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(72) Inventors; and
(71) Applicants : **STUART, Martin, A.** [US/US]; 3612 W. Victory Blvd., Burbank, CA 91505 (US). **CUNNINGHAM, Stephen, L.** [US/US]; 2306 Glen Canyon Road, Altadena, CA 91001 (US).

(74) Agents: **BODI, Robert, F.** et al.; Pearne & Gordon LLP, 1801 East 9th Street, Suite 1200, Cleveland, OH 44114 (US).

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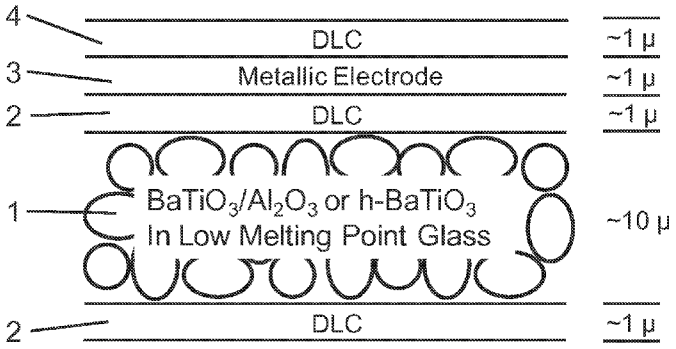


FIG. 1

(57) Abstract: A device and method for providing electrical energy storage of high specific energy density. The device contains a plurality of layers of high dielectric constant material, such as Barium Titanate or Hexagonal Barium Titanate, sandwiched between electrode layers made up of a variety of possible conducting materials. The device includes additional insulating layers, such as Diamond Like Carbon Coating, between the electrodes that provide for very high breakdown voltages. Layers are created by a variety of methods and assembled to form the device that is the High Energy Density Storage Device.

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High Energy Density Storage Device

BACKGROUND

[0001] Capacitors are devices that store electrical energy on a dielectric material between two conductive electrodes, usually metal. Their architecture has followed a path that started as a metal sleeve on the outside and inside of a glass jar (called a Leyden Jar). Today, materials with very high dielectric constants are used in geometries that maximize the area of the electrodes while at the same time providing dielectric thicknesses that result in high breakdown voltages. The combination of high dielectric constant, high voltage, and high electrode surface area leads to an energy storage capability with very high specific energy (energy per unit volume).

[0002] Recently it has been reported (U.S. Pat. No. 7,023,687, incorporated herein by reference) that very small particles of Barium Titanate ($BaTiO_3$) coated with a layer of Alumina (Al_2O_3) can have very high dielectric constants (values near 20,000) when they are preferentially oriented by an external electric field. The cited inventors have chosen to fill the gaps between the particles with a plastic (the chosen plastic is PET) so as to increase the breakdown voltage of the dielectric layer and to hold the particles in place. This solution uses powdered metal (Aluminum) to create the conducting electrodes. In order to access the increased dielectric constant of the $BaTiO_3$ material, a high voltage is applied to the matrix between the electrodes while the system is held at a temperature high enough for the PET to be soft to allow the $BaTiO_3$ particles to orient. The layer of $BaTiO_3$ particles needs to be relatively thin in order to have a high enough field strength to cause the preferential orientation. One problem has been the fact that most dielectric materials used in this application have a breakdown voltage that is lower than the voltage needed for the orientation effect. The inventors reported that the breakdown voltage can be held just above the required value if the $BaTiO_3$ particles are densely packed in the PET matrix of the dielectric layer.

[0003] Even more recent is an application in Japan by the Japanese Aerospace Exploration Agency and TDK (US patent application pub. No. 2011/0059838 for Dielectric Ceramic Composition, incorporated herein by reference). The material in this

application is also $BaTiO_3$ made with an additional small amount of Lanthanum, Cerium, Vanadium, or Bismuth. This addition and processing method provides a hexagonal form of $BaTiO_3$ which has a measured dielectric constant of 160,000.

[0004] However, there are problems with practical devices based on this architecture using PET. If the $BaTiO_3$ coated particles have a lower density in some areas of the plastic matrix, then a lower breakdown voltage will be experienced in that specific area. This results in local current breakdown with high heating and subsequent destruction of the device. This susceptibility to catastrophic breakdown is further exacerbated by a residual heating effect in the powdered metal electrodes due to a resistance from metal particle to particle, and to a residual heating effect in the $BaTiO_3$ material due to charging and discharging. While this effect may be small, the temperature effect is evident in the charge/discharge operation and important for the life and reliability of the device. These concerns can therefore severely limit the maximum allowed applied voltage to the device and thereby limit the amount of energy storage, limiting the utility of the resulting device.

SUMMARY

[0005] Examples of a new method and design is provided that inserts a thin layer of an electrically insulating material with a high breakdown voltage and very good heat conductivity between the electrode and the dielectric material. The insulating material, for example Diamond Like Carbon (DLC), can be deposited in thin layers by a number of different methods described below. The specific thicknesses and the method of deposition can vary depending upon the desired energy density and size of the final device.

[0006] In one example embodiment, the reliability of the device can be considerably improved over previous embodiments by encasing the $BaTiO_3$ in a low melting temperature glass (LMG), such as, but not limited to, Mitsui's 380C frit glass (US 6,355,586 incorporated by reference), instead of PET. Then, a thin layer of Diamond Like Carbon (DLC) is deposited on both faces of the dielectric layer prior to applying a thin metal film. The DLC serves the function of increasing to a very high level the breakdown voltage of the sandwich (the breakdown voltage of DLC film can be 10,000

volts/micron assuming at least 70% is in the tetrahedral carbon structure, usually specified as sp^3 structure) while providing good heat conductivity. A safe voltage range is chosen, typically at about half the breakdown voltage.

[0007] The glass or ceramic can be sintered, fused or melted at a temperature below 400C. This temperature limit is important since Diamond Like Carbon (DLC) can graphitize at or above this temperature. While the glass is soft, a high voltage is applied to orient the $BaTiO_3/Al_2O_3$ particles and the particles remain oriented as the structure cools.

[0008] Other embodiments using different electrode material, different layer thicknesses, and different voltages are possible, some of which are described below. The critical parameters for sizing the High Energy Density Storage Device are: 1) the breakdown voltage of the DLC insulation layers, 2) the maximum applied field allowed by the $BaTiO_3$ to keep its high dielectric constant, and 3) the maximum voltage (DC) that can be practically generated in the external power supply.

[0009] Provided is a device for storing energy, comprising: a first insulating layer comprising an electrically insulating material having at least good heat conductivity; a dielectric layer comprising particles dispersed in an electrically insulating material, the particles including $BaTiO_3$; a first conducting electrode layer; a second conducting electrode layer; anda second insulating layer comprising the electrically insulating material having at least good heat conductivity. The dielectric layer is provided between the first conducting electrode layer and the second conducting electrode layer.

[0010] Also provided is a device for storing energy, comprising: a plurality of insulating layers each comprising carbon at least partially organized in a diamond-like structure; a plurality of dielectric layers each comprising particles dispersed in an electrically insulating material, the particles including BaTiO3; and a plurality of conducting electrode layers. The plurality of conducting electrode layers are interleaved with the plurality of dielectric layers and the plurality of insulating layers to form an electric capacitor device adapted for storing energy obtained from an electrical voltage source connected to the device.

[0011] Further provided is a device for storing energy, comprising: a plurality of insulating layers each comprising carbon at least partially organized in a diamond-like structure acting as an electrical insulator and having at least good heat conducting properties; a plurality of dielectric layers including $BaTiO_3$; and a plurality of conducting electrode layers. The plurality of conducting electrode layers are interleaved with the plurality of dielectric layers and the plurality of insulating layers to form an electric capacitor device adapted for storing energy obtained from an electrical voltage source connected to the device.

[0012] Still further provided is a device for storing energy, comprising: a plurality of insulating layers comprising an electrically insulating material having at least good heat conductivity; a plurality of dielectric layers; and a plurality of conducting electrode layers. The plurality of conducting electrode layers are interleaved with the plurality of dielectric layers and the plurality of insulating layers to form an electric capacitor device adapted for storing energy obtained from an electrical voltage source connected to the device. Furthermore, the device is adapted for storing energy at an energy density of greater than 10 kilojoules per cubic centimeter.

[0013] Also provided are devices with additional combinations and arrangements of the above features, along with additional example embodiments, some, but not all of which, are described hereinbelow in more detail.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] For a fuller understanding of the nature of the present invention, reference should be made to the following detailed description taken in conjunction with the accompanying drawings.

[0015] **FIG. 1** shows a schematic of an example sandwich structure of the $BaTiO_3/Al_2O_3$ or h-$BaTiO_3$ particles in a low melting point glass between layers of Diamond Like Carbon (DLC) with single electrode.

[0016] **FIG. 2** shows a schematic of an example of thin metal foil coated with DLC.

[0017] **FIG. 2a** shows a schematic similar to **FIG. 2** with the addition of a layer of magnetic material.

[0018] **FIG. 3** shows a schematic of an example of metal foil with matched thermal expansion coefficient completely encased in h-$BaTiO_3$ and sintered glass.

[0019] **FIG. 4** shows a schematic of an example with metal foil coated on only one side with h-$BaTiO_3$ and sintered glass.

[0020] **FIG. 5** shows a schematic of a standalone layer of powdered h-$BaTiO_3$ held in place with a low melting point glass or a plastic matrix.

[0021] **FIG. 6** shows a schematic of a single layer with metal electrode and $BaTiO_3$ deposited on a glass or metal carrier.

[0022] **FIG. 7** shows a schematic of a multilayer structure created by PLD for low voltage/high capacitance applications.

[0023] **FIG. 8** shows a schematic of the interleaving layers of the electrodes for the complete device.

[0024] **FIG. 9** is a plot showing the energy density of an example embodiment where all applied voltages are at their limiting value.

[0025] **FIG. 10** is a plot showing the energy density in a cubic centimeter for the example energy storage device for the case that the external voltage is limited to 10,000 volts.

DETAILED DESCRIPTION OF EXAMPLE EMBODIMENTS

[0026] Note that throughout this document, the term DLC is used to describe diamond-like-carbon, a material that may come in various forms, all comprising carbon that displays properties similar to those of diamond, like hardness giving good wear properties, slickness, and that can have high electrical insulation capability, while also having good to excellent heat conducting capability, such as the thermal conductivities in the range of metals (in the tens to many hundreds of W/m-K), to the excellent thermal conductivity of pure diamond (around 1000 W/m-K). However, some forms of DLC may even have semiconductor properties. This DLC material typically includes carbon

at least partially organized in a diamond-like structure, and may contain significant amounts of sp^3 hybridized carbon atoms. Unlike pure diamond, DLC materials can be made flexible and amorphous. In some of its forms, DLC material may contain actual synthetic diamond material. For the purposes of this disclosure, DLC formulations are preferred that offer high electrical insulating capabilities while also having good to excellent heat conducting capabilities. Other materials having similar properties, such as diamond composites and diamond powders, among others (such as specialized polymers or ceramics that may include diamond-like or actual diamond materials), could be substituted for the DLC material described below.

[0027] **FIG. 1** shows a schematic of the layered structure of an example storage device having a $BaTiO_3$ layer structure **1** with $BaTiO_3/Al_2O_3$ or h-$BaTiO_3$ particles dispersed in an insulating matrix, such as a low melting point glass (where h-$BaTiO_3$ is in the hexagonal structure and has higher dielectric properties than the more common cubic structure). The $BaTiO_3$ layer **1** is coated on top and bottom by a layer **2** of DLC. A metal electrode **3** is deposited on the top DLC layer **2**. Multiples of the layers shown in FIG. 1 are sandwiched together in the final storage device as desired to obtain the preferred storage capacity (see, e.g., Fig. 8 and accompanying discussion). The outermost metal electrode layer **3** is coated with an external DLC layer **4** to electrically insulate the storage device. The thicknesses of the layers can be varied as needed, and thus illustrate only one embodiment of this device, in particular where the applied voltages are limited to be below 20,000 volts. This limitation is set by the thickness of the DLC layers between electrodes. By varying the thickness of the DLC layers between the electrodes, the limiting voltage can be changed up or down, with increasing voltages leading to thicker DLC layers.

[0028] Although Aluminum particles for the electrode can be used, as in previous approaches, the current carrying capacity of the metal electrode film can be increased for applications with rapid charge/discharge cycles by adding or exclusively using Molybdenum, especially where the film thickness is critical, since Molybdenum has a very low expansion coefficient. In a large cross section device, this would be desirable to reduce the effect of expansion in the metal of the electrode. Alternatively, an alloy of Ni and Fe can be used to match the expansion coefficient of the Low Melting Point glass

and/or the DLC by altering the ratio of Ni to Fe to obtain the desired result. Since the entire device can be encapsulated in DLC or another sealing coating, the electrode can be protected from the effects of oxidation that otherwise might preclude the use of such an alloy.

[0029] Another alternative candidate for the metal electrode would be to use a coating of copper onto the DLC coated h-$BaTiO_3$ layer, at an elevated temperature up to 400C. If processed at this temperature, the copper layer upon cool down to ambient temperatures would contract. This permits the use of metal with higher expansion ratios than the composite of h-$BaTiO_3$/DLC layer. This method would permit the use of lower cost metals within the storage device, because the higher Coefficient of Thermal Expansion (CTE) metal would shrink within a cavity inside the DLC encapsulation mentioned. This is an expansion contraction fabrication method. Additionally this method relies on the DLC releasing from the metal it encapsulates. To facilitate this effect there may be an atom-thick release layer similar to, but reverse from, the ZnO layer mentioned in **FIG. 6** to facilitate hexagonal crystal formation.

[0030] Another alternative for the metal electrode is to use a commercial variation of 430 stainless steel as a substrate which can be obtained at 1 mil thickness (without a custom fixture) or less (with holding fixture). This material in foil form would permit roll-to-roll fabrication as the Coefficient of Thermal Expansion (CTE) is close to that of the h-$BaTiO_3$ dielectric. In this case, the $BaTiO_3$ would be deposited and grown in the h-$BaTiO_3$ form via a suitable hexagonal seed layer, such as Zinc Oxide. This would be followed by a heat and cool down at a proscribed rate. This process would have the advantage of allowing for a more robust metal, during set up, in the roll-to-roll coater. Alternatively, if desired, Titanium or Molybdenum foil could be used in this arrangement as well.

[0031] The electrodes of the full device are typically interleaved, with alternating electrode layers connected to opposite ends of the device (as shown in **FIG. 8**). One advantage of this construction with layers of DLC is that the very high heat conductivity of diamond will allow the residual heat load in the device to be conducted efficiently to the sides (90 degrees from the electrode ends) where it can be removed by any number of heat transfer methods. For example, assuming two-1 micron DLC layers adjacent to a 10

micron h-$BaTiO_3$ or $BaTiO_3$-Al_2O_3 particle layer, and a 1 micron thick electrode layer as shown in **FIG. 1**, the cross section of the side of the device would have a 15% surface area of DLC for conducting heat.

[0032] While specific film thicknesses are shown in the figure, they are only illustrative of the various choices a designer could make. The thickness of the DLC layer is related to the maximum desired voltage of the device. Lower voltages would permit the choice of thinner DLC layers, and, indeed, any of the layers could be changed by the designer to tailor a device for specific tasks and applications. For fabrication of thick DLC layers, trace amounts of various metals, such as Titanium, Tungsten, Cobalt, or various others mixed with carbon in low percentages, can be used to create a stress relieve layer. Additionally, lowering the radiance levels of the laser on the pure carbon target will create sp^2 (graphite) layers which are also stress relief layers. Stress relief is desired for thick layers to prevent cracking.

[0033] The manufacture of these layered storage devices can be accomplished via the use of several standard technologies. The preferred method is high speed Pulsed Laser Deposition (PLD) which can be accomplished in a roll-to-roll coater. Magnetron sputtering in a roll-to-roll Chemical Vapor Deposition (CVD) coater would also be a viable method, as would planar CVD, reactive CVD or Plasma Assisted Chemical Vapor Deposition (PACVD) . These deposition methods are existing art and are used for other applications, but can be applied to manufacture the disclosed devices.

[0034] When using PLD to manufacture the device, any of several pulsed lasers can be used. These include the Neodymium doped Yttrium Aluminum Garnet (Nd:YAG), the Neodymium doped Yttrium Vanadate (Nd:$YbVO_4$), the Chromium doped Alexandrite (Cr:$BeAl_2O_4$), or the Titanium doped Sapphire lasers. Other lasers can also be used, in particular if they are pulsed and have high power density in the focused spot. For high growth rates, this process best utilizes lasers exhibiting both high radiance per pulse and high average power. Lasers in this class are usually considered military systems. The laser is focused on a high purity carbon target with an energy density in the range 10^8 to 10^{10} (or more) Watts per square centimeter. This energy density is desired to create a plume of single carbon ions (lower energies tend to create clusters or strings of carbon atoms). The desired pulse width would be in the range of tens of nanoseconds, which is a

usual pulse length for Q-switched lasers (or down to the picosecond range if they are mode locked). The pulse repetition rate will be function of which laser gain material is actually used, and is usually in the range of several to several tens of kilohertz for the Q-switched systems. This method is existing art, although the growth rate for the DLC is fairly slow.

[0035] Several methods are proposed herein to increase the growth rate and the quality of the Diamond Like Carbon surface. At high PLD growth rates, one of the problems is that clusters of carbon atoms that are not in the sp^3 diamond structure impinge on the substrate. To improve the quality and rate of growth of the PLD films, the carbon plume is confined and directed to the substrate by several possible methods, the simplest of which is electrostatically charged baffles or electrodes. Additional methods would include using a quadrupole antenna or radio frequency (RF) antenna. The use of RF frequency (for example in the Microwave frequency range to couple to the carbon-carbon bond) can both serve to focus the beam and to break up any clumps of carbon atoms within the ejected material. A third alternate method is to use a portion of the laser beam in a second beam path to irradiate the plume in flight. This second beam can be at the primary frequency or at a harmonically converted frequency (or combination of both) of the source laser.

[0036] In the architecture described in **FIG. 1**, a completed envisioned device could have 10,000 or more layers per foot of height, with the length, from centerline assumed, but not limited to, 6 inches and the width from heat sink to heat sink assumed, but not limited to, 1.5 inches. Such a device would have very high energy density. For example, with a dielectric constant for $BaTiO_3$ of 160,000 as reported for one composition compared to 20,000 reported for another composition, and an applied voltage of 5,000 volts, the device will hold up to ~2.8×10^9 Joules (this is ~3 Gigajoules or about 775 kilowatt-hours) of energy in a cubic foot of material.

[0037] There are two major alternative construction techniques described below. The first (shown in **FIGS. 2-5**) is based on a coated insulated electrode built upon a metal foil that is expansion matched to DLC or CTE contraction encapsulation fabricated method. A schematic of this electrode is shown in **FIG. 2**. A metal foil strip **5** which is as wide as the Energy Storage Unit (ESU) device is coated on both sides and edges and one

end by a layer of DLC **6**. For this example, the metal foil **5** is 2 mils thick or less, the desired value being the minimum practical thickness._The DLC layer **6** is between 1/40 mil and 1 mil in thickness, the desired value being determined by the maximum applied voltage.

[0038] **FIGS. 3-5** show three alternative ways to add layers of $BaTiO_3$ to the electrode in **FIG. 2** to form the ESU structure. In each case, the $BaTiO_3$ layer is interleaved with the metal foil electrode in **FIG. 2** to create the multi-layered capacitor that is the ESU.

[0039] The hexagonal or doped formulation of $BaTiO_3$ can also be a powder that is mechanically added to an interleaved structure of DLC on metal electrode similar to that shown in **FIG. 2**. This design variant has the advantage of particle self-alignment after construction. This version would have the advantage of the simplest construction lending itself to automated assembly.

[0040] An additional variation of the electrode shown in **FIG. 2a** is to add a layer of high magneto-coercive material **11** on the outside of the DLC layer, such that the current flow through the electrode will set up a magnetically opposed force. This will have the effect of slowing the current and thus limiting the discharge rate. This would be desirable for situations in consumer applications such as hybrid car power cells, where for safety reasons a designer would want to limit the short circuit current in crashes and/or power system malfunctions.

[0041] In **FIG. 3**, a carrier metal strip **5** (for example, the commercially available nickel-cobalt ferrous alloy of Kovar® or the nickel-iron alloy Invar®) for which the coefficient of thermal expansion is matched to that of $BaTiO_3$ in sintered glass is coated on both sides. The dimensions are approximate. The coating material **7** is powdered h-$BaTiO_3$ mixed with glass particles which are ultimately sintered or hot pressed to form a layer. The metal foil **5** is from 1 to 3 mils thick, and the $BaTiO_3$ layers **7** can range from 1/4 to 40 mil in thickness depending upon the desired energy density.

[0042] In **FIG. 4**, the carrier metal strip **8**, similar to **FIG. 3**, is coated on only one side **9** with $BaTiO_3$. Here the layers are from 1 to 3 mils thick, with the dimension of the electrode **8** as thin as is practical.

[0043] Finally, the $BaTiO_3$ layer may be self supporting with no metal substrate when it is made up of particles suspended in a low melting point glass or in a plastic matrix or just mechanically applied to interleaved structures. This example is shown in the schematic of **FIG. 5**. The thickness of the $BaTiO_3$ layer **10** is determined by what is practical based on the machinery used. As will be shown below, the desired thickness depends upon the applied voltage and the desired energy density. All of the example configurations shown in **FIGS. 3-5** are provided sandwiched between electrodes as shown in **FIG. 2** in making the ESU device.

[0044] Additional alternate constructions are shown in **FIGS. 6** and **7**. These constructions are based on the ability to create layers using Pulsed Laser Deposition (PLD). In each case, a carrier (either a boron-silicate glass, e.g., about 2 mils thick, or a metal layer of matched thermal expansion to $BaTiO_3$ such as Kovar or an iron/nickel mix) is coated with various layers deposited using PLD.

[0045] In the example of **FIG. 6**, the substrate **17** is first coated with a very thin layer **16** of Zinc Oxide (ZnO). This layer need only be thick enough to establish a crystalline structure, as small as a few tens of angstroms. This layer is desired so that the $BaTiO_3$ structure **15** that is grown next has the preferred hexagonal structure with the desired z-axis perpendicular to the surface. This aligns the axis of the high dielectric constant with the axis of the ESU. Next, a layer of DLC **2** is deposited with a thickness, e.g., at least 1 micron (1/25 mil). Next is provided a layer of metal **3** that serves as an electrode which is then coated by another layer **2** of DLC. The DLC on both sides of the metal electrode serves the purpose of providing a good insulation barrier to prevent current from flowing even at very high applied voltages. The ESU is ultimately assembled by interleaving multiple structures where the carrier may or may not be removed.

[0046] **FIG.7** shows another example arrangement having a monolithic structure created using PLD that is similar to devices created for integrated circuits. On a metal or glass carrier **17**, alternating layers **2** of DLC and metallic electrode **3** are sandwiched between layers **18** of $BaTiO_3$ grown on Zinc Oxide coated substrates **16**. The full size structure would contain an even number of $BaTiO_3$ layers, with the limit only imposed by practical considerations for the number of PLD layers possible without opening the

vacuum chamber. Once a multi layer structure is made, many of them can be sandwiched together to form the full ESU.

[0047] These example alternate structures for the ESU are 1) based on the high dielectric constant of $BaTiO_3$ or one of its doped derivatives, and 2) use the insulating and thermal properties of DLC. There are a number of variations within these general principles for the exact thicknesses of any of the layers, and even the ordering and number of intermediate layers. The exact details will be governed by the practicality of the various mechanical implementations, and the methodology is not limited to any one specific design.

[0048] **FIG. 8** shows schematically an example of how the electrodes of the example energy storage devices can be interleaved. The left electrode **20** has comb-like fingers **26** of layers that are interleaved with the fingers **25** of the right electrode **21**. The material between the electrodes **24** can be any of the example layers of materials deposited on the metallic electrodes or metal foils shown in **FIGS. 1-6**. The total number of layers is arbitrary. The final device is encapsulated in a jacket **22** of DLC, which can serve as an electrical insulator and, if necessary for large devices, a thermal path to a cooling system.

[0049] **FIG. 9** shows a plot of the energy density values that are possible for various thicknesses of $BaTiO_3$ and DLC layers for some of the example embodiments. In each case, the electrode thickness is assumed to be about 25 microns. The plots assume the lower value of the dielectric constant for $BaTiO_3$ from the previous compositions of 20,000. The maximum applied field across the $BaTiO_3$ is limited to about 500 Volts per micron based on data showing that the dielectric constant is virtually unchanged up to fields of this strength. The breakdown voltage for the DLC is assumed to be 10,000 Volts per micron, which is appropriate for the sp^3 (diamond) structure. The $BaTiO_3$ layer is not assumed to add any protection against voltage breakdown. Finally, the maximum voltage available from the external power supply is assumed to be limited to about 125,000 Volts for this example. The figure shows the energy density in kilojoules per cubic centimeter for four different thicknesses of DLC and as the thickness of the $BaTiO_3$ increases up to about 254 microns (10 mils).

[0050] The curves in **FIG. 9** show the energy per cubic centimeter (cc) imposed by the above chosen voltage limits. For thicknesses of $BaTiO_3$ below about 200 microns, the maximum energy density per cc is determined by the applied field limitation of 500 Volts per micron of $BaTiO_3$. For thicknesses of $BaTiO_3$ above 250 microns, the energy density per cc is limited by the maximum possible applied voltage of about 125,000 volts. For the case where the DLC layer thickness is 5 microns, the limit is determined by the breakdown voltage of the DLC of 10,000 Volts per micron. This figure shows that the specific choice of these design parameters depends upon the ultimate desired energy density and the ease of manufacturing the layers of certain thicknesses. For a large range of variables, the energy density has the very high value in the range of about 10 kilojoules per cubic centimeter.

[0051] The curves in the plot of **FIG. 10** show the example design for the case where the maximum applied voltage is limited to about 10,000 volts. For layers thinner than about 20 microns, the voltage is limited by the applied field limitation of 500 Volts per micron. For layers thicker than about 20 microns, the energy density decreases because the applied voltage is constant and the capacitance decreases since it is inversely related to the thickness between electrodes. As the layers get thinner the number of layers that are needed to create a 1 cm thick stack becomes very large. So, again, there is a tradeoff between ease of manufacturing, thicknesses of layers, applied voltage, and energy density.

EXAMPLE APPLICATIONS

[0052] The energy densities obtained with the device described herein exceed by a factor greater than 5 the energy density of Lithium-Ion batteries of existing technologies. Furthermore, the device can typically be more rapidly charged, and won't degrade in the manner often seen in rechargeable batteries, and thus may need be replaced less often. The device also typically has less internal current leakage, and thus stays charged longer. The resulting improved device can then be utilized for applications where high-energy density mobile power sources are desired. For example, such a device can be used to power an electric automobile, aircraft, ship, or other transportation device, effectively replacing storage batteries with a more energy-dense, and less

environmentally toxic, solution. Furthermore, the dense energy storage will allow for more compact and mobile use of devices requiring large amounts of energy, such as for powering mobile LASERs, electromagnetic weapons (e.g., rail guns), and other such devices.

[0053] In addition, the energy storage device could be utilized in arrays of devices for energy storage on a large scale, such as for storing wind or solar electrical energy during peak generation for use at other times when the wind or sun are not available. Also, applications include systems that involve long unattended operational lifetimes, such as powering remote sensors, micro space satellites, or even deep space probes, or systems where recharging capability may be infrequent.

[0054] Also, the device can be used on a small scale as a replacement in any device using batteries. This includes portable devices ranging in any size from flashlights to computers, cell phones, and watches. This concept taken to miniature extremes would have all of these features on an integrated circuit in a nano robotic application. One such example would be for a covert listening or locating device about the size of a grain of salt.

[0055] Many other example embodiments of the invention can be provided through various combinations of the above described features. Although the invention has been described hereinabove using specific examples and embodiments, it will be understood by those skilled in the art that various alternatives may be used and equivalents may be substituted for elements and/or steps described herein, without necessarily deviating from the intended scope of the invention. Modifications may be necessary to adapt the invention to a particular situation or to particular needs without departing from the intended scope of the invention. It is intended that the invention not be limited to the particular implementations and embodiments described herein, but that the claims be given their broadest reasonable interpretation to cover all novel and non-obvious embodiments, literal or equivalent, disclosed or not, covered thereby.

CLAIMS

What is claimed is:

1 A device for storing energy, comprising:

a first insulating layer comprising an electrically insulating material having at least good heat conductivity;

a dielectric layer comprising particles dispersed in an electrically insulating material, said particles including $BaTiO_3$;

a first conducting electrode layer;

a second conducting electrode layer; and

a second insulating layer comprising the electrically insulating material having at least good heat conductivity, wherein

said dielectric layer is provided between said first conducting electrode layer and said second conducting electrode layer.

2. The device of claim 1, wherein said electrically insulating material is glass.

3. The device of claim 1, wherein said particles also include Al_2O_3.

4. The device of claim 1, wherein the $BaTiO_3$ of said particles is at least partially organized in a hexagonal structure.

5. The device of claim 1, wherein said electrically insulating material having at least good heat conductivity includes carbon at least partially organized in a diamond-like structure.

6. The device of claim 1, wherein said electrically insulating material having at least good heat conductivity includes diamond.

7. The device of claim 1, wherein said first insulating layer and/or said second insulating layer is about 1 micron thick or less.

8. The device of claim 1, wherein one or both of said first conducting layer or said second conducting layer includes material having a Coefficient of Thermal Expansion that is close to that of the dielectric layer.

9. The device of claim 1, further comprising a layer including a high magneto-coercive material.

10. The device of claim 1, further comprising a layer including zinc oxide.

11. The device of claim 1, wherein one or both of said first conducting layer or said second conducting layer includes a metal foil encapsulated in a material including carbon at least partially organized in a diamond-like structure.

12. A device for storing energy, comprising:

a plurality of insulating layers each comprising carbon at least partially organized in a diamond-like structure;

a plurality of dielectric layers each comprising particles dispersed in an electrically insulating material, said particles including $BaTiO_3$; and

a plurality of conducting electrode layers; wherein

said plurality of conducting electrode layers are interleaved with said plurality of dielectric layers and said plurality of insulating layers to form an electric capacitor device adapted for storing energy obtained from an electrical voltage source connected to said device.

13. The device of claim 12, wherein said electrically insulating material is glass.

14. The device of claim 12, wherein said particles also include Al_2O_3.

15. The device of claim 12, wherein the $BaTiO_3$ of said particles is at

least partially organized in a hexagonal structure.

16. The device of claim 12, wherein insulating layers are about 1 micron thick or less.

17. The device of claim 12, wherein at least some of said conducting layers include material having a Coefficient of Thermal Expansion that is close to that of the dielectric layers.

18. The device of claim 12, further comprising one or more layers including a high magneto-coercive material.

19. The device of claim 12, further comprising one or more layers including zinc oxide.

20. A device for storing energy, comprising:

a plurality of insulating layers each comprising carbon at least partially organized in a diamond-like structure acting as an electrical insulator and having at least good heat conducting properties;

a plurality of dielectric layers including $BaTiO_3$; and

a plurality of conducting electrode layers, wherein

said plurality of conducting electrode layers are interleaved with said plurality of dielectric layers and said plurality of insulating layers to form an electric capacitor device adapted for storing energy obtained from an electrical voltage source connected to said device.

21. The device of claim 20, further comprising one or more layers including a high magneto-coercive material.

22. The device of claim 20, further comprising one or more layers including zinc oxide.

23. The device of claim 20, wherein at least some of said conducting layers include material having a Coefficient of Thermal Expansion that is close to that of the dielectric layers.

24. A device for storing energy, comprising:

a plurality of insulating layers comprising an electrically insulating material having at least good heat conductivity;

a plurality of dielectric layers; and

a plurality of conducting electrode layers, wherein

said plurality of conducting electrode layers are interleaved with said plurality of dielectric layers and said plurality of insulating layers to form an electric capacitor device adapted for storing energy obtained from an electrical voltage source connected to said device, and wherein

said device is adapted for storing energy at an energy density of greater than 10 kilojoules per cubic centimeter.

25. The device of claim 24, wherein said energy density is at least 15 kilojoules per cubic centimeter.

26. The device of claim 24, wherein said plurality of insulating layers each include carbon at least partially organized in a diamond-like structure acting as an electrical insulator and having at least good heat conducting properties.

27. The device of claim 24, wherein each of said dielectric layers includes particles comprising $BaTiO_3$.

28. The device of claim 27, wherein said particles are dispersed in a matrix of insulating material.

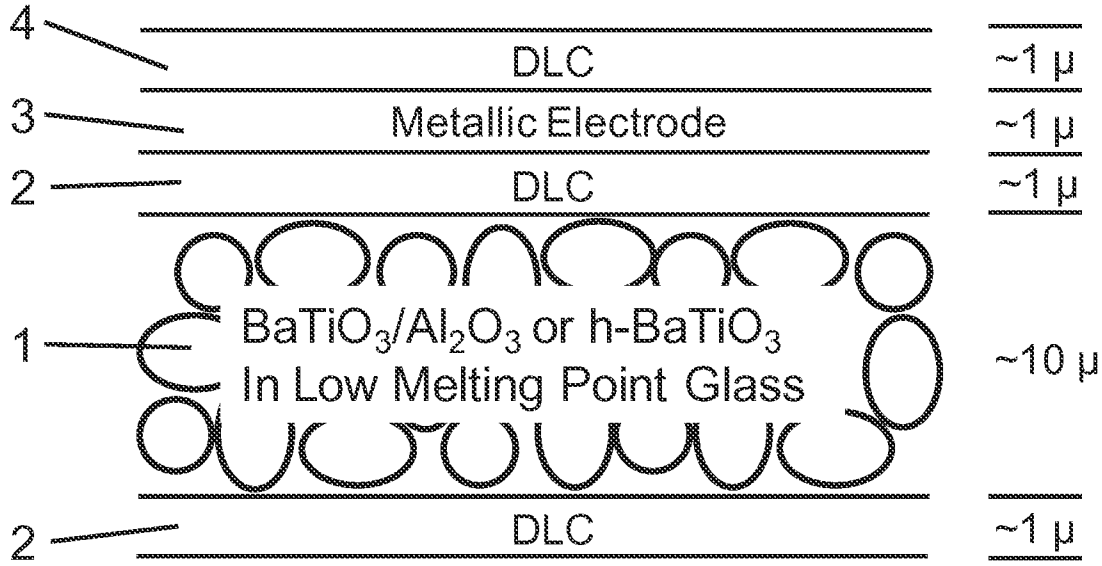

4
DLC
~1 μ
3
Metallic Electrode
~1 μ
2
DLC
~1 μ
1
$BaTiO_3/Al_2O_3$ or h-$BaTiO_3$
In Low Melting Point Glass
~10 μ
2
DLC
~1 μ

FIG. 1

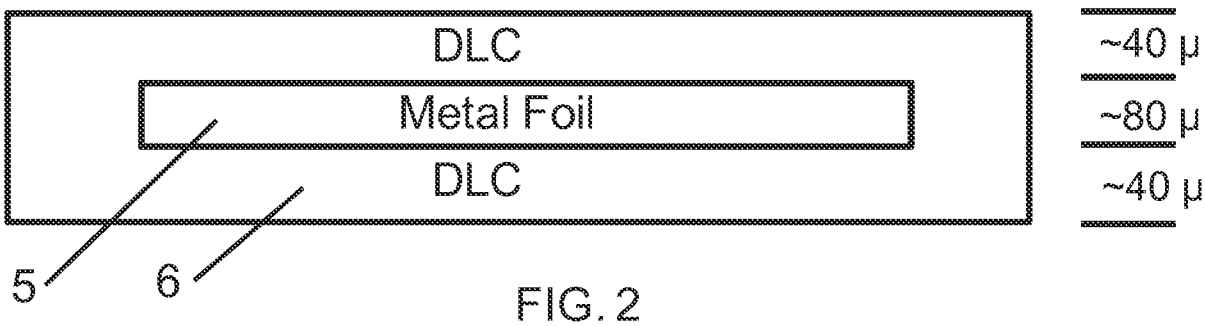

DLC
~40 μ
Metal Foil
~80 μ
DLC
~40 μ
5
6

FIG. 2

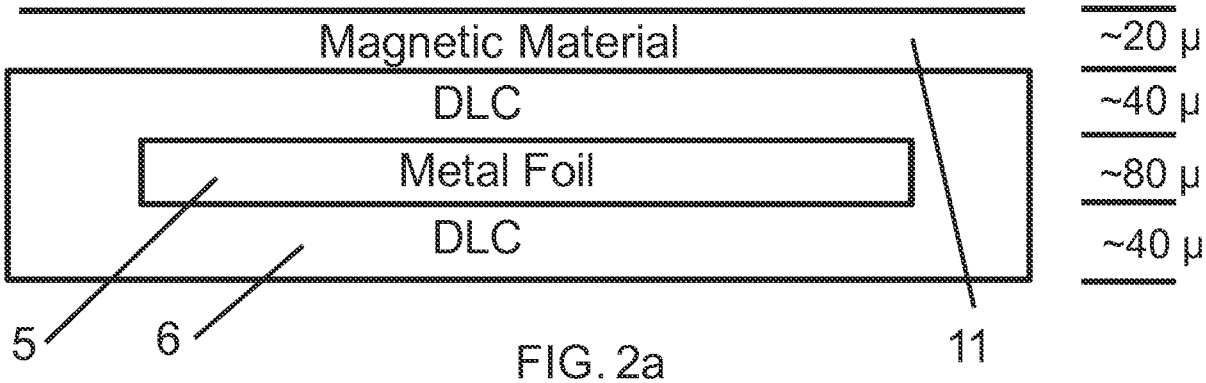


FIG. 2a

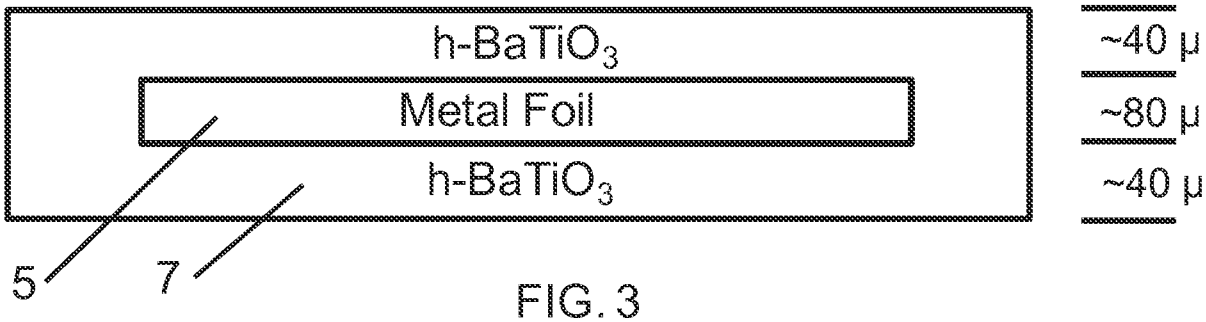


FIG. 3

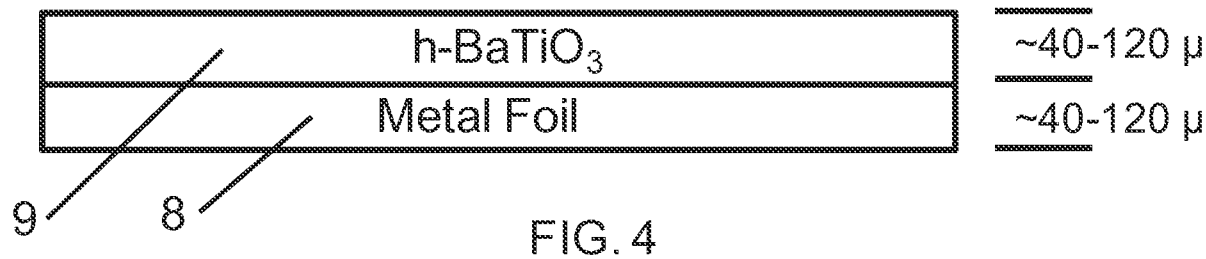


FIG. 4


h-BaTiO3
~40-240 µ
10

FIG. 5

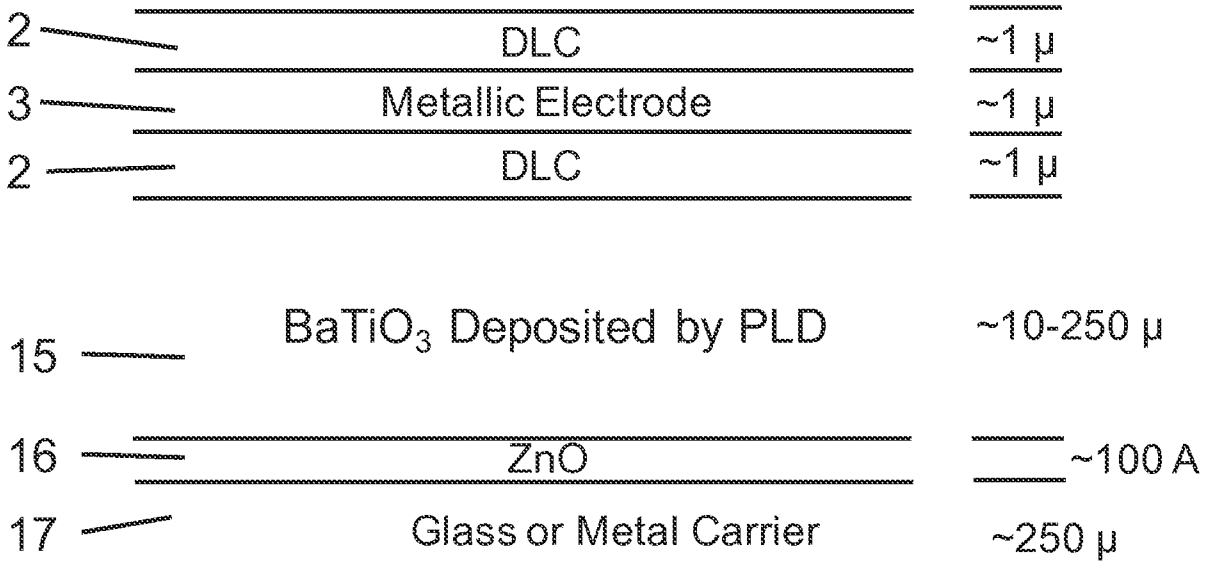

2
DLC
~1 µ
3
Metallic Electrode
~1 µ
2
DLC
~1 µ
15
BaTiO3 Deposited by PLD
~10-250 µ
16
ZnO
~100 A
17
Glass or Metal Carrier
~250 µ

FIG. 6

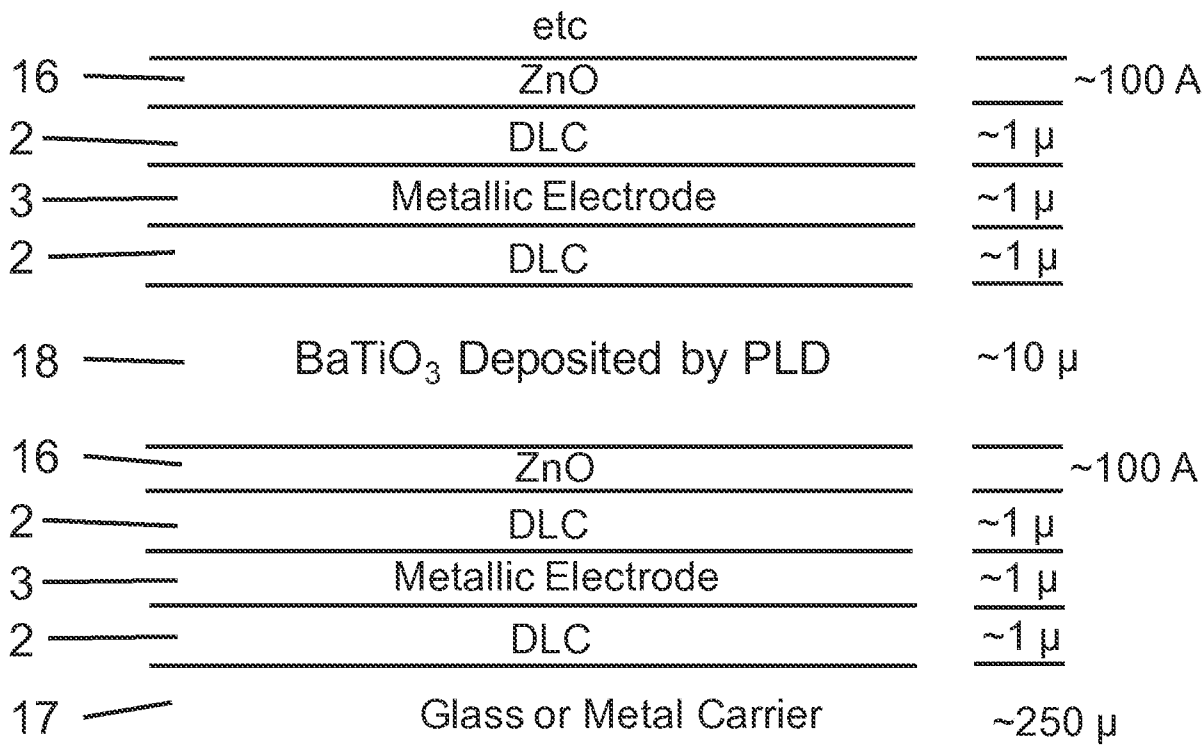

etc
16
ZnO
~100 A
2
DLC
~1 µ
3
Metallic Electrode
~1 µ
2
DLC
~1 µ
18
BaTiO3 Deposited by PLD
~10 µ
16
ZnO
~100 A
2
DLC
~1 µ
3
Metallic Electrode
~1 µ
2
DLC
~1 µ
17
Glass or Metal Carrier
~250 µ

FIG. 7

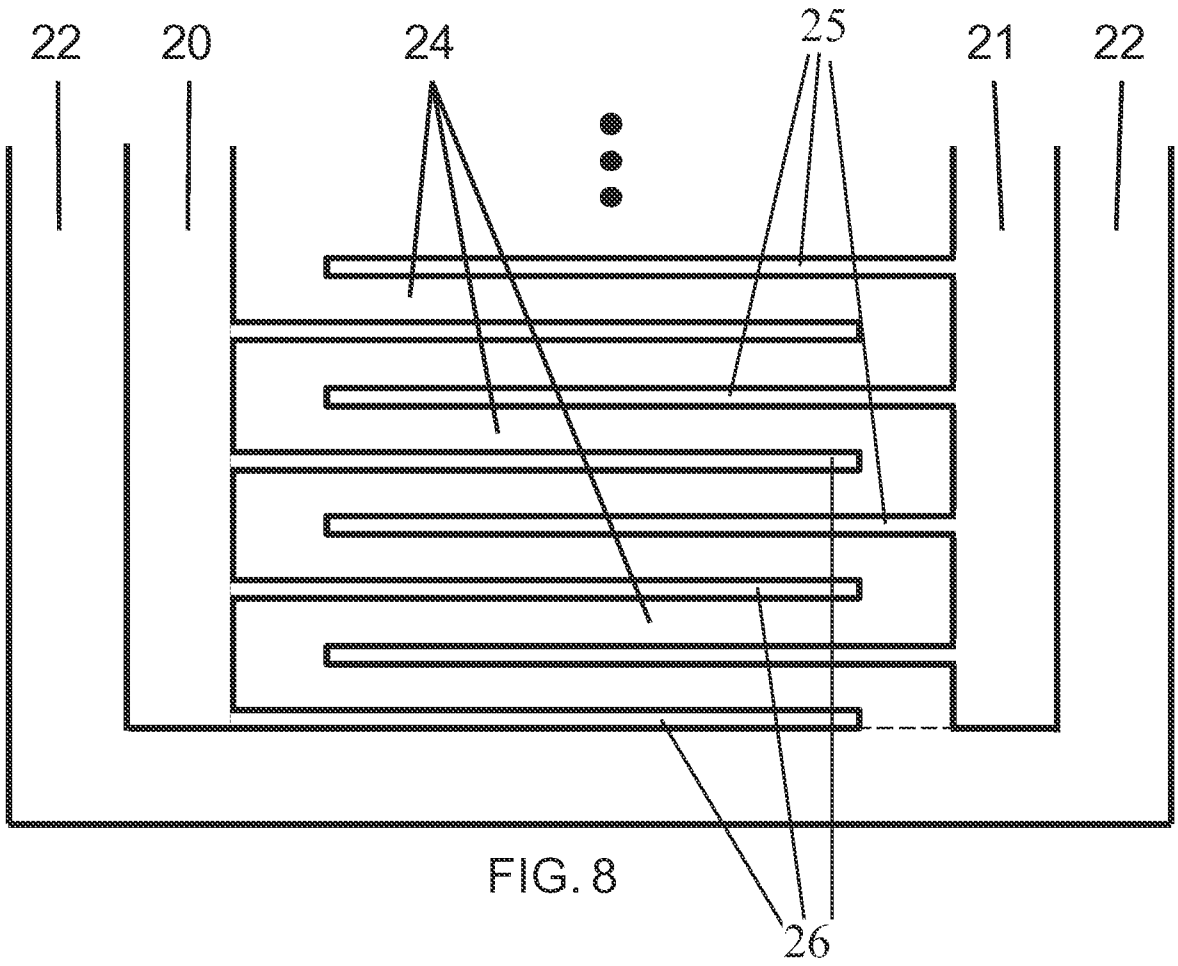


FIG. 8

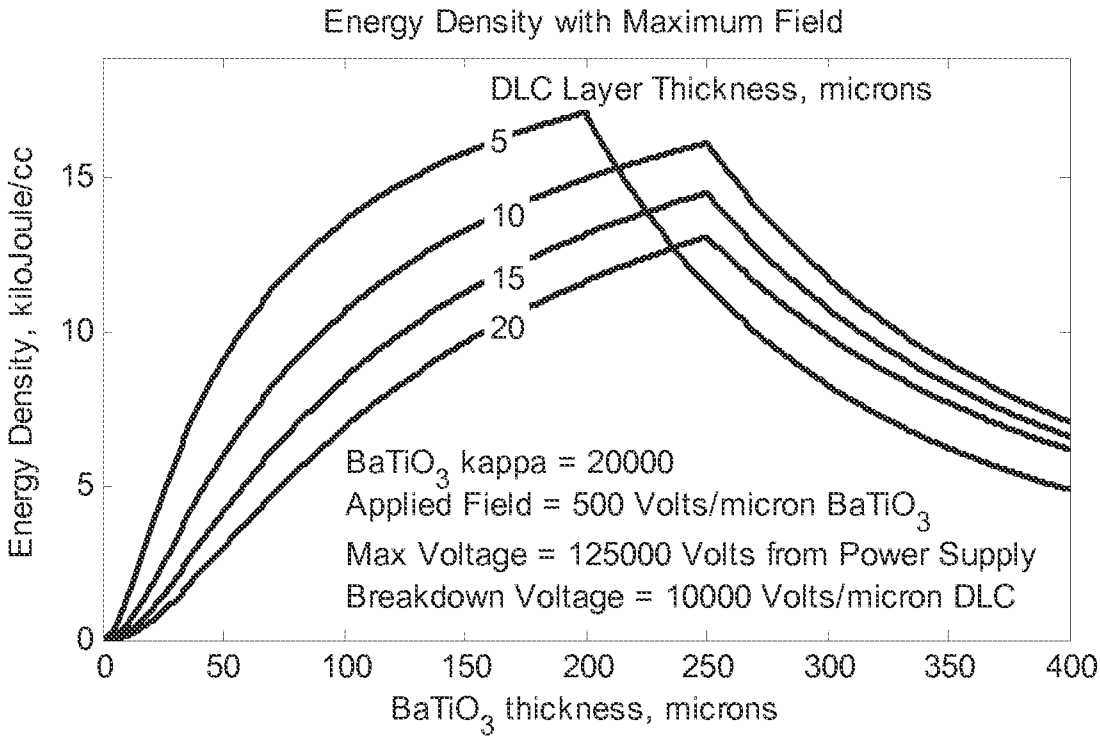

Energy Density with Maximum Field
DLC Layer Thickness, microns
5
10
15
20
BaTiO3 kappa = 20000
Applied Field = 500 Volts/micron BaTiO3
Max Voltage = 125000 Volts from Power Supply
Breakdown Voltage = 10000 Volts/micron DLC
Energy Density, kiloJoule/cc
0
5
10
15
0
50
100
150
200
250
300
350
400
BaTiO3 thickness, microns

FIG. 9

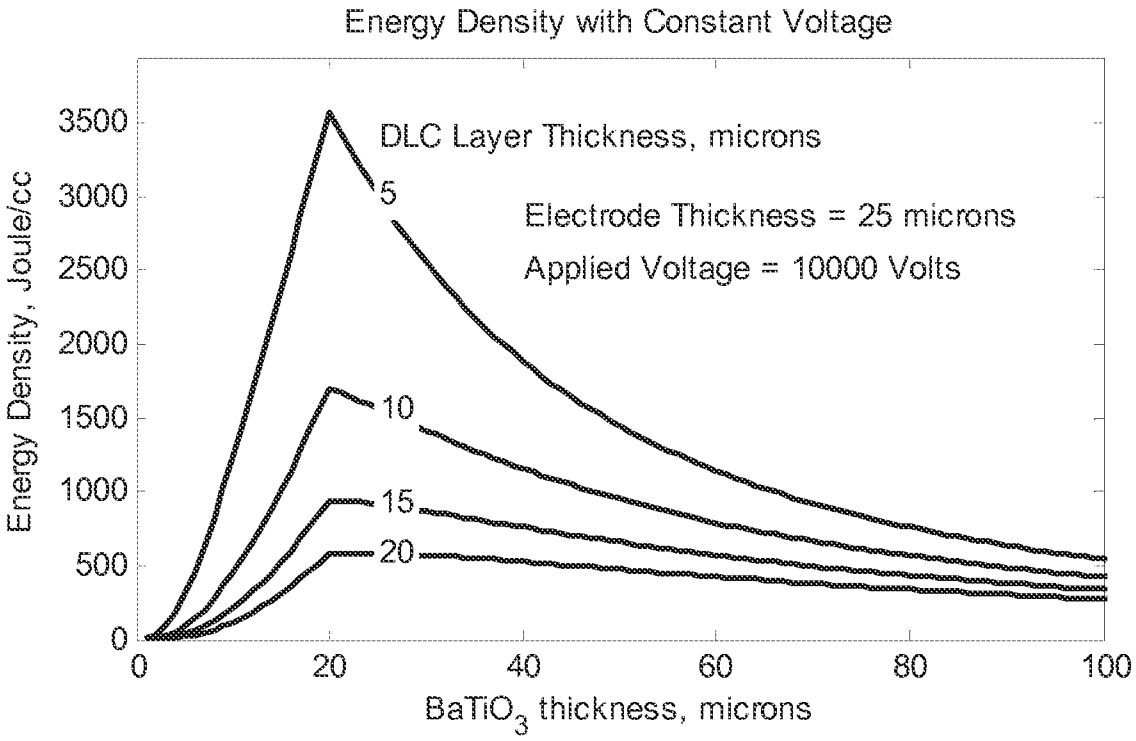

Energy Density with Constant Voltage
DLC Layer Thickness, microns
5
10
15
20
Electrode Thickness = 25 microns
Applied Voltage = 10000 Volts
Energy Density, Joule/cc
3500
3000
2500
2000
1500
1000
500
0
0
20
40
60
80
100
BaTiO3 thickness, microns

FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/064944

A. CLASSIFICATION OF SUBJECT MATTER

H01G 4/018(2006.01)i, H01G 4/228(2006.01)i

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)

H01G 4/018; H05K 3/46; H01G 4/30; H01G 4/12; C04B 35/46; H01B 3/12

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: insulating layer, barium titanate, dielectric layer, electrode layer, diamond-like structure

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2005-285968 A (KYOCERA CORP) 13 October 2005 See the abstract, figures 1-2 and claims 1-3.	1-28
A	JP 2008-227093 A (TDK CORP) 25 September 2008 See the abstract and claims 1-3.	1-28
A	JP 2009-292671 A (KYOCERA CORP) 17 December 2009 See the abstract, figures 1-2 and claims 1-3.	1-28

☐ 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 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
22 MARCH 2013 (22.03.2013)	**25 MARCH 2013 (25.03.2013)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer JOEN, Han Cheol Telephone No. 82-42-481-8464

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2012/064944

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2005-285968 A	13.10.2005	JP 4578134 B2	10.11.2010
JP 2008-227093 A	25.09.2008	None	
JP 2009-292671 A	17.12.2009	CN 102066286 A	18.05.2011
		TW 200952010 A	16.12.2009
		US 2011-0085281 A1	14.04.2011
		US 8305732 B2	06.11.2012
		WO 2009-147893 A1	10.12.2009