

SURFACE MODIFIED SUBSTRATES AND RELATED METHODS

FIELD

[001] The present disclosure relates to surface modified substrates and related methods.

CROSS-REFERENCE TO RELATED APPLICATIONS

[002] This application claims the benefit under 35 USC 119 of U.S. Provisional Patent Application No. 63/529,321 filed on Jul. 27, 2023, the disclosure of which is hereby incorporated herein by reference in its entirety.

BACKGROUND

[003] Semiconductor and microelectronic device manufacturing methods require processing steps that use reactive process materials, such as plasma, in surface treatments. Manufacturing substrates with a protective coating to provide chemical, physical, and/or electrical resistance to these surface treatments remains an ongoing challenge.

SUMMARY

[004] Some embodiments relate to a substrate. In some embodiments, the substrate comprises a first region comprising an aluminum fluoride. In some embodiments, the substrate comprises a second region comprising an aluminum alloy. In some embodiments, the first region is above the second region. In some embodiments, a concentration of the aluminum fluoride decreases from the first region to the second region.

[005] Some embodiments relate to a substrate. In some embodiments, the substrate comprises a first region comprising a magnesium fluoride. In some embodiments, the substrate comprises a second region comprising a magnesium-containing aluminum alloy. In some embodiments, the substrate comprises a third region comprising an aluminum fluoride. In some embodiments, the third region is between the first region and the second region. In some embodiments, a

concentration of the magnesium fluoride decreases from the first region to the third region. In some embodiments, a concentration of the aluminum fluoride decreases from the third region to the second region.

- [006] Some embodiments relate to a method. In some embodiments, the method comprises exposing a substrate to a fluorine-containing vapor sufficient to form at least one of a first region comprising at least one of an aluminum fluoride, a magnesium fluoride, or any combination thereof; a second region comprising an aluminum alloy; a third region comprising at least one of an aluminum fluoride, a magnesium fluoride, or any combination thereof. In some embodiments, the first region is above the second region. In some embodiments, the third region, when present, is between the first region and the second region.

DRAWINGS

- [007] Some embodiments of the disclosure are herein described, by way of example only, with reference to the accompanying drawings. With specific reference now to the drawings in detail, it is stressed that the embodiments shown are by way of example and for purposes of illustrative discussion of embodiments of the disclosure. In this regard, the description taken with the drawings makes apparent to those skilled in the art how embodiments of the disclosure may be practiced.
- [008] **FIG. 1** is a flowchart of a method for modifying a surface of a substrate, according to some embodiments.
- [009] **FIG. 2** is a schematic diagram of at least a portion of a cross-section of a substrate having a modified surface, according to some embodiments.
- [0010] **FIG. 3** is a schematic diagram of at least a portion of a cross-section of a substrate having a modified surface, according to some embodiments.
- [0011] **FIG. 4** depicts a depth profile of a substrate having a modified surface, according to some embodiments.
- [0012] **FIG. 5** depicts a depth profile of a substrate having a modified surface, according to some embodiments.
- [0013] **FIG. 6** depicts a depth profile of a substrate having a modified surface, according to some embodiments.

DETAILED DESCRIPTION

- [0014] Among those benefits and improvements that have been disclosed, other objects and advantages of this disclosure will become apparent from the following description taken in conjunction with the accompanying figures. Detailed embodiments of the present disclosure are disclosed herein; however, it is to be understood that the disclosed embodiments are merely illustrative of the disclosure that may be embodied in various forms. In addition, each of the examples given regarding the various embodiments of the disclosure are intended to be illustrative, and not restrictive.
- [0015] Any prior patents and publications referenced herein are incorporated by reference in their entireties.
- [0016] Throughout the specification and claims, the following terms take the meanings explicitly associated herein, unless the context clearly dictates otherwise. The phrases "in one embodiment," "in an embodiment," and "in some embodiments" as used herein do not necessarily refer to the same embodiment(s), though they may. Furthermore, the phrases "in another embodiment" and "in some other embodiments" as used herein do not necessarily refer to a different embodiment, although it may. All embodiments of the disclosure are intended to be combinable without departing from the scope or spirit of the disclosure.
- [0017] As used herein, the term "based on" is not exclusive and allows for being based on additional factors not described, unless the context clearly dictates otherwise. In addition, throughout the specification, the meaning of "a," "an," and "the" include plural references. The meaning of "in" includes "in" and "on."
- [0018] Conventional coatings can be applied to the surfaces of substrates useful in microelectronic fabrication (e.g., semiconductor fabrication) to protect against chemical resistance, physical resistance, and electrical resistance. Due to limitations with respect to the conventional coatings and processes for forming the conventional coatings, the resulting coated substrates have numerous disadvantages. Conventional coatings are non-uniform in thickness and non-conformal with the underlying surface. In addition, these problems are exacerbated

by substrates with high-aspect ratio features (e.g., deep trenches, etc.). Forming a conformal and uniform coating on high-aspect ratio substrates remains an ongoing challenge.

[0019] Some embodiments disclosed herein overcome all or at least some of the challenges of conventional coatings by providing surface modified substrates and processes for modifying surfaces of substrates. In some embodiments, for example, the surface of the substrate is exposed to a vapor that reacts with metals present in the substrate, thereby resulting in a modified surface that exhibits improved chemical resistance, physical resistance, and/or electrical resistance, among other things. These modified surfaces can protect the substrate, without a coating or other material being deposited on the surface of the substrate. Using a reactive vapor to modify the surface of the substrate provides access to uniform and conformal surface modifications on high-aspect ratio substrates, with difficult to access features, because the reactive vapor is readily and easily exposed to all surfaces of high-aspect ratio substrates.

[0020] **FIG. 1** is a flowchart of a method 100 for modifying a surface of a substrate, according to some embodiments. As shown in **FIG. 1**, the method comprises one or more of the following steps: obtaining 102 a substrate; obtaining 104 a reactive vapor; and exposing 106 the substrate to the reactive vapor sufficient to modify a surface of the substrate.

[0021] At step 102, the substrate is obtained. The substrate can comprise a substrate useful in microelectronic fabrication, such as, for example and without limitation, semiconductor fabrication. The substrate can be a high-aspect ratio substrate, such as, for example and without limitation, a substrate having an aspect ratio of 2:1 to 2000:1 or 20:1 to 2000:1. The aspect ratio of the substrate can refer to a ratio of two of a width, a depth, a height, a length, or a diameter, in any combination. In some embodiments, for example, the aspect ratio refers to the ratio of a depth of a circular hole (e.g., a pore, etc.) to a diameter of the circular hole (e.g., the pore, etc.). In some embodiments, the aspect ratio refers to the ratio of a depth of a non-circular hole (e.g., a trench, etc.) to a width of the non-circular hole (e.g., the trench, etc.). Non-limiting examples of substrates, including high-aspect ratio substrates,

include, without limitation, at least one of a membrane, a showerhead, a liner, a tube, a gas line, a valve, an injector, a tray, or any combination thereof.

[0022] The substrate may have an aspect ratio of 20:1 to 2000:1, or any range or subrange between 20:1 and 2000:1. In some embodiments, the substrate may have an aspect ratio of 50:1 to 2000:1, 100:1 to 2000:1, 200:1 to 2000:1, 300:1 to 2000:1, 400:1 to 2000:1, 500:1 to 2000:1, 600:1 to 2000:1, 700:1 to 2000:1, 800:1 to 2000:1, 900:1 to 2000:1, 1000:1 to 2000:1, 1100:1 to 2000:1, 1200:1 to 2000:1, 1300:1 to 2000:1, 1400:1 to 2000:1, 1500:1 to 2000:1, 1600:1 to 2000:1, 1700:1 to 2000:1, 1800:1 to 2000:1, 1900:1 to 2000:1, 20:1 to 1900:1, 20:1 to 1800:1, 20:1 to 1700:1, 20:1 to 1600:1, 20:1 to 1500:1, 20:1 to 1400:1, 20:1 to 1300:1, 20:1 to 1200:1, 20:1 to 1100:1, 20:1 to 1000:1, 20:1 to 900:1, 20:1 to 800:1, 20:1 to 700:1, 20:1 to 600:1, 20:1 to 500:1, 20:1 to 400:1, 20:1 to 300:1, 20:1 to 200:1, 20:1 to 100:1, or 20:1 to 50:1.

[0023] In some embodiments, the substrate comprises an aluminum (Al) component. In some embodiments, the aluminum component comprises elemental aluminum (e.g., aluminum metal). In some embodiments, the aluminum component comprises a molecular aluminum (e.g., aluminum is a part of a molecule). In some embodiments, the aluminum component comprises an aluminum cation (e.g., Al^+ , Al^{+2} , Al^{+3} , etc.). In some embodiments, the aluminum component comprises anodized aluminum. In some embodiments, the aluminum component comprises an aluminum alloy. In some embodiments, the aluminum alloy comprises at least one of a copper component, an iron component, a manganese component, a silicon component, a zinc component, a magnesium component, a chromium component, a titanium component, or any combination thereof. In some embodiments, reference to a metal component refers to at least one of an elemental form of the metal, a molecular form of the metal, an ionic form of the metal, or any combination thereof. In some embodiments, the substrate does not comprise a magnesium component. In some embodiments, the substrate comprises a magnesium component.

[0024] In some embodiments, the substrate comprises at least 50% to 99% by weight of the aluminum component based on a total weight of the substrate, or any range or

subrange between 50% and 99% by weight of the aluminum component based on the total weight of the substrate. In some embodiments, the substrate comprises 50% to 95%, 50% to 90%, 50% to 85%, 50% to 80%, 50% to 75%, 50% to 70%, 50% to 65%, 50% to 60%, 50% to 55%, 55% to 99%, 60% to 99%, 65% to 99%, 70% to 99%, 75% to 99%, 80% to 99%, 85% to 99%, 90% to 99%, or 95% to 99%. In some embodiments, the substrate is entirely aluminum and comprises 100% by weight of the aluminum component based on the total weight of the substrate. In some embodiments, the substrate comprises less than 10% by weight of the iron component based on the total weight of the substrate. For example, in some embodiments, the substrate comprises 0.01% to 10%, 0.01% to 9%, 0.01% to 8%, 0.01% to 7%, 0.01% to 6%, 0.01% to 5%, 0.01% to 4%, 0.01% to 3%, 0.01% to 2%, 0.01% to 1%, 0.01% to 0.1%, 0.1% to 10%, 1% to 10%, 2% to 10%, 3% to 10%, 4% to 10%, 5% to 10%, 6% to 10%, 7% to 10%, 8% to 10%, or 9% to 10% by weight of the iron component based on the total weight of the substrate.

[0025] At step 104, the reactive vapor is obtained. In some embodiments, the reactive vapor comprises a fluorine component. In some embodiments, the reactive vapor comprises a fluorine-containing vapor. In some embodiments, the fluorine-containing vapor comprises a fluorine component that reacts or is reactive with the aluminum component of the substrate. In some embodiments, the fluorine-containing vapor comprises a fluorine component that reacts or is reactive with the magnesium component of the substrate. In some embodiments, the fluorine-containing vapor comprises a fluorine component that reacts or is reactive with the aluminum component of the substrate and with the magnesium component of the substrate.

[0026] In some embodiments, the fluorine component comprises a molecular fluorine source vapor, which may be derived from a liquid or solid. In some embodiments, the fluorine component comprises molecular fluorine. In some embodiments, the fluorine component is not ionic, substantially not ionic, not processed (e.g., by adding energy other than heat) to form plasma, or any combination thereof. In some embodiments, the fluorine component comprises at least one of a fluorinated organic compound, a perfluorinated organic compound, or any combination

thereof. In some embodiments, for example, the fluorine component comprises at least one of a fluorinated alkane, a perfluorinated alkane, a fluorinated alkene, a perfluorinated alkene, or any combination thereof, wherein any one or more of which may be linear or branched. In some embodiments, the fluorine-containing vapor comprises at least one of CF_4 , C_2F_4 , C_3F_6 , C_4F_8 , CHF_3 , $\text{C}_2\text{H}_2\text{F}_2$, C_2F_6 , HF , CH_3F , or any combination thereof.

[0027] In some embodiments, the fluorine component comprises a vaporized fluorinated polymer. In some embodiments, for example, obtaining the reactive vapor comprises heating a fluorinated polymer to a temperature sufficient to vaporize at least a portion of the fluorinated polymer. In some embodiments, the fluorine component comprises a gaseous fluorinated polymer derived from a non-gaseous fluorinated polymer (e.g., a solid or a liquid phase fluorinated polymer). In some embodiments, the fluorinated polymer comprises a homopolymer or a copolymer. In some embodiments, the fluorinated polymer comprises a copolymer of at least one fluoroolefin monomer and optionally at least one non-fluorinated co-monomer. In some embodiments, the fluorinated polymer may be fluorinated (i.e., partially fluorinated), perfluorinated, or may include non-fluorine halogen atoms, such as, for example and without limitation, chlorine. In some embodiments, a molecular fluorine source may be liquid or solid at room temperature, but that vaporizes at the process temperatures disclosed herein. Non-limiting examples of fluoropolymers include, without limitation, at least one of the following: polymerized perfluoroalkylethylene having a $\text{C}_1\text{-C}_{10}$ perfluoroalkyl group, polytetrafluoroethylene (PTFE), tetrafluoroethylene/perfluoro(alkyl vinyl ether) copolymer (PFA), tetrafluoroethylene/hexafluoropropylene copolymer (FEP), tetrafluoroethylene/perfluoro(alkyl alkenyl ether)/hexafluoropropylene copolymer (EPA), polyhexafluoropropylene, ethylene/tetrafluoroethylene copolymer (ETFE), poly trifluoroethylene, polyvinylidene fluoride (PVDF), polyvinyl fluoride (PVF), polychlorotrifluoroethylene (PCTFE), ethylene/chlorotrifluoroethylene copolymer (ECTFE), or any combination thereof.

[0028] At step 106, the substrate is exposed to the reactive vapor sufficient to modify a surface of the substrate. In some embodiments, the exposing comprises flowing

the reactive vapor into a chamber containing the substrate. In some embodiments, the exposing comprises contacting the reactive vapor with at least one surface of the substrate. In some embodiments, the exposing comprises pumping the reactive vapor into a chamber containing the substrate. In some embodiments, the exposing comprises discharging the reactive vapor into a chamber containing the substrate. In some embodiments, the exposing comprises introducing the reactive vapor into a chamber containing the substrate. In some embodiments, the exposing comprises feeding the reactive vapor into a chamber containing the substrate.

[0029] In some embodiments, the exposing proceeds under conditions sufficient to modify a surface of the substrate. For example, the conditions of the exposing may comprise at least one of a temperature of 200 °C to 600 °C, a pressure of 760 Torr (e.g., atmospheric pressure), a duration of 1 millisecond to 15 hours, or any combination thereof. In some embodiments, the exposing proceeds at or to a temperature of 250 °C to 600 °C, 300 °C to 600 °C, 350 °C to 600 °C, 400 °C to 600 °C, 450 °C to 600 °C, 500 °C to 600 °C, 550 °C to 600 °C, 200 °C to 550 °C, 200 °C to 500 °C, 200 °C to 450 °C, 200 °C to 400 °C, 200 °C to 350 °C, 200 °C to 300 °C, or 200 °C to 250 °C, or any range or subrange between 200 °C and 600 °C. In some embodiments, the exposing comprises heating the substrate at or to one or more of the aforementioned temperatures between 200 °C and 600 °C, or any range or subrange between 200 °C and 600 °C.

[0030] In some embodiments, the exposing proceeds at a pressure in a range of 100 Torr to 1000 Torr, or any range or subrange between 100 Torr and 1000 Torr. In some embodiments, for example, the exposing proceeds at a pressure of 100 Torr to 900 Torr, 100 Torr to 850 Torr, 100 Torr to 800 Torr, 100 Torr to 750 Torr, 100 Torr to 700 Torr, 100 Torr to 650 Torr, 100 Torr to 600 Torr, 100 Torr to 550 Torr, 100 Torr to 500 Torr, 100 Torr to 450 Torr, 100 Torr to 400 Torr, 100 Torr to 350 Torr, 100 Torr to 300 Torr, 100 Torr to 250 Torr, 100 Torr to 200 Torr, 100 Torr to 150 Torr, 150 Torr to 1000 Torr, 200 Torr to 1000 Torr, 250 Torr to 1000 Torr, 300 Torr to 1000 Torr, 350 Torr to 1000 Torr, 400 Torr to 1000 Torr, 450 Torr to 1000 Torr, 500 Torr to 1000 Torr, 550 Torr to 1000 Torr, 600 Torr to 1000 Torr, 650 Torr to

1000 Torr, 700 Torr to 1000 Torr, 750 Torr to 1000 Torr, 800 Torr to 1000 Torr, 850 Torr to 1000 Torr, 900 Torr to 1000 Torr, or 950 Torr to 1000 Torr. In some embodiments, the exposing proceeds at atmospheric pressure.

[0031] In some embodiments, the exposing proceeds for a duration of 1 millisecond to 14 hours, 1 millisecond to 13 hours, 1 millisecond to 12 hours, 1 millisecond to 11 hours, 1 millisecond to 10 hours, 1 millisecond to 9 hours, 1 millisecond to 8 hours, 1 millisecond to 7 hours, 1 millisecond to 6 hours, 1 millisecond to 5 hours, 1 millisecond to 4 hours, 1 millisecond to 3 hours, 1 millisecond to 2 hours, 1 millisecond to 1 hour, 1 millisecond to 30 minutes, 1 millisecond to 15 minutes, 1 millisecond to 1 minute, 1 millisecond to 30 seconds, 1 millisecond to 1 second, 1 hour to 15 hours, 2 hours to 15 hours, 3 hours to 15 hours, 4 hours to 15 hours, 5 hours to 15 hours, 6 hours to 15 hours, 7 hours to 15 hours, 8 hours to 15 hours, 9 hours to 15 hours, 10 hours to 15 hours, 11 hours to 15 hours, 12 hours to 15 hours, 13 hours to 15 hours, 14 hours to 15 hours, or any range or subrange between 1 millisecond and 15 hours.

[0032] In some embodiments, the exposing is sufficient to modify at least one surface of the substrate so as to form at least one of a first region, a second region, a third region, or any combination thereof. In some embodiments, the exposing is sufficient to modify at least one surface of the substrate so as to form a first region and a second region, wherein the first region is above the second region. In regards to this application “above” may mean outermost layer or outside of the first layer in a three dimensional embodiment. In some embodiments, the exposing is sufficient to modify at least one surface of the substrate so as to form a first region, a second region, and a third region, wherein the third region is located between the first region and the second region.

[0033] In some embodiments, the first region is an outermost region of the substrate relative to the second region and/or the third region. In some embodiments, the first region is the region comprising the modified surface(s) of the substrate. In some embodiments, a surface is modified when at least a portion of the surface or components thereof react with the reactive vapor, for example, to chemically change the substrate, wherein the chemically changed portion of the substrate is

or comprises the first region. In some embodiments, the first region comprises all vapor-exposed and/or gas-exposed surfaces of the substrate. For example, in some embodiments, the first region comprises all surfaces in direct contact with, or in fluid communication with, the reactive vapor. In some embodiments, the first region extends from a surface of the substrate to a first depth beneath the surface of the substrate.

[0034] In some embodiments, the second region is a region that does not include any surface of the substrate. In some embodiments, the second region is a region of the substrate that has not reacted with the reactive vapor. In some embodiments, the second region is the region of the substrate that has reacted less with the reactive vapor than the first region and/or the third region. In some embodiments, the second region extends from about the first region to a second depth, wherein the second depth is greater than the first depth. In some embodiments, when the third region is present, the second region extends from about the third region to a second depth, wherein the second depth is greater than the first depth and the depth of the third region. In some embodiments, the substrate does not comprise the second region (e.g., when the substrate is exposed for a sufficient duration so as to chemically change the entire substrate).

[0035] In some embodiments, the third region is a region that does not include any surface of the substrate. In some embodiments, the third region is a modified region of the substrate. That is, in some embodiments, a region is modified when at least a portion of the region or components thereof react with the reactive vapor, for example, to chemically change the substrate, wherein the chemically changed portion of the substrate in the third region is different from the chemically changed portion of the substrate in the first region. In some embodiments, the third region is different (e.g., chemically different) from the first region. In some embodiments, the third region is located between the first region and the second region. In some embodiments, the substrate does not comprise the third region (e.g., when the substrate does not comprise magnesium).

[0036] In some embodiments, the first region comprises at least one of aluminum fluoride. In some embodiments, the first region comprises a magnesium fluoride. In some

embodiments, the third region comprises an aluminum fluoride. In some embodiments, the second region comprises an aluminum alloy. In some embodiments, the second region comprises a magnesium-containing aluminum alloy. In some embodiments, the first region comprises an aluminum fluoride and the second region comprises an aluminum alloy, wherein a concentration of the aluminum fluoride gradually decreases from the first region to the second region. In some embodiments, the first region comprises a magnesium fluoride, the second region comprises a magnesium-containing aluminum alloy, and the third region comprises an aluminum fluoride, wherein the third region is located between the first region and the second region, wherein a concentration of the magnesium fluoride gradually decreases from the first region to the third region and/or the second region, wherein a concentration of the aluminum fluoride gradually decreases from the third region to the second region.

[0037] In some embodiments, the fluorine component from the fluorine-containing vapor reacts with the aluminum component of the substrate to form the first region. In some embodiments, the fluorine component from the fluorine-containing vapor reacts with the magnesium component of the substrate to form the first region. In some embodiments, the fluorine component from the fluorine-containing vapor reacts with the aluminum component of the substrate to form the third region.

[0038] In some embodiments, the modified surface is present on all exposed surfaces of the substrate, including features that have a high aspect ratio (e.g., holes, channels, internal plenums, metal membranes). In some embodiments, the modified surface is a corrosion-resistant surface that protects against corrosion. In some embodiments, the modified surface is a passivated surface of the substrate.

[0039] In some embodiments, at least a portion of the first region has a depth of 1 nm to 50 μm , or any range or subrange therebetween. For example, in some embodiments, at least a portion of the first region has a depth of less than 5 μm , less than 1 μm , or less than 250 nm. In some embodiments, at least a portion of the first region has a depth of 100 nm to 250 nm, 1 nm to 4 μm , 1 nm to 3 μm , 1 nm to 2 μm , 1 nm to 1 μm , 1 nm to 900 nm, 1 nm to 850 nm, 1 nm to 800 nm, 1 nm to 750 nm, 1 nm to 700 nm, 1 nm to 650 nm, 1 nm to 600 nm, 1 nm to 550 nm,

1 nm to 450 nm, 1 nm to 400 nm, 1 nm to 350 nm, 1 nm to 300 nm, 1 nm to 250 nm, 1 nm to 200 nm, 1 nm to 150 nm, 1 nm to 100 nm, 1 nm to 50 nm, 50 nm to 5 μ m, 100 nm to 5 μ m, 200 nm to 5 μ m, 300 nm to 5 μ m, 400 nm to 5 μ m, 500 nm to 5 μ m, 600 nm to 5 μ m, 700 nm to 5 μ m, 800 nm to 5 μ m, 900 nm to 5 μ m, 1 μ m to 5 μ m, 2 μ m to 5 μ m, 3 μ m to 5 μ m, 4 μ m to 5 μ m, 1 nm to 750 nm, 1 nm to 500 nm, 2 nm to 500 nm, 1 nm to 250 nm, 20 nm to 125 nm, 20 nm to 250 nm, 20 nm to 500 nm, 50 nm to 500 nm, 50 nm to 400 nm, 50 nm to 300 nm, 50 nm to 200 nm, 15 nm to 200 nm, 20 nm to 50 nm, 10 nm to 40 nm, 30 nm to 50 nm, 1 nm to 5 μ m, 1 μ m to 5 μ m, 1 μ m to 4 μ m, 1 μ m to 3 μ m, 1 μ m to 2 μ m, 5 nm to 5 μ m, 1 nm to 1 μ m, or 10 nm to 5 μ m.

[0040] In some embodiments, at least a portion of the second region has a depth of 1 nm to 50 μ m, or any range or subrange therebetween. For example, in some embodiments, at least a portion of the second region has a depth of less than 5 μ m, less than 1 μ m, or less than 250 nm. In some embodiments, at least a portion of the second region has a depth of 100 nm to 250 nm, 1 nm to 4 μ m, 1 nm to 3 μ m, 1 nm to 2 μ m, 1 nm to 1 μ m, 1 nm to 900 nm, 1 nm to 850 nm, 1 nm to 800 nm, 1 nm to 750 nm, 1 nm to 700 nm, 1 nm to 650 nm, 1 nm to 600 nm, 1 nm to 550 nm, 1 nm to 450 nm, 1 nm to 400 nm, 1 nm to 350 nm, 1 nm to 300 nm, 1 nm to 250 nm, 1 nm to 200 nm, 1 nm to 150 nm, 1 nm to 100 nm, 1 nm to 50 nm, 50 nm to 5 μ m, 100 nm to 5 μ m, 200 nm to 5 μ m, 300 nm to 5 μ m, 400 nm to 5 μ m, 500 nm to 5 μ m, 600 nm to 5 μ m, 700 nm to 5 μ m, 800 nm to 5 μ m, 900 nm to 5 μ m, 1 μ m to 5 μ m, 2 μ m to 5 μ m, 3 μ m to 5 μ m, 4 μ m to 5 μ m, 1 nm to 750 nm, 1 nm to 500 nm, 2 nm to 500 nm, 1 nm to 250 nm, 20 nm to 125 nm, 20 nm to 250 nm, 20 nm to 500 nm, 50 nm to 500 nm, 50 nm to 400 nm, 50 nm to 300 nm, 50 nm to 200 nm, 15 nm to 200 nm, 20 nm to 50 nm, 10 nm to 40 nm, 30 nm to 50 nm, 1 nm to 5 μ m, 1 μ m to 5 μ m, 1 μ m to 4 μ m, 1 μ m to 3 μ m, 1 μ m to 2 μ m, 5 nm to 5 μ m, 1 nm to 1 μ m, or 10 nm to 5 μ m.

[0041] In some embodiments, at least a portion of the third region has a depth of 1 nm to 50 μ m, or any range or subrange therebetween. For example, in some embodiments, at least a portion of the third region has a depth of less than 5 μ m, less than 1 μ m, or less than 250 nm. In some embodiments, at least a portion of

the third region has a depth of 100 nm to 250 nm, 1 nm to 4 μm , 1 nm to 3 μm , 1 nm to 2 μm , 1 nm to 1 μm , 1 nm to 900 nm, 1 nm to 850 nm, 1 nm to 800 nm, 1 nm to 750 nm, 1 nm to 700 nm, 1 nm to 650 nm, 1 nm to 600 nm, 1 nm to 550 nm, 1 nm to 450 nm, 1 nm to 400 nm, 1 nm to 350 nm, 1 nm to 300 nm, 1 nm to 250 nm, 1 nm to 200 nm, 1 nm to 150 nm, 1 nm to 100 nm, 1 nm to 50 nm, 50 nm to 5 μm , 100 nm to 5 μm , 200 nm to 5 μm , 300 nm to 5 μm , 400 nm to 5 μm , 500 nm to 5 μm , 600 nm to 5 μm , 700 nm to 5 μm , 800 nm to 5 μm , 900 nm to 5 μm , 1 μm to 5 μm , 2 μm to 5 μm , 3 μm to 5 μm , 4 μm to 5 μm , 1 nm to 750 nm, 1 nm to 500 nm, 2 nm to 500 nm, 1 nm to 250 nm, 20 nm to 125 nm, 20 nm to 250 nm, 20 nm to 500 nm, 50 nm to 500 nm, 50 nm to 400 nm, 50 nm to 300 nm, 50 nm to 200 nm, 15 nm to 200 nm, 20 nm to 50 nm, 10 nm to 40 nm, 30 nm to 50 nm, 1 nm to 5 μm , 1 μm to 5 μm , 1 μm to 4 μm , 1 μm to 3 μm , 1 μm to 2 μm , 5 nm to 5 μm , 1 nm to 1 μm , or 10 nm to 5 μm .

[0042] In some embodiments, the modified surface of the substrate is formed by a vapor deposition process. Examples of vapor deposition processes include, without limitation, at least one of a chemical vapor deposition (CVD) process, a digital or pulsed chemical vapor deposition process, a plasma-enhanced cyclical chemical vapor deposition process (PECCVD), a flowable chemical vapor deposition process (FCVD), an atomic layer deposition (ALD) process, a thermal atomic layer deposition, a plasma-enhanced atomic layer deposition (PEALD) process, a metal organic chemical vapor deposition (MOCVD) process, a plasma-enhanced chemical vapor deposition (PECVD) process, or any combination thereof.

[0043] In some embodiments, the substrate has an aluminum fluoride content of 60% to 80% as measured by XPS, or any range or subrange between 60% and 80%. For example, in some embodiments, the fluoride content of the substrate may be 61% to 80%, 62% to 80%, 63% to 80%, 64% to 80%, 65% to 80%, 66% to 80%, 67% to 80%, 68% to 80%, 69% to 80%, 70% to 80%, 71% to 80%, 72% to 80%, 73% to 80%, 74% to 80%, 75% to 80%, 76% to 80%, 77% to 80%, 78% to 80%, or 79% to 80%. In some embodiments, the fluoride content of the substrate may be 60% to 79%, 60% to 78%, 60% to 77%, 60% to 76%, 60% to 75%, 60% to 74%, 60% to 73%, 60% to 72%, 60% to 71%, 60% to 70%, 60% to 69%, 60% to 68%, 60%

to 67%, 60% to 66%, 60% to 65%, 60% to 64%, 60% to 63%, 60% to 62%, or 60% to 61%. In some embodiments, the aluminum fluoride content is the content of aluminum fluoride in the first region. In some embodiments, the aluminum fluoride content is the content of aluminum fluoride in the third region.

[0044] In some embodiments, the substrate comprises magnesium fluoride. In some embodiments, the substrate has an aluminum fluoride content of 3% to 15% as measured by XPS, or any range or subrange between 3% and 15%. For example, in some embodiments, the fluoride content of the substrate may be 4% to 15%, 5% to 15%, 6% to 15%, 7% to 15%, 8% to 15%, 9% to 15%, 10% to 15%, 11% to 15%, 12% to 15%, 13% to 15 %, or 14% to 15%. In some embodiments, the fluoride content of the substrate may be 3% to 14%, 3% to 13%, 3% to 12%, 3% to 11%, 3% to 10%, 3% to 9%, 3% to 8%, 3% to 7%, 3% to 6%, 3% to 5%, or 3% to 4%. In some embodiments, the substrate has a magnesium fluoride content of 20% and 40%. For example, in some embodiments, the magnesium fluoride content of the substrate may be 21% to 40%, 22% to 40%, 23% to 40%, 24% to 40%, 25% to 40%, 26% to 40%, 27% to 40%, 28% to 40%, 29% to 40%, 30% to 40 %, 31% to 40%, 32% to 40%, 33% to 40%, 34% to 40%, 35% to 40%, 36% to 40%, 37% to 40%, 38% to 40%, or 39% to 40%. In some embodiments, the magnesium fluoride content of the substrate may be 20% to 39%, 20% to 38%, 20% to 37%, 20% to 36%, 20% to 35%, 20% to 34%, 20% to 33%, 20% to 32%, 20% to 31%, 20% to 30%, 20% to 29%, 20% to 28%, 20% to 27%, 20% to 26%, 20% to 25%, 20% to 24%, 20% to 23%, 20% to 22%, or 20% to 21%. In some embodiments, the magnesium fluoride content is the content of magnesium fluoride in the first region.

[0045] In some embodiments, the substrate comprises anodized Al. In some embodiments, the substrate has an aluminum fluoride content of 20% to 40% as measured by XPS, or any range or subrange between 20% and 40%. For example, in some embodiments, the fluoride content of the substrate may be 21% to 40%, 22% to 40%, 23% to 40%, 24% to 40%, 25% to 40%, 26% to 40%, 27% to 40%, 28% to 40%, 29% to 40%, 30% to 40 %, 31% to 40%, 32% to 40%, 33% to 40%, 34% to 40%, 35% to 40%, 36% to 40%, 37% to 40%, 38% to 40%, or 39% to 40%.

In some embodiments, the fluoride content of the substrate may be 20% to 39%, 20% to 38%, 20% to 37%, 20% to 36%, 20% to 35%, 20% to 34%, 20% to 33%, 20% to 32%, 20% to 31%, 20% to 30%, 20% to 29%, 20% to 28%, 20% to 27%, 20% to 26%, 20% to 25%, 20% to 24%, 20% to 23%, 20% to 22%, or 20% to 21%.

[0046] **FIG. 2** is a schematic diagram of at least a portion of a cross-section of a substrate 200 having a modified surface, according to some embodiments. For example, in some embodiments, the substrate 200 has a first surface and a second surface opposite the first surface, wherein only the first surface of the substrate 200 is shown. As shown in **FIG. 2**, in some embodiments, the substrate 200 comprises a first region 202 and a second region 204. In some embodiments, the first region 202 is above the second region 204. In some embodiments, the first region 202 comprises aluminum fluoride. In some embodiments, the second region 204 comprises aluminum alloy. In some embodiments, the substrate 200 does not comprise magnesium. In some embodiments, the substrate is formed according to the methods disclosed herein. Any of the substrates, first regions, second regions, and other aspects disclosed herein may be used here, without departing from the scope of this disclosure.

[0047] **FIG. 3** is a schematic diagram of at least a portion of a cross-section of a substrate 300 having a modified surface, according to some embodiments. For example, in some embodiments, the substrate 300 has a first surface and a second surface opposite the first surface, wherein only the first surface of the substrate 300 is shown. As shown in **FIG. 3**, in some embodiments, the substrate 300 comprises a first region 302, a second region 306, and a third region 304. In some embodiments, the third region 304 is located between the first region 302 and the second region 306. In some embodiments, the first region 302 comprises magnesium fluoride. In some embodiments, the third region 304 comprises aluminum fluoride. In some embodiments, the second region 306 comprises aluminum alloy. In some embodiments, the substrate 300 comprises magnesium. In some embodiments, the substrate is formed according to the methods disclosed herein. Any of the substrates, first regions, second regions, third regions, and other aspects disclosed herein may be used here, without departing from the scope of this disclosure.

[0048] **FIG. 4** depicts a depth profile of a substrate having a modified surface, according to some embodiments. As shown in **FIG. 4**, the first region 402 of the substrate comprises magnesium fluoride, the second region 406 of the substrate (not shown) comprises magnesium-containing aluminum alloy, and the third region 404 of the substrate comprises aluminum fluoride and magnesium fluoride, wherein the third region 404 of the substrate is located between the first region 402 and the second region 406.

[0049] **FIG. 5** depicts a depth profile of a substrate having a modified surface, according to some embodiments. As shown in **FIG. 5**, the first region 502 of the substrate comprises aluminum fluoride and the second region 504 of the substrate comprises aluminum alloy. The substrate does not comprise magnesium (e.g., Al1100). The aluminum fluoride (AlF_3) content is at least 50% down to a depth of approximately 200 nm (first region 502). The second region 504 comprises a mixture of the aluminum fluoride and aluminum alloy. The fluorine content is at least 20% down to a depth of approximately 500 nm, and at least 5% down to a depth of approximately 1200 nm. The aluminum content is at least 50% starting at a depth of about 300 nm or greater.

[0050] **FIG. 6** depicts a depth profile of a substrate having a modified surface, according to some embodiments. As shown in **FIG. 6**, the first region 602 of the substrate comprises magnesium fluoride, the second region 606 of the substrate comprises magnesium-containing aluminum alloy, and the third region 604 of the substrate comprises aluminum fluoride, magnesium fluoride, and aluminum alloy, wherein the third region 604 of the substrate is located between the first region 602 and the second region 606. The magnesium fluoride (MgF_2) content is at least 50% down to a depth of approximately 800 nm (first region 602). The third region 604 comprises a mixture of the magnesium fluoride, aluminum fluoride, and aluminum alloy. The fluorine content is at least 20% down to a depth of approximately 2500 nm. The aluminum content is at least 50% starting at a depth of approximately 1800 nm.

[0051] ASPECTS

[0052] Various Aspects are described below. It is to be understood that any one or more of the features recited in the following Aspect(s) can be combined with any one or more other Aspect(s).

Aspect 1. A substrate comprising:

a first region comprising an aluminum fluoride; and

a second region comprising an aluminum alloy,

wherein the first region is above the second region;

wherein a concentration of the aluminum fluoride decreases from the first region to the second region.

Aspect 2. The substrate according to Aspect 1, wherein the substrate has an aspect ratio of 20:1 to 2000:1, wherein the aspect ratio is a ratio of two of a width, a depth, a height, a length, or a diameter.

Aspect 3. The substrate according to any one of Aspects 1-2, wherein the substrate comprises:

at least 50% by weight of aluminum based on a total weight of the substrate; and

less than 10% by weight of iron based on the total weight of the substrate.

Aspect 4. The substrate according to any one of Aspects 1-3, wherein the substrate comprises anodized Al.

Aspect 5. The substrate according to any one of Aspects 1-4, wherein the substrate does not comprise magnesium or less than 1% of magnesium.

Aspect 6. The substrate according to any one of Aspects 1-5, wherein the first region extends from a surface of the substrate to a depth of 2 nm to 5 μm .

Aspect 7. The substrate according to any one of Aspects 1-6, wherein the first region has a fluoride content of up to 100% as measured by XPS.

Aspect 8. The substrate according to any one of Aspects 1-7, wherein the first region has a fluorine content of 60% to 80% as measured by XPS.

Aspect 9. The substrate according to any one of Aspects 1-8, wherein the first region has a fluorine content of 20% to 40% as measured by XPS.

Aspect 10. The substrate according to any one of Aspects 1-9, wherein the first region is an outermost region of the substrate.

Aspect 11. A substrate comprising:

- a first region comprising a magnesium fluoride;

- a second region comprising a magnesium-containing aluminum alloy; and

- a third region comprising an aluminum fluoride;

- wherein the third region is between the first region and the second region;

- wherein a concentration of the magnesium fluoride decreases from the first region to the third region;

- wherein a concentration of the aluminum fluoride decreases from the third region to the second region.

Aspect 12. The substrate according to Aspect 11, wherein the substrate has an aspect ratio of 20:1 to 2000:1, wherein the aspect ratio is a ratio of two of a width, a depth, a height, a length, or a diameter.

Aspect 13. The substrate according to any one of Aspects 11-12, wherein the substrate comprises:

- at least 50% by weight of aluminum based on a total weight of the substrate; and

- less than 10% by weight of iron based on the total weight of the substrate.

Aspect 14. The substrate according to any one of Aspects 11-13, wherein the substrate comprises anodized Al.

Aspect 15. The substrate according to any one of Aspects 11-14, wherein:

the first region has a magnesium content of 20% to 40% as measured by XPS;

the second region has a fluorine content of 10% to 60% as measured by XPS.

Aspect 16. A method comprising:

exposing a substrate to a fluorine-containing vapor sufficient to form at least one of:

a first region comprising at least one of an aluminum fluoride, a magnesium fluoride, or any combination thereof;

a second region comprising an aluminum alloy; and

a third region comprising at least one of an aluminum fluoride, a magnesium fluoride, or any combination thereof;

wherein the first region is above the second region;

wherein the third region, when present, is between the first region and the second region.

Aspect 17. The method according to Aspect 16, wherein a fluorine component from the fluorine-containing vapor reacts with a magnesium component of the substrate to form the first region.

Aspect 18. The method according to any one of Aspects 16-17, wherein a fluorine component from the fluorine-containing vapor reacts with an aluminum component of the substrate to form the first region.

Aspect 19. The method according to any one of Aspects 16-18, wherein the fluorine-containing vapor comprises at least one of CF₄, C₂F₄, C₃F₆, C₄F₈, CHF₃, C₂H₂F₂, C₂F₆, HF, CH₃F, a vaporized fluorinated polymer, or any combination thereof.

Aspect 20. The method according to any one of Aspects 16-19, wherein the exposing comprises heating at least a portion of the substrate at or to a

temperature of 200 °C to 600 °C and exposing the substrate to the fluorine-containing vapor for a duration of 1 millisecond to 15 hours.

It is to be understood that changes may be made in detail, especially in matters of the construction materials employed and the shape, size, and arrangement of parts without departing from the scope of the present disclosure. This Specification and the embodiments described are examples, with the true scope and spirit of the disclosure being indicated by the claims that follow.

CLAIMS

WHAT IS CLAIMED IS:

1. A substrate comprising:
a first region comprising an aluminum fluoride; and
a second region comprising an aluminum alloy,
wherein the first region is above the second region;
wherein a concentration of the aluminum fluoride decreases from the first region to the second region.
2. The substrate of claim 1, wherein the substrate has an aspect ratio of 2:1 to 2000:1, wherein the aspect ratio is a ratio of two of a width, a depth, a height, a length, or a diameter.
3. The substrate of claim 1, wherein the substrate comprises:
at least 50% by weight of aluminum based on a total weight of the substrate;
and
less than 10% by weight of iron based on the total weight of the substrate.
4. The substrate of claim 1, wherein the substrate comprises anodized Al.
5. The substrate of claim 1 wherein the substrate does not comprise magnesium.
6. The substrate of claim 1, wherein the first region extends from a surface of the substrate to a depth of 2 nm to 5 μm .
7. The substrate of claim 1, wherein the first region has a fluoride content of up to 100% as measured by XPS.
8. The substrate of claim 1, wherein the first region has a fluorine content of 60% to 80% as measured by XPS.
9. The substrate of claim 5, wherein the first region has a fluorine content of 20% to 40% as measured by XPS.
10. The substrate of claim 1, wherein the first region is an outermost region of the substrate.

11. A substrate comprising:
 - a first region comprising a magnesium fluoride;
 - a second region comprising a magnesium-containing aluminum alloy; and
 - a third region comprising an aluminum fluoride;
 - wherein the third region is between the first region and the second region;
 - wherein a concentration of the magnesium fluoride decreases from the first region to the third region;
 - wherein a concentration of the aluminum fluoride decreases from the third region to the second region.
12. The substrate of claim 11, wherein the substrate has an aspect ratio of 2:1 to 2000:1, wherein the aspect ratio is a ratio of two of a width, a depth, a height, a length, or a diameter.
13. The substrate of claim 11, wherein the substrate comprises:
 - at least 50% by weight of aluminum based on a total weight of the substrate;
 - and
 - less than 10% by weight of iron based on the total weight of the substrate.
14. The substrate of claim 11, wherein the substrate comprises anodized Al.
15. The substrate of claim 11, wherein:
 - the first region has a magnesium content of 20% to 40% as measured by XPS;
 - the second region has a fluorine content of 10% to 60% as measured by XPS.
16. A method comprising:
 - exposing a substrate to a fluorine-containing vapor sufficient to form at least one of:
 - a first region comprising at least one of an aluminum fluoride, a magnesium fluoride, or any combination thereof;
 - a second region comprising an aluminum alloy; and

a third region comprising at least one of an aluminum fluoride, a magnesium fluoride, or any combination thereof;

wherein the first region is above the second region;

wherein the third region, when present, is between the first region and the second region.

17. The method of claim 16, wherein a fluorine component from the fluorine-containing vapor reacts with a magnesium component of the substrate to form the first region.

18. The method of claim 16, wherein a fluorine component from the fluorine-containing vapor reacts with an aluminum component of the substrate to form the first region.

19. The method of claim 16, wherein the fluorine-containing vapor comprises at least one of CF_4 , C_2F_4 , C_3F_6 , C_4F_8 , CHF_3 , $\text{C}_2\text{H}_2\text{F}_2$, C_2F_6 , HF , CH_3F , a vaporized fluorinated polymer, or any combination thereof.

20. The method of claim 16, wherein the exposing comprises heating at least a portion of the substrate at or to a temperature of 200 °C to 600 °C and exposing the substrate to the fluorine-containing vapor for a duration of 1 millisecond to 15 hours.