAHTI, Lassi**; c/o Beneq Oy, Olarinluoma 9, 02200 Espoo (FI).

(74) Agent: **PAPULA OY**; P.O.Box 981, 00101 Helsinki (FI).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

(54) Title: A FILM OF RARE EARTH METAL OXIDE ON A SURFACE OF A SUBSTRATE

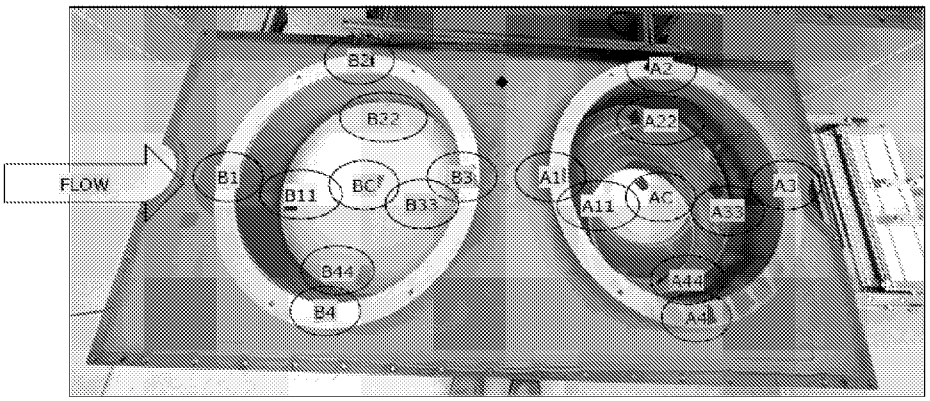

Fig. 1

(57) Abstract: A method for producing a film of rare earth metal oxide on a surface of a substrate is disclosed. The method comprises, in a reaction space, in any order the alternating steps of: a) exposing a deposition surface to an alcohol-based precursor for oxygen such that at least a portion of said alcohol-based precursor for oxygen gets adsorbed onto the deposition surface of the substrate, and subsequently purging the deposition surface with an inert gas for a first period of time of 1 - 180 seconds; and b) exposing a deposition surface to a precursor for rare earth metal such that at least a portion of said precursor for rare earth metal gets adsorbed onto the deposition surface of the substrate, and subsequently purging the deposition surface with an inert gas for a second period of time. Further is disclosed the use of the method.

WO 2024/256745 A1

A FILM OF RARE EARTH METAL OXIDE ON A SURFACE OF A SUBSTRATE

FIELD OF THE INVENTION

The present disclosure relates to a method for producing a film of rare earth metal oxide on a surface of a substrate. The present disclosure further relates to the use of the method.

BACKGROUND OF THE INVENTION

Yttrium oxide, as well as other rare earth metal oxides, is known to be a hygroscopic material. Water adsorption into the oxide is often strong and desorption slow. In processes like atomic layer deposition (ALD) this results in adverse processing conditions and non-uniformity of the produced film of rare earth metal oxide. There remains a need for a method enabling to fabricate a film of rare earth metal oxide with properties suitable for further applications.

SUMMARY

A method for producing a film of rare earth metal oxide on a surface of a substrate is disclosed. The method comprises, in a reaction space, in any order the alternating steps of:

a) exposing a deposition surface to an alcohol-based precursor for oxygen such that at least a portion of said alcohol-based precursor for oxygen gets adsorbed onto the deposition surface of the substrate, and subsequently purging the deposition surface with an inert gas for a first period of time of 1 - 180 seconds; and

b) exposing a deposition surface to a precursor for rare earth metal such that at least a portion of said precursor for rare earth metal gets adsorbed onto the deposition surface of the substrate, and

subsequently purging the deposition surface with an inert gas for a second period of time.

Further is disclosed the use of the method as disclosed in the current specification for reducing the amount of moisture in the produced film of rare earth metal oxide on a surface of a substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are included to provide a further understanding of the method and the substrate and constitute a part of this specification, illustrate embodiments and together with the description help to explain the principles of the above. In the drawings:

Fig. 1 illustrates the test setup used in example 1.

DETAILED DESCRIPTION

A method for producing a film of rare earth metal oxide on a surface of a substrate is disclosed. The method comprises, in a reaction space, in any order the alternating steps of:

a) exposing a deposition surface to an alcohol-based precursor for oxygen such that at least a portion of said alcohol-based precursor for oxygen gets adsorbed onto the deposition surface of the substrate, and subsequently purging the deposition surface with an inert gas for a first period of time of 1 - 180 seconds; and

b) exposing a deposition surface to a precursor for rare earth metal such that at least a portion of said precursor for rare earth metal gets adsorbed onto the deposition surface of the substrate, and subsequently purging the deposition surface with an inert gas for a second period of time.

Further is disclosed the use of the method as disclosed in the current specification for reducing the

amount of moisture in the produced film of rare earth metal oxide on a surface of a substrate.

The method may be used to produce a film of rare earth metal oxide on the surface of the substrate, wherein the film of rare earth metal oxide exhibits a uniform thickness. The thickness uniformity of the produced film of rare earth metal oxide may be measured by using e.g. an ellipsometer. In this specification, unless otherwise stated, the term "uniform thickness" or "thickness uniformity" may be taken to refer to a film that with a thickness of 100 – 2000 nm exhibits a thickness uniformity of +/- 5 % over the whole area of the film.

The inventor surprisingly found out that using an alcohol-based precursor for oxygen in the method as disclosed in the current specification enabled to reduce or remove moisture from the film during the production process while in addition being able to reduce the period of time used for purging the reaction space with an inert gas. Rare earth metal oxide is a material that may easily bind moisture thereto that may not be easily removed during the production process. The moisture bound to the rare earth metal oxide has the adverse effect of the produced film lacking uniform thickness and thus having a visual appearance that may not be suitable for further applications. The property of the rare earth metal oxide to bind moisture thereto increases the growth rate of the film which may thus affect the uniformity of the thickness in an adverse manner.

In this specification, unless otherwise stated, the term "the surface", "surface of the substrate", or "deposition surface", is used to address the surface of the substrate or the surface of the already formed film, layer, or deposit on the substrate. Therefore, the terms "surface", "surface of the substrate", and "deposition surface" include the surface of the substrate which has not yet been exposed to any precursors

and the surface which has been exposed to one or more precursors. The "deposition surface" thus changes during the deposition process when chemicals get chemisorbed onto the surface.

The method may be carried out as an industrial scale method in a reaction space of a volume of at least 40 dm^3, or at least 100 dm^3, or at least 150 dm^3. The method as disclosed in the current specification has the added utility of enabling the production of a rare earth metal oxide film in a largescale industrial process, wherein the purging away water or moisture from the reaction space after the use water as a precursor for oxygen has traditionally been a slow process leaving residual moisture in the film. The method as disclosed in the current specification has the added utility of enabling one to produce a film of uniform film thickness in a largescale process while simultaneously keeping the production time on an economically useful level.

In one embodiment, the method is carried out in a reaction space of a volume of at most 250 dm^3.

The growth rate of the film of rare earth metal oxide may be 0.1 - 10 Å/deposition cycle, or 0.3 - 2 Å/deposition cycle, 0.5 - 1.5 Å/deposition cycle, wherein each deposition cycle comprises or consists of a) and b). The inventor surprisingly found out that using the alcohol-based precursor for oxygen, the growth rate of the film can be lowered whereby a film of rare earth metal oxide of uniform thickness can be produced in large scale production process. The use of the alcohol-based precursor in the method has the desired effect of reducing the amount of moisture present in the produced film that would affect in the thickness uniformity in an adverse manner.

The rare earth metal may be selected from scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

In one embodiment, the rare-earth metal is yttrium or europium.

According to the International Union of Pure and Applied Chemistry (IUPAC) the lanthanides as well as yttrium and scandium are considered rare-earth metals.

The rare earth metal oxide may be scandium oxide, yttrium oxide, lanthanum oxide, cerium oxide, praseodymium oxide, neodymium oxide, samarium oxide, europium oxide, gadolinium oxide, terbium oxide, dysprosium oxide, holmium oxide, erbium oxide, thulium oxide, ytterbium oxide, or lutetium oxide, or any combination or mixture thereof. The rare earth metal oxide may be yttrium oxide, cerium oxide, dysprosium oxide, erbium oxide, or gadolinium oxide, or any combination or mixture thereof. In one embodiment, the rare earth metal oxide is yttrium oxide.

Different precursors, to be used in the method disclosed in the current specification for producing the film of rare earth metal oxide, are generally available and will be obvious to the skilled person based on the current specification.

In this specification, unless otherwise stated, the term “alcohol-based precursor for oxygen”, is used to address an organic compound that include a hydroxyl group, consisting of an oxygen atom and a hydrogen atom, bonded to a carbon atom. Alcohols may be represented by the general formula of ROH, where R may be an alkyl group or a substituted alkyl group.

The alcohol-based precursor for oxygen may be a methanol-based precursor for oxygen, an ethanol-based precursor for oxygen, a propanol-based precursor for oxygen, an isopropanol-based precursor for oxygen, a butanol-based precursor for oxygen, a 2-butanol-based precursor for oxygen, or a tert-butanol-based precursor for oxygen. In one embodiment, the alcohol-based precursor for oxygen is selected from a group consisting

of methanol, ethanol, propanol, isopropanol, butanol, 2-butanol, and tert-butanol. In one embodiment, the alcohol-based precursor for oxygen is ethanol or isopropanol.

In one embodiment, the precursor for rare earth metal is selected from a group consisting of a precursor for scandium, a precursor for yttrium, a precursor for lanthanum, a precursor for cerium, a precursor for praseodymium, a precursor for neodymium, a precursor for samarium, a precursor for europium, a precursor for gadolinium, a precursor for terbium, a precursor for dysprosium, a precursor for holmium, a precursor for erbium, a precursor for thulium, a precursor for ytterbium, and a precursor for lutetium.

The precursor for rare earth metal may be e.g. a precursor containing cyclopentadienyl ligands, amine ligands, or a heteroleptic containing both. As an example only, tris(methylcyclopentadienyl)yttrium ($(MeCp)_3Y$) and yttrium tris(N,N'-diisopropylacetamidinate) may be mentioned, but any other suitable precursors for rare earth metal may be used.

The substrate may be formed of silicon, ceramic, metal, and/or glass. In one embodiment, the substrate is formed of metal. The metal may be porous metal. The glass may be porous glass. In one embodiment, the substrate is formed of silicon.

In one embodiment, the alternating steps of a) and b) are repeated one or more times. The alternating steps of a) and b) may be repeated one or more times until the desired film thickness is reached. The method may comprise forming a film of rare earth metal oxide having a total thickness of 100 – 5000 nm, or 150 – 4000 nm, or 200 – 3000 nm, or 300 – 2500 nm, or 400 - 2000 nm.

The film of rare-earth metal oxide may be fabricated on the surface of the substrate in a reaction space with an atomic layer deposition (ALD) type

process. When the film of rare-earth metal oxide is fabricated on the surface of the substrate by an ALD-type process excellent conformality and uniformity may be achieved for the formed film.

The ALD-type process is a method for depositing uniform and conformal deposits, layers, or films over substrates of various shapes, even over complex three-dimensional structures. In the ALD-type process, the substrate is alternately exposed to at least two different precursors (chemicals), usually one precursor at a time, to form on the substrate a deposit, a layer, or a film by alternately repeating essentially self-limiting surface reactions between the surface of the substrate (on the later stages, naturally, the surface of the already formed layer, deposit, or film on the substrate) and the precursors. As a result, the deposited material is "grown" on the substrate molecule layer by molecule layer.

The distinctive feature of the ALD-type process is that the surface to be deposited is exposed to two or more different precursors in an alternate manner with usually a purging period in between the precursor pulses. During a purging period the deposition surface is exposed to a flow of gas which does not react with the precursors used in the process. This inert gas, often also called the carrier gas or the purge gas, is therefore inert towards the precursors used in the process and removes e.g. surplus precursor and by-products resulting from the chemisorption reactions of the previous precursor pulse. This purging can be arranged by different means. The basic requirement of the ALD-type process is that the deposition surface is purged between the introduction of a precursor for a metal and a precursor for a non-metal. The purging period ensures that the gas phase growth is limited and only surfaces exposed to the precursor gas participate in the growth.

Purging the deposition surface in a) may be carried out by purging the deposition surface with an inert gas for a first period of time of 1 – 180 seconds, or 1 – 120 seconds, or 2 – 100 seconds, or 3 – 60 seconds, or 4 - 30 seconds, or 5 – 25 seconds. The inventor surprisingly found out that the purging time may be essentially reduced when using an alcohol-based precursor for oxygen. Being able to reduce the purging time has the added utility of making the process more economical to use.

Purging the reaction space in b) may be carried out by purging the deposition surface with an inert gas for a second period of time of 1 – 180 seconds, or 1 – 120 seconds, or 2 – 100 seconds, or 3 – 60 seconds, or 4 - 30 seconds, or 5 – 25 seconds.

The alternate or sequential exposure of the deposition surface to different precursors can be carried out in different manners. In a batch type process at least one substrate is placed in a reaction space, into which precursor and purge gases are being introduced in a predetermined cycle. Spatial atomic layer deposition is an ALD-type process based on the spatial separation of precursor gases or vapors. The different precursor gases or vapors can be confined in specific process areas or zones while the substrate passes by. In the continuous ALD-type process constant gas flow zones separated in space and a moving substrate are used in order to obtain the time sequential exposure. By moving the substrate through stationary zones, providing precursor exposure and purging areas, in the reaction space, a continuous coating process is achieved enabling roll-to-roll coating of a substrate. In continuous ALD-type process the cycle time depends on the speed of movement of the substrate between the gas flow zones.

Other names besides atomic layer deposition (ALD) have also been employed for these types of processes, where the alternate introduction of or

exposure to two or more different precursors lead to the growth of the layer, often through essentially self-limiting surface reactions. These other names or process variants include atomic layer epitaxy (ALE), atomic layer chemical vapour deposition (ALCVD), and corresponding plasma enhanced, photo-assisted and electron enhanced variants. Unless otherwise stated, also these processes will be collectively addressed as ALD-type processes in this specification.

The method as disclosed in the current specification has the added utility of one being able to produce a film of rare earth metal oxide of uniform thickness with economically suitable process conditions. The method as disclosed in the current specification has the added utility of exhibiting a reduced growth rate of the film. The method as disclosed in the current specification has the further added utility of the time period used for purging the deposition surface may be reduced.

EXAMPLES

Reference will now be made in detail to the described embodiments.

The description below discloses some embodiments in such a detail that a person skilled in the art is able to utilize the method based on the disclosure. Not all steps of the embodiments are discussed in detail, as many of the steps will be obvious for the person skilled in the art based on this specification.

As presented above the ALD-type process is a method for depositing uniform and conformal films or layers over substrates of various shapes. Further, as presented above in ALD-type processes the layer or film is grown by alternately repeating, essentially self-limiting, surface reactions between a precursor and a surface to be coated. The prior art discloses many different apparatuses suitable for carrying out an ALD-

type process. The construction of a processing tool suitable for carrying out the methods in the following embodiments will be obvious to the skilled person in light of this disclosure. The tool can be *e.g.* a conventional ALD tool suitable for handling the process chemicals. Many of the steps related to handling such tools, such as delivering a substrate into the reaction space, pumping the reaction space down to a low pressure, or adjusting gas flows in the tool if the process is done at atmospheric pressure, heating the substrates and the reaction space etc., will be obvious to the skilled person. Also, many other known operations or features are not described here in detail nor mentioned, in order to emphasize relevant aspects of the various embodiments of the invention.

A film of rare earth metal oxide may be prepared on the surface of a substrate as exemplified below. This exemplary embodiment may be fabricated by bringing the substrate into a reaction space of a typical reactor tool, *e.g.* a tool suitable for carrying out an ALD-type process e.g. as a batch-type process. The reaction space may subsequently be pumped down to a pressure suitable for forming a film of rare earth metal oxide, using *e.g.* a mechanical vacuum pump, or in the case of atmospheric pressure ALD systems and/or processes, flows are typically set to protect the deposition zone from the atmosphere. The substrate can be heated to a temperature suitable for forming the film by the used method. The substrate can be introduced to the reaction space through *e.g.* an airtight load-lock system or simply through a loading hatch. The substrate can be heated *in situ* by *e.g.* resistive heating elements which also heat the entire reaction space or *ex situ*.

After the substrate and the reaction space have reached the targeted temperature and other conditions suitable for deposition, the surface of the substrate can be conditioned such that the different layers may

be essentially directly deposited on the surface. This conditioning of the surface commonly includes chemical purification of the surface of the substrate from impurities and/or oxidation. Especially removal of oxide is beneficial when the surface has been imported into the reaction space via an oxidizing environment, e.g. when transporting the exposed substrate from one deposition tool to another. The details of the process for removing impurities and/or oxide from the surface of the substrate will be obvious to the skilled person in view of this specification. In some embodiments of the invention the conditioning can be done ex-situ, *i.e.* outside the tool suitable for ALD-type processes. An example of an ex-situ conditioning process is etching for 1 min in a 1 % HF solution followed by rinsing in DI-water. Another example of an ex-situ conditioning process is exposing the substrate to ozone gas or oxygen plasma to remove organic impurities from the substrate surface in the form of volatile gases.

After the surface of the substrate has been conditioned, an alternate exposure of the deposition surface to different chemicals is started, to form a film of rare earth metal oxide directly on the surface of the substrate.

The precursors are suitably introduced into the reaction space in their gaseous form. This can be realized by first evaporating the precursors in their respective source containers which may or may not be heated depending on the properties of the precursor chemical itself. The evaporated precursor can be delivered into the reaction space by *e.g.* dosing it through the pipework of the reactor tool comprising flow channels for delivering the vaporized precursors into the reaction space. Controlled dosing of vapor into the reaction space can be realized by valves installed in the flow channels or other flow controllers. These valves

are commonly called pulsing valves in a system suitable for ALD-type deposition.

Also other mechanisms of bringing the substrate into contact with a chemical inside the reaction space may be conceived. One alternative is to make the surface of the substrate (instead of the vaporized chemical) move inside the reaction space such that the substrate moves through a region occupied by a gaseous chemical.

A reactor suitable for ALD-type deposition comprises a system for introducing inert gas, such as nitrogen or argon into the reaction space such that the reaction space can be purged from surplus chemical and reaction by-products before introducing the next chemical into the reaction space. This feature together with the controlled dosing of vaporized precursors enables alternately exposing the surface of the substrate to precursors without significant intermixing of different precursors in the reaction space or in other parts of the reactor. In practice the flow of inert gas is commonly continuous through the reaction space throughout the deposition process and only the various precursors are alternately introduced to the reaction space with the carrier gas. Obviously, purging of the reaction space does not necessarily result in complete elimination of surplus precursors or reaction by-products from the reaction space but residues of these or other materials may always be present.

Following the step of various preparations, film of rare earth metal oxide is deposited in the deposition surface by exposing the deposition surface to alternately repeated surface reactions of selected precursors, one precursor at a time, until a predetermined thickness of the film is achieved. This can be carried out in a reaction space by the alternating steps of:

a) exposing a deposition surface to an alcohol-based precursor for oxygen such that at least a portion of said alcohol-based precursor for oxygen gets adsorbed

onto the deposition surface of the substrate, and subsequently purging the deposition surface with an inert gas for a first period of time of 1 – 180 seconds; and

b) exposing a deposition surface to a precursor for rare earth metal such that at least a portion of said precursor for rare earth metal gets adsorbed onto the deposition surface of the substrate, and subsequently purging the deposition surface with an inert gas for a second period of time.

Each exposure of the deposition surface to a precursor, results in formation of additional deposit on the deposition surface as a result of adsorption reactions of the corresponding precursor with the deposition surface. Thickness of the film on the surface of the substrate can be increased by repeating the exposure to the different precursors one or more times. The thickness of the film is increased until a targeted thickness is reached, after which the alternate exposures are stopped and the process is ended. As a result of the deposition process a film of rare earth metal oxide is formed on the surface of the substrate.

The following example describes how a film of rare earth metal oxide can be fabricated on a surface of a substrate.

EXAMPLE 1 - Forming a film of rare earth metal oxide on a substrate

In this example a film of rare earth metal oxide on a surface of a substrate in an ALD-type process. The used test setup is presented in Fig. 1. Thus, substrate samples to be coated with the formed films were placed on different spots on two bowls placed in the reaction chamber. The gas flow direction is indicated with an arrow. The following parameters were used in this example:

alcohol-based precursor for oxygen: ethanol
a first period (purging): 30 s
a precursor for rare earth metal: $(MeCp)_3Y$
a second period of time (purging): 30 s
substrate: silicon
Temperature: 250 °C

Firstly, the deposition surface was exposed to ethanol for 1 second, followed by purging the deposition surface for a first period of time of 30 seconds with an inert gas (N_2). Then the deposition surface was exposed to tris(methylcyclopentadienyl)yttrium ($(MeCp)_3Y$) for 2 seconds, followed by purging the deposition surface for a second period of time of 30 seconds with the inert gas (N_2). This cycle was repeated 350 times after which process was stopped and the coated substrate was cooled to room temperature.

A comparative example 1 was carried out in otherwise similar manner but the precursor for oxygen was water instead of ethanol.

The formed films were subjected to measurement as to their thickness uniformity over the film by ellipsometry used in the reaction chamber. The measurement points are indicated in Fig. 1 (B1, B2, B3, B4, A1, A2, A3, and A4 are on the edges of the bowls and B11, B22, B33, B44, BC, A11, A22, A33, A44, and AC are on the bottoms of the bowls). The results are presented in the below table:

Example 1		Comparative example 1	
Measurement point	Thickness (nm)	Measurement number	Thickness (nm)
B1	29.75	B1	67
B4	29.76	B4	66.4
B3	30.1	B3	66.9
B2	29.3	B2	68.1
B11	25.1	B11	54

B22	25.3	B22	58.5
B33	24.3	B33	57.4
B44	24.24	B44	57.8
BC	30	BC	70
A1	24.3	A1	59.5
A2	26	A2	59
A3	26.4	A3	56
A4	26.2	A4	62
A11	23.98	A11	42.3
A22	24.3	A22	45
A33	23.78	A33	45.6
A44	24.57	A44	48.00
AC	27	AC	56.3

The thickness average for example 1 was 26.36 nm with RSD (relative standard deviation) of 8.97 % and GPC (growth per cycle) of 0.075 nm/cycle. In a similar manner the thickness average for comparative example 1 was 57.77 nm with RSD of 14.47 % and GPC of 0.165 nm/cycle.

From the above results one may see that the GPC is lower for example 1 than for the comparative example. There is also much less variation in thickness between different part of the rare earth metal film in the film of example 1 compared to the film of the comparative example 1.

It is obvious to a person skilled in the art that with the advancement of technology, the basic idea may be implemented in various ways. The embodiments are thus not limited to the examples described above; instead they may vary within the scope of the claims.

The embodiments described hereinbefore may be used in any combination with each other. Several of the embodiments may be combined together to form a further embodiment. A method or a use as disclosed herein, may

comprise at least one of the embodiments described hereinbefore. It will be understood that the benefits and advantages described above may relate to one embodiment or may relate to several embodiments. The embodiments are not limited to those that solve any or all of the stated problems or those that have any or all of the stated benefits and advantages. It will further be understood that reference to 'an' item refers to one or more of those items. The term “comprising” is used in this specification to mean including the feature(s) or act(s) followed thereafter, without excluding the presence of one or more additional features or acts.

CLAIMS

1. A method for producing a film of rare earth metal oxide on a surface of a substrate, wherein the method comprises, in a reaction space, in any order the alternating steps of:

a) exposing a deposition surface to an alcohol-based precursor for oxygen such that at least a portion of said alcohol-based precursor for oxygen gets adsorbed onto the deposition surface of the substrate, and subsequently purging the deposition surface with an inert gas for a first period of time of 1 - 180 seconds; and

b) exposing a deposition surface to a precursor for rare earth metal such that at least a portion of said precursor for rare earth metal gets adsorbed onto the deposition surface of the substrate, and subsequently purging the deposition surface with an inert gas for a second period of time.

2. The method of claim 1, wherein the method is carried out as an industrial scale method in a reaction space of a volume of at least 40 dm^3, or at least 100 dm^3, or at least 150 dm^3.

3. The method of any one of the preceding claims, wherein the growth rate of the film of rare earth metal oxide is 0.1 - 10 Å/deposition cycle, or 0.3 - 2 Å/deposition cycle, 0.5 - 1.5 Å/deposition cycle, wherein each deposition cycle comprises or consists of a) and b).

4. The method of any one of the preceding claims, wherein the alcohol-based precursor for oxygen is selected from a group consisting of methanol-based precursor for oxygen, ethanol-based precursor for oxygen, propanol-based precursor for oxygen, isopropanol-based precursor for oxygen, butanol-based precursor for oxygen, 2-butanol-based precursor for oxygen, and tert-butanol-based precursor for oxygen.

5. The method of any one of the preceding claims, wherein the precursor for rare earth metal is

selected from a group consisting of a precursor for scandium, a precursor for yttrium, a precursor for lanthanum, a precursor for cerium, a precursor for praseodymium, a precursor for neodymium, a precursor for samarium, a precursor for europium, a precursor for gadolinium, a precursor for terbium, a precursor for dysprosium, a precursor for holmium, a precursor for erbium, a precursor for thulium, a precursor for ytterbium, and a precursor for lutetium.

6. The method of any one of the preceding claims, wherein purging the reaction space in a) is carried out by purging the deposition surface with an inert gas for a first period of time of 1 – 120 seconds, or 2 – 100 seconds, or 3 – 60 seconds, or 4 - 30 seconds, or 5 – 25 seconds.

7. The method of any one of the preceding claims, wherein purging the reaction space in b) is carried out by purging the deposition surface with an inert gas for a second period of time of 1 – 180 seconds, or 1 – 120 seconds, or 2 – 100 seconds, or 3 – 60 seconds, or 4 - 30 seconds, or 5 – 25 seconds.

8. The method of any one of the preceding claims, wherein the substrate is formed of silicon, ceramic, metal, and/or glass.

9. The method of any one of the preceding claims, wherein the film of rare-earth metal oxide is fabricated on the surface of the substrate in a reaction space with an atomic layer deposition type process.

10. Use of the method of any one of the preceding claims for reducing the amount of moisture in the produced film of rare earth metal oxide on a surface of a substrate.

11. The use of claim 10, wherein the method is used to produce a film of rare earth metal oxide on the surface of the substrate, wherein the film of rare earth metal oxide exhibits a uniform thickness.

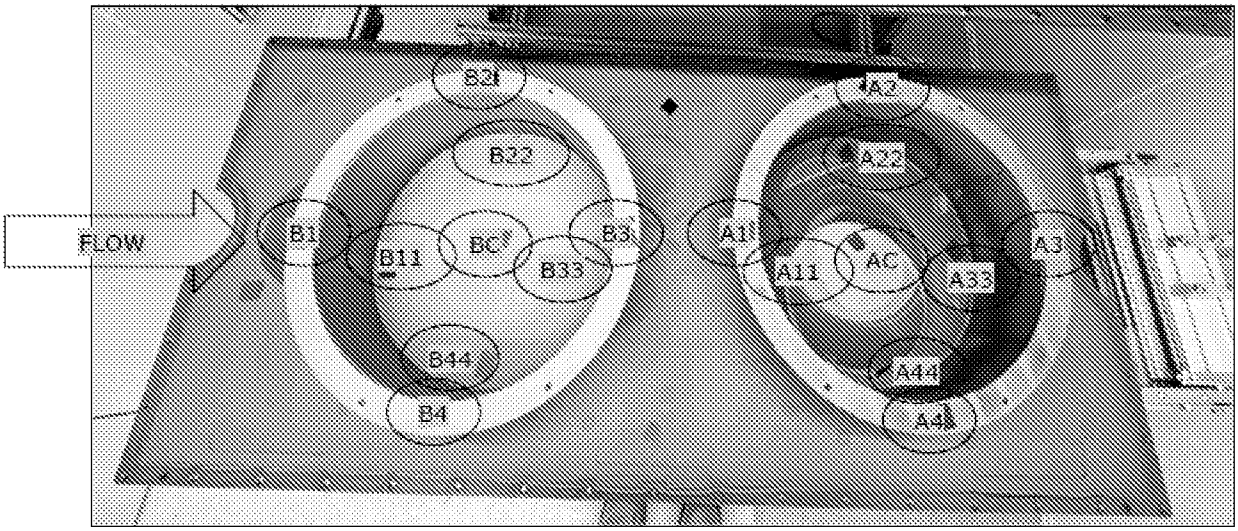

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2024/050235

A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C16/40 C23C16/455 H01L21/02 C23C16/44
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 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 practicable, search terms used)

EPO-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 2021/021822 A1 (APPLIED MATERIALS INC [US]) 4 February 2021 (2021-02-04) paragraphs [0079], [0081], [0084] - [0086], [0090]; figures 1-4, 7	1-11
X	WO 2021/071567 A1 (APPLIED MATERIALS INC [US]) 15 April 2021 (2021-04-15) paragraph [0027] - paragraph [0030]; claims 1, 6 paragraph [0014]	1-11
X	US 2019/348273 A1 (TANG FU [US] ET AL) 14 November 2019 (2019-11-14) paragraphs [0049], [0051], [0053] - [0055], [0057]; claims 1, 3, 7 paragraphs [0044], [0046], [0077]	1-11

☐ 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 application or patent 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	Date of mailing of the international search report
26 July 2024	13/08/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Engelen, Karen

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/FI2024/050235

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2021021822 A1	04-02-2021	KR 20220038482 A	28-03-2022
		TW 202113118 A	01-04-2021
		US 2021032745 A1	04-02-2021
		US 2024003003 A1	04-01-2024
		WO 2021021822 A1	04-02-2021
WO 2021071567 A1	15-04-2021	CN 114502769 A	13-05-2022
		EP 4041933 A1	17-08-2022
		JP 2022551859 A	14-12-2022
		KR 20220079618 A	13-06-2022
		US 2024076776 A1	07-03-2024
		WO 2021071567 A1	15-04-2021
US 2019348273 A1	14-11-2019	KR 20190128558 A	18-11-2019
		TW 201947059 A	16-12-2019
		TW 202344708 A	16-11-2023
		US 2019348273 A1	14-11-2019
		US 2023015724 A1	19-01-2023
		US 2024186138 A1	06-06-2024