

## **MODIFIED METAL FOIL CAPACITORS AND METHODS FOR MAKING SAME**

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

**[0001]** This application claims the benefit of and priority to U.S. Provisional Application No. 63/199,229, filed on December 15, 2020, which is hereby incorporated by reference in its entirety.

### **FIELD**

**[0002]** The present disclosure relates to electronic devices generally and more specifically to metal-based, e.g., aluminum-based capacitors, having high capacitance and their use in embedded circuits and integrated circuits.

### **BACKGROUND**

**[0003]** Capacitor devices have numerous applications in the electronic, electrical, and micro-electrical fields. They are useful for energy storage. Aluminum capacitors, specifically, are commonly used in compact devices due to their high capacitance density, relatively high voltage compatibility, and relatively low cost. Capacitors generally include high surface area to achieve high capacitance values and are commonly arranged as a pair of thin electrodes separated by a dielectric and rolled into a tight cylindrical structure to optimize the surface area per unit volume. A high surface area per unit volume, resulting in a high capacitance, is desirable because it allows for increased energy storage.

**[0004]** Typically, capacitors are manufactured by forming a porous high-purity foil which is then anodized. The pores are then impregnated with a liquid or a polymer electrolyte. Such capacitors have high surface area, and, when alumina is used as the dielectric, have a dielectric constant of approximately 10. Capacitors formed by tunnel etching, however, have upper limits for capacitance.

### **SUMMARY**

**[0005]** The term embodiment and like terms are intended to refer broadly to all of the subject matter of this disclosure and the claims below. Statements containing these terms should be understood not to limit the subject matter described herein or to limit the meaning or scope of the claims below. Embodiments of the present disclosure covered herein are defined by the claims below, not this summary. This summary is a high-level overview of various

aspects of the disclosure and introduces some of the concepts that are further described in the Detailed Description section below. This summary is not intended to identify key or essential features of the claimed subject matter, nor is it intended to be used in isolation to determine the scope of the claimed subject matter. The subject matter should be understood by reference to appropriate portions of the entire specification of this disclosure, any or all drawings and each claim.

**[0006]** In some aspects, the present disclosure is directed to a metal foil capacitor, comprising a modified metal foil comprising a base metal, preferably an aluminum foil. The metal foil capacitor may satisfy at least two of the following conditions: (a) the modified metal foil has a surface area of at least 10 times greater than an unmodified metal foil; (b) the modified metal foil has a dielectric constant (k) of at least 5; (c) the modified metal foil has a thickness of at least 1 micron; and/or (d) the modified metal foil comprises at least one metal in addition to the base metal, wherein the at least one metal is present in an amount of at least 0.01 wt.% based on the total weight of the modified metal foil. In some aspects, conditions (a) and (b) are satisfied. In some aspects, conditions (a) and (c) are satisfied. In some aspects, conditions (a) and (d) are satisfied. In some aspects, conditions (b) and (c) are satisfied. In some aspects, conditions (b) and (d) are satisfied. In some aspects, conditions (c) and (d) are satisfied. In some aspects, conditions (a), (b) and (c) are satisfied. In some aspects, conditions (a), (b) and (d) are satisfied. In some aspects, conditions (b), (c) and (d) are satisfied. In some aspects, conditions (a), (b), (c) and (d) are satisfied. The dielectric constant (k) may be at least 10. The at least one metal in addition to the base metal (e.g., aluminum, copper, gold, silver, nickel, zinc) may be titanium, zirconium, or combinations thereof. The at least one metal in addition to the base metal may be present from 0.01 to 30 wt.%, based on the total weight of the modified metal foil. The modified metal foil may comprise a total of from 0.01 to 30 wt.% titanium and zirconium, based on the total weight of the modified metal foil.

**[0007]** In some aspects, the present disclosure is directed to a modified aluminum foil and methods of forming a layer of alumina over the modified aluminum foil by anodizing the modified aluminum foil.

**[0008]** In some aspects, the present disclosure is directed to methods of forming the modified metal foil, e.g., modified aluminum foil. The method may comprise glancing angle deposition (GLAD). In some aspects, the method further comprises atomic layer deposition (ALD) and/or electroless metal deposition. The ALD may be used to form a deposited layer comprising at least one of Al, Si, Al oxide, Ti oxide, Al nitride, Ti nitride, or combinations thereof. Depending on the conductivity of the deposited layer, the layer may act as a dielectric

layer or cathode. The electroless metal deposition may comprise electroless nickel deposition (ELNi), electroless aluminum deposition, electroless copper deposition, electroless silver deposition, or combinations thereof.

[0009] Other objects and advantages will be apparent from the following detailed description of non-limiting examples.

#### BRIEF DESCRIPTION OF THE FIGURE

[0010] The specification makes reference to the following appended figures, in which use of like reference numerals in different figures is intended to illustrate like or analogous components.

[0011] FIG. 1 provides a schematic illustration of a process sequence for GLAD/ALD/electroless metal deposition (e.g., Elni) on a metallic foil such as an aluminum foil for capacitors.

[0012] FIG. 2A provides an SEM micrograph showing a 50KX planar view of a specific example of an aluminum GLAD film with a nominal thickness of 487 nm deposited on an aluminum foil.

[0013] FIG. 2B provides an SEM micrograph showing a 50KX planar view of the aluminum GLAD film shown in FIG. 2A after deposition of an Al<sub>2</sub>O<sub>3</sub> ALD film with a nominal thickness of 10 nm.

[0014] FIG. 3A provides an SEM micrograph showing a 50KX planar view of a specific example of a titanium GLAD film with a nominal thickness of 1000 nm deposited on an aluminum foil.

[0015] FIG. 3B provides an SEM micrograph showing a 50KX planar view of the titanium GLAD film shown in FIG. 3A after deposition of an Al<sub>2</sub>O<sub>3</sub> ALD film with a nominal thickness of 10 nm.

#### DETAILED DESCRIPTION

##### [0016] **Definitions**

[0017] As used herein, the terms “invention,” “the invention,” “this invention” and “the present invention” are intended to refer broadly to all of the subject matter of this patent application and the claims below. Statements containing these terms should be understood not to limit the subject matter described herein or to limit the meaning or scope of the patent claims below.

**[0018]** All ranges disclosed herein are to be understood to encompass any and all subranges subsumed therein. For example, a stated range of “1 to 10” should be considered to include any and all subranges between (and inclusive of) the minimum value of 1 and the maximum value of 10; that is, all subranges beginning with a minimum value of 1 or more, e.g. 1 to 6.1, and ending with a maximum value of 10 or less, e.g., 5.5 to 10. Unless stated otherwise, the expression “up to” when referring to the compositional amount of an element means that element is optional and includes a zero percent composition of that particular element. Unless stated otherwise, all compositional percentages are in weight percent (wt. %).

**[0019]** As used herein, the meaning of “a,” “an,” and “the” includes singular and plural references unless the context clearly dictates otherwise.

**[0020]** As used herein, the meaning of “room temperature” can include a temperature of from about 15 °C to about 30 °C, for example about 15 °C, about 16 °C, about 17 °C, about 18 °C, about 19 °C, about 20 °C, about 21 °C, about 22 °C, about 23 °C, about 24 °C, about 25 °C, about 26 °C, about 27 °C, about 28 °C, about 29 °C, or about 30 °C.

**[0021]** **Introduction**

**[0022]** **[0008]** Described herein are metal foils (e.g., aluminum, copper, silver, gold, nickel, or zinc foils), that may be anodized and used as capacitors. The metal foils are formed by methods that result in high capacitance, due to increasing the surface area and/or dielectric constant of the metal foil. The disclosed capacitors employ the modified metal foil and an oxide layer (e.g., alumina or titania) to act as a dielectric. In part due to their high capacitance, the capacitors described herein are useful as components of integrated and embedded circuits, for example. The metal foils described herein have high capacitance due to increased surface area, an increased dielectric constant, and/or decreased thickness of the dielectric layer.

**[0023]** Capacitance is defined as  $C=EA/d$ , where C is capacitance, E is the dielectric constant, A is the surface area, and d is the thickness of the dielectric layer. As used herein, dielectric constant is also referred to as (k). While in conventional methods the surface area and thickness may be modestly modified to increase capacitance, i.e., by increasing the surface area and decreasing the thickness, the value of the dielectric constant cannot readily be modified. By using the methods described herein, the capacitance may be increased by greater amounts than previously known because of changes to the surface area, dielectric constant, and thickness. In some aspects, the dielectric constant is greater than 10. In some aspects, the surface area of the capacitor foil is at least 10 times greater than an unmodified metal foil. In some aspects, the capacitor foil has a dielectric constant (k) of at least 15. In some aspects, the

thickness of the foil is from 1 micron to 500 microns. In some aspects, the capacitor foil comprises at least one metal (e.g., a dopant) in addition to the base metal.

**[0024]     Capacitor**

**[0025]**     As described herein, the capacitor comprises a modified metal foil such as an aluminum foil, a copper foil, a gold foil, a silver foil, a nickel foil, a zinc foil, or the like. The metal foil may be made of any pure metal or alloy with good electrical conductivity. The foil may be anodized to form a thin oxide layer. Disclosed herein are methods for forming the capacitor foil which result in capacitors with superior properties, especially as compared with capacitors with foils prepared by tunnel etching.

**[0026]**     In some aspects, the capacitor has a capacitance of at least 10 times greater than a capacitor containing an unmodified metal foil, e.g., at least 15 times greater, at least 20 times greater, at least 25 times greater, at least 30 times greater, at least 35 times greater, at least 40 times greater, at least 45 times greater, at least 50 times greater, at least 55 times greater, at least 60 times greater, at least 65 times greater, at least 70 times greater, at least 75 times greater, at least 80 times greater, at least 85 times greater, at least 90 times greater, at least 95 times greater, at least 100 times greater, at least 105 times greater, 110 times greater, at least 115 times greater, at least 120 times greater, at least 125 times greater, at least 130 times greater, at least 135 times greater, at least 140 times greater, at least 145 times greater, at least 150 times greater, at least 155 times greater, at least 160 times greater, at least 165 times greater, at least 170 times greater, at least 175 times greater, at least 180 times greater, at least 185 times greater, at least 190 times greater, at least 195 times greater, or at least 200 times greater.

**[0027]**     In some aspects, the capacitor has a capacitance of at least 25% greater than a capacitor containing a foil prepared by tunnel etching, e.g., at least 30%, at least 35%, at least 40%, at least 45%, at least 50%, at least 55%, at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 95%, at least 100%, at least 105%, at least 110%, at least 115%, at least 120%, at least 125%, at least 130%, at least 135%, at least 140%, at least 145%, at least 150%, at least 155%, at least 160%, at least 165%, at least 170%, at least 175%, at least 180%, at least 185%, at least 190%, at least 195%, at least 200%, at least 205%, at least 210%, at least 215%, at least 220%, at least 225%, at least 230%, at least 235%, at least 240%, at least 245%, and/or at least 250%.

**[0028]**     In some aspects, the capacitor foil has a surface area of at least 10 times greater than an unmodified metal foil, e.g., e.g., at least 15 times greater, at least 20 times greater, at least 25 times greater, at least 30 times greater, at least 35 times greater, at least 40 times greater, at

least 45 times greater, at least 50 times greater, at least 55 times greater, at least 60 times greater, at least 65 times greater, at least 70 times greater, at least 75 times greater, at least 80 times greater, at least 85 times greater, at least 90 times greater, at least 95 times greater, at least 100 times greater, at least 105 times greater, 110 times greater, at least 115 times greater, at least 120 times greater, at least 125 times greater, at least 130 times greater, at least 135 times greater, at least 140 times greater, at least 145 times greater, at least 150 times greater, at least 155 times greater, at least 160 times greater, at least 165 times greater, at least 170 times greater, at least 175 times greater, at least 180 times greater, at least 185 times greater, at least 190 times greater, at least 195 times greater, or at least 200 times greater.

**[0029]** In some aspects, the capacitor foil has a dielectric constant (k) of at least 5, at least 6, at least 7, at least 8, at least 9, at least 10, at least 11, at least 12, at least 13, at least 14, at least 15, at least 16, at least 17, at least 18, at least 19, at least 20, at least 21, at least 22, at least 23, at least 24, at least 25, at least 26, at least 27, at least 28, at least 29, at least 30, at least 31, at least 32, at least 33, at least 34, at least 35, at least 36, at least 37, at least 38, at least 39, at least 40, at least 41, at least 42, at least 43, at least 44, at least 45, at least 46, at least 47, at least 48, at least 49, at least 50, at least 51, at least 52, at least 53, at least 54, at least 55, at least 56, at least 57, at least 58, at least 59, at least 60, at least 61, at least 62, at least 63, at least 64, at least 65, at least 66, at least 67, at least 68, at least 69, at least 70, at least 71, at least 72, at least 73, at least 74, at least 75, at least 76, at least 77, at least 78, at least 79, at least 80, at least 81, at least 82, at least 83, at least 84, at least 85, at least 86, at least 87, at least 88, at least 89, at least 90, at least 91, at least 92, at least 93, at least 94, at least 95, at least 96, at least 97, at least 98, at least 99, or at least 100. In terms of ranges, the capacitor foil may have a dielectric constant from 5 to 100, from 10 to 75, from 15 to 50, or from 20 to 45.

**[0030]** In some aspects, the capacitor foil may have a thickness from 1 to 200  $\mu\text{m}$ , from 5 to 200  $\mu\text{m}$ , from 10 to 200  $\mu\text{m}$ , from 15 to 195  $\mu\text{m}$ , from 25 to 175  $\mu\text{m}$ , from 50 to 150  $\mu\text{m}$ , at least 1  $\mu\text{m}$ , at least 5  $\mu\text{m}$ , at least 10  $\mu\text{m}$ , at least 15  $\mu\text{m}$ , at least 20  $\mu\text{m}$ , at least 25  $\mu\text{m}$ , at least 30  $\mu\text{m}$ , at least 35  $\mu\text{m}$ , at least 40  $\mu\text{m}$ , at least 45  $\mu\text{m}$ , at least 50  $\mu\text{m}$ , at least 55  $\mu\text{m}$ , at least 60  $\mu\text{m}$ , at least 65  $\mu\text{m}$ , at least 70  $\mu\text{m}$ , at least 75  $\mu\text{m}$ , at least 80  $\mu\text{m}$ , at least 85  $\mu\text{m}$ , at least 90  $\mu\text{m}$ , at least 95  $\mu\text{m}$ , at least 100  $\mu\text{m}$ , at least 105  $\mu\text{m}$ , at least 110  $\mu\text{m}$ , at least 115  $\mu\text{m}$ , at least 120  $\mu\text{m}$ , at least 125  $\mu\text{m}$ , at least 130  $\mu\text{m}$ , at least 135  $\mu\text{m}$ , at least 140  $\mu\text{m}$ , at least 145  $\mu\text{m}$ , at least 150  $\mu\text{m}$ , at least 155  $\mu\text{m}$ , at least 160  $\mu\text{m}$ , at least 165  $\mu\text{m}$ , at least 170  $\mu\text{m}$ , at least 175  $\mu\text{m}$ , at least 180  $\mu\text{m}$ , at least 185  $\mu\text{m}$ , at least 190  $\mu\text{m}$ , at least 195  $\mu\text{m}$ , at least 200  $\mu\text{m}$ , at least 205  $\mu\text{m}$ , at least 210  $\mu\text{m}$ , at least 215  $\mu\text{m}$ , at least 220  $\mu\text{m}$ , at least 225  $\mu\text{m}$ , at least 230  $\mu\text{m}$ , at least 235  $\mu\text{m}$ , at least 240  $\mu\text{m}$ , at least 245  $\mu\text{m}$ , at least 250  $\mu\text{m}$ , at least 255  $\mu\text{m}$ , at least 260

μm, at least 265 μm, at least 270 μm, at least 275 μm, at least 280 μm, at least 285 μm, at least 290 μm, at least 295 μm, at least 300 μm, at least 305 μm, at least 310 μm, at least 315 μm, at least 320 μm, at least 325 μm, at least 330 μm, at least 335 μm, at least 340 μm, at least 345 μm, at least 350 μm, at least 355 μm, at least 360 μm, at least 365 μm, at least 370 μm, at least 375 μm, at least 380 μm, at least 385 μm, at least 390 μm, at least 395 μm, at least 400 μm, at least 405 μm, at least 410 μm, at least 415 μm, at least 420 μm, at least 425 μm, at least 430 μm, at least 435 μm, at least 440 μm, at least 445 μm, at least 450 μm, at least 455 μm, at least 460 μm, at least 465 μm, at least 470 μm, at least 475 μm, at least 480 μm, at least 485 μm, at least 490 μm, at least 495 μm, or at least 500 μm.

**[0031]** In some aspects, the dielectric layer (an alumina layer, a titania layer, an oxide of Si, Zn, Zr, Ta, Hf, Nb, Ba, Sr, Pb, La, Y, St, or a combination of two or more oxides formed by anodizing or co-deposition on the modified metal foil), may have a thickness from about 5 nm to about 100 nm, such as from 10 nm to 90 nm, from 20 nm to 80 nm, from 40 nm to 60 nm, 5 nm, 10 nm, 15 nm, 20 nm, 25 nm, 30 nm, 35 nm, 40 nm, 50 nm, 55 nm, 60 nm, 65 nm, 70 nm, 75 nm, 80 nm, 85 nm, 90 nm, 95 nm, or 100 nm.

**[0032]** In some aspects, the capacitor foil comprises at least one metal in addition to the base metal (e.g., aluminum). In some aspects, the at least one metal is in the form of a dopant or in the form of a surface coating, and it comprises Ti, Si, Zn, Zr, Ta, Hf, La, Y, Sr or combinations thereof wherein the at least one metal is present in an amount of at least 0.01 wt.%, based on the total weight of the capacitor foil, at least 1.25 wt.%, at least 1.5 wt.%, at least 1.75 wt.%, at least 2 wt.%, at least 2.25 wt.%, at least 2.5 wt.%, at least 2.75 wt.%, at least 3 wt.%, at least 3.25 wt.%, at least 3.5 wt.%, at least 3.75 wt.%, at least 4 wt.%, at least 4.25 wt.%, at least 4.5 wt.%, at least 4.75 wt.%, at least 5 wt.%, at least 5.25 wt.%, at least 5.5 wt.%, at least 5.75 wt.%, at least 6 wt.%, at least 6.25 wt.%, at least 6.5 wt.%, at least 6.75 wt.%, at least 7 wt.%, at least 7.25 wt.%, at least 7.5 wt.%, at least 7.75 wt.%, at least 8 wt.%, at least 8.25 wt.%, at least 8.5 wt.%, at least 8.75 wt.%, at least 9 wt.%, at least 9.25 wt.%, at least 9.5 wt.%, at least 9.75 wt.%, at least 10 wt.%, at least 10.25 wt.%, at least 10.5 wt.%, at least 10.75 wt.%, at least 11 wt.%, at least 11.25 wt.%, at least 11.5 wt.%, at least 11.75 wt.%, at least 12 wt.%, at least 12.25 wt.%, at least 12.5 wt.%, at least 12.75 wt.%, at least 13 wt.%, at least 13.25 wt.%, at least 13.5 wt.%, at least 13.75 wt.%, at least 14 wt.%, at least 14.25 wt.%, at least 14.5 wt.%, at least 14.75 wt.%, at least 15 wt.%, at least 15.25 wt.%, at least 15.5 wt.%, at least 15.75 wt.%, at least 16 wt.%, at least 16.25 wt.%, at least 16.5 wt.%, at least 16.75 wt.%, at least 17 wt.%, at least 17.25 wt.%, at least 17.5 wt.%, at least 17.75 wt.%, at least 18 wt.%, at least 18.25 wt.%, at least 18.5 wt.%, at least 18.75 wt.%, at least 19 wt.%, at least

19.25 wt.%, at least 19.5 wt.%, at least 19.75 wt.%, at least 20 wt.%, at least 20.25 wt.%, at least 20.5 wt.%, at least 20.75 wt.%, at least 21 wt.%, at least 21.25 wt.%, at least 21.5 wt.%, at least 21.75 wt.%, at least 22 wt.%, at least 22.25 wt.%, at least 22.5 wt.%, at least 22.75 wt.%, at least 23 wt.%, at least 23.25 wt.%, at least 23.5 wt.%, at least 23.75 wt.%, at least 24 wt.%, at least 24.25 wt.%, at least 24.5 wt.%, at least 24.75 wt.%, at least 25 wt.%, at least 25.25 wt.%, at least 25.5 wt.%, at least 25.75 wt.%, at least 26 wt.%, at least 26.25 wt.%, at least 26.5 wt.%, at least 26.75 wt.%, at least 27 wt.%, at least 27.25 wt.%, at least 27.5 wt.%, at least 27.75 wt.%, at least 28 wt.%, at least 28.25 wt.%, at least 28.5 wt.%, at least 28.75 wt.%, at least 29 wt.%, at least 29.25 wt.%, at least 29.5 wt.%, at least 29.75 wt.%, or at least 30 wt.%. In terms of exemplary ranges, the at least one metal may be present from 1 wt.% to 30 wt.%, 1.25 wt.% to 29 wt.%, 1.5 wt.% to 28 wt.%, 2 wt.% to 25 wt.%, or 3 wt.% to 20 wt.%, or any of the values contained above.

**[0033]** In some aspects, the capacitor has at least two of the above characteristics, e.g., at least three, or all four, including dielectric constant, surface area, thickness, and/or level of dopant.

**[0034]** In some aspects, the capacitor foil may have a surface area of at least 10 times greater than an unmodified metal foil. In some aspects, the capacitor foil may have a surface area of at least 10 times greater than an unmodified metal foil, and the foil may have a dielectric constant (k) of at least 5. In some aspects, the capacitor foil may have a surface area of at least 10 times greater than an unmodified metal foil, and the foil may have a thickness of at least 1 micron. In some aspects, the capacitor foil may have a surface area of at least 10 times greater than an unmodified metal foil and at least one metal in addition to the base metal (e.g., aluminum), wherein the at least one metal is present in an amount of at least 0.01 wt.%, based on the total weight of the capacitor foil.

**[0035]** In some aspects, the capacitor foil may have a surface area of at least 10 times greater than an unmodified metal foil, the foil may have a dielectric constant (k) of at least 5, and the foil may have a thickness of at least 1 micron. In some aspects, the capacitor foil may have a surface area of at least 10 times greater than an unmodified metal foil, the foil may have a dielectric constant (k) of at least 5, and the foil may comprise at least one metal in addition to the base metal (e.g., aluminum), wherein the at least one metal is present in an amount of at least 0.01 wt.%, based on the total weight of the capacitor foil.

**[0036]** In some aspects, the capacitor foil may have a surface area of at least 10 times greater than an unmodified metal foil, the foil may have a dielectric constant (k) of at least 5, the foil may have a thickness of at least 1 micron, and the foil may comprise at least one metal

in addition to the base metal (e.g., aluminum), wherein the at least one metal is present in an amount of at least 0.01 wt.%, based on the total weight of the capacitor foil.

**[0037]** In some aspects, the capacitor foil may have a dielectric constant ( $k$ ) of at least 5, and a thickness of at least 1 micron. In some aspects, the foil may have a dielectric constant ( $k$ ) of at least 5, and the foil may have at least one metal in addition to the base metal (e.g., aluminum), wherein the at least one metal is present in an amount of at least 0.01 wt.%, based on the total weight of the capacitor foil.

**[0038]** In some aspects, the capacitor foil may have a dielectric constant ( $k$ ) of at least 5, a thickness of at least 1 micron, and at least one metal in addition to the base metal (e.g., aluminum), wherein the at least one metal is present in an amount of at least 0.01 wt.%, based on the total weight of the capacitor foil.

**[0039]** In some aspects, the foil may have a thickness of at least 1 micron, and the foil may have at least one metal in addition to the base metal (e.g., aluminum), wherein the at least one metal is present in an amount of at least 0.01 wt.%, based on the total weight of the capacitor foil.

**[0040] Glancing Angle Deposition**

**[0041]** In some embodiments, capacitor foils described herein may be formed by using glancing angle deposition (GLAD) to deposit pure Al, pure Ti, Al alloys with Ti, Cu, Ag, Au, Zr, Zn, Si, Hf, La, Y, Ta, Sr; Ti alloys with Al, Cu, Ag, Au, Zr, Zn, Si, Hf, La, Y, Ta, Sr; pure Cu, Ag, Au, Zr, Zn, Si, Hf, La, Y, Ta, Sr; or any combinations of these pure metals or alloys. Metals that form a natural oxide layer with high dielectric constant may be beneficial to use, as their natural oxide film may contribute to the performance of the dielectric layer deposited by the ALD film.

**[0042]** GLAD is a nanofabrication technique used for fabricating porous thin films. In a common physical vapor deposition process, the angle  $\theta$  between incoming particle flux and substrate normal is fixed close to  $0^\circ$ . Modifying the angle  $\theta$ , however, represents an additional degree of freedom for influencing film morphology. Tilting the substrate to an oblique angle of incidence  $\theta > 70^\circ$  leads to the formation of a thin film consisting of separated tilted nanocolumns. A metal foil with titled nanocolumns may be referred to as a modified metal foil in this disclosure, and the tilted nanocolumns may be referred to as surface modifications. This is called oblique angle deposition (OAD), whereas the combination of an oblique angle of incidence  $\theta$  and simultaneous substrate rotation is called GLAD. GLAD is described in US Patent No. 6,206,065 and US Pub. No. 2015/0140213, the entire contents and disclosures of which are incorporated by reference.

**[0043]** The porous thin film may be generated in other ways. For example, the porous thin film may be generated through physical vapor deposition (PVD), chemical vapor deposition (CVD), or etching.

**[0044]** In some aspects, the method may further include atomic layer deposition (ALD) and/or electroless nickel deposition (ELNi). The atomic layer deposition may be used to deposit Al, Si, Al oxide, Ti oxide, Al nitride, Ti nitride, or any combinations of Al, Si, Al alloy oxides, Al alloy nitrides, Ti alloy oxides, ruthenium, ruthenium oxide,  $\text{MnO}_2$ , strontium ruthenate, or Ti alloy nitrides. Depending on the conductivity, the deposited film may act as a dielectric layer or cathode. Additionally or alternatively, the dielectric layer may be formed through anodization of the metal foil. The dielectric layer, formed through ALD or ALD, may be one of the following:  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{HfSiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{La}_2\text{O}_3$ ,  $\text{LaAlO}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{TiO}_2$ ,  $\text{BaTiO}_3$ ,  $\text{SiTrO}_3$ ,  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ , or  $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ ,  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ,  $\text{ZrO}_2$ , or  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ , for example. The electroless deposition may also be used to deposit other metals with high conductivity, including Ni, Cu, Ag, Al, or others. This may eliminate the need for the application of a conductive polymer (and the additional steps associated with that) in the conventional fabrication of capacitors, which can improve productivity, reduce cost, and potentially improve performance. Additionally or alternatively, thiophene, polyaniline, or P3HT can be deposited using electropolymerization. In certain aspects, a multi-step method comprises a GLAD-ALD-ELNi processing line. A schematic is shown in FIG. 1. The processing line may be fit into a reel-reel metallic foil, e.g., an aluminum foil. The foil may then be subjected to GLAD to apply a structured metallic layer. Next, the structured metallic layer may be encapsulated in an ultra-thin oxide film via ALD. The dielectric constant of the ultra-thin oxide film may be at least 5.

**[0045]** In some aspects, the method may further include deposition of any conductor made of metal, alloy, metallic composites, or combinations thereof.

**[0046]** In some aspects, the method may further comprise physical vapor deposition (PVD) and/or chemical vapor deposition (CVD) of any conductor made of metal, alloy, metallic composites, or combinations thereof.

**[0047]** Next, the encapsulated film may be coated with a metallic coating process by using Elni. By coating the film with a metal such as nickel, the structured surface formed by GLAD and ALD is protected and it is also a conductive counter-electrode.

**[0048]** The surface area of the foils made according to this method may be at least 10 times greater than an unmodified foil, The thickness of the foil may be at least 1 micron.

**[0049]** The following examples will serve to further illustrate the present invention without, at the same time, however, constituting any limitation thereof. On the contrary, it is to

be clearly understood that resort may be had to various embodiments, modifications and equivalents thereof which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the invention. During the studies described in the following examples, conventional procedures were followed, unless otherwise stated. Some of the procedures are described below for illustrative purposes.

### **EXAMPLES**

#### **[0050]**     Example 1

**[0051]**     An aluminum film having a nominal thickness of 487 nm was deposited by GLAD on an aluminum foil. An SEM micrograph is shown in FIG. 2A.

#### **[0052]**     Example 2

**[0053]**     An Al<sub>2</sub>O<sub>3</sub> film having a nominal thickness of 10 nm was deposited onto the film of Example 1. An SEM micrograph is shown in FIG. 2B. The average capacitance of the GLAD/ALD deposited film was then measured. The results are reported in Table 1 below.

#### **[0054]**     Example 3

**[0055]**     A titanium film having a nominal thickness of 1000 nm was deposited by GLAD on an aluminum foil. An SEM micrograph is shown in FIG. 3A.

#### **[0056]**     Example 4

**[0057]**     An Al<sub>2</sub>O<sub>3</sub> film having a nominal thickness of 10 nm was deposited onto the film of Example 3. An SEM micrograph is shown in FIG. 3B. The average capacitance of the GLAD/ALD deposited film was then measured. The results are reported in Table 1 below.

| <b>TABLE 1</b> |                   |                  |                                |                                                |                           |
|----------------|-------------------|------------------|--------------------------------|------------------------------------------------|---------------------------|
| <b>Example</b> | <b>Metal Foil</b> | <b>GLAD film</b> | <b>ALD film</b>                | <b>Average Capacitance (μF/cm<sup>2</sup>)</b> | <b>Standard Deviation</b> |
| Example 2      | Al                | Al               | Al <sub>2</sub> O <sub>3</sub> | 3.72                                           | 1.53E-07                  |
| Example 3      | Al                | Ti               | Al <sub>2</sub> O <sub>3</sub> | 117                                            | 1.67E-05                  |

#### **[0058]**     Example 5

**[0059]**     In general, capacitors formed using the methods described herein had a capacitance density of about 1.8-2.2 μF/mm<sup>2</sup> at 100 kHz, an equivalent series resistance of about 30-160 mΩ\*mm<sup>2</sup> and an insulation resistance of about 10-15 MΩ\*mm<sup>2</sup>.

### **ILLUSTRATIVE ASPECTS**

**[0060]**     As used below, any reference to a series of aspects (e.g., “Aspects 1-4”) or non-enumerated group of aspects (e.g., “any previous or subsequent aspect”) is to be understood

as a reference to each of those aspects disjunctively (e.g., “Aspects 1-4” is to be understood as “Aspects 1, 2, 3, or 4”).

**[0061]** Aspect 1 is a method for forming a metal foil capacitor, comprising: (a) providing a metal substrate; (b) modifying the metal substrate to generate a porous thin film on the metal substrate; (c) forming a dielectric layer on the porous thin film of the metal substrate; (d) depositing a cathode layer conformal with the dielectric layer using atomic layer deposition or using electroless deposition; and (e) depositing a metal layer on the cathode layer using electroless deposition to form the metal foil capacitor.

**[0062]** Aspect 2 is the method of any previous or subsequent aspect, wherein the metal substrate comprises aluminum.

**[0063]** Aspect 3 is the method of any previous or subsequent aspect, wherein (b) comprises physical vapor deposition (PVD), chemical vapor deposition (CVD), glancing angle deposition (GLAD), or etching.

**[0064]** Aspect 4 is the method of any previous or subsequent aspect, wherein (c) comprises depositing the dielectric layer on the porous thin film of the metal substrate using atom layer deposition.

**[0065]** Aspect 5 is the method of any previous or subsequent aspect, wherein (c) comprises anodizing the porous thin film of the metal substrate.

**[0066]** Aspect 6 is the method of any previous or subsequent aspect, wherein the dielectric layer comprises alumina.

**[0067]** Aspect 7 is the method of any previous or subsequent aspect, wherein the dielectric layer further comprises an oxide of titanium (Ti), silicon (Si), zinc (Zn), zirconium (Zr), tantalum (Ta), hafnium (Hf), lanthanum (La), yttrium (Y), strontium (St), or a combination thereof.

**[0068]** Aspect 8 is the method of any previous or subsequent aspect, wherein the metal layer comprises one or more of nickel (Ni), copper (Cu), silver (Ag), or aluminum (Al).

**[0069]** Aspect 9 is the method of any previous or subsequent aspect, wherein a dielectric constant (k) of the metal foil capacitor is at least 5, such as from 5 to 100, or more.

**[0070]** Aspect 10 is the method of any previous or subsequent aspect, wherein the dielectric constant (k) is at least 10.

**[0071]** Aspect 11 is the method of any previous or subsequent aspect, wherein the metal substrate or the porous thin film comprises at least 0.01% by weight of an additional metal, such as from 0.01% by weight to 1% by weight, or more.

**[0072]** Aspect 12 is the method of any previous or subsequent aspect, wherein the additional metal is titanium (Ti), silicon (Si), zinc (Zn), zirconium (Zr), tantalum (Ta), hafnium (Hf), lanthanum (La), yttrium (Yt), or strontium (St).

**[0073]** Aspect 13 is the method of any previous or subsequent aspect, wherein the additional metal is present from 0.01 to 30 wt.%, based on the total weight of the metal substrate.

**[0074]** Aspect 14 is the method of any previous or subsequent aspect, wherein the dielectric layer is at most 100 nanometers thick, such as from 5 nanometer thick to 100 nanometers.

**[0075]** Aspect 15 is the method of any previous or subsequent aspect, wherein the metal foil capacitor has an average capacitance of at least 1  $\mu\text{F}/\text{mm}^2$ , such as from 1  $\mu\text{F}/\text{mm}^2$  to 5  $\mu\text{F}/\text{mm}^2$ , or more.

**[0076]** Aspect 16 is the method of any previous or subsequent aspect, wherein the metal foil capacitor has a capacitance of at least about 1.8  $\mu\text{F}/\text{mm}^2$  at 100 kHz, such as from about 1.8  $\mu\text{F}/\text{mm}^2$  at 100 kHz to about 5  $\mu\text{F}/\text{mm}^2$  at 100 kHz, or more.

**[0077]** Aspect 17 is the method of any previous or subsequent aspect, wherein the cathode layer comprises titanium nitride.

**[0078]** All patents, publications, and abstracts referenced herein are incorporated herein by reference in their entirety. The foregoing description of the embodiments, including illustrated embodiments, has been presented only for the purpose of illustration and description and is not intended to be exhaustive or limiting to the precise forms disclosed. Numerous modifications, adaptations, and uses thereof will be apparent to those skilled in the art.