Notice

DESCRIPTION CN106584976A

A highly conductive graphene/copper-based composite material and its preparation method

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一种高导电石墨烯/铜基层状复合材料及其制备方法

[0001]

Technical Field

技术领域

[0002]

This invention belongs to the field of highly conductive metal-based composite materials, specifically relating to a highly conductive graphene/copper-based matrix composite material and its preparation method.

本发明属于高导电金属基复合材料材料领域，具体的，涉及一种高导电石墨烯/铜基层状复合材料及其制备方法。

[0003]

Background Technology

背景技术

[0004]

In recent years, with the development of electronics and conduction technology, fields such as electrode materials and signal fidelity have put forward higher requirements for the conduction performance of conductors than pure silver (≥62.9×10⁶S/m, 108% IACS) (IACS is the International Standard for Annealed Copper).

近年来，随着电子、传导技术的发展，电极材料、信号保真等领域对导体的传导性能提出了高于纯银(≥62.9×10⁶S/m，108%IACS)的要求(IACS为国际退火铜标准)。

A literature search of existing technologies revealed that literature (1) "Copper Better than Silver: Electrical Resistivity of the Grain-Free Single-Crystal Copper Wire" (Crystal Growth & Design, Vol. 10, No. 6, 2010, 2780-2784) prepared copper single crystals by rotational pulling and then obtained single-crystal copper wires using electrical discharge wire cutting technology. The conductivity (65.7 × 10 NER^{2} S/m, 113% IACS) was higher than that of pure silver. Literature (2) "Fabrication of the best conductor from single-crystal copper and the contribution of grain boundaries to the Debye" Based on the best conductor made from single-crystal copper and the contribution of grain boundaries to the Debye temperature (CrystEngComm, 2012, 14, 1463–1467), hot isostatic pressing technology was introduced to further reduce the point defect density inside the material, making the conductivity of single-crystal copper wire (67.9 × 10^{3} S/m, 117% IACS) higher than that of single-crystal silver (67.1 × 10^{4} S/m, 115% IACS), which can meet the current development requirements of electronic and conduction technologies for high conductivity.

对现有技术的文献检索发现，文献(1)“Copper Better than Silver:Electrical Resistivityof the Grain-Free Single-Crystal Copper Wire”(铜优于银：单晶铜线的电阻率)(Crystal Growth&Design, Vol.10,No.6,2010,2780-2784)通过旋转提拉法制备铜单晶，然后利用电火花线切割技术获得单晶铜导线，电导率(65.7×10⁶S/m，113%IACS)高于纯银，文献(2)“Fabrication of the best conductor from single-crystal copper and thecontribution of grain boundaries to the Debye temperature”(由单晶铜制造最好的导体及晶界对德拜温度的贡献)(CrystEngComm, 2012,14,1463–1467)在此基础上引入热等静压技术，进一步降低材料内部的点缺陷密度，使单晶铜导线的电导率(67.9×10⁶S/m，117%IACS)高于单晶银(67.1×10⁶S/m，115%IACS)，可以满足当前电子、传导技术对于高导电性能的发展要求。

However, the single crystal preparation technology using the spin-pulling method has extremely harsh production conditions, and the yield of single crystals is low, resulting in extremely high production costs.

但是通过旋转提拉法制备单晶技术对生产条件极为苛刻，而且单晶的成品率较低，生产成本极高。

[0005]

Since its discovery in 2004, graphene has received great attention due to its excellent conductivity.

石墨烯自2004年发现以来，因优异的传导性能受到了极大的关注。

As a reinforcing agent, graphene's extremely high electrical conductivity and electron mobility make it possible for copper-based composite materials to achieve or even exceed the electrical conductivity of pure silver.

作为增强体，石墨烯所具有的极高电导率和电子迁移率为铜基复合材料的电导率达到甚至超过纯银提供了可能。

Reference (3) "Enhanced Mechanical Properties of Graphene/Copper Nanocomposites Using a Molecular-Level Mixing Process" first utilizes the molecular-level mixing of oxidized graphene nanosheets in aqueous solution with copper ions through electrostatic adsorption to obtain graphene oxide/copper ions (GO/Cu²⁺), and then obtains reduced graphene oxide/copper (rGO/Cu) nanocomposites through oxidation, reduction and discharge plasma sintering. However, the electrical conductivity of this nanocomposite material is only 50% IACS. Analysis revealed that this was due to the high defect density of graphene oxide, which severely reduced the original high conductivity of graphene, thus preventing the improvement of the conductivity of the composite material. Reference (4) "Fabrication of in-situ grown graphene reinforced Cu matrix composites" first disperses a solid carbon source on the surface of spherical micron copper powder, and then uses CVD technology to convert the solid carbon source into graphene grown along the surface of the spherical copper powder to obtain graphene-copper composite powder. Finally, the densification of the CVD graphene-copper composite material is completed by hot pressing sintering. The CVD technology used in this composite material introduces graphene with a relatively low defect density, which significantly improves the electrical conductivity of the composite material (99.1% IACS) compared to the electrical conductivity of the rGO/Cu composite material in reference (3) (50% IACS), but still does not exceed the level of the international annealed soft copper standard. Analysis revealed that the main reasons were: (1) the copper substrate is polycrystalline, and the large number of grain boundaries increases the scattering of charge carriers, thus increasing the resistance; (2) due to the two-dimensional atomic layer structure and anisotropic properties of graphene, the powder sintering technology causes graphene to be dispersed in the composite material without orientation, which is not conducive to the intrinsic properties of graphene's two-dimensional high conductivity and high electron mobility, resulting in the conductivity of CVD graphene-copper composite material being lower than the international standard for annealed copper.

文献(3)“Enhanced Mechanical Properties of Graphene/CopperNanocomposites Using a Molecular-Level Mixing Process”(使用分子级混合工艺机械性能提高的石墨烯/铜纳米复合材料)首先利用水溶液中氧化状态的石墨烯纳米片与铜离子通过静电剂吸附进行分子级混合，获得氧化石墨烯/铜离子(GO/Cu²⁺)，之后通过氧化、还原和放电等离子体烧结获得还原氧化石墨烯/铜(rGO/Cu)纳米复合材料。 然而该纳米复合材料的电导率只有50%IACS。 通过分析发现这是由于氧化石墨烯具有高的缺陷密度，严重降低了石墨烯原有的高电导率，致使复合材料电导率并不能得到提高。 文献(4)“Fabrication of in-situ grown graphene reinforced Cu matrix composites”(制备原位生长石墨烯增强铜基复合材料)首先将固体碳源分散在球形微米铜粉表面，之后利用CVD技术将固体碳源转化为沿球形铜粉表面生长的石墨烯，获得石墨烯-铜复合粉末再通过热压烧结完成CVD石墨烯-铜复合材料的致密化。 该复合材料中使用的CVD技术引入了缺陷密度相对较低的石墨烯，使得复

合材料电导率(99.1%IACS)较文献(3)中rGO/Cu复合材料的电导率(50%IACS)有显著提高，但仍没有超过国际退火软铜标准的水平。 通过分析发现，主要是(1)铜基底为多晶态，大量的晶界界面增加了载流子的散射，从而使得电阻增加；(2)由于石墨烯具有二维原子层结构特征和性质各项异性，而该粉末烧结技术导致石墨烯在复合材料内部呈无取向分散，不利于发挥石墨烯二维高导、高电子迁移率的本征特性，导致CVD石墨烯-铜复合材料的电导率低于国际退火铜标准。

[0006]

Summary of the Invention

发明内容

[0007]

To address the shortcomings of existing technologies, the purpose of this invention is to provide a highly conductive graphene/copper-based composite material and its preparation method. The electrical conductivity of the prepared material exceeds the international standard for annealed copper and is even higher than that of pure silver.

针对现有技术的不足，本发明的目的是提供一种高导电石墨烯/铜基层状复合材料及其制备方法，制备的材料电导率突破国际退火铜标准，甚至高于纯银。

[0008]

Based on long-term research, this invention finds that to prepare graphene/copper composite materials with conductivity exceeding international annealed copper standards and even higher than pure silver, the following is required: (1) the substrate has a microstructure of single-crystal copper or close to single-crystal copper; (2) high-conductivity CVD graphene is introduced; and (3) a microstructure is constructed in which graphene is spread along the plane and oriented in the substrate, which is conducive to giving full play to the intrinsic properties of graphene's two-dimensional high conductivity and high electron mobility.

本发明根据长期的研究发现，要制备电导率突破国际退火铜标准甚至高于纯银的石墨烯/铜复合材料需要：(1)基底具有单晶铜或接近单晶铜的微结构组织；(2)引入高电导的CVD石墨烯，以及(3)构建石墨烯在基底内呈沿平面铺展、取向分布，有利于发挥石墨烯二维高导、高电子迁移率的本征性能的微观构型。

Based on the above research findings, this invention provides the following highly conductive graphene/copper-based matrix composite material and its preparation method.

基于上述研究发现，本发明提供以下高导电石墨烯/铜基层状复合材料及其制备方法。

[0009]

According to a first aspect of the present invention, a highly conductive graphene/copper substrate-based composite material is provided, wherein the composite material is composed of alternating composites of CVD graphene and plate-shaped copper substrate to form a layered structure, wherein the substrate in the thickness direction of the layer is monocrystalline and exhibits a highly oriented (111) crystal plane, and the substrate in the horizontal direction of the layer is monocrystalline or polycrystalline.

根据本发明的第一方面，提供一种高导电石墨烯/铜基层状复合材料，所述复合材料由CVD石墨烯与板状铜基底交替复合构成层状结构，层内厚度方向基底为单晶态，且表现为高度取向(111)晶面，层内水平方向基底为单晶或多晶态。

[0010]

Preferably, graphene is uniformly deposited on the upper and lower surfaces of the plate-shaped copper substrate, and the copper substrate is induced to preferentially align along (111) to obtain a sandwich-shaped graphene-coated copper substrate.

优选地，所述板状铜基底上下表面均匀沉积石墨烯，并诱导铜基底沿(111)择优取向，得到三明治状的石墨烯包覆铜基底。

[0011]

Preferably, in the sandwich-shaped graphene-coated copper substrate, the copper substrate is a foil or plate, the layer thickness of the copper substrate is 1μm to 500μm, and the purity of the copper substrate is ≥99%.

优选地，所述的三明治状的石墨烯包覆铜基底中，铜基底为箔材或板材，铜基底的层厚为1μm～500μm，铜基底的纯度≥99%。

[0012]

Preferably, in the sandwich-shaped graphene-coated copper substrate, the number of graphene layers is 1 to 10.

优选地，所述的三明治状的石墨烯包覆铜基底中，石墨烯的层数为1～10层。

[0013]

Preferably, the number of copper foil substrates is two or more.

优选地，所述铜箔基底的片数为2片以上。

[0014]

According to a second aspect of the present invention, a method for preparing a highly conductive graphene/copper-based matrix composite material is provided, comprising:

根据本发明的第二方面，提供一种高导电石墨烯/铜基层状复合材料的制备方法，包括：

[0015]

First, graphene was uniformly deposited on the upper and lower surfaces of a plate-shaped copper substrate using chemical vapor deposition (CVD) technology, and the copper substrate was induced to preferentially align along (111) to obtain a sandwich-shaped graphene-coated copper foil.

首先利用化学气相沉积(CVD)技术，在板状铜基底上下表面均匀沉积石墨烯，并诱导铜基底沿(111)择优取向，得到三明治状的石墨烯包覆铜箔；

[0016]

Multiple graphene sheets are then coated onto a copper substrate and densified by hot pressing and sintering to obtain a highly conductive graphene/copper substrate composite material.

再将多片石墨烯包覆铜基底经热压烧结致密化，得到高导电石墨烯/铜基层状复合材料。

[0017]

Preferably, in the graphene-coated copper substrate, the copper substrate is highly crystalline, highly oriented along the (111) crystal plane, with a thickness of 1μm to 500μm and a purity of ≥99%.

优选地，所述的石墨烯包覆铜基底中，铜基底为高度结晶、沿(111)晶面高度取向，厚度1μm～500μm，纯度≥99%。

[0018]

Preferably, in the graphene-coated copper substrate, the copper substrate grains are monocrystalline in the thickness direction of the copper foil and monocrystalline or polycrystalline in the horizontal in-plane direction.

优选地，所述的石墨烯包覆铜基底中，铜基底晶粒在铜箔厚度方向为单晶态，在面内水平方向为单晶或多晶态。

[0019]

Preferably, in the highly conductive graphene/copper substrate composite material, the number of sandwich-shaped graphene sheets covering the copper substrate is two or more.

优选地，所述的高导电石墨烯/铜基层状复合材料中，所使用的三明治状的石墨烯包覆铜基底的片数为2片或以上。

[0020]

Preferably, the carbon source required for graphene growth in the preparation of the sandwich-shaped graphene-coated copper substrate includes one of gaseous and solid states, and the number of graphene layers grown is 1 to 10.

优选地，所述三明治状的石墨烯包覆铜基底制备中石墨烯生长所需的碳源种类包括气态和固态中的一种，所生长石墨烯的层数为1～10层。

[0021]

Preferably, the hot pressing densification includes one of hot pressing sintering under vacuum or gas protection, electric discharge plasma sintering, and microwave sintering.

优选地，所述的热压烧结致密化包括真空或者气体保护下热压烧结、放电等离子体烧结、微波烧结中的一种。

[0022]

In the preparation method of the present invention, graphene is grown on the surface of a copper substrate by chemical vapor deposition (CVD) to form a sandwich-shaped graphene coating on the copper substrate. Since the honeycomb lattice of graphene and the (111) crystal plane lattice of copper have a good matching relationship, the reduction of interface energy is the driving force. After graphene deposition and growth, the grains on the surface of the copper substrate are significantly increased, and the crystal planes undergo orientation transformation. The copper substrate tends to be preferentially oriented towards the (111) crystal plane.

在本发明制备方法中，通过化学气相沉积(CVD)技术使石墨烯生长于铜基底表面形成三明治状的石墨烯包覆铜基底，由于石墨烯蜂巢晶格与铜(111)晶面晶格具有良好的匹配关系，以界面能降低为驱动力，在经过石墨烯沉积生长之后，铜基底表面晶粒显著增大，并且晶面发生了取向转变，铜基底趋向于(111)晶面择优取向分布。

In the process of preparing highly conductive graphene/copper substrate composite material, hot pressing sintering densification causes further grain orientation transformation of the sandwich-shaped graphene-coated copper substrate, further improving its crystal integrity and preferred orientation, and enabling the copper substrate to grow into a single crystal state in the thickness direction.

在制备高导电石墨烯/铜基层状复合材料的过程中，热压烧结致密化使三明治状的石墨烯包覆铜基底发生进一步晶粒取向转变，其结晶完整度和择优取向进一步提升，使得铜基底厚度方向晶粒生长为单晶态。

During the hot pressing densification process, the simultaneous application of high temperature and high pressure significantly reduces the internal defect density of the material. Due to the transformation of grain orientation promoted by graphene, the (111) crystal plane exhibits an arrangement similar to a single crystal long-range order inside the material, effectively reducing the scattering effect of defects on electron transport.

在热压烧致密化结过程中，高温高压的同时施加使材料内部缺陷密度大幅降低，由于石墨烯促进的晶粒取向的转变，(111)晶面在材料内部呈现出一种近似于单晶长程有序的排列方式，有效降低缺陷对电子传输产生的散射作用。

Hot pressing and sintering densification increased the bonding energy of the graphene-copper interface inside the sandwich-shaped graphene-coated copper substrate by 200 times.

The graphene-copper interface with high bonding strength is conducive to the transport of charge carriers, which further improves the conductivity of the sample, reaching a level higher than that of pure silver.

热压烧结致密化使三明治状的石墨烯包覆铜基底内部石墨烯-铜界面的结合能得到了200倍的提高，具有高结合强度的石墨烯-铜界面有利于载流子的传输，使样品的导电性能得到进一步提高，达到了高于纯银的水平。

Currently widely used graphene derivatives, such as (reduced) graphene oxide, have high defect density, which increases electron scattering and severely reduces the intrinsic high conductivity of graphene. In contrast, graphene grown by CVD technology has high structural integrity and exhibits the intrinsic high conductivity of graphene.

目前广泛使用的石墨烯衍生物，如(还原)氧化石墨烯，具有高的缺陷密度，加大了对电子的散射，严重降低了石墨烯本征的高电导率，而CVD技术生长石墨烯结构完整性高，表现出石墨烯高电导的本征性能。

Meanwhile, even with the introduction of CVD graphene, as reported in the background literature (3, 4), when graphene is randomly and unorientedly distributed inside the substrate, the probability of carrier migration along different directions increases, and the utilization rate of the intrinsic high conductivity of graphene in two dimensions decreases, thus increasing scattering and resistance. However, the layered composite material constructed here allows graphene to spread in a planar and oriented manner inside the substrate, which is conducive to the high-speed migration of carriers, thereby obtaining high conductivity.

与此同时，即使引入CVD石墨烯，但如背景技术中文献(3，4)所报道，当石墨烯在基底内部呈杂乱无序、无取向分布时，载流子沿不同方向迁移几率增加，相应的石墨烯二维高电导本征性能利用率降低，从而散射和电阻也增加，而此处所构建的层状复合材料使得石墨烯在基底内呈平面铺展、取向分布，有利于载流子的高速迁移，从而得到高的电导率。

[0023]

Compared with the prior art, the present invention has the following beneficial effects:

与现有技术相比，本发明具有以下有益效果：

[0024]

(1) The good layered reinforcement/substrate configuration design makes the conduction orientation of charge carriers in graphene uniform, and the utilization efficiency of graphene as a charge carrier transport channel is high, giving full play to the intrinsic characteristics of

graphene's two-dimensional high conductivity; at the same time, the introduction of CVD graphene-copper interface which is conducive to charge carrier transport overcomes the lack of resistance reduction of composite heterostructure interfaces in other composite materials.

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(1)良好的层状增强体/基底构型设计，使得载流子在石墨烯中的传导取向统一，石墨烯作为载流子传输通道的利用效率高，充分发挥了石墨烯二维高导的本征特性；同时引入利于载流子传输的CVD石墨烯-铜界面，克服了其它复合材料中复合异质界面降低电阻的不足。

[0025]

(2) The electrical conductivity of copper-based composite materials is higher than that of pure silver.

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(2)铜基复合材料的导电性能高于纯银。

The growth of graphene causes a change in the grain orientation of the copper substrate, and the hot-pressing sintering densification process makes the material exhibit a near-single-crystal long-range ordered arrangement, which greatly reduces the internal defect density of the material.

石墨烯的生长促使铜基底晶粒取向发生转变，热压烧结致密化过程使材料内部呈现出一种近似于单晶长程有序的排列方式，材料内部缺陷密度大幅降低。

[0026]

(3) Easy to produce.

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(3)易于生产。

Chemical vapor deposition (CVD) technology using sandwich-shaped graphene-coated copper substrates and hot-pressing densification technology using highly conductive graphene/copper-based matrix composites are suitable for large-scale production.

三明治状的石墨烯包覆铜基底制备的化学气相沉积技术和高导电石墨烯/铜基层状复合材料制备的热压烧结致密化技术适于大规模生产。

[0027]

Attached Figure Description

附图说明

[0028]

Other features, objects, and advantages of the present invention will become more apparent from the following detailed description of non-limiting embodiments with reference to the accompanying drawings:

通过阅读参照以下附图对非限制性实施例所作的详细描述，本发明的其它特征、目的和优点将会变得更明显：

[0029]

Figure 1. Schematic diagram of the structure of the highly conductive graphene/copper base matrix composite material;

图1高导电石墨烯/铜基层状复合材料的结构示意图；

[0030]

Figure 2. Distribution and morphology of graphene on the surface of a copper substrate in a sandwich-shaped graphene-coated copper substrate;

图2三明治状的石墨烯包覆铜基底中铜基底表面石墨烯分布和形貌；

[0031]

Figure 3 Electron backscatter diffraction (EBSD) on a copper substrate, showing the crystal orientation of the copper substrate after CVD growth of graphene.

图3铜基底电子背散射衍射(EBSD)，CVD生长石墨烯后铜基底晶面取向；

[0032]

Figure 4 shows the metallographic cross-section of the highly conductive graphene/copper-based layered composite material. The layered structure is monocrystalline in the thickness direction and monocrystalline or polycrystalline in the intralayer direction.

图4高导电石墨烯/铜基层状复合材料金相截面，层状结构厚度方向为单晶态，层内方向为单晶或多晶态；

[0033]

Figure 5 shows that the graphene/copper interface serves as a rapid channel for carrier transport within the highly conductive graphene/copper base composite material.

图5石墨烯/铜界面成为高导电石墨烯/铜基层状复合材料内部载流子传输的快速通道。

[0034]

Detailed Implementation

具体实施方式

[0035]

The present invention will now be described in detail with reference to specific embodiments.

下面结合具体实施例对本发明进行详细说明。

The following examples will help those skilled in the art to further understand the present invention, but do not limit the invention in any way.

以下实施例将有助于本领域的技术人员进一步理解本发明，但不以任何形式限制本发明。

It should be noted that those skilled in the art can make several modifications and improvements without departing from the concept of this invention.

应当指出的是，对本领域的普通技术人员来说，在不脱离本发明构思的前提下，还可以做出若干变形和改进。

These all fall within the scope of protection of this invention.

这些都属于本发明的保护范围。

[0036]

In the following examples, the copper substrate with a sandwich-like graphene coating has a purity of ⩾99% and a graphene coverage of ⩾95%.

以下实施例中三明治状的石墨烯包覆铜基底的铜基底纯度⩾99%，石墨烯覆盖率⩾95%。

In the preparation of highly conductive graphene/copper-based matrix composites, the hot-pressing temperature for densification by hot-pressing sintering is 700–1000°C, the pressure is 10–200MPa, and the time is 10–90 minutes.

制备高导电石墨烯/铜基层状复合材料过程中，热压烧结致密化的热压温度为700～1000°C，压力为10～200MPa，时间10～90分钟。

The sample was prepared in sheet form with a planar size of 10mm × 5mm for conductivity measurement, and the process was carried out in accordance with the process flow shown in Figure 1.

制备样品为片状，平面尺寸为10mm×5mm，用于电导率测量，并遵照图1所示的工艺流程实施。

[0037]

The room temperature resistivity (ρ) of the material was measured using an EPS-300 probe station from Ecopia, South Korea, and calculated using formula , where C is the probe correction factor, I is the input current, V is the output voltage, is the sample thickness correction factor, is the sample shape and measurement position correction factor, W is the sample thickness, d is the sample width, and S is the probe spacing.

材料的室温电阻率(ρ)采用韩国Ecopia公司EPS-300探针台测量，由公式 计算得出，其中C为探针修正系数，I为输入电流，V为输出电压， 为样品厚度修正系数， <img file="

BDA0001167297530000053.TIF" he="95" img-content="drawing" img-format="tif" inline="no" orientation="portrait" wi="121"/> 为样品形状与测量位置修正系数，W为样品厚度，d为样品宽度，S为探针间距。

[0038]

Example 1

实施例1

[0039]

First, a single layer of graphene with a coverage of ⩾95% was grown on a 500μm thick copper substrate using chemical vapor deposition, with methane gas as the carbon source, to obtain a sandwich-shaped graphene-coated copper substrate with a grain size ⩾300μm in the copper substrate surface; then, two graphene-coated copper substrates were vacuum hot-pressed and sintered to obtain a highly conductive graphene/copper substrate composite material.

首先，将厚度为单层，覆盖率⩾95%的石墨烯利用化学气相沉积生长于500μm厚铜基底表面，碳源为甲烷气体，得到三明治状的石墨烯包覆铜基底，铜基底面内晶粒尺寸⩾300μm；再将2片石墨烯包覆铜基底进行真空热压烧结得到高导电石墨烯/铜基层状复合材料。

The electrical conductivity of the obtained layered composite material is (66.2×10 S/m, 114% IACS), which is higher than that of pure silver and meets the requirements for use.

获得的层状复合材料的电导率为(66.2×10⁶S/m，114%IACS)，高于纯银，满足使用要求。

[0040]

Example 2

实施例2

[0041]

First, a single layer of graphene with a coverage of ⩾95% was grown on the surface of a 100μm thick copper substrate using chemical vapor deposition, with acetylene gas as the carbon source, to obtain a sandwich-shaped graphene-coated copper substrate with an in-plane grain size of ⩾300μm. Then, five graphene-coated copper substrates were hot-pressed and sintered under an argon atmosphere to obtain a highly conductive graphene/copper-based composite material.

首先，将厚度为单层，覆盖率≥95%的石墨烯利用化学气相沉积生长于100μm厚铜基底表面，碳源为乙炔气体，得到三明治状的石墨烯包覆铜基底，铜基底面内晶粒尺寸≥300μm；再将5片石墨烯包覆铜基底在氩气气氛保护下进行热压烧结得到高导电石墨烯/铜基层状复合材料。

The electrical conductivity of the obtained layered composite material is (67.2 × 10^{1} NER^{1} S /m, 116% IACS), which is higher than that of pure silver and meets the requirements for use.

获得的层状复合材料的电导率为(67.2×10⁶S/m，116%IACS)，高于纯银，满足使用要求。

[0042]

Example 3

实施例3

[0043]

First, a single layer of graphene with a coverage of ≥95% was grown on a 40μm thick copper substrate using chemical vapor deposition with methane gas as the carbon source, resulting in a sandwich-shaped graphene-coated copper substrate with a grain size ≥300μm within the copper substrate surface. Then, 10 graphene-coated substrates were subjected to discharge plasma sintering to obtain a highly conductive graphene/copper substrate composite material.

首先，将厚度为单层，覆盖率≥95%的石墨烯利用化学气相沉积生长于40μm厚铜基底表面，碳源为甲烷气体，得到三明治状的石墨烯包覆铜基底，铜基底面内晶粒尺寸≥300μm；再将10片石墨烯包覆基底进行放电等离子体烧结得到高导电石墨烯/铜基层状复合材料。

The electrical conductivity of the obtained layered composite material is (66.9×10⁶S/m, 115%IACS), which is higher than that of pure silver and meets the requirements for use.

获得的层状复合材料的电导率为(66.9×10⁶S/m，115%IACS)，高于纯银，满足使用要求。

[0044]

Example 4

实施例4

[0045]

First, a single layer of graphene with a coverage of ≥95% was grown on a 3μm thick copper substrate using chemical vapor deposition with methane gas as the carbon source, resulting in a sandwich-shaped graphene-coated copper substrate with an in-plane grain size of ≥300μm. Then, 50 graphene-coated copper substrates were hot-pressed and sintered under an argon atmosphere to obtain a highly conductive graphene/copper substrate composite material.

首先，将厚度为单层，覆盖率≥95%的石墨烯利用化学气相沉积生长于3μm厚铜基底表面，碳源为甲烷气体，得到三明治状的石墨烯包覆铜基底，铜基底面内晶粒尺寸≥300μm；再将50片石墨烯包覆铜基底在氩气气氛保护下进行热压烧结得到高导电石墨烯/铜基层状复合材料。

The electrical conductivity of the obtained layered composite material is (67.8 × 10^{12} S/m, 117% IACS), which is higher than that of pure silver and meets the requirements for use.

获得的层状复合材料的电导率为(67.8×10⁶S/m，117%IACS)，高于纯银，满足使用要求。

[0046]

Example 5

实施例5

[0047]

First, graphene with a thickness of 2-3 layers and a coverage of ⩾95% is grown on the surface of a 30μm thick copper substrate by chemical vapor deposition, with PMMA solid as the carbon source, to obtain a sandwich-shaped graphene-coated copper substrate with a grain size of ⩾300μm in the copper substrate surface; then, 6 graphene-coated copper substrates are microwave sintered to obtain a highly conductive graphene/copper substrate composite material.

首先，将厚度为2～3层，覆盖率⩾95%的石墨烯利用化学气相沉积生长于30μm厚铜基底表面，碳源为PMMA固体，得到三明治状的石墨烯包覆铜基底，铜基底面内晶粒尺寸⩾300μm；再将6片石墨烯包覆铜基底进行微波烧结得到高导电石墨烯/铜基层状复合材料。

The electrical conductivity of the obtained layered composite material is (67.0×10⁶S/m, 116%IACS), which is higher than that of pure silver and meets the requirements for use.

获得的层状复合材料的电导率为(67.0×10⁶S/m，116%IACS)，高于纯银，满足使用要求。

[0048]

Example 6

实施例6

[0049]

First, graphene with a thickness of 6 to 10 layers and a coverage of ⩾95% is grown on the surface of a 100 μm thick copper substrate using chemical vapor deposition. The carbon source is solid PMMA, resulting in a sandwich-shaped graphene-coated copper substrate with an in-plane grain size of ⩾300 μm. Then, four graphene-coated copper substrates are vacuum hot-pressed and sintered to obtain a highly conductive graphene/copper-based composite material.

首先，将厚度为6～10层，覆盖率⩾95%的石墨烯利用化学气相沉积生长于100μm厚铜基底表面，碳源为PMMA固体，得到三明治状的石墨烯包覆铜基底，铜基底面内晶粒尺寸⩾300μm；再将4片石墨烯包覆铜基底进行真空热压烧结得到高导电石墨烯/铜基层状复合材料。

The obtained layered composite material has an electrical conductivity of (66.4 × 10^{14} S/m, 114% IACS), which is higher than that of pure silver and meets the requirements for use.

获得的层状复合材料的电导率为(66.4×10⁶S/m，114%IACS)，高于纯银，满足使用要求。

[0050]

Comparative Example 1

比较实施例1

[0051]

First, a single layer of graphene with a coverage of ≥95% was grown on the surface of a 30μm thick copper substrate using chemical vapor deposition with methane gas as the carbon source, resulting in a sandwich-shaped graphene-coated copper substrate with an in-plane grain size of ≥300μm. The graphene on the surface of the graphene-coated copper substrate was then removed to obtain the copper substrate. Next, three sandwich-shaped graphene-coated copper substrates and three copper substrates were alternately stacked and sintered under argon atmosphere to obtain a highly conductive graphene/copper substrate composite material.

首先，将厚度为单层，覆盖率≥95%的石墨烯利用化学气相沉积生长于30μm厚铜基底表面，碳源为甲烷气体，得到三明治状的石墨烯包覆铜基底，铜基底面内晶粒尺寸≥300μm；将石墨烯包覆铜基

底表面石墨烯去除得到铜基底；再将3片三明治状的石墨烯包覆铜基底与3片铜基底交替堆叠排列，在氩气气氛保护下进行热压烧结得到高导电石墨烯/铜基层状复合材料。

The electrical conductivity of the layered composite material was obtained as (65.6×10^{1} S/m, 113% IACS), which is higher than that of pure silver and meets the application requirements.

获得层状复合材料电导率为(65.6×10⁶S/m，113%IACS)，高于纯银，满足使用要求。

[0052]

Comparative Example 2

比较实施例2

[0053]

First, a 30μm thick copper substrate was annealed at the same temperature as graphene chemical vapor deposition growth without the introduction of a carbon source to obtain an annealed copper substrate with an in-plane grain size of ≤150μm. Then, monolayer graphene was transferred to the upper and lower surfaces of the annealed copper substrate. Six annealed copper substrates with transferred monolayer graphene were hot-pressed and sintered under argon atmosphere protection to obtain a layered composite material.

首先，将30μm厚铜基底在石墨烯化学气相沉积生长相同的温度环境下进行退火处理，无碳源引入，得到退火铜基底，铜基底面内晶粒尺寸≤150μm；将单层石墨烯转移到退火铜基底上下表面；将6片转移有单层石墨烯的退火铜基底在氩气气氛保护下进行热压烧结得到层状复合材料。

The electrical conductivity of the composite material was (54.2 × 10^{1} S/m, 93% IACS), which is lower than that of pure copper and does not meet the requirements for use.

获得复合材料电导率为(54.2×10⁶S/m，93%IACS)，低于纯铜，不满足使用要求。

[0054]

Comparative Example 3

比较实施例3

[0055]

First, a 30μm thick copper substrate was annealed at the same temperature as graphene chemical vapor deposition growth without the introduction of a carbon source to obtain an annealed copper substrate with an in-plane grain size of ≤150μm. Six annealed copper substrates were then hot-pressed and sintered under an argon atmosphere to obtain a bulk copper material.

首先，将30μm厚铜基底在石墨烯化学气相沉积生长相同的温度环境下进行退火处理，无碳源引入，得到退火铜基底，铜基底面内晶粒尺寸≤150μm；将6片退火铜基底在氩气气氛保护下进行热压烧结得到铜块体材料。

The electrical conductivity of the obtained bulk copper material is (55.6×10⁶S/m, 96% IACS), which is lower than that of pure copper and does not meet the requirements for use.

获得铜块体材料电导率为(55.6×10⁶S/m，96%IACS)，低于纯铜，不满足使用要求。

[0056]

Table 1 shows the process parameters and final material properties for each embodiment, with the electrical conductivity given as the result of room temperature testing.

表1给出的是各实施例中的工艺参数和最终材料性能，给出的电导率为室温测试结果。

[0057]

Table 1. Process parameters and final material properties for each embodiment.

表1各实施例中的工艺参数和最终材料性能

[0060]

This invention prepares a sandwich-shaped graphene-coated copper substrate by growing graphene on the surface of a copper substrate through chemical vapor deposition. The graphene growth process promotes significant growth of the copper substrate grains and changes the orientation of the crystal planes. The crystal planes on the surface of the copper substrate tend to be distributed with (111) crystal planes, and the grains grow into a single crystal state in the thickness direction of the copper substrate.

本发明在铜基底表面通过化学气相沉积生长石墨烯制备三明治状的石墨烯包覆铜基底，石墨烯生长过程促进铜基底晶粒显著长大，并且晶面发生了取向转变，铜基底表面晶面趋向于(111)晶面分布，同时在铜基底的厚度方向晶粒生长为单晶状态。

During the sintering densification process of preparing highly conductive graphene/copper base composite material, the simultaneous application of high temperature and high pressure significantly reduces the internal defect density of the material. Due to the transformation of grain orientation promoted by graphene, the (111) crystal plane exhibits an arrangement similar to a single crystal long-range order inside the material, effectively reducing the scattering effect of defects on electron transport.

在制备高导电石墨烯/铜基层状复合材料的烧结致密化过程中，高温高压的同时施加使材料内部缺陷密度大幅降低，由于石墨烯促进的晶粒取向的转变，(111)晶面在材料内部呈现出一种近似于单晶长程有序的排列方式，有效降低缺陷对电子传输产生的散射作用。

Hot pressing and sintering densification significantly improved the bonding energy of the graphene-copper interface inside the sandwich-shaped graphene-coated copper substrate. The copper-CVD graphene interface leveraged the intrinsic two-dimensional high conductivity of graphene to become a fast channel for charge carrier transport, further improving the conductivity of the sample to the level of pure silver.

热压烧结致密化使三明治状的石墨烯包覆铜基底内部石墨烯-铜界面的结合能得到了显著的提高，铜-CVD石墨烯界面发挥了石墨烯二维高导的本征特性成为载流子传输的快速通道，使样品的导电性能得到进一步提高，达到了纯银的水平。

The highly conductive graphene/copper-based composite material prepared by this invention has high conductivity, exceeding that of pure silver, and is easy to produce, making it suitable for use as an interconnect material in various types of chips.

本发明所制得的高导电石墨烯/铜基层状复合材料电导率高，超过纯银的传导水平，且易于生产，可用作各类的芯片中的互连材料。

[0061]

The above are some preferred embodiments of the present invention. It should be understood that the present invention has other embodiments, such as changing the preparation of the sandwich-shaped graphene-coated copper substrate, the number of graphene layers, the number of copper substrate sheets, and the values of the densification hot pressing sintering parameters in the above embodiments. This is easy to implement for those skilled in the art.

以上为本发明的部分优选实施例，应当理解的是，本发明还有其他的实施方式，比如改变上述实施例中的三明治状的石墨烯包覆铜基底制备、石墨烯层数、铜基底片数以及致密化热压烧结参数取值，这对本领域的技术人员来说，是很容易实现的。

[0062]

Although the present invention has been described in detail through the above preferred embodiments, it should be understood that the above description should not be considered as a limitation of the present invention.

尽管本发明的内容已经通过上述优选实施例作了详细介绍，但应当认识到上述的描述不应被认为是对本发明的限制。

After reading the above, those skilled in the art will find that various modifications and substitutions to this invention will be readily apparent.

在本领域技术人员阅读了上述内容后，对于本发明的多种修改和替代都将是显而易见的。

Therefore, the scope of protection of this invention should be defined by the appended claims.

因此，本发明的保护范围应由所附的权利要求来限定。