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(54) Title: COMPOSITE GRAPHENE OXIDE FILM

Figure 1

(57) Abstract: A thermal management article includes a graphite sheet from between about 10 micron and 100 micron thick with an in-plane thermal conductivity at least 250 W/mK. The graphite sheet has a graphene oxide coating having a thickness from between 0.1 micron to about 30 micron.
COMPOSITE GRAPHENE OXIDE FILM

[001] Electronics designers are constantly pushing device architecture to thinner and more lightweight configurations. The desire for smaller devices having more complicated power requirements necessarily requires close attention to thermal management. For example, processors, integrated circuits and displays typically operate efficiently only under a certain range of threshold temperatures. Further, heat-generating components within a device can produce areas of higher temperature than surrounding areas. This can affect surrounding components as well as negatively affect the user experience. Of course, any thermal management element should not otherwise affect the performance of the electronic device. There is therefore a need in the art for a thin thermal management article having thermal conductivity and electrically insulated coating sufficient for use in electronic devices.

SUMMARY OF THE INVENTION

[002] According to one aspect, a thermal management article includes graphite sheet from between about 10 micron and 100 micron thick and having an in-plane thermal conductivity at least 250 W/mK and having opposed major surfaces. A graphene oxide coating is disposed on at least one of the opposed major surfaces with a thickness from between about 0.1 micron to about 30 micron.

[003] According to another aspect, a method of producing a thermal management article includes providing a graphite sheet having a thickness from between about 10 micron and about 100 micron and in-plane thermal conductivity of at least 250 W/mK and opposed major surfaces. A graphene oxide powder is dispersed in a solvent to form a graphene oxide suspension. The graphene oxide suspension is applied to the graphite sheet to form a graphene oxide coating less than 20 microns thick.
BRIEF DESCRIPTION OF THE DRAWINGS

[004] Figure 1 is a side view of a composite thermal management article.

DETAILED DESCRIPTION

[005] With reference now to Fig. 1, a thermal management article is shown and generally indicated by the numeral 10. Thermal management article is a composite article, including a graphite sheet or foil 12 and at least one coating layer 14. The coating layer 14 may be applied to a first major surface 16 of the graphite sheet 12. Optionally, as shown in Fig. 1, the coating layer 14 may be applied to both the first major surface 16 and to the opposed second major surface 18 of the flexible graphite layer 12. For purposes of the present disclosure, graphite sheet or graphite foil may be any graphite in the form of a sheet or foil that exhibits anisotropic thermal and/or electrical properties. As will be discussed herein below in greater detail, exemplary graphite sheet may include compressed exfoliated graphite, pyrolytic graphite and heat treated graphitizable polymers.

[006] Compressed exfoliated graphite may be produced by treating particles of graphite, such as natural graphite flake, with an intercalant of, e.g. a solution of sulfuric and nitric acid. Upon exposure to high temperature, the intercalant within the graphite decomposes and volatilizes, causing the particles of intercalated graphite to expand in dimension as much as about 80 or more times its original volume in the direction perpendicular to the crystalline planes of the graphite. The exfoliated graphite particles are vermiciform in appearance, and are therefore commonly referred to as worms. The worms may be compressed together into flexible sheets that, unlike the original graphite flakes, can be formed and cut into various shapes.
[007] Pyrolytic graphite commonly refers to the carbon materials produced through a gas-phase carbonization process. The gas-phase deposition of carbon occurs on a surface through the contact of hydrocarbons upon a substrate through the pyrolysis of hydrocarbons in the gas phase and deposition on the substrate surface. The large aromatic molecules produced by dehydrogenation and polymerization of hydrocarbons collide with the high-temperature substrate surface to form the deposit.

[008] Heat treated graphitizable polymers, can be made from a polymer material heated to at least 2000°C. According to this method, graphite films with high crystallinity can be created by the solid-state carbonization of graphitizable polymers, for example an aromatic polyimide film, followed by a high temperature heat treatment. The carbonization and heat treatment may take place as a two-step process, the first step at a substantially lower temperature than the second step. During the first step of carbonizing a the graphitizable film, which occurs by bringing the film to a temperature of at least about 600°C, up to about 1800°C, for a time sufficient to substantially carbonize the film. The graphitization process includes a higher temperature (i.e., at least 2000°C and up to about 3200°C) heat treatment with the temperature of the heat treatment resulting in alignment of the carbon atoms to nearly perfectly aligned carbon layers.

[009] The graphite sheet 12 advantageously has an in-plane thermal conductivity of greater than 250 W/mK, more advantageously greater than 400 W/mK, still more advantageously greater than 1000 W/mK, and still more advantageously greater than 1400 W/mK. In other embodiments, graphite sheet has an in-plane thermal conductivity of from between 250 W/mK and 2000 W/mK. In still further embodiments, the graphite sheet has an in-plane thermal conductivity of from between about 250 W/mK and about 600 W/mK. In other embodiments, the graphite sheet has an in-plane thermal conductivity of from between about 900 W/mK and about 1600 W/mK.
[010] Graphite sheet 12 advantageously has a thickness less than 100 microns, more
advantageously less than 50 microns and still more advantageously less than 20 microns. In
further embodiments, graphite sheet 12 has a thickness from between about 5 microns to
about 3 millimeters. In further embodiments, graphite sheet 12 has a thickness from between
about 10 microns and about 100 microns. In still further embodiments, the graphite sheet 12
has a thickness from between about 10 microns and about 50 microns. In certain
embodiments, the graphite sheet has a density of at least 1.0 grams/cc, still more
advantageously at least 1.2 grams/cc and yet more advantageously at least 1.4 grams/cc. In
further embodiments, the graphite sheet has a density of from between about 1.0 grams/cc
and about 2.2 grams/cc. In still further embodiments, the graphite sheet has a density of from
between about 1.4 grams/cc and about 2.0 grams/cc.

[011] Coating layer 14 is advantageously graphene oxide, which is a compound material
comprised of carbon, oxygen, and hydrogen. The material is commonly synthesized from
natural graphite, resulting in a brown-colored powder that generally retains the layer structure
of graphite but with a larger and more irregular spacing. The structure and properties of
graphite oxide depend on particular synthesis method and degree of oxidation. The material
commonly conserves the layer structure the precursor graphite, but the layers tend to be
generally buckled and the interlayer spacing is about 0.7 nanometers, which is approximately
two times larger than that of graphite.

[012] In one embodiment, coating layer 14 has a thickness from between about 0.1 microns
and about 30 microns. In further embodiments coating layer 14 has a thickness from between
about 1.0 microns and about 10 microns thick. In still further embodiments, the coating layer
14 is from between about 10 microns and about 20 microns thick. In still other embodiments,
coating layer 14 has a thickness from between about 0.1 microns and about 5.0 microns. In
further embodiments, the coating layer has a thickness advantageously less than 20 microns, more advantageously less than 10 microns and still more advantageously less than 5 microns. [013] In another embodiment, a chemical bonding agent may be used to bond together coating layer 14 and graphite sheet 12. Examples of suitable bonding agents might include, for example, a resin-hardener system or cement. Advantageously, however, coating layer 14 adheres to graphite sheet 12 in the absence of a bonding agent. In the absence of chemical bonding, the graphene oxide coating layer 14 is adhered to the graphite sheet by other mechanisms, such as dispersion forces (otherwise referred to as “van der Waals forces”) and/or electrostatic forces. The strength of these forces is dependent on the distance between graphene oxide and the graphite sheet, as well as their respective geometry. At the microscopic level, the graphene oxide coating layer 14 is comprised of generally flat crystallites with a relatively large surface area to thickness ratio. This structure provides a large area for dispersion and electrostatic forces to enable adhesion. Further, the smoothness (lack of microscopic roughness) of the graphene oxide coating layer 14 allows the distance between layer 14 and the graphite sheet 12 to be minimized, enabling a strong adhesion.

[014] The graphene oxide is an electrical insulator wherein the individual graphene oxide layers are advantageously aligned substantially with the plane of the major surface to which it is attached. Accordingly, in one embodiment, the coating layer 14 is anisotropic, wherein it exhibits different properties in the in-plane direction verses the thru-plane direction. In one embodiment, in-plane thermal conductivity may be from between about 2 W/mK to about 10 W/mK. In other embodiments, the in-plane thermal conductivity may be greater than about 2 W/mK.

[015] In one embodiment, in-plane electrical conductivity, using a multi-meter, of the coating layer 14 is from between about $1.0 \times 10^{-3}$ S/m to about $0.1 \times 10^{-3}$ S/m. In other embodiments, the in-plane electrical conductivity of the coating layer 14 is from between
about 0.8 x 10^{-3} S/m to about 0.3 x 10^{-3} S/m. In still further embodiments, the in-plane electrical conductivity of the coating layer 14 is advantageously less than about 1.5 x 10^{-3} S/m, still more advantageously less than about 1.0 x 10^{-3} S/m, and still more advantageously less than about 0.5 x 10^{-3} S/m. In one embodiment through-plane electrical conductivity, as measured using frequency sweeps, of coating layer 14 is from between about 1.0 x 10^{-4} S/m to about 1.0 x 10^{-5} S/m when measured at 106 Hz. In other embodiments, the through-plane electrical conductivity of coating layer 14 is from between about 2.0 x 10^{-5} S/m to about 8.0 x 10^{-5} S/m when measured at 106 Hz. In still further embodiments, the through-plane electrical conductivity of coating layer 14 is less than about 1.0 x 10^{-4} S/m when measured at 106 Hz.

In still further embodiments, the through-plane electrical conductivity of coating layer 14 is less than about 0.5 x 10^{-4} S/m when measured at 106 Hz. In further embodiments, through-plane electrical conductivity of coating layer 14 is from between about 10^{-7} S/m to about 10^{-11} S/m when measured at 10^{-3} Hz. In still further embodiments, the through-plane electrical conductivity of coating layer 14 is less than about 1.0 x 10^{-7} S/m and more advantageously less than about 1.0 x 10^{-10} S/m when measured at 10^{-1} Hz. The electrically insulating behavior results from a combination of the graphene oxide’s sp3 bonding structure and the presence of air in the interlayer spaces.

[016] The above thermal management article may be produced in accordance with any one or more of the following methods. In one embodiment, graphene oxide powder may be dispersed in water or another polar solvent in concentrations ranging from about 0.1 mg/ml to about 5 mg/ml. This powder may be dispersed in water or other polar solvents to generate a suspension containing single-layer graphene oxide sheets. Advantageously, dispersion of the graphene oxide sheets may be aided with sonication or any other suitable form of agitation. Graphene oxide in solution may then be assembled into a multi-layered film by any one or more of the following methods.
[017] In one embodiment, the graphene oxide suspension is filtered over a fine-pored membrane having pore sizes from between about 100 nm to about 500 nm in diameter. Advantageously, the filtering process may be aided with the use of a vacuum. The thus formed graphene oxide multi-layer film may then be removed from the filter medium and applied to one or both major surfaces of graphite sheet 12. As discussed above, application of the graphene oxide film may be performed with or without the use of an adhesive. In such a manner, the graphene oxide coating layer 14 is arranged in a flat, aligned film with only trace solvent remaining between the coating layer 14 and graphite sheet 12.

[018] In another embodiment, an electric field is applied the graphene oxide suspension (the individual graphene oxide sheets assume a negative charge when suspended in water). The single-layer graphene oxide sheets in the suspension move toward a conductive positively charged surface and deposit into a flat, aligned multi-layer film under the appropriate conditions. The graphene oxide film may then be transferred to the graphite sheet 12 (e.g., via a sacrificial layer). Alternately, because the graphite sheet 12 is electrically conductive, electrophoretic deposition is advantageously performed directly onto graphite sheet 12.

[019] In yet another embodiment, the graphene oxide suspension may be sprayed onto one or both major surfaces of graphite sheet 12 to form a multi-layer graphene oxide coating layer 14. Advantageously, the graphite sheet 12 may be heated to encourage evaporation of the solvent, leaving behind the graphene oxide film.

[020] In still another embodiment, the graphene oxide suspension may be coated onto a substrate in a roller application or printing (e.g. gravure type printing) or the like. According to this method, achieving the desired thickness may require multiple coating and drying/evaporation steps. Further, the substrate material may be heated to encourage evaporation of the solvent. The graphene oxide film may then be transferred to the graphite
sheet 12 (e.g., via a sacrificial layer). Alternately, the printing/rolling is advantageously performed directly onto graphite sheet 12.

[021] Although preferred embodiments of the disclosure have been described using specific terms, devices, and methods, such description is for illustrative purposes only. The words used are words of description rather than of limitation. It is to be understood that changes and variations may be made by those of ordinary skill in the art without departing from the spirit or the scope of the present disclosure, which is set forth in the following claims. In addition, it should be understood that aspects of the various embodiments may be interchanged both in-whole or in-part. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained therein.
CLAIMS

I claim:

1. A thermal management article comprising:
   a graphite sheet from between about 10 micron and 100 micron thick and having an in-plane thermal conductivity at least 250 W/mK and having opposed major surfaces; and a graphene oxide coating disposed on at least one of said opposed major surfaces having a thickness from between about 0.1 micron to about 30 micron.

2. The thermal management article according to claim 1 wherein said graphene oxide coating is secured to said major surface in the absence of a chemical adhesive.

3. The thermal management article according to claim 1 wherein said graphene oxide coating has an in-plane thermal conductivity greater than about 2 W/mK.

4. The thermal management article according to claim 1 wherein said graphene oxide coating through-plane electrical conductivity is less than about $1.0 \times 10^{-4}$ S/m when measured at $10^6$ Hz.

5. The thermal management article according to claim 1 wherein said graphite sheet comprises compressed exfoliated natural graphite, pyrolytic graphite or heat treated graphitizable polymer.

6. The thermal management article according to claim 1 wherein said graphene oxide coating thickness less than about 10 microns.

7. The thermal management article according to claim 1 wherein said graphene oxide coating thickness less than about 5 microns.

8. A method of producing a thermal management article comprising:
   providing a graphite sheet having a thickness from between about 10 micron and about 100 micron and in-plane thermal conductivity of at least 250 W/mK and opposed major surfaces;
dispersing a graphene oxide powder in a solvent to form a graphene oxide suspension;
applying said graphene oxide suspension to said graphite sheet to form a graphene oxide coating less than 20 microns thick.

9. The method according to claim 8 wherein said step of applying said graphene oxide suspension comprises applying an electric field to said graphene oxide suspension; positively charging at least one of said opposed major surfaces of said graphite sheet; and electrophoretically depositing a flat, aligned multi-layer graphene oxide film on said at least one of said opposed major surfaces.

10. The method according to claim 8 wherein said step of applying said graphene oxide suspension comprises spraying said graphene oxide suspension onto at least one of said opposed major surfaces of said graphite sheet; evaporating said solvent to form a multi-layer graphene oxide film.

11. The method according to claim 8 wherein said step of applying said graphene oxide suspension comprises filtering said graphene oxide suspension over a fine-pored membrane to form a flat, aligned graphene oxide film; removing said graphene oxide film from said filter medium; and applying said graphene oxide film to at least one of said opposed major surfaces of said graphite sheet.
Figure 1