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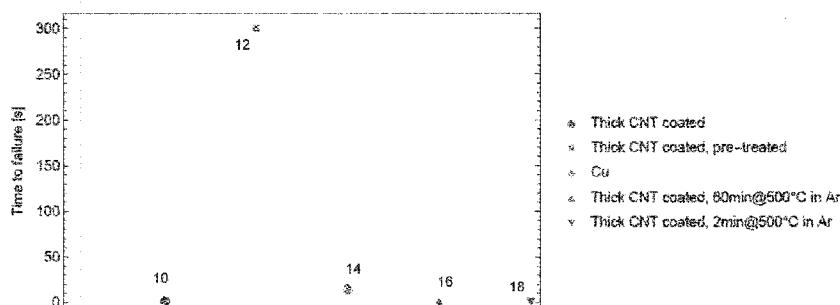
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(54) **Title:** COATED ELECTRICAL CONDUCTORS AND METHODS FOR THEIR MANUFACTURE

**Fig. 1**

(57) **Abstract:** A method of manufacturing a coated electrical conductor is disclosed. The method includes coating an exposed surface of a copper-based conductor with a coating comprising carbon nanotubes, and subjecting the coated conductor to a heat treatment step in an oxidising atmosphere at a temperature of at least 200°C. The resultant coated electrical conductor is also disclosed.

COATED ELECTRICAL CONDUCTORS AND METHODS FOR THEIR MANUFACTURE

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5 Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 609057.

FIELD OF THE INVENTION

The present invention relates to coated electrical conductors and to methods of
10 manufacturing coated electrical conductors. The invention has particular applicability to
treatment of copper-based electrical conductors, but is not necessarily of only exclusive
applicability to such conductors.

RELATED ART

15 Copper wires are commonly used as electrical conductors in a variety of applications and
in a multitude of external conditions. However, copper electrical conductors exposed to
high current densities typically show increased resistance over time and increased losses.
Increased resistance of the copper electrical conductor leads to increased heating of said
20 conductor, ultimately leading to failure of the conductor.

Heating a copper electrical conductor in an oxidising atmosphere such as air encourages
the formation of copper oxide on the surface of said conductor. Copper oxide (e.g.
copper (I) oxide, or cuprous oxide, Cu_2O) is more resistive than metallic copper. As such,
25 the available cross-sectional area of the copper conductor for current transport is
effectively reduced by the formation of copper oxide. This increases the resistance of the
copper conductor, which in turn causes additional heating of the copper conductor.
Additional heating increases the rate of oxygen diffusion into the wire. Over time the
copper oxide layer grows in thickness, consuming more of the copper, and the available
30 cross-sectional area of the copper conductor for current transport is reduced accordingly.

Electromigration is the gradual transport of material caused by momentum transfer between conducting electrons and metal atoms in a conductor. This effect is particularly significant in applications where high direct current densities are used. Electrical
5 conductors exposed to high current densities for extended periods of time are prone to failure caused by excessive electromigration of the electrical conductor. The combination of oxidation of the copper conductor reducing the effective cross-sectional area, combined with electromigration, causes copper conductors to fail after a period of use.

10

For many applications, it would be beneficial to provide an improvement in the current carrying capabilities and durability under high current density of copper conductors. For example, one suitable application would be internal wiring in circuit boards. As circuit board dimensions tend to be reduced in each generation of new devices, it is desirable to
15 continue to reduce the wiring dimensions as well. As a result, the current density that needs to be carried by the remaining conductor increases. Electromigration is already a known failure mechanism in circuit board wiring. In order to further reduce the dimensions of circuit board wiring, it is desirable to develop processes which provide copper conductors with increased tolerance to the effects of operating in an oxidising
20 environment and electromigration.

Methods of protecting copper conductors from oxidation are known in the art. For example an insulating polymer coating can be provided around a copper wire. This can reduce the rate of oxidation of the wire. However, suitable polymer coatings are prone to
25 melting or burning when exposed to moderate temperatures, or when the conductor itself is raised to a high temperature as a result of high current density, for example a sudden spike in network current or an overloading of the wiring system.

Alternatively, copper-based electrical conductors can be coated with tin-based coatings.

30 Similar to polymer coatings, tin-based coatings reduce the rate of oxidation of the copper

conductor by preventing direct exposure of the copper surface to the atmosphere.

However, tin-based coatings are only stable up to temperatures of about 150°C. When exposed to higher temperatures, the tin will diffuse into the copper conductor. As the tin diffuses into the copper conductor, the conductivity of the conductor is reduced. At even
5 higher temperatures, tin melts (the melting point of tin is about 230°C).

SUMMARY OF THE INVENTION

Carbon nanotube coatings for copper conductors are also known. WO 2014/189549

10 discloses carbon nanotube composite conductors, formed from a copper conductor and a carbon nanotube coating. The copper conductor is dipped into a dispersion containing carbon nanotubes to produce a carbon nanotube coating on the surface of the copper conductor. WO 2014/189549 discloses that the carbon nanotube coating increases the conductivity of the composite conductor compared to an uncoated copper conductor.

15

WO 2014/189549 also discloses a method of annealing the composite conductor. WO 2014/189549 discloses composite conductors heated in an inert or reducing atmosphere for at least 1 hour. It is suggested that the annealing may be performed at temperatures up to 1000°C. WO 2014/189549 discloses embodiments annealed at 400°C and 500°C
20 for 10 and 15 hours respectively.

The present invention primarily concerns copper-based electrical conductors. The terms “conductor”, “conductivity” and “conduction” are intended to refer to electrical conductor, electrical conductivity and electrical conduction, unless the context demands otherwise.

25

Oxidation of copper conductors significantly limits the lifetime of the copper conductor. This problem is observed in most copper wires and cables. This problem is particularly significant when the copper conductor is operated at high ambient temperatures and/or when the copper conductor is used to carry high current densities. In order to reduce the
30 effect of oxidation on a copper conductor and extend the lifetime of copper conductors, it

is desirable to develop a coating which extends the lifetime of the copper conductor compared to an uncoated copper conductor.

Coatings including carbon nanotubes have been developed for copper conductors to
5 form composite conductors. Some of these composite conductors are reported to have increased conductivity compared to an uncoated copper conductor as electrical current is thought to be carried in the carbon nanotube coating in addition to the electrical current in the copper conductor. See, for example, WO 2014/189549.

10 However, the carbon nanotube coatings known in the art do not improve the lifetime of a copper conductor. In fact, the carbon nanotube coatings known in the art can reduce the lifetime of the copper conductor. This is because the carbon nanotube coatings known in the art can act as thermally insulating layers. Therefore, when a composite conductor known in the art is subjected to a high current density, the temperature of the copper wire
15 is increased (compared with a comparable bare copper wire) due to a reduction in heat loss from the surface of the copper wire. This accelerates the failure mechanisms of the copper conductor (oxidation and/or electromigration).

The present invention has been devised in order to address at least one of the above
20 problems. Preferably, the present invention reduces, ameliorates, avoids or overcomes at least one of the above problems.

In a general aspect, the present invention treats a conductor such as a copper-based conductor with a carbon nanomaterial-based coating such as a carbon nanotube-based
25 coating and a subsequent heat treatment step in an oxidising environment. This is found to improve certain aspects of the electrical performance of the conductor.

In a first preferred aspect, the present invention provides a method of manufacturing a coated electrical conductor, the method including the steps:

30 i) providing a copper-based electrical conductor;

- ii) coating an exposed surface of said conductor with a coating comprising carbon nanotubes; and
- iii) subjecting the coated conductor to a heat treatment step in an oxidising atmosphere at a temperature of at least 200°C .

5

By providing a coating including carbon nanotubes and subsequently heat treating the coated conductor in an oxidising atmosphere, the operational lifetime of the coated conductor can be extended compared to an uncoated copper conductor.

- 10 Without wishing to be limited by theory, the present inventors have found that by covering a copper conductor with a coating including carbon nanotubes and subsequently heat treating the coated conductor in an oxidising atmosphere, a barrier layer is formed on the outer surface of the coated conductor. This barrier layer includes carbon nanotubes and copper oxide. The present inventors have found that the
- 15 presence of this barrier layer reduces the rate of diffusion of oxygen to the copper conductor. This in turn extends the lifetime of the coated copper conductor. The formation of the barrier layer, is considered at the time of writing to be relevant to extending the lifetime of the coated conductor. In particular, the heat treatment step should be carried out in an oxidising atmosphere in order to supply the oxygen necessary
- 20 to form the copper oxide in the barrier layer.

- The inventors have also found, surprisingly, that this heat treatment step further promotes the diffusion of carbon nanotubes present at the surface of the coated conductor into the copper conductor itself. The inventors consider, again without wishing
- 25 to be limited by theory, that the diffusion of carbon nanotubes into the surface of the copper conductor reduces the rate of formation of copper oxide at the surface of the copper conductor (the interface between the copper conductor and the coating) by offering a special stabilisation mechanism. By this stabilisation mechanism, the migration copper atoms are limited by the interaction between the copper-based

conductor and the carbon nanotube surface. Hence, the rate of degradation of the conductor is slowed, thereby further increasing the lifetime of the copper conductor.

5 Optionally, after the heat treatment, the coated conductor is cooled to below 100°C. This is preferred in particular where the heat treatment step is a pre-treatment step, in order to prepare the coated conductor for its intended use as an electrical conductor, e.g. carrying substantial current density for extended periods of time.

10 Optionally, the copper-based conductor may be a copper alloy. In the case of a copper alloy, a suitable copper alloy comprises one or more of: tin, bismuth, iron, lead, molybdenum, in addition to the copper base. Other elements may also be included in the copper alloy. Suitable copper alloys are well known in the art.

15 Preferably, in the heat treatment step of the first aspect of the invention, the heat is provided by an external heat source. Heating using an external heat source is advantageous for carrying the method of the present invention on an industrial scale. Suitable external heat sources include electrical furnaces or ovens (e.g. a tube furnace can be used in a continuous process in which an elongate coated conductor is pulled through the furnace). Alternatively, heat can be provided by a burner. Heating can also
20 be provided irradiation, e.g. by a laser. Using a laser as an external heat source is advantageous as the coated conductor can be rapidly heated.

25 Alternatively, in another preferred embodiment, the heat is provided by resistive heating of the conductor itself, by passing an electrical current through the copper-based conductor. Heating the coated conductor using electrical current is advantageous for controlling the heat delivered to the interface between the coating and the copper conductor.

Alternatively, the treatment applied to the coated conductor may include RF/microwave induced heating, or indeed any other activation providing a similar effect to a heat treatment.

- 5 Preferably the coated conductor is subjected to the heat treatment for at least 1 second. By subjecting the conductor to a heat treatment for at least this duration, the barrier layer formed due to the heat treatment reduces the rate at which the copper-based conductor is oxidised. The preferred heat treatment duration is dependent on the heat source used for the heat treatment process, and the maximum temperature achieved in the heat
- 10 treatment profile. As such, the heat treatment duration may alternatively be less than 1 second by rapidly heating the coated conductor to a high temperature above the minimum temperature required. Preferably, the coated conductor is subjected to the heat treatment for up to 1 hour, more preferably up to 5 minutes, and still more preferably up to about a minute. In a preferred embodiment, about 30 second has been found to be
- 15 suitable.

- Preferably, the carbon nanotubes used in the method of the first aspect comprise multi-walled carbon nanotubes, although single wall CNTs can be used. By using multi-walled carbon nanotubes the structural integrity of the inner wall of the carbon nanotube is
- 20 preserved, should the outer layer be sacrificed through carbide formation. As such, the multi-walled nanotubes have increased heat resistance compared to single-walled nanotubes when used in combination with a copper-based alloy. It is also realised that one property of the nanotubes useful for preventing migration of copper atoms through the coating is the shear strength of the interface between the coating and the copper-
- 25 based conductor. As multi-walled nanotubes tend to have a larger diameter than single-walled nanotubes, the shear strength reinforcement of the interface provided by multi-walled nanotubes is increased compared to that provided by single-walled nanotubes. Additionally, multi-walled nanotubes appear to provide increased resistance to copper migration through the coating compared to single-walled nanotubes.

Preferably, the carbon nanotubes also have an average length of at least 0.3 μ m. The carbon nanotubes may have an average length of not more than 20mm. For example their average length may be not more than 3mm, not more than 2mm or not more than 1mm. Their average length may be not more than 100 μ m, for example. It is considered
5 that the average length of the carbon nanotubes affects the uniformity of the coating coated on the exposed surface of the copper-based conductor. If the average length of the carbon nanotubes is too small (e.g. less than 300nm), then it is difficult to produce a sufficiently thick coating of carbon nanotubes on the copper-conductor. If the average length of the carbon nanotubes is too large, then the coating produced is not suitably
10 uniform. A uniform coating thickness is preferred in order to ensure that the lifetime of the coated conductor is consistent along the length of the conductor. The average length of the carbon nanotubes and the average diameter of the carbon nanotubes can be measured by scanning electron microscope (SEM) in a manner well known to the person skilled in the art.

15 Preferably, the thickness of the coating is at least 0.5 μ m. Thinner coatings are in principle possible, but a thickness of 0.5 μ m is found to provide beneficial effects. Preferably the thickness is measured in the direction normal to the exposed surface of the copper-based conductor. This direction is referred to in this disclosure as the
20 "thickness direction".

Preferably, the coating is formed on the copper-based conductor by dip coating the conductor in a coating dispersion which includes carbon nanotubes and a carrier liquid. By forming the coating using dip coating, a uniform coating with uniform thickness can be
25 produced. Other coating formation processes are also suitable. For example, spray coating can be used.

Preferably, the coating dispersion has a concentration of carbon nanotubes of at least 0.1%wt based on the weight of the coating dispersion. Preferably, the coating dispersion
30 has a concentration of carbon nanotubes of at most 10%wt based on the weight of the

coating dispersion. A concentration of carbon nanotubes within this range produces a coating dispersion viscosity suitable for coating a copper-conductor with a uniform coating. The concentration of carbon nanotubes in the solution may be measured by thermogravimetric analysis.

5

Preferably, the coating dispersion also includes a surfactant with a concentration of at least 0.1%wt based on the weight of the coating dispersion. Preferably, the coating dispersion also includes a surfactant with a concentration of at most 10%wt based on the weight of the coating dispersion. Including a concentration of surfactant above the lower limit identified above helps to disperse the carbon nanotubes within the coating dispersion. Including a surfactant concentration below the upper limit identified above ensures that the surfactant does not influence the properties of the coating during the heat treatment step. More preferably the surfactant used is dodecyl benzene sulfonic acid sodium salt. Other suitable surfactants will be apparent to the skilled person in the light of the present disclosure.

10

15

Preferably the carrier liquid for the coating dispersion is water. However, other solvents, for example, acetone or ethanol can be used as a carrier liquid. In general, a solvent may be used as the carrier liquid as long as the processing time is such that no substantial and deleterious evaporation of the liquid occurs during processing of the dispersion.

20

Preferably, the dispersion consists of the carbon nanotubes, surfactant and carrier liquid only, alongside incidental impurities.

25

In a second preferred aspect, the present invention provides a coated electrical conductor obtained by, or obtainable by, the method of the first aspect of the invention.

In a third preferred aspect of the present invention a coated electrical conductor

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comprising a copper-based electrical conductor and a coating covering at least part of an

exposed surface of said conductor is provided. The coating comprises carbon nanotubes wherein an outer surface of the coating presents a barrier layer comprising copper oxide and carbon nanotubes.

- 5 Preferably, the thickness of the barrier layer is such that a ratio between a cross-sectional area of the barrier layer and a cross-sectional area of the coating, when viewed in a cross-sectional plane including the thickness direction is at least 1%. The thickness of the barrier layer is preferably such that a ratio between a cross-sectional area of the barrier layer and a cross-sectional area of the coating, when viewed in a cross-sectional
10 plane including the thickness direction is less than 90%.

Preferably, the coating of the second aspect of the present invention has an average thickness normal to the surface of the copper-based electrical conductor which is at least 0.5 μ m. Preferably, the coating of the second aspect of the present invention has an
15 average thickness normal to the surface of the copper-based electrical conductor which is not greater than 1000 μ m. Coatings which have a thickness less than the lower limit identified above are considered to not provide a sufficient diffusion barrier to oxygen reaching the copper-based conductor. As such, a sufficient lifetime improvement of the coated conductor is not realised in coating which are too thin. Coatings which have a
20 thickness greater than the upper limit identified above are highly thermally insulating. This results in heat generated in the copper-based conductor when operated at high current densities not being efficiently dissipated to the surroundings, and the lifetime of the coated conductor can therefore be reduced.

- 25 It is considered that the present invention may have particular applicability in terms of the treatment of relatively thick coatings, in the sense that the heat treatment applied to the coating may provide a greater benefit for relatively thick coatings compared with relatively thin coatings. Accordingly, in some preferred embodiments, the thickness of the coating may be at least 1 μ m thick, more preferably at least 10 μ m thick, more
30 preferably at least 50 μ m thick, more preferably at least 100 μ m thick.

Preferably, at an interface between the coating and the copper-based conductor, carbon nanotubes are at least partially embedded in the copper-based conductor. The spatial frequency of carbon nanotubes crossing the interface between the coating and the copper-based conductor is greater than $0.1\mu\text{m}^{-1}$. It is speculated that the mechanism for the migration of carbon nanotubes into the copper-based conductor is diffusion-based. Carbon nanotubes which cross or partially cross the interface between the coating and the copper-based conductor appear to decrease the rate at which the copper-based conductor is oxidised. Therefore, when the carbon nanotubes that cross the interface between the coating and the copper-based conductor are distributed across the copper-based conductor according to the minimum spatial frequency, the lifetime of the coated conductor is increased accordingly. Furthermore, the heat dissipation of the coated conductor is improved by having a spatial frequency of carbon nanotubes crossing the interface at or above the specified limit. This in turn reduces the rate of oxygen and copper diffusion, thus increasing the lifetime of the conductor.

The first, second and third aspects of the invention provide the technical benefit of a coated copper electrical conductor having increased lifetime compared to an uncoated copper electrical conductor. Furthermore, the coating provided by the invention has the additional advantage of being capable of being heat resistant up to temperatures of 1000°C , as the coating comprises carbon nanotubes. Additionally, the coating has a lower density than some other coatings known in the art to reduce the rate of oxidation of a copper conductor.

In an alternative aspect of the present invention a method of manufacturing a coated electrical conductor is provided, the method including the steps:

- i) providing an electrical conductor;
- ii) coating an exposed surface of said conductor with a coating comprising carbon nanotubes or other carbon nanomaterial; and

iii) subjecting the coated conductor to a heat treatment step in an oxidising atmosphere at a temperature of at least 200°C and optionally cooling the coated conductor to below 100°C.

5 In this alternative aspect, the electrical conductor is made from a material suitable for conduction of high current densities, for example, copper, aluminium, gold or the like. This alternative aspect provides the technical benefit of a coated electrical conductor having increased lifetime compared to an uncoated electrical conductor. Furthermore, the coating provided by the invention has the additional advantage of being capable of
10 being heat resistant up to temperatures of 1000°C, as the coating comprises carbon nanotubes. Additionally, the coating has a lower density than some other coatings known in the art to reduce the rate of oxidation of an electrical conductor

In another alternative aspect of the present invention a method of manufacturing a
15 coated electrical conductor is provided, the method including the steps:
i) providing a copper-based electrical conductor, or other electrical conductor;
ii) coating an exposed surface of said conductor with a coating comprising carbon nanomaterial; and
iii) subjecting the coated conductor to a heat treatment step in an oxidising
20 atmosphere at a temperature of at least 200°C and optionally cooling the coated conductor to below 100°C.

In this alternative aspect, the carbon nanomaterial preferably comprises carbon nanotubes, or graphene, or a mixture of such materials. Preferably the coating also
25 comprises metallic particles. Preferably the metallic particles are nano-scale metallic particles.

This alternative aspect of the present invention provides the technical benefit of a coated copper electrical conductor having increased lifetime compared to an uncoated copper
30 electrical conductor. Furthermore, the coating provided by the invention has the

additional advantage of being capable of being heat resistant up to temperatures of 1000°C, as the coating comprises carbon nanomaterials. Additionally, the coating has a lower density than some other coatings known in the art to reduce the rate of oxidation of a copper conductor.

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Any aspect of the invention may be combined with any other. Also, one or more of the optional or preferred features set out with respect to an aspect of the invention may be combined with another aspect of the invention, in any suitable combination, unless the context demands otherwise.

10

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will now be described by way of example with reference to the accompanying drawings in which:

15

Fig. 1 – Experimental data comparing the effect of different treatments for copper wires on the lifetime of the copper wires.

20

Fig. 2A – Experimental data showing the composition of a carbon nanotube coating including the barrier layer as measured by Energy Dispersive X-ray spectroscopy (EDX), and a corresponding SEM micrograph of the analysed section.

25

Fig. 2B – Experimental data showing the composition of an interface between a carbon nanotube coating and a copper wire as measured by Energy Dispersive X-ray spectroscopy (EDX), and a corresponding SEM micrograph of the analysed section.

Fig. 3 – Experimental data showing the time to failure for uncoated copper wires which have been heat treated, and uncoated copper wires which have not been heat treated.

Fig. 4 – Experimental data showing the effect of heat treatment time on the lifetime of coated copper wires.

Fig. 5 – Experimental data showing the effect of heat treatment temperature, expressed
5 in terms of heat treatment current density, on the lifetime of coated copper wires.

Fig. 6A – Experimental data showing the effect of temperature versus time during exposure to a current density of 356 A/mm^2 for various sample coated wires.

10 Fig. 6B - Experimental data showing the effect of temperature versus resistance during exposure to a current density of 356 A/mm^2 for various sample coated wires.

Fig. 7 – Experimental data showing resistance versus current for the last three cycling measurements before fatal damage of a coated copper wire and an uncoated copper
15 wire.

Fig. 8A – SEM image of a coated copper wire after application of 2.6A at 2700 magnification.

20 Fig. 8B – SEM image of a coated copper wire after application of 2.8A at 5000 magnification.

Fig. 8C – SEM image of a coated copper wire after application of 3.0A at 21000 magnification.

25

Fig. 9A – SEM image of an uncoated copper wire after application of 3.2A sufficient to cause failure of the wire at 3600 magnification.

Fig. 9B – SEM image of an uncoated copper wire after application of 3.4A sufficient to
30 cause failure of the wire at 4500 magnification.

Figs. 10A and 10B – Experimental data showing the development of resistance versus current for an uncoated copper wire (Fig. 10A) and a carbon nanotube coated wire (Fig. 10B) during 20 cycles to 2.6 A.

5

Figs 11A-11C – SEM image of a copper wire with a carbon nanotube coating, the coating exposed to an increasing number of current cycles of 2.6A: A) 2 cycles shown at 26000 magnification, B) 3 cycles shown at 36000 magnification, C) 20 cycles shown at 26000 magnification.

10

Figs 11D-11F – SEM image of a copper wire with a carbon nanotube coating, the coating exposed to an increasing number of current cycles of 2.6A: A) 10 cycles shown at 8000 magnification, B) 15 cycles shown at 85000 magnification, C) 20 cycles shown at 26000 magnification.

15

Figs. 12A-12D – Images produced by EDX measurement of a carbon nanotube coated copper wire after 18 cycles to 2.6 A according to Experiment 7. Fig. 12A shows a secondary electron (SE) image, Figs 12B-12D show carbon (C), oxygen (O) and copper (Cu), respectively.

20

Fig. 13 – Experimental data showing resistance versus current for various carbon nanotube coated copper wires and uncoated copper wires. The insets show magnifications of region II, III, and IV (top left, top right and bottom inset respectively).

25 Figs. 14A-14F – SEM images of sample CNT9 close to the longitudinal middle of the wire (Fig. 14A, shown at 4500 magnification) and further away (Fig. 14B, shown at 29000 magnification), SEM images of sample CNT10 (Fig. 14C, shown at 4500 magnification and Fig. 14D, shown at 33000 magnification), and SEM images of sample CNT7 (Fig. 14E, shown at 25000 magnification and Fig. 14F shown at 11000 magnification).

30

Figs. 15A and 15B - SEM images of sample CNT7 with decreasing distance to the breaking point (shown at 7000 and 5000 magnification respectively).

5 Figs. 16A and 16B – Variation in barrier layer thickness and carbon nanotube diffusion distance at the interface between the copper-based conductor and the coating for variation in heat treatment current density.

10 Figs. 17A and 17B - Variation in barrier layer thickness and carbon nanotube diffusion distance at the interface between the copper-based conductor and the coating for variation in heat treatment duration.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS, AND FURTHER
OPTIONAL FEATURES OF THE INVENTION**

15 An embodiment of the first aspect present invention is a method of manufacturing a coated electrical conductor according to an embodiment of the second and third aspects of the invention.

A copper conductor with a cross-sectional diameter of at least 0.0001 mm is provided.

20 Preferably the diameter of the copper conductor is at least 0.001mm, 0.005mm, 0.01mm, 0.05mm, or 0.1mm. A maximum diameter of the copper conductor is 100cm, for example. Preferably the maximum diameter of the conductor is 50cm, 10cm, 5cm, 1cm, 5mm, 1mm, or 0.5mm. Most preferably the diameter of the copper wire is about 0.15mm. Copper conductors with a diameter less than the minimum diameter are difficult to coat

25 with the coating, as the wires are a comparable size to the carbon nanotubes. Copper conductors with a diameter larger than the maximum diameter are so large relative to the coating that the coating is not as effective.

Preferably the copper conductor is copper wire, with a round or circular cross-section.

30 However, the skilled person would understand that other cross-sectional shapes, for

example, triangular, rectangular, or elliptical are equally suitable for the method of the present embodiment.

The copper-based electrical conductor is an electrical conductor that is substantially made from copper, or a copper alloy. Preferably the copper-based conductor is at least 90 %wt copper compared to the total weight of the copper-based conductor. More preferably, the copper-based conductor is at least 95%wt, 99%wt, 99.9%wt or 99.99%wt copper based on the weight of the copper based conductor. As such, the copper-based conductor may be pure copper.

In the case of a copper alloy, suitable copper alloys comprise one or more of: tin, bismuth, iron, lead, molybdenum, in addition to the copper base.

An exposed surface of the copper-based conductor is coated by a coating comprising carbon nanotubes. The exposed surface of the copper-based conductor is considered to be any surface of the copper conductor exposed to atmosphere prior to coating. The total exposed surface area of the copper-based conductor can be less than the total surface area of the copper-based conductor. For example, part of the surface area may be covered by another part such as a circuit board or electrical contacts to the ends of the copper conductor. Not all of the exposed surface area of the copper-based conductor needs to be coated by the coating. Preferably at least 10% of the total exposed surface area of the copper-based conductor is coated by the coating. More preferably at least 30%, 50%, 60%, 70%, 80%, 90%, 95% or 100% of the total exposed surface area of the copper-based conductor is coated by the coating.

A coating provided by an embodiment of the first aspect of the present invention comprises carbon nanotubes. Preferably, the copper-based conductor is coated with the coating by dipping the copper-based conductor into a coating dispersion comprising carbon nanotubes and a carrier liquid for dispersing the carbon nanotubes. Preferably the liquid is water, e.g. distilled water. Alternatively, the carrier liquid can be acetone,

ethanol, or any other suitable liquid that can be removed without leaving traces at a temperature suitable for use with the coated conductor.

The carbon nanotubes dispersed in the coating dispersion may be obtained from commercial suppliers or grown using typical methods known in the art for producing carbon nanotubes such as chemical vapour deposition. Single walled or multi-walled carbon nanotubes may be used. Preferably, the carbon nanotubes are predominantly multi-walled carbon nanotubes. At least in part, this is because multi-walled carbon nanotubes are not prone to bunching. MWNTs also have an outer layer that can be sacrificed during carbide formation, are less prone to entanglement and have a higher diameter, which is considered to be advantageous when it comes to preventing copper migration.

The carbon nanotubes dispersed in the solution will range in length due to the nature of carbon nanotube growth. One characterising measure for the length of carbon nanotubes is the average length of the carbon nanotubes. The average length of a batch of carbon nanotubes is measured by measuring the lengths of individual carbon nanotubes from a SEM image.

The average length of the carbon nanotubes in the coating dispersion (and thereby in the coating of the coated conductor as well) is at least $0.05\mu\text{m}$. Preferably, the average length of the carbon nanotubes is at least $0.1\mu\text{m}$, $0.5\mu\text{m}$, $1\mu\text{m}$ or $10\mu\text{m}$. The maximum average length of the carbon nanotubes can be substantial, for example up to 20mm . The average length can be up to 3mm , up to 2mm or up to 1mm , for example.

Preferably, the maximum average length of the carbon nanotubes is $500\mu\text{m}$, $100\mu\text{m}$, $50\mu\text{m}$, $30\mu\text{m}$, $20\mu\text{m}$, $10\mu\text{m}$, or $5\mu\text{m}$. By ensuring the average length of the carbon nanotubes is at least $0.05\mu\text{m}$, the viscosity of the coating dispersion is such that a uniform coating can be formed on the copper-based conductor. Where suitable, by ensuring that the average length of the carbon nanotubes is not too high, the coating formed on the conductor can be provided with a uniform thickness.

The coating dispersion according to an embodiment of the present invention preferably also contains a surfactant. More preferably the surfactant is sodium dodecylbenzenesulfonate (SDBS). Alternatively, for example, sodium dodecyl sulfate (SDS) could be used as a surfactant. Other surfactants that have been shown to solubilise carbon nanotubes in the literature would also be suitable. The presence of a surfactant in the coating dispersion helps to disperse the carbon nanotubes so that a more uniform coating can be produced. In a particularly preferred embodiment, a minimum concentration of surfactant present in the coating dispersion is 0.1%wt of the total solution. More preferably a minimum concentration of the surfactant present in the coating dispersion is 0.5%wt, 1%wt or 2%wt of the total solution. A maximum concentration of surfactant present in the coating dispersion is preferably 10%wt of the total solution. More preferably, a maximum concentration of surfactant present in the coating dispersion is 5%wt of the total solution. By ensuring that the concentration of surfactant in the coating dispersion is within this range, the viscosity of the coating dispersion is such that a more uniform coating of carbon nanotubes is provided on the exposed surfaces of the copper conductor when it is dip coated in the coating dispersion.

The heat treatment step according to an embodiment of the first aspect of the present invention involves subjecting the coated conductor to a heat treatment step in an oxidising atmosphere at a temperature of at least 200°C (see also the preferred alternative temperature ranges given below) and cooling the coated conductor to below 100°C. In one preferred embodiment, the heat treatment is provided by heating the coated conductor with an external heat source. The external heat source is preferably an oven, a heat gun or a torchflame. Alternatively laser heating can be used. Other known methods applicable to heating a coated wire sample would be equally suitable. Heating using an external heat source is advantageous for carrying the method of the present invention on an industrial scale. Heat treatment using an external heat source can also be used to control the rate of heating of the coated conductor. This can be used to

reduce the chance of burnout of the carbon nanotubes when heating the coated conductor to high temperatures.

Alternatively, in another preferred embodiment of the first aspect of the present invention
5 the heat treatment is provided by resistive heating by passing an electrical current
through the copper-based conductor in order to heat the copper-based conductor and the
coating. Heating the coated conductor using electrical current is advantageous for
controlling the heat delivered to the interface between the coating and the copper-based
conductor. The amount of heating provided to the copper-based conductor depends on
10 the resistivity of the copper-based conductor and the current density supplied. For
example, a 0.15mm diameter copper wire exposed to a current density of 356 A/mm² will
heat to a stable temperature after 6s.

The heat treatment according to an embodiment of the first aspect of the present
15 invention is carried out in an oxidising atmosphere. An oxidising atmosphere is an
atmosphere around the coated conductor which allows for the formation of a barrier layer
on the exposed surface of the coated conductor, wherein the barrier layer comprises
copper oxide. As such, it will be understood by the skilled person that the oxidising
atmosphere is required for the formation of copper oxide in the barrier layer.
20 Furthermore, it will be understood by the skilled person that a reducing atmosphere or an
inert atmosphere is not an oxidising atmosphere, as a reducing or inert atmosphere will
not allow for the formation of copper oxide in the barrier layer. In one embodiment of the
method, the oxidising atmosphere is air. Alternatively, in another embodiment, the
oxidising atmosphere may be produced inside a controlled atmosphere chamber with an
25 additional supply of oxygen. The additional supply of oxygen may be provided as an
oxygen gas supply to the chamber, or alternatively the oxygen may be provided through
the decomposition of at least one chemical compound within the chamber.

Preferably, the coated conductor is subjected to a heat treatment step according to an
30 embodiment of the first aspect of the present invention for a duration of at least 1s. More

preferably, the duration of the heat treatment step is at least 5s, 10s, 1 minute, 10 minutes, 1 hour, or 5 hours. Subjecting the coated conductor to a heat treatment of minimum duration allows for sufficient time for copper to diffuse to the surface of the coating in order to form the barrier layer. Preferably the coated conductor is subjected to

5 a heat treatment step of a maximum duration of 100 hours. More preferably, the maximum heat treatment step duration is 50 hours, 10 hours, 5 hours, 1 hour, 30 minutes or 10 minutes. Subjecting the coated conductor to a heat treatment beyond the maximum duration will result in excessive oxidation of the coating and the copper-based conductor, thus reducing the effectiveness of the present invention. The skilled person

10 will understand that the optimum duration for the heat treatment step will depend on the temperature of the heat treatment step as well as the dimensions of the coating and the copper conductor. A particularly preferred heat treatment duration is 30s.

The heat treatment temperature is preferably at least 300°C, more preferably at least

15 400°C. The heat treatment temperature is preferably at most 1000°C, more preferably at most 900°C, at most 800°C, or at most 700°C. The suitable heat treatment temperature for a particular coating may additionally depend on the duration of the heat treatment, with the suitable duration of the heat treatment varying inversely with the heat treatment temperature.

20 The heat treatment step according to an embodiment of the first aspect of the present invention also includes a cooling step. The heat treated coated conductor should be cooled to at least 100°C. Preferably the heat treated coated conductor should be cooled to room temperature. The cooling step provides separation between the heat treatment

25 and further stressing of the coated conductor. As such, the increase in lifetime of the coated conductor is realised after the coated conductor is cooled.

A second aspect of the present invention is a coated electrical conductor. The coated electrical conductor comprises a copper-based electrical conductor and a coating

30 covering at least part of an exposed surface of said conductor.

Preferably, the copper-based conductor has a cross-sectional diameter of at least 0.0001 mm. More preferably the diameter of the copper-based conductor is at least 0.001mm, 0.005mm, 0.01mm, 0.05mm, or 0.1mm. Preferably, a maximum diameter of the copper-based conductor is 100cm. More preferably the maximum diameter of the copper-based conductor is 50cm, 10cm, 5cm, 1cm, 5mm, 1mm, or 0.5mm. Most preferably the diameter of the copper-based conductor is 0.15mm or 0.1mm.

Preferably the copper-based conductor is copper wire, with a round or circular cross-section. However, the skilled person would understand that other cross-sectional shapes are equally suitable for the method of the present embodiment.

The copper-based electrical conductor is an electrical conductor that is substantially made from copper, or a copper alloy. Preferably the copper-based conductor is at least 90 %wt copper compared to the total weight of the copper-based conductor. More preferably, the copper-based conductor is at least 95%wt, 99%wt, 99.9%wt or 99.99%wt copper compared to the total weight of the copper-based conductor. As such, the copper-based conductor may be pure copper.

The coating used according to an embodiment of the second or third aspect of the present invention comprises carbon nanotubes, wherein an outer surface of the coating further includes a barrier layer comprising copper oxide and carbon nanotubes. The barrier layer is formed when a copper-based conductor coated with a coating comprising carbon nanotubes is subjected to a heat treatment step. The heat treatment step is carried out at a temperature of at least 200°C in an oxidising atmosphere. The heat treatment step forms a barrier layer on the outer exposed surface of the coating. The barrier layer comprises carbon nanotubes and copper oxide. The copper oxide is formed due to the heat treatment in an oxidising atmosphere. The copper in the copper oxide of the barrier layer is a result of copper diffusion from the copper conductor. Forming a barrier layer at the outer surface of the barrier layer is advantageous as it reduces the

rate of oxygen diffusion to copper conductor. Therefore, the rate at which the copper-based conductor oxidises is reduced, thus the lifetime of the coated conductor is increased compared to an uncoated copper-based conductor.

- 5 A ratio between the cumulative cross-sectional area of the barrier layer and the total cross-sectional area of the coating (which includes the barrier layer but not the copper conductor) is typically greater than 10% and less than 100%. Preferably the cross-sectional area of the coating layer is calculated by taking a cross-sectional view of the coated conductor perpendicular to the intended direction of current flow in the copper-based conductor, for example using SEM microscopy. Alternatively, a cross-section may
10 be taken aligned with the intended direction of current flow. In a particularly preferred embodiment, the thicknesses of the barrier layer and the coating are uniform such that the ratio of the cross-sectional area of the barrier layer and the cross-sectional area of the coating are not dependent on the orientation of the cross-section taken, provided that
15 the cross section passes through the centre of the conductor.

In a preferred embodiment of the second aspect the ratio between the cross-sectional area of the barrier layer and the cross-sectional area of the coating is at least 20%, at least 30% at least 40%, at least 50% or at least 60%. By increasing the amount of
20 barrier layer present in the coating, the rate of oxygen diffusion is further attenuated, thus increasing the lifetime of the coated conductor. Preferably, the ratio is also not more than 99%, not more than 95%, not more than 90% or not more than 80%. Increasing the cross-sectional area of the barrier layer beyond a certain point reduces the lifetime of the coated conductor. However, it is considered that a coated conductor with a barrier layer
25 which has a cross-sectional area 100% of the coating cross-sectional area would still show an improved lifetime compared to an uncoated conductor.

In a preferred embodiment of the second aspect of the present invention, carbon nanotubes cross the interface between the coating and the copper-based conductor. As
30 such, some of the carbon nanotubes extend into the bulk of the copper-based conductor.

At the time of writing, it is not clear whether this change is brought about by a diffusion of the carbon nanotubes into the copper-based conductor, or a diffusion of the copper-based conductor into the coating, or a combination of both effects. When carbon nanotubes cross the interface between the coating and the copper-based conductor, the rate of oxidation of the copper-based conductor is reduced when exposed to electrical current. Thus the lifetime of the coated conductor is extended compared to an uncoated copper-based conductor. Furthermore, carbon nanotubes preferably cross the interface at a spatial frequency of at least $0.1 \mu\text{m}^{-1}$. The spatial frequency of carbon nanotubes crossing the interface into the copper is measured by EDX analysis of the interface between the copper-based conductor and the coating according to an embodiment of the second aspect of the invention. As shown in Fig. 2b, the relatively high presence of carbon relative to copper and oxygen in the region 750nm to 1200nm indicates the presence of a carbon nanotube diffused into the copper. Multiple regions along the coated conductor may preferably be analysed in order to accurately assess the spatial frequency of the diffused carbon nanotubes. By increasing the spatial frequency of diffused carbon nanotubes, the rate of oxidation of the copper based-conductor is further attenuated.

Examples

The technical advantages provided by the present invention are further illustrated in the following examples.

Experiment 1

Copper wires with a diameter of 0.125mm were coated with a coating comprising carbon nanotubes. The coatings had a thickness of about 22 μm . The diameters of the carbon nanotubes in the coatings ranged from 50 to 200 nm. The average length of the carbon nanotubes was in the range 3-4 μm . The coated copper wires were subjected to a range of different surface treatments. The different treatments are as follows:

10: Thick coating comprising carbon nanotubes, no additional treatment.

12: Thick coating comprising carbon nanotubes that was heat treated in air with: 30s at 3.2A, followed by 30s at 3.4A, followed by 30s at 3.6A.

14: Uncoated copper wire, with no additional treatment.

16: Thick coating comprising carbon nanotubes, heat treated at 500°C for 60 min in Ar atmosphere (inert atmosphere) (heating rate of 20 °C per minute, cooling took about an hour).

5 18: Thick coating comprising carbon nanotubes, heat treated at 500°C for 2 min in Ar atmosphere (inert atmosphere) (heating rate of 20 °C per minute, cooling took about an hour).

The copper wires were then tested to failure under a constant current of 3.8 A. Fig. 1 is a graph showing the time to failure for each wire tested. Fig. 1 shows that inclusion of a heat treatment step in an oxidising atmosphere (air in this case) significantly increases the lifetime of the conductor. The lifetime of the uncoated copper wire 14 is greater than the lifetime of a copper wire 10 coated with a thick coating of carbon nanotubes but without heat treatment. Therefore, merely coating a copper wire with a thick coating of carbon nanotubes is detrimental to the lifetime of the copper wire. Similarly, heat treating a copper wire with a thick carbon nanotube coating in an inert atmosphere (samples 16, 18) does not improve the lifetime of the copper wire compared to the uncoated copper wire. In contrast, a carbon nanotube coating combined with a heat treatment step in an oxidising atmosphere (sample 12) according to an embodiment of the present invention significantly increases the lifetime of the copper wire.

Experiment 2

Figs. 2A and 2B show EDX line maps and corresponding SEM images of a carbon nanotube coating and the interface between the coating and a copper wire treated at 331 A/mm² for five minutes, the coated conductor produced according to an embodiment of the present invention. Fig. 2A shows that the outer layer of the CNT coated Cu wires after the 300 s of treatment consisted of CuO and Cu₂O intervened with CNTs. Fig. 2B shows that at the interface between the copper wire and the coating, carbon nanotubes have diffused into copper wire as evidenced by the composition variation in the graph produced by EDX measurements.

Figs. 2A and 2B show carbon nanotubes that had diffused into the Cu matrix of the wire, where they again could have acted as heat sinks and thereby prevented the destruction of the wire by efficient heat transport out of the wire.

5

Experiment 3

Different heat treatment times and currents were tested and the effect on the lifetime at higher current densities evaluated. The results presented in this section have been measured on a 0.125mm diameter copper wire with thin coatings below 10 μm thickness.

- 10 Different heat treatment times, namely 0, 30, 60 and 120 s, were tested with a heat treatment current density of 283 A/mm² and a test current density of 305 A/mm². The varying heat treatment current densities (293, 288, 284, 261, 244 A/mm²) were all applied for 60 s.
- 15 The exact parameters of dependency vary with the coating thickness, copper wire diameter, test current and heat treatment current and the results presented are only a guideline for a general trend in dependency. In order to show that the extended lifetime after heat treatment at lower current densities is not an effect of the copper material itself, an uncoated copper wire, diameter 0.125 mm was also heat treated at 244 A/mm² for 60
- 20 s and then exposed to 293 A/mm².

In Fig. 3, resistance versus time for a copper wire heat treated in this manner and two conventional wires are shown. It is evident that the heat treatment does not affect the lifetime of the uncoated copper wire.

25

- The results for varying heat treatment times at fixed current density are shown in Fig. 4. The coated wire that was not heat treated at low current densities, shown at 0 s heat treatment time, is instantly destroyed. The uncoated copper wire lasted 24 ± 4 s under corresponding conditions. With increasing heat treatment time, the time to failure under
- 30 high current density also increased. It seems as though the time to failure saturates with

further increasing heat treatment time, resulting in a time to failure of 418 ± 100 s after 120 s of heat treatment. The large error bar is explained by the varying diameter of the coating thickness between samples, the effect of which becomes even more pronounced as the heat treatment time is increased.

5

The results for varying heat treatment current densities for fixed time of 60s are shown in Fig. 5. All heat treated wires last longer than non-heat treated coated wires, that decomposed immediately, or uncoated copper wires that broke after 24 ± 4 s as shown above. Heat treatment at low current densities of below 265A/mm^2 led to an increase in lifetime by up to a factor of 9.

10

A heat treatment at a current density of 283 A/mm^2 led to the highest increase in time to failure, before a decrease in time to failure was observed for heat treatments at even higher current densities. The best heat treatment current density and duration for this particular case were found to be 60s at 283A/mm^2 . This can be explained by the movement of carbon nanotubes into the copper matrix, without wishing to be limited by theory. A too high current density will lead to immediate surface oxidation and reduced movement of carbon nanotubes. A too low current density will not lead to enough movement of carbon nanotubes, whereas the right current density will lead to enough carbon nanotube movement, without increasing the oxide layer too much. A low time will not allow enough movement of carbon nanotubes, whereas, once a certain threshold of movement has been reached, further treatment will only slightly increase the properties as most of the diffusion has taken place. Hence, a medium time and current density are ideal as heat treatment settings.

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Another indication supporting the hypothesis of CNT migration into the Cu matrix and thereby affecting temperature and resistance was found by testing a coated wire and a coated wire with a heat treatment according to an embodiment of the present invention at current densities over 356A/mm^2 . It was found that exposure of a wire with a thick coating to a current density of e.g. 343A/mm^2 led to immediate destruction of the wire.

30

The middle piece of material was completely destroyed over a centimetre range, and not just broken in one point as in the cases observed before at lower current densities or thinly coated/uncoated copper wires at higher current densities. The lifetime of uncoated copper wire and thinly coated wire in this region was low, but they were not as
5 immediately decomposed as the thickly coated wires.

If the thickly coated wires were however first pre-treated according to an embodiment of the present invention, this effect did not set in. After treatment of the thickly coated wires at a current of 331 A/mm² for five minutes, exposure to a current of 356 A/mm² did not
10 lead to instant destruction as observed before.

Experiment 4

In this experiment a series of copper wires were prepared with different coatings. The copper wires were then subjected to a current density of 356A/mm² wherein the
15 resistance and temperature of the wires was measured over time.

In Figs. 6A and 6B the temperature of two thickly coated wires as prepared, a thickly coated wire that was heat treated and an uncoated wire are shown versus time and resistance respectively. The thickly coated wires showed a sharp increase in
20 temperature after only two seconds of treatment at high current, whereas the “pre-treated” and the uncoated wires showed a lower temperature, which increased over time (not shown). In the temperature versus resistance plot (Fig. 6B), a nearly linear increase of temperature with resistance can be seen for the heat treated wire, except in the region of constant temperature between about 0.49Ω and 0.53Ω, until failure is observed. The
25 thickly coated wires showed a sharp increase in temperature at low values of resistance, hence the higher temperature is not just a results of an intrinsically higher resistance value. The uncoated wires showed similar temperatures for identical resistance values, but no linear section, allowing for the longer lifetime of the correctly coated wires as they were held at lower temperature and resistance for an extended period of time.

The temperature values for the measurements on the coated wires are considered to be more accurate than the uncoated copper wire ones, as the surface was coated with carbon nanotubes, which are black-body radiators.

- 5 The emissivity could hence be set fairly accurately for these wires. The bare copper wires' temperatures are only a lower boundary again, especially in the first seconds before oxidation has set in, as emissivity changes with the surface oxidation. Both sets of samples show however lower apparent temperatures due to the small surface area. The larger offset in emissivity for the bare copper wires could explain why the thick, pre-
10 treated wire's temperature appears to be higher than the one of the bare copper wire in Fig. 6B.

Experiment 5

- This experiment studied the resistance development of the carbon nanotube coated and
15 uncoated copper wires in dependency of applied current. The resistance data was linked to SEM/EDX images and an understanding of the principal processes during current increase, cycling and prolonged exposure to high currents obtained.

- Uncoated copper wires of 0.1mm diameter were coated with carbon nanotubes from
20 liquid suspension. The carbon nanotubes, predominantly MWNTs, were grown in a horizontal c-CVD furnace setup and dispersed in distilled water with the aid of SDBS as surfactant. Post heat treatment and resting was combined to produce a solution suitable for homogenous coating of the copper wires.

- 25 For measurement of resistance versus applied current, a current source (TTi CPX400SP DC Power Supply) and a nanovoltmeter (Keithley 2182A) were used, both regulated and monitored via a GBIP interface. The sample holder consisted of four copper blocks, two of them stacked and separated from the other two by a distance of 7 cm. The current was supplied via the bottom copper block and the sample was clamped between two
30 stacked blocks. Voltage was measured at the upper copper blocks. The sample holder

was placed inside a sealed containment during the measurements in order to prevent air fluctuations. The current could be set to cycle up to a maximum value and back to zero while the voltage was read by a computer.

- 5 Additionally to the ampacity tests, the wires were taken for SEM and EDX evaluation after the measurements to determine the composition and observe the effects on the carbon nanotube layer.

10 In Fig. 7 the last three resistance versus current cycling curves leading up to destruction of the wires are shown for both uncoated copper wires and carbon nanotube coated copper wires. The uncoated copper wires failed at a lower maximum current, i.e. 3.2A, whereas the carbon nanotube coated wires failed at 3.4A. Identical currents led to a higher resistance and irreversible hysteresis was observed at lower applied currents for the uncoated copper wires. The final measurement of the carbon nanotube coated wire
15 shows resistance values higher than the final uncoated copper wire.

Experiment 6

An uncoated copper wire and a copper wire with a carbon nanotube coating were subjected to heat treatments of increasing temperature. The heat treatment was
20 provided by subjecting the copper wires to increasing electrical current. The composition of the surface of each conductor was analysed after each heat treatment.

Maximum current [A]	Composition carbon nanotube coated Cu wire	Composition uncoated copper wire
< 2	CNT	Cu
2.2	CNT	Cu ₂ O + Cu
2.4	CNT + Cu ₂ O	Cu ₂ O + Cu
2.6	CNT + Cu ₂ O	Cu ₂ O
2.8	CuO+ Cu ₂ O	CuO + Cu ₂ O
3.0	CuO	CuO + Cu ₂ O
3.2	CuO+ Cu ₂ O	CuO + Cu ₂ O
3.4	CuO	-

Table 1

- 5 Table 1 shows the composition of the wire surface after application of the different currents. It should be noted that the exact values, once oxidation starts, depends on the measurement parameters as the temperature thereafter does not reach equilibrium anymore due to the oxidation process. In general, with increasing current, the copper wires are expected to oxidise and cuprous oxide (Cu₂O) will be formed. For even higher
- 10 currents, cupric oxide (CuO) may be developed on the surface. On the uncoated copper wire, this process is homogeneously taking place over all of the surface, resulting in an increasingly thick layer of cuprous and cupric oxide. The carbon nanotube coated wire shows development of copper oxide species, but the formation is taking place less homogeneously due to the carbon nanotube coating. In Fig. 8A, the formation of copper
- 15 oxide in the carbon nanotube layer is visible (treated to 2.6A). With increasing current, the amount of carbon nanotubes on the surface is reduced and larger copper oxide areas develop (see Fig. 8B, treated to 2.8A), until the complete surface is covered in copper oxide and no carbon nanotubes are visible. Destruction of the surface and imaging of the lower layer reveals that the carbon nanotubes are covered and surrounded by a thick
- 20 oxide layer. In Fig. 8C (treated to 3.0A), the surface below the cuprous oxide has been

imaged. Carbon nanotubes are clearly visible on this interlayer surface. Some of the carbon nanotubes are closely intervened with the oxide.

Images of both samples treated up to the breaking point are shown in Figs. 9A and 9B (treated to 3.2A for the pure and 3.4A for the coated wire respectively). On the uncoated copper wire's surface large copper grains were formed. In contrast, the carbon nanotube wire's surface consisted of a more dendritic structure. No carbon nanotubes could be found on the surface. This indicates a slower diffusion in the carbon nanotube coated material, which allowed for finer reassembly of the Cu grains.

The observed formation of an initial Cu_2O layer and the subsequent development of CuO on the surface is in agreement with the generally observed oxidation of copper wires at elevated temperatures. De Los Santos Valladares et al. observed oxidation behaviour during exposure of thin Cu layers to high temperatures that is in agreement with the observations made in this experiment. It supports the hypothesis of initial development of Cu_2O and subsequent CuO formation. They explained the oxidation process by the initial adsorption of oxygen atoms onto the copper surface, followed by nucleation of oxides, preferably on structural defects. These initially small oxide islands grow into a surface-covering layer and, for further increase of the oxide layer, diffusion is required. De Los Santos Valladares et al. assume Cu diffusion from the Cu layer to the oxide/oxygen interface as oxidation rate determining factor. They assume that, once the Cu layer is completely consumed, formation of CuO starts. Cu_2O and CuO formation will be overlapping in our work as the wire under test is significantly larger than material tested by De Los Santos Valladares et al. They also investigated electrical resistance versus annealing temperature and found four dominant regions, namely $\text{Cu} + \text{Cu}_2\text{O}$, Cu_2O , $\text{Cu}_2\text{O} + \text{CuO}$ and CuO . The first region showed an exponential increase of resistance with temperature, which comes to a halt once all the Cu is consumed and stays constant in the pure Cu_2O region, until a decrease in resistivity for the $\text{Cu}_2\text{O} + \text{CuO}$ region is found. This decrease is commonly observed in the oxidation process of Cu and

not yet fully understood at the time of writing. The last region also shows an initial decrease in resistance, followed by a high increase for temperatures above 800°C.

Experiment 7

5 In order to understand the formation of oxides on the wire's surface and the effect of the carbon nanotube coating more thoroughly, the current was cycled up to 2.6A for an increasing number of cycles next. The resistance of an uncoated copper wire and a coated copper wire during 20 cycles is shown in Figs. 10A and Figs. 10B respectively. The darkest shade curve shows the first cycle, the lightest one the last. One can see
10 that the resistance is increasing with increasing cycle number, more so for the uncoated copper wire than for the carbon nanotube coated one. In order to understand the cause of this, SEM images were taken at each of the cycling steps and representative SEM images are shown in Figs. 11A-11F.

15 It is evident that, with increasing cycle numbers, the surface coverage with copper oxide increases. After two cycles (Fig. 11A), most of the surface is still uniformly covered in carbon nanotubes, only disrupted by a few spots of copper oxide. After one more cycle, about half of the surface is covered in carbon nanotubes and an image of the interface reveals incorporation of the carbon nanotubes into the copper oxide layer (Fig. 11B).
20 With further increase of the number of cycles, more and more of the outer surface is covered in copper oxide and the carbon nanotubes are absorbed into the oxide layer, until, after 20 cycles (Fig. 11C), all the carbon nanotubes are found at the bottom of the copper oxide layer, sandwiched between the copper oxide layer and the underlying copper wire.

25

The uncoated copper wire undergoes a similar transformation with increasing number of cycles. In Figs. 11D-11F the evolution of the copper oxide layer on an uncoated copper wire with increasing number of cycles is shown. The interface images show an increase in the thickness of the copper oxide layer with number of cycles (Fig. 11D through to Fig.
30 11F). In Fig. 11F, whiskers can additionally be seen on the surface of the wire.

In Figs. 12A-12D, a secondary electron image and EDX images of different elemental components of the carbon nanotube coated copper wire's interface after 18 cycles are shown. Carbon nanotubes are embedded within the copper oxide layer at the interface
 5 between the oxide layer and the copper wire.

These results are in agreement with the above described formation of enclosure of carbon nanotubes in the oxide network. Both the carbon nanotube coated wire and the uncoated copper wire show increasing amount of oxide on the surface. The carbon
 10 nanotube coating acts as a barrier between the oxide and the copper wire and could potentially have reduced the growth of further oxide due to suppressed copper and oxygen diffusion to the copper/copper oxide interface.

Experiment 8

15 In order to understand the dynamics of the process better, single cycle measurements with high point density were conducted. The current was slowly increased to the respective failure points and the resistance versus current curves fitted with models for the growth dynamics of CuO and Cu₂O on the wires' surface.

20 Plots for both a carbon nanotube coated copper wire and an uncoated copper wire, treated up to their failure point at around 2.7 A, is shown in Fig. 13. The plot has been divided into four distinct regions, relating to different stages of oxidation of the wire.

In order to model the behaviour of the resistance in region II, the current was related to
 25 the temperature of the material, as no oxidation occurred and an increase of resistance was ascribed purely to heating of the material:

$$R(I) = R_0 + R_0 \alpha_0 \rho / (S D A^2) I^2,$$

with the resistance R_0 , temperature coefficient α_0 , both at room temperature, the specific heat S , the cross sectional area A , the density D and the resistivity ρ .

Fitting of the data to the model yielded:

$$R_{CNT,b(I)} = (0.139 \pm 0.001) + (0.0224 \pm 0.0005) I^2$$

for the carbon nanotube coated copper wire and:

$$R_{Cu,b(I)} = (0.143 \pm 0.002) + (0.0233 \pm 0.0003) I^2$$

5 for the uncoated copper wire respectively.

The carbon nanotube coated copper wire shows both a lower intersection with the y-axis, and hence a lower initial resistance value, as well as a lower slope, resulting in a reduced increase of resistance with current compared to the uncoated copper wire.

10

The resistance behaviour in region III is dominated by the onset of Cu_2O growth and the resulting reduction of metallic copper material for low resistance conduction.

The resistance in this region is assumed to be proportional to the sum of the resistance of the unoxidised copper conductor, which is continuously heating up due to the Joule heating shown in region III and an additional resistance term caused by the reduction in conducting material available due to the formation of the Cu_2O layer on top of the wire.

The resistance at a certain current, in accordance with the exponential increase indicated by De Los Santos Valladares⁹ in the $Cu + Cu_2O$ region, and the afore derived parabolic relation between temperature and current, is given as:

20

$$R(I) = R_{b(I)} + n \exp[m I^2],$$

where n and m are constants including both the growth of the Cu_2O layer and the dependence of the resistance of this layer on the temperature.

For the carbon nanotube coated copper wire, the fit yielded:

$$25 \quad R_{CNT,c(I)} = R_{CNT,b(I)} + (0.00066 \pm 0.00005) \exp[(0.74 \pm 0.02) I^2],$$

and for the uncoated copper wire:

$$R_{Cu,c(I)} = R_{Cu,b(I)} + (0.00061 \pm 0.00001) \exp[(0.82 \pm 0.02) I^2].$$

The pre-factor in the exponent can be interpreted as an efficient activation energy for the growth process of the oxide layer, indicating a lower value for carbon nanotube coated

30

copper wire which explains the decreased deterioration of the carbon nanotube coated copper wire with applied current.

In region IV, an onset of CuO growth was found. This accounts for the further increase in

- 5 R. The copper wires all behaved fairly similar, with a strong increase in resistance after 2.6A and the failure shortly after.

Carbon nanotube coated copper wires showed a much more moderate increase in resistance with increasing current. This can be explained by the lower rate of oxidation
10 due to suppression of diffusion by the presence of carbon nanotubes. The dependency of the resistance on current in this region additionally strongly varied between the coated wires. Some coated wires (cf. CNT7 in Fig. 13) showed an additional dip in increase at around 2.75A ($\sim 0.5 \Omega$). This was not observed for CNT9 and only moderately for CNT10.

- 15 When comparing SEM images of these samples, one has to make sure to compare images with roughly the same distance to the breaking point of the sample, as this point will be the one with highest temperature and hence biggest effect on the wires' structure.

- Images of sample CNT9 are shown in Figs. 14A and 14B, for a point close to the
20 (longitudinal) middle of the wire (Fig. 14A) and about a half way towards the middle (Fig. 14B). The image close to the middle shows no carbon nanotubes, the image taken further away, below the oxide layer on top, shows carbon nanotubes in close proximity to the underlying copper wire and with additional spheres of copper on top.

- 25 For CNT10, about half way from the middle, the same carbon nanotube image as for CNT9 was obtained. Closer to the middle of the wire, carbon nanotubes could be found on the copper/copper oxide interface, which were closely intervened with the Cu layer and partially consumed or enclosed within a Cu layer (Fig. 14C and 14D). Fig. 14C shows the surface closer to the middle of the wire where carbon nanotubes can be seen

between the Cu particles. Partial consumption of the carbon nanotubes as well decoration with Cu particles is visible.

The images of CNT7 show a change of the coating with decreasing distance to the middle of the wire. About halfway from the middle, carbon nanotubes are plenty and in close proximity to copper spheres (as shown in Figs. 15A and 15B). Some of the carbon nanotubes pierced through copper spheres and close interfaces were observed. In Fig. 14E, at a position closer to the middle, the size of the copper islands had grown and covered carbon nanotubes partially, until, as shown in Fig. 14F, fewer carbon nanotubes were visible on the surface. They seemed to have been absorbed into the copper matrix and partially also consumed in this process.

From the observation of different carbon nanotube coated wires during the last phase before failure, slow absorption of the carbon nanotubes into the copper wire's matrix seems to be the main cause for the dip in increase in resistance. Especially the non-presence of carbon nanotubes in the middle of the wire in sample CNT9, which did not show a dip, and the different stages of carbon nanotube consumption close to the middle of samples CNT10 and CNT7 support this hypothesis. CNT7, which performs better than sample CNT10, has less consumed CNTs on its surface than sample CNT10.

We assume that the carbon nanotubes additionally act as heat sink at this stage, supporting the reduction of increase of R.

We identified four regions in the destruction process of the wires. An initial region (0-0.14 Ω), followed by a region in which the resistance was dominated by a response to the increased temperature ($\sim$ 0.14-0.21 Ω). The third region demarked the onset of Cu₂O growth ($\sim$ 0.21-0.45 Ω), the last one is dominated by Cu growth ($>$ 0.45 Ω). This development was seen both in the resistance response as well as in SEM/EDX characterisations. These improvement of carbon nanotube coated wires over uncoated copper wires was mainly attributed to reduced oxidation of the surface, followed by subsequent slower oxidation of the complete wire structure. Initially due to the protection

of the surface by carbon nanotubes, then by reduced diffusion of oxygen and copper through the copper structure, as the carbon nanotube sank below the copper oxide layer and formed a barrier between the copper wire and the oxidation layer. Additional effects of reduced temperature, i.e. carbon nanotubes acting as heat sink within the copper matrix are also possible mechanisms for the benefits provided by the present invention.

Experiment 9

Copper wires were coated with a coating of thickness $<10\mu\text{m}$ comprising carbon nanotubes. The coated wires were then subjected to a heat treatment by resistive heating in air. Samples were subjected to a heat treatment current density of $283\text{A}/\text{mm}^2$ for a range of different times. Another set of samples were each subjected to different heat treatment current densities for 60s. The thickness of the oxide layer for each of the samples was measured using an SEM to image the cross-section of the coated wires in the thickness direction. The distance of diffusion of the carbon nanotubes through the interface between the copper-based conductor and the coating was also measured using SEM imaging.

Fig. 16A shows the effect of heat treatment current density on the thickness of the barrier layer (oxide layer). It can be seen that for a heat treatment current density of $246\text{ A}/\text{mm}^2$ the thickness of the barrier layer is about 220 nm. In contrast, for the heat treatments performed at current densities above $285\text{ A}/\text{mm}^2$, the thickness of the barrier layer appears to have plateaued at a higher level. As also suggested by Fig. 5, the highest heat treatment current densities do not produce the optimal increase in conductor lifetime

Fig. 16B shows the average distance the nanowires have migrated into the copper wires at the interface between the coating and the copper wire after being subjected to the different heat treatment current densities. The average migration distance is measured by analysing SEM images of cross-sections of the coated conductor.

Fig 17A shows the effect of heat treatment duration on the thickness of the barrier layer formed. These experiments show that after 30s a 2.5µm barrier layer is formed in the coating. Heat treatment times longer than 60s show that the thickness of the barrier appeared to plateau at a higher level.

5

Fig. 17B shows the distance the nanowires have migrated into the copper wires at the interface between the coating and the copper wire after being subjected to a heat treatment current density of 283A/mm² for varying periods of time. The nanowires were observed to have migrated 2µm after only 30s heat treatment time. Similar to the coating thickness, the distance of migration appears to plateau at a higher level (here about 8µm) after 60s treatment time.

10

While the invention has been described in conjunction with the experiments and exemplary embodiments described above, many equivalent modifications and variations will be apparent to those skilled in the art when given this disclosure. Accordingly, the exemplary embodiments of the invention set forth above are considered to be illustrative and not limiting. Various changes to the described embodiments may be made without departing from the spirit and scope of the invention.

15

20 All references referred to above and/or below are hereby incorporated by reference.

Non-patent document references

De Los Santos Valladares, L., et al. "Crystallization and electrical resistivity of Cu₂O and CuO obtained by thermal oxidation of Cu thin films on SiO₂/Si substrates." Thin Solid Films 520, pp. 6368–6374 (2012).

25

CLAIMS

1. A method of manufacturing a coated electrical conductor, the method including the steps:

- 5 i) providing a copper-based electrical conductor;
- ii) coating an exposed surface of said conductor with a coating comprising carbon nanotubes; and
- iii) subjecting the coated conductor to a heat treatment step in an oxidising atmosphere at a temperature of at least 200°C .

10

2. A method according to claim 1 wherein an external heat source provides the heat for the heat treatment step.

3. A method according to claim 1 wherein an electrical current is passed through the
15 copper-based electrical conductor in order to provide the heat for the heat treatment step, via resistive heating.

4. A method according to any one of the preceding claims wherein the coated conductor is subjected to the heat treatment step for at least 1 second.

20

5. A method according to any one of the preceding claims wherein the carbon nanotubes comprise multi-walled carbon nanotubes with an average length of at least 1 µm and not more than 20 mm.

25 6. A method according to any one of the preceding claims wherein the thickness of the coating is at least 1 µm, and not more than 1000 µm.

7. A method according to any one of the preceding claims wherein the coating is formed on the conductor by dipping the conductor in a coating dispersion, the coating
30 dispersion including a carrier liquid and said carbon nanotubes.

8. A method according to claim 7 wherein the coating dispersion has a concentration of carbon nanotubes between 0.1 wt% and 10wt%, based on the weight of the coating dispersion.

5

9. A method according to claim 7 or claim 8 wherein the coating dispersion also includes a surfactant with a concentration between 1 wt% and 10 wt%, based on the weight of the coating dispersion.

10 10. A method according to any one of claims 1 to 9 wherein, after the heat treatment, the coated conductor is cooled to below 100°C.

11. A coated electrical conductor comprising:

a copper-based electrical conductor;

15 a coating covering at least part of an exposed surface of said conductor, the coating comprising carbon nanotubes, wherein

an outer surface of the coating presents a barrier layer comprising copper oxide and carbon nanotubes, wherein the thickness of the barrier layer is such that a ratio between a cross-sectional area of the barrier layer and a cross-sectional area of the
20 coating, when viewed in a cross sectional plane including the thickness direction, is greater than 1% and less than 50%.

12. A coated electrical conductor according to claim 11 wherein the average thickness of the coating in a thickness direction perpendicular to the surface of the
25 copper-based electrical conductor is at least 1 µm, and not more than 1000 µm.

13. A coated electrical conductor according to claim 11 or claim 12 wherein, at an interface between the coating and the copper-based conductor, carbon nanotubes are at least partially embedded in the copper-based conductor, the spatial frequency of carbon

nanotubes crossing the interface between the coating and the copper-based conductor being at least $0.1\mu\text{m}^{-1}$, when measured along the interface.

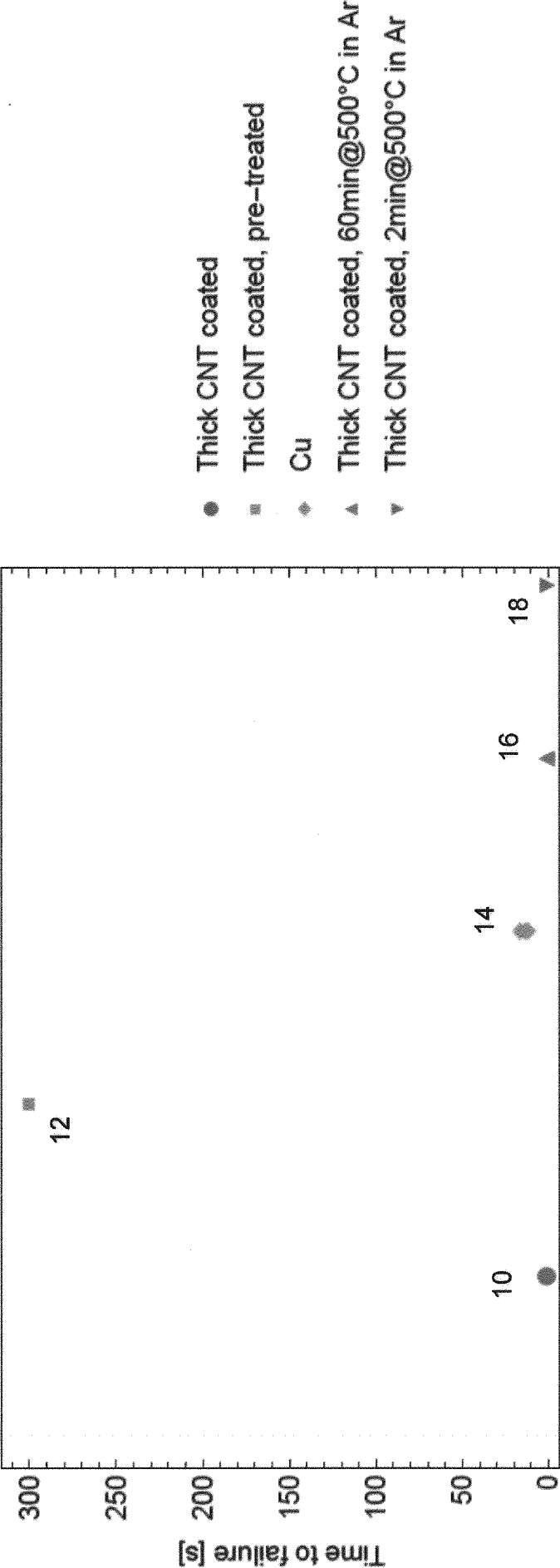
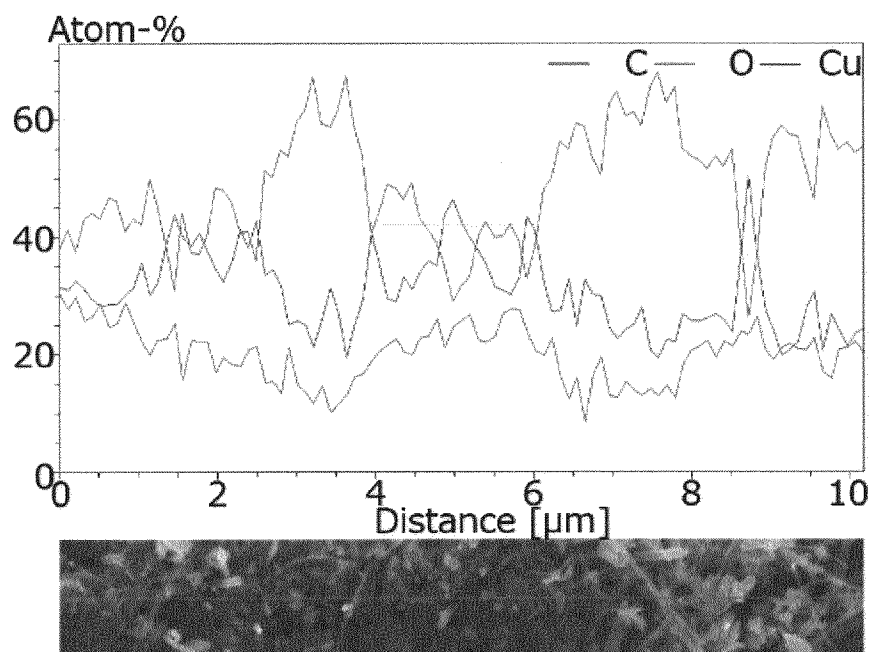
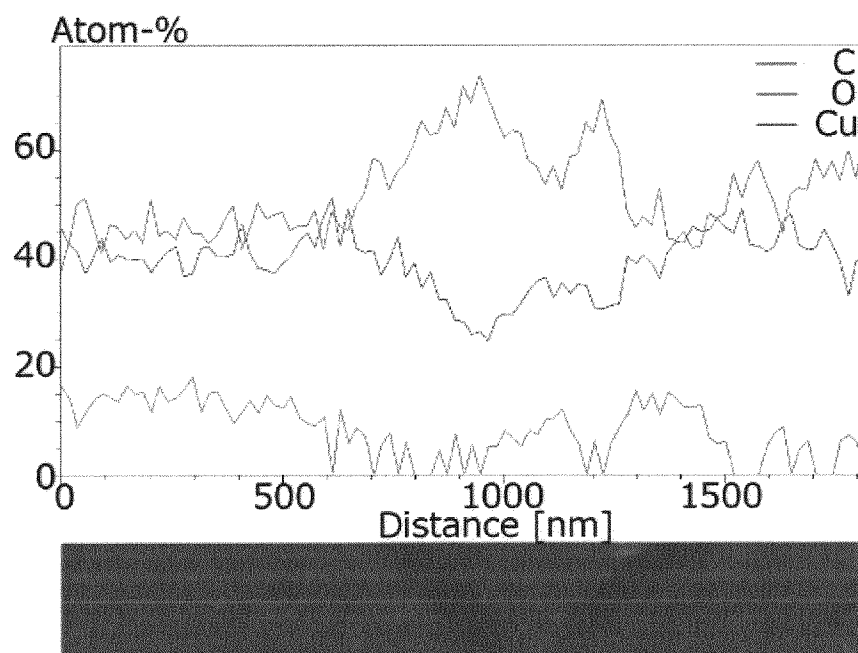
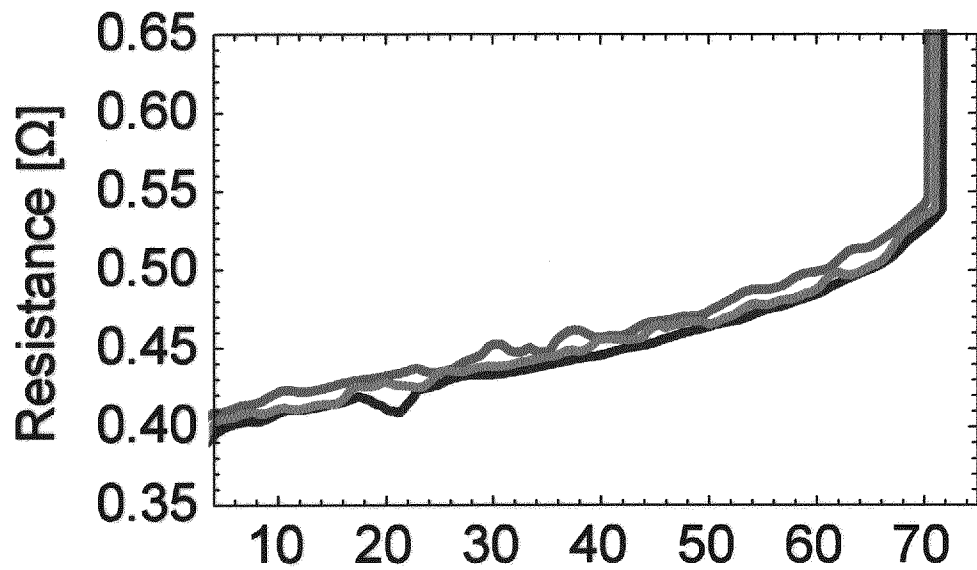


Fig. 1

**Fig. 2A****Fig. 2B**

— 3.6A — 3.6A — 3.6A, pre-treated



Time to failure [10⁴s] **Fig. 3**

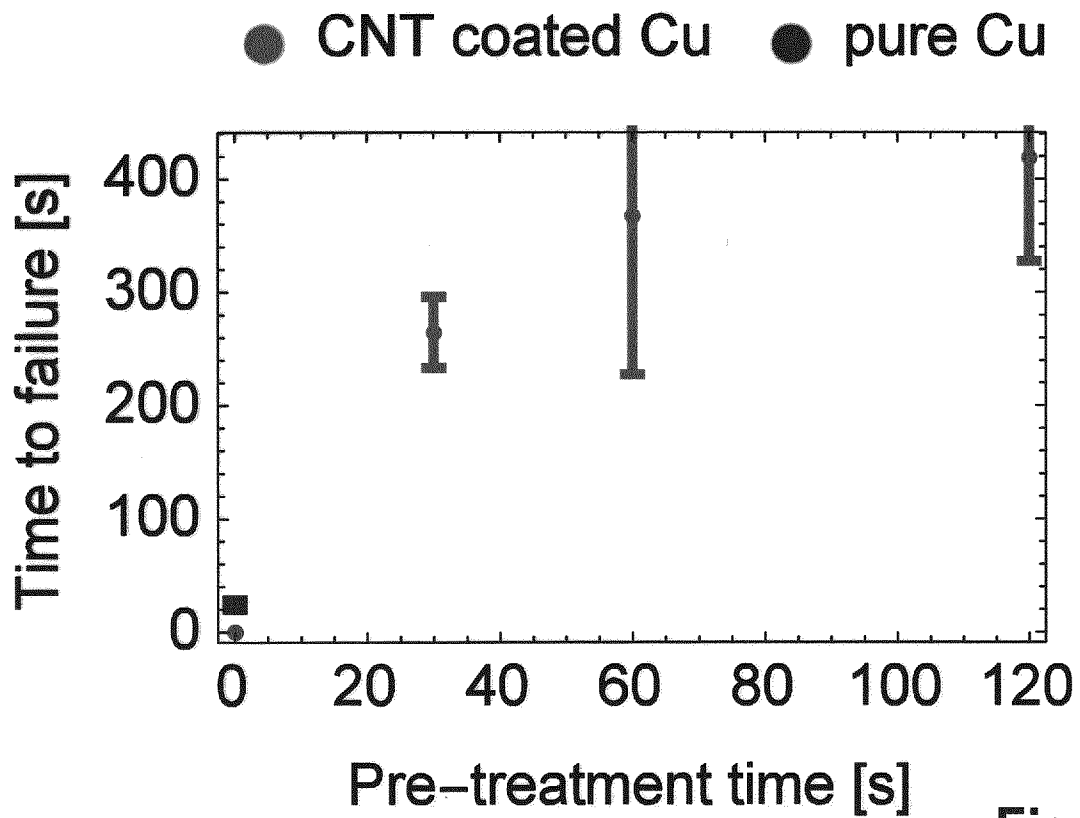
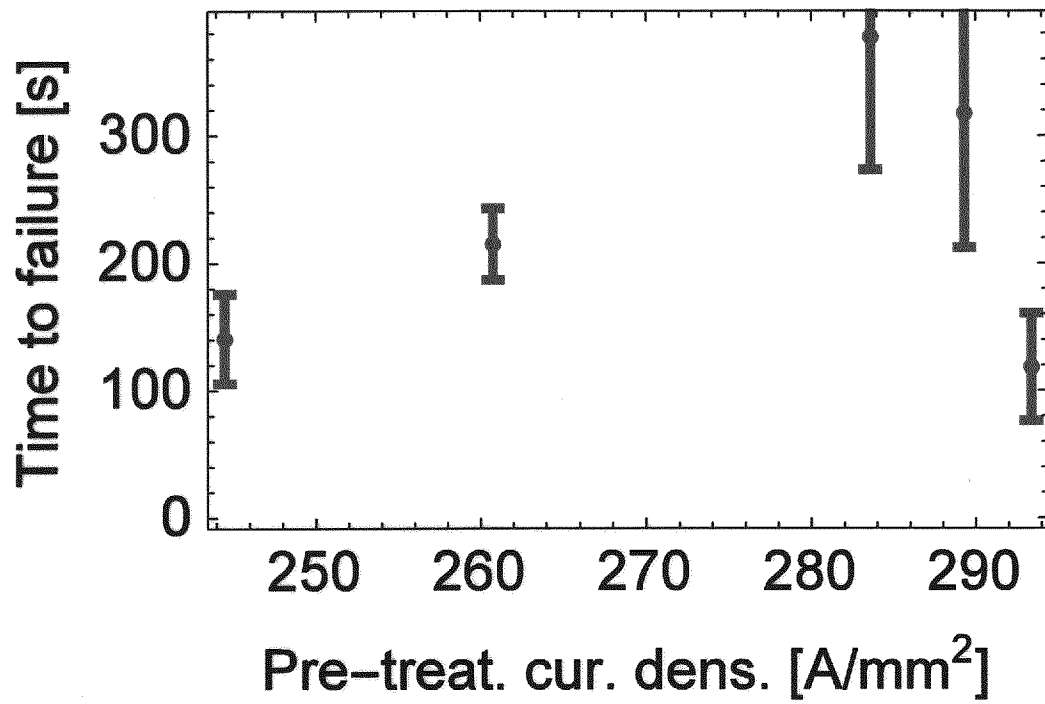
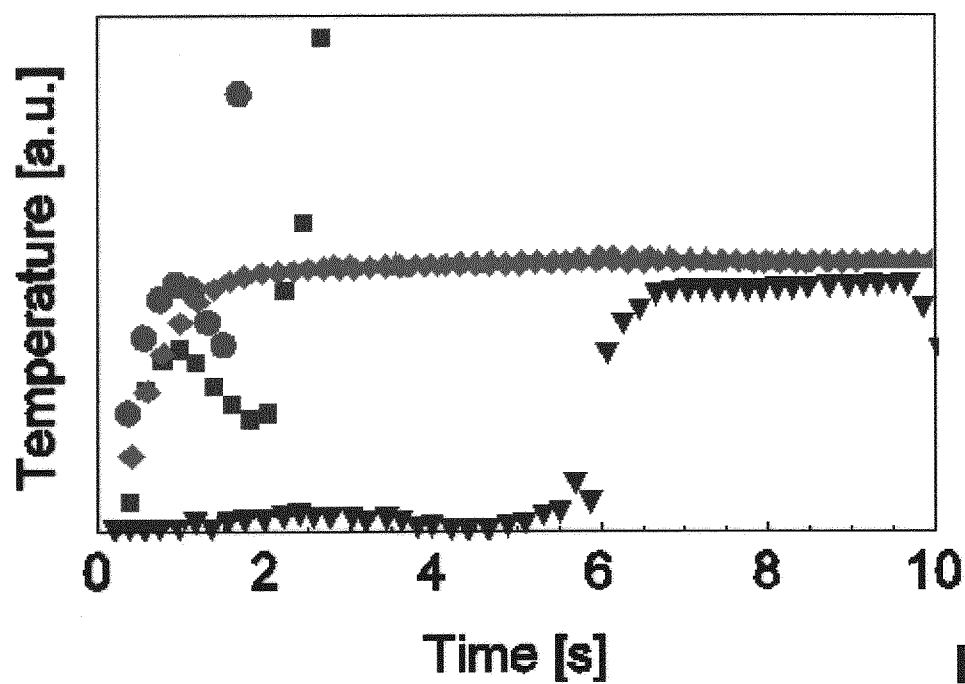
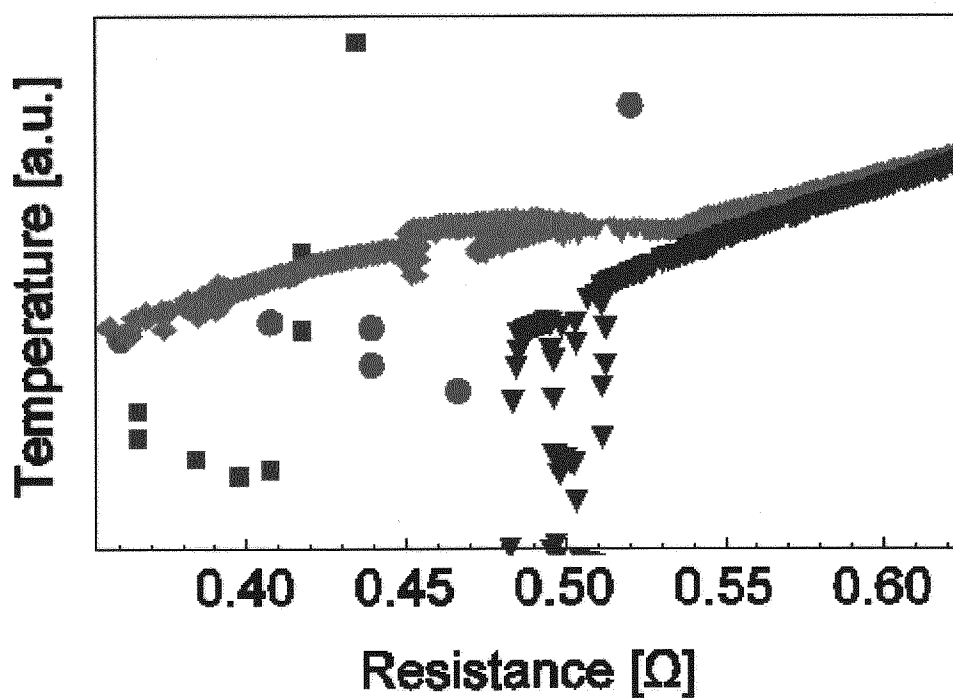
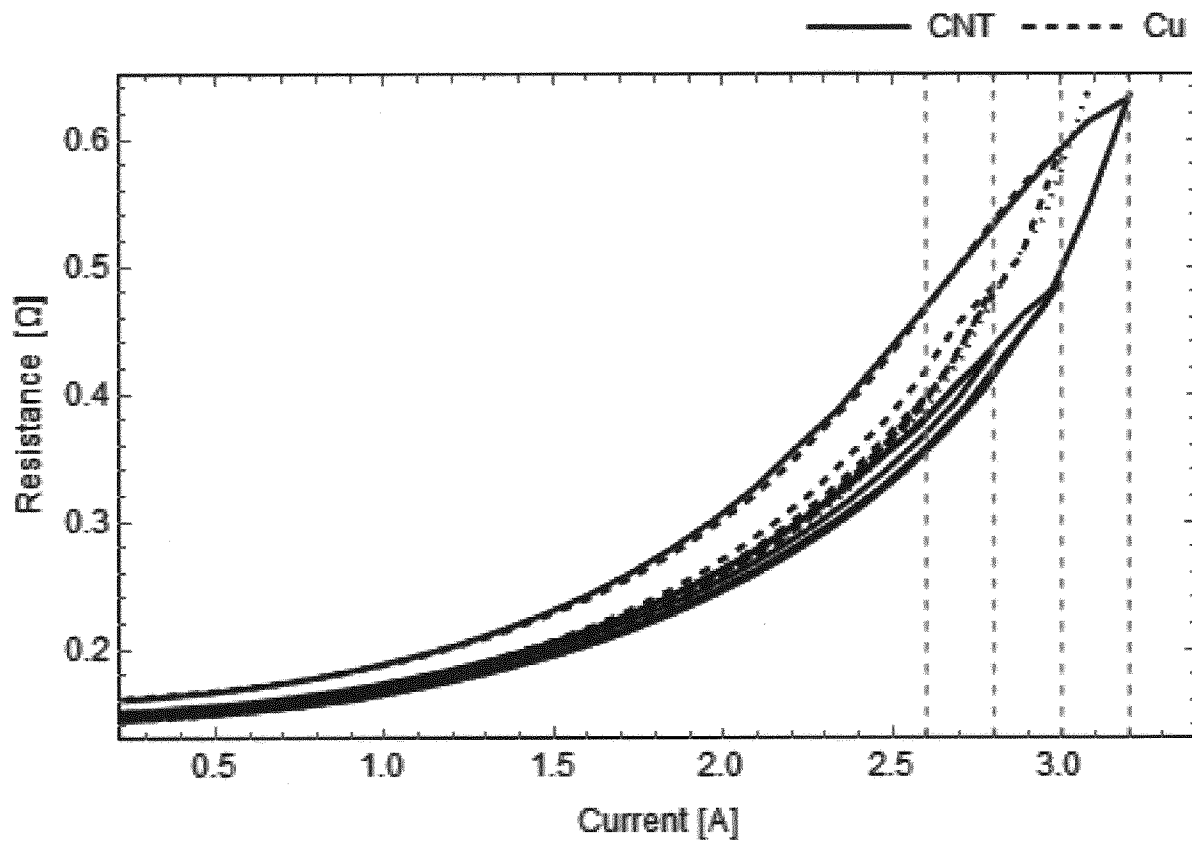


Fig. 4

**Fig. 5**

- thick ● thick
- thick, pre-treated ● bare

Fig. 6AFig. 6B

**Fig. 7**

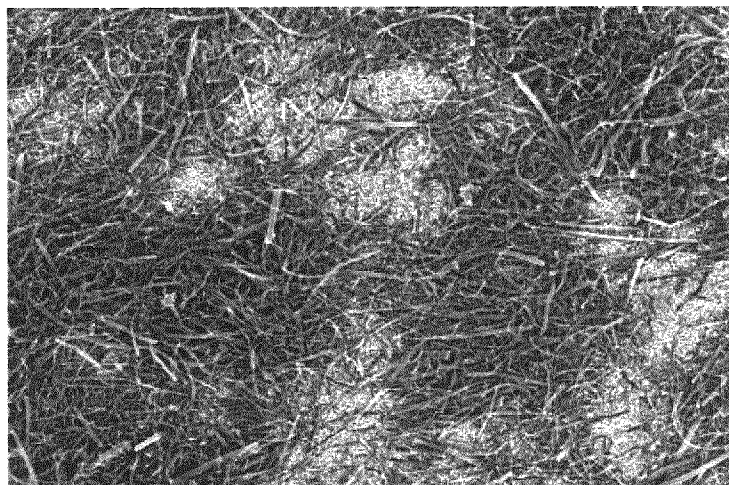


Fig. 8A

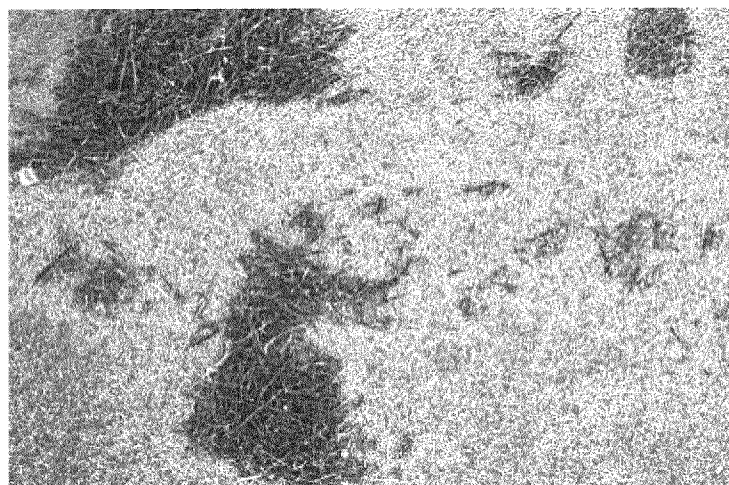


Fig. 8B

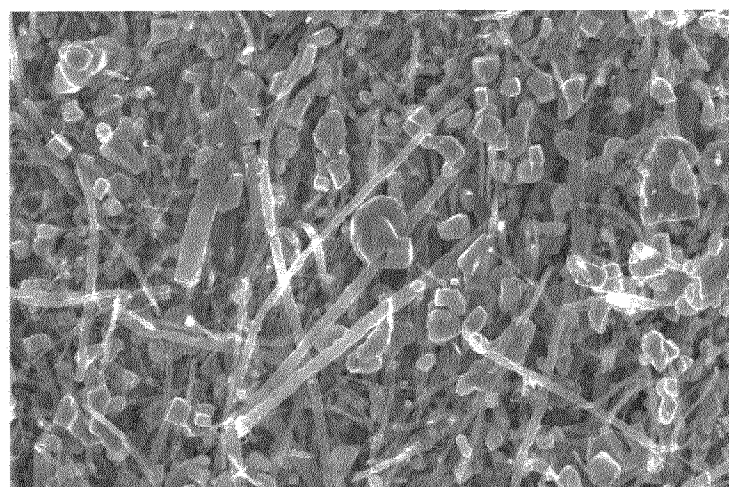


Fig. 8C

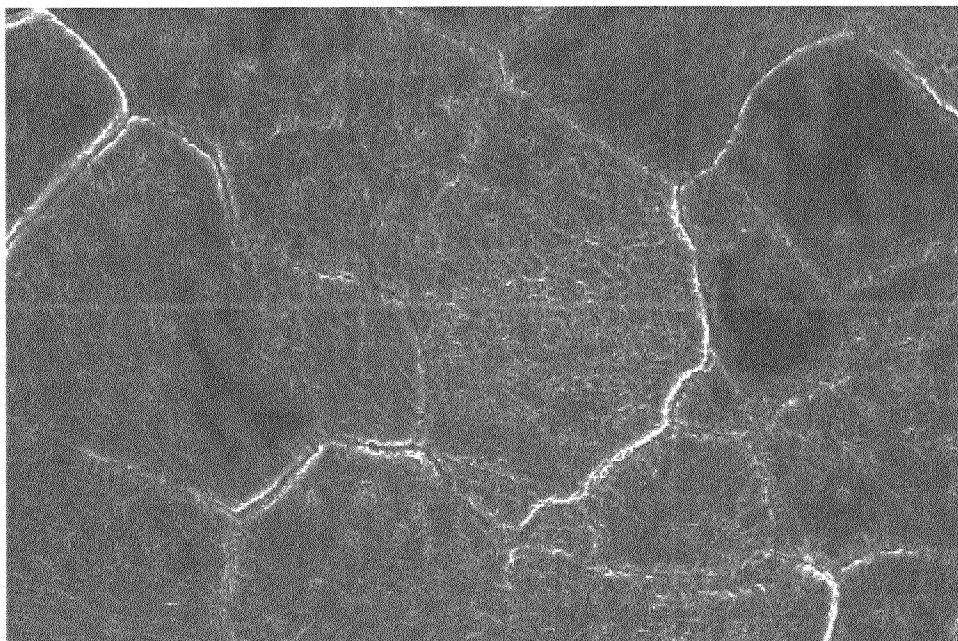


Fig. 9A

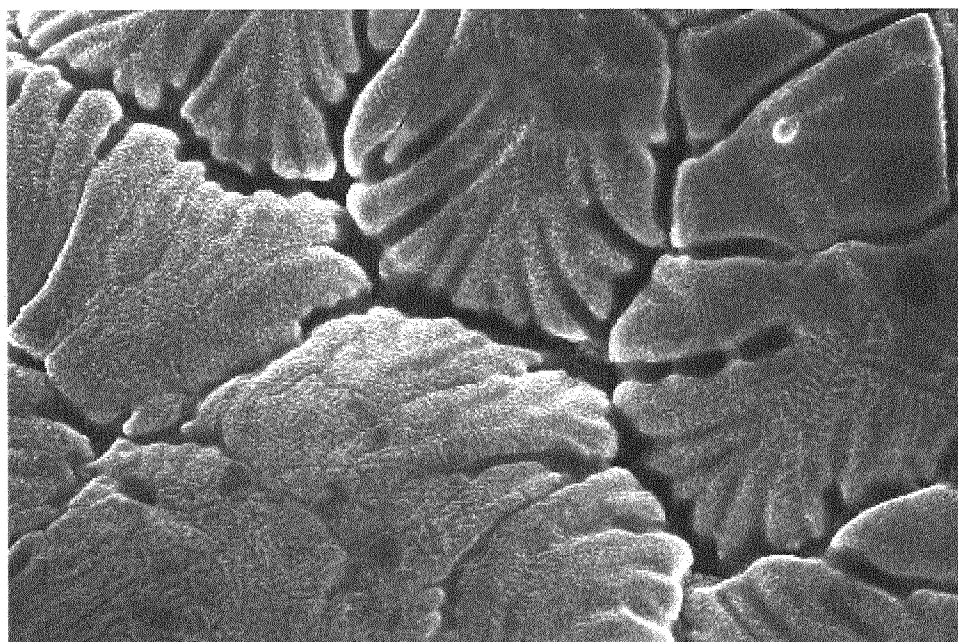
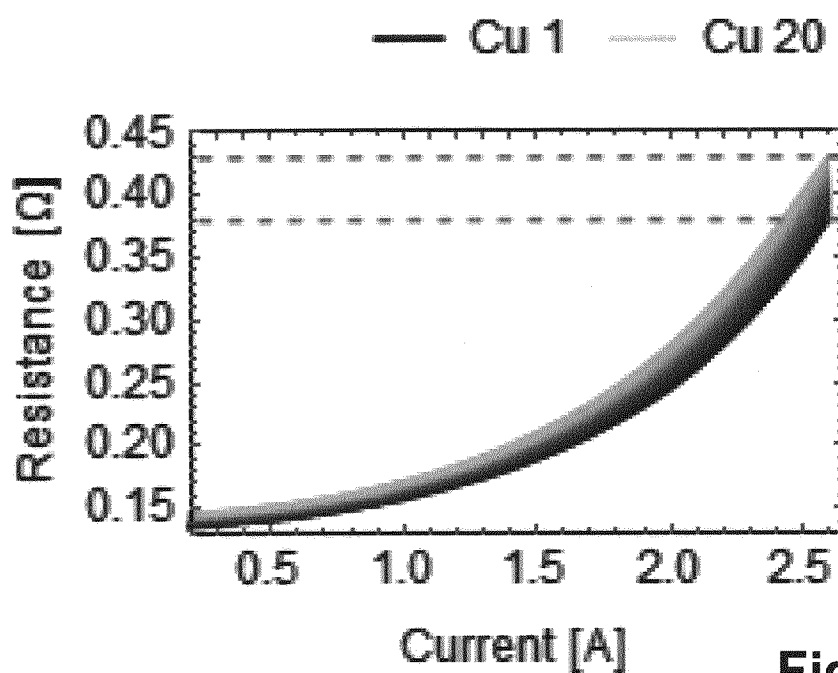
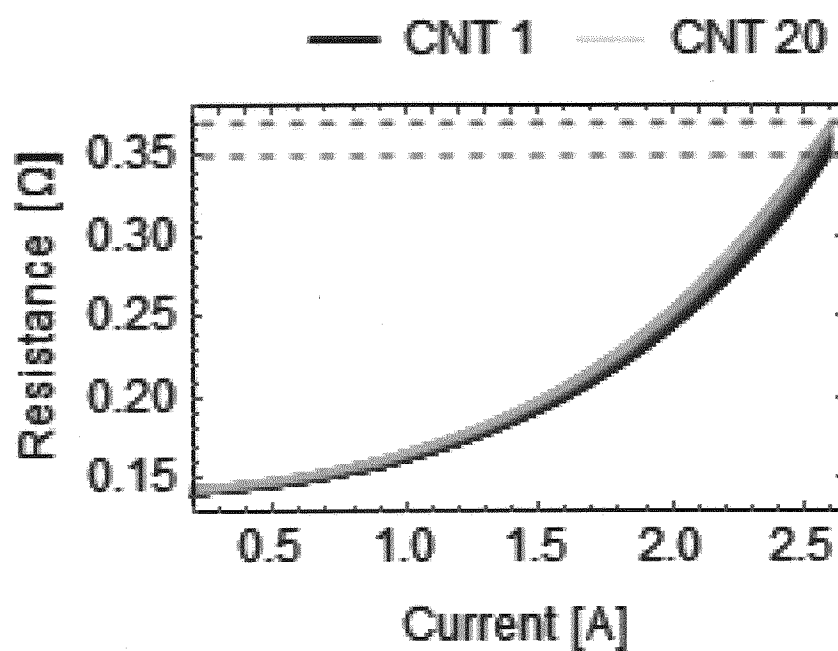
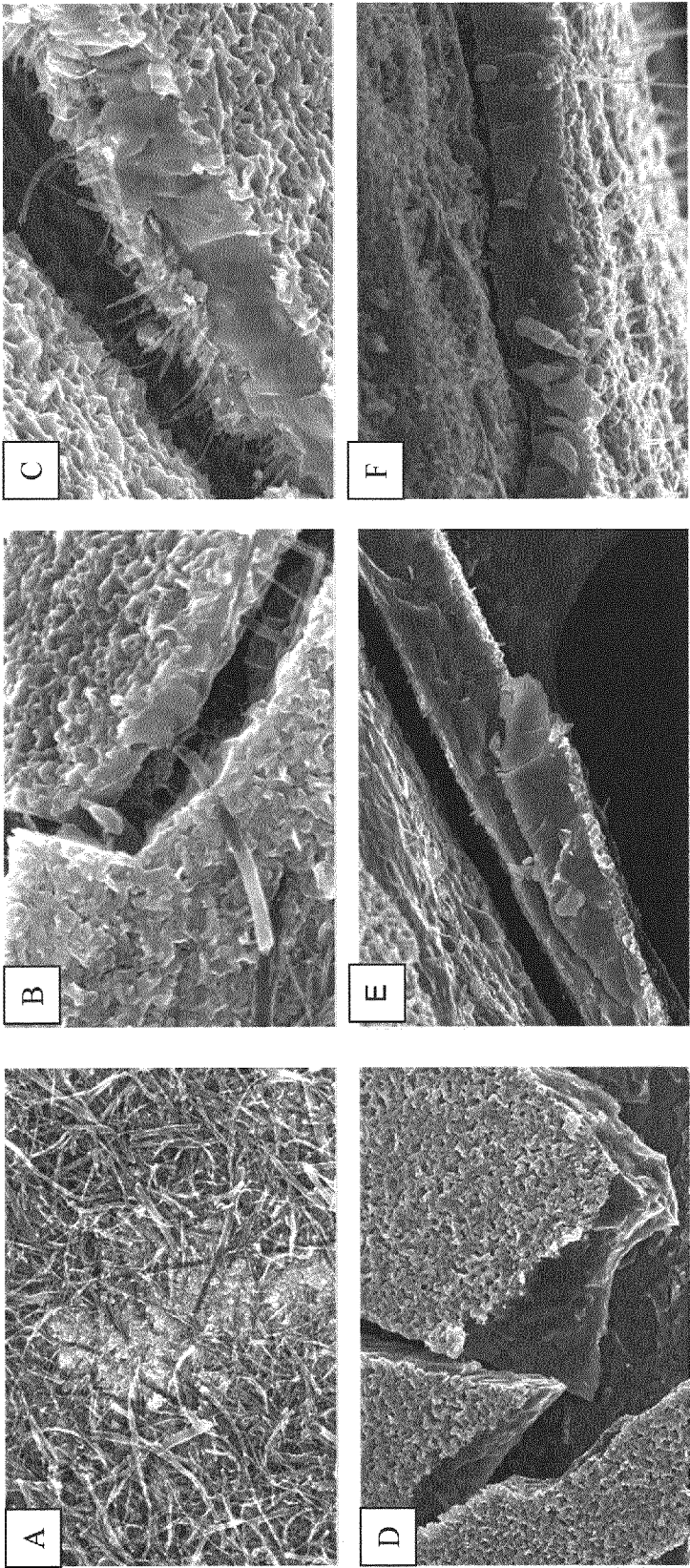


Fig. 9B

**Fig. 10A****Fig. 10B**



Figs. 11A – 11F

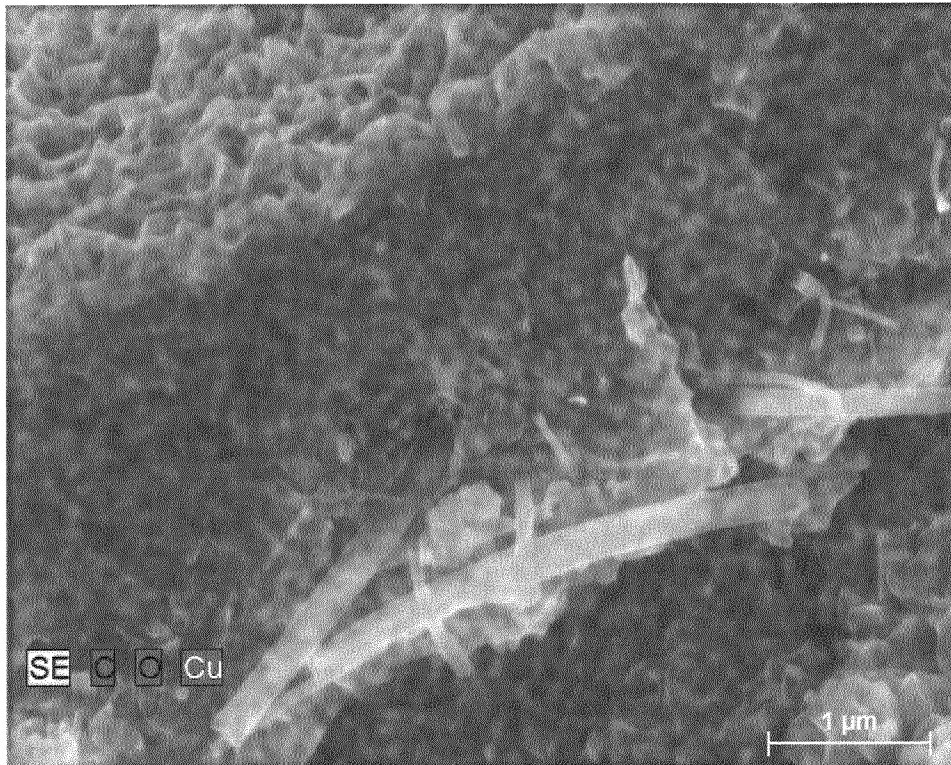


Fig. 12A

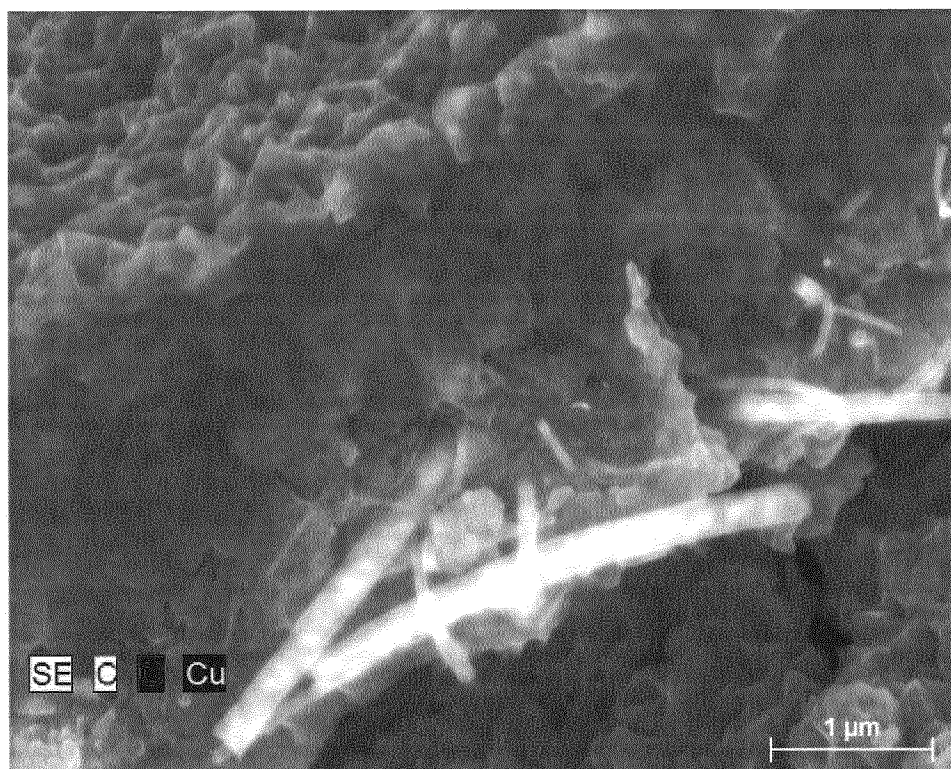


Fig. 12B

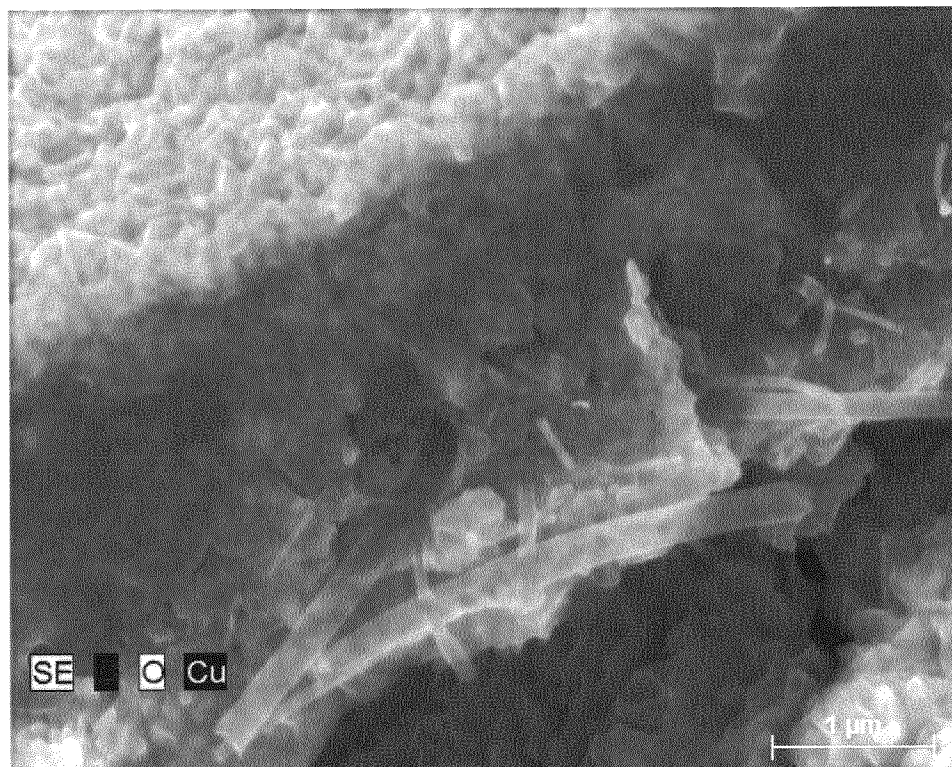


Fig. 12C

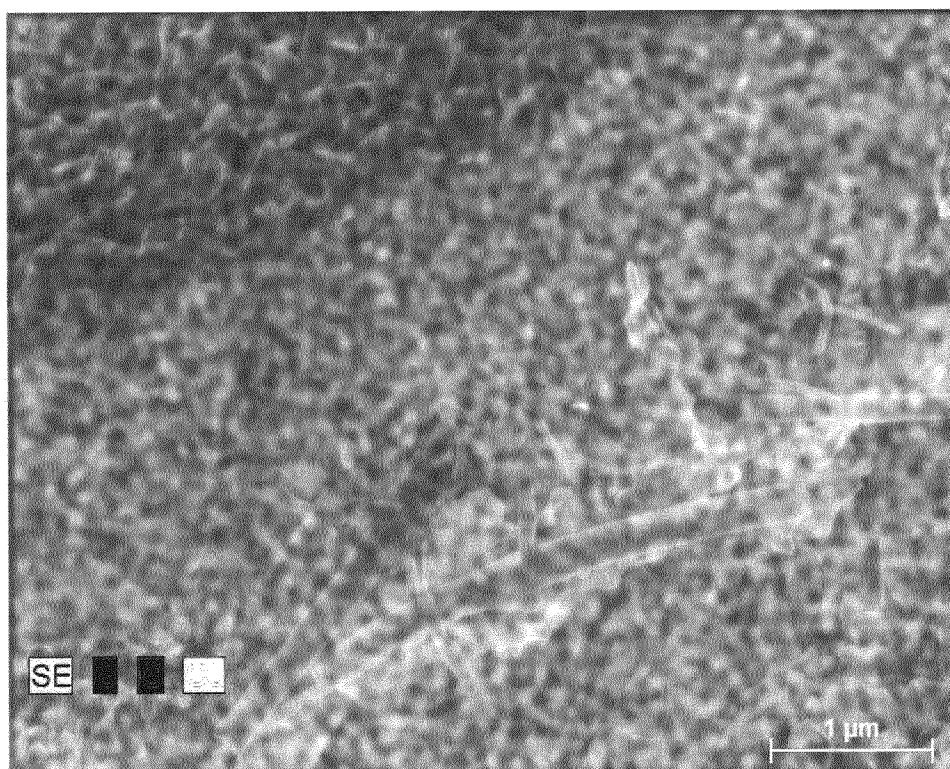
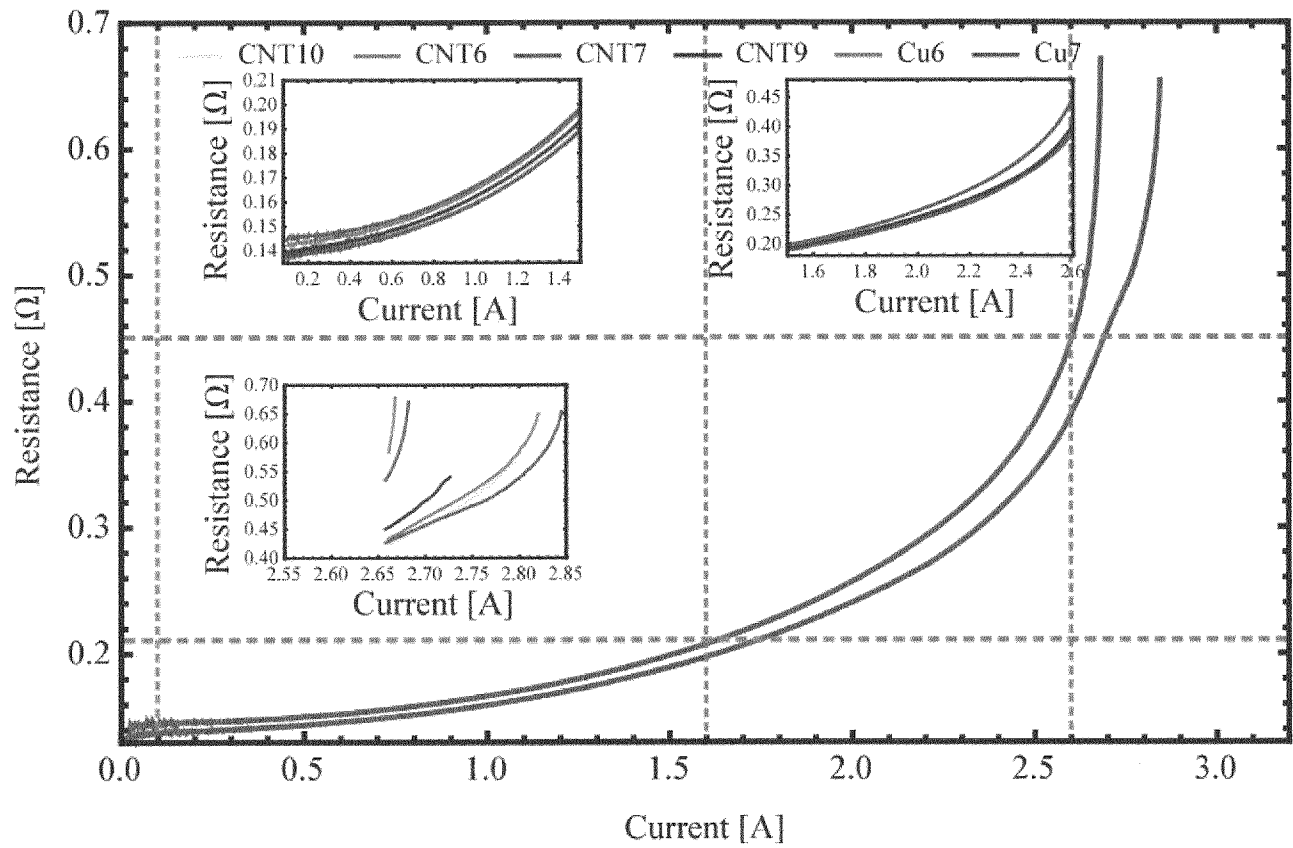
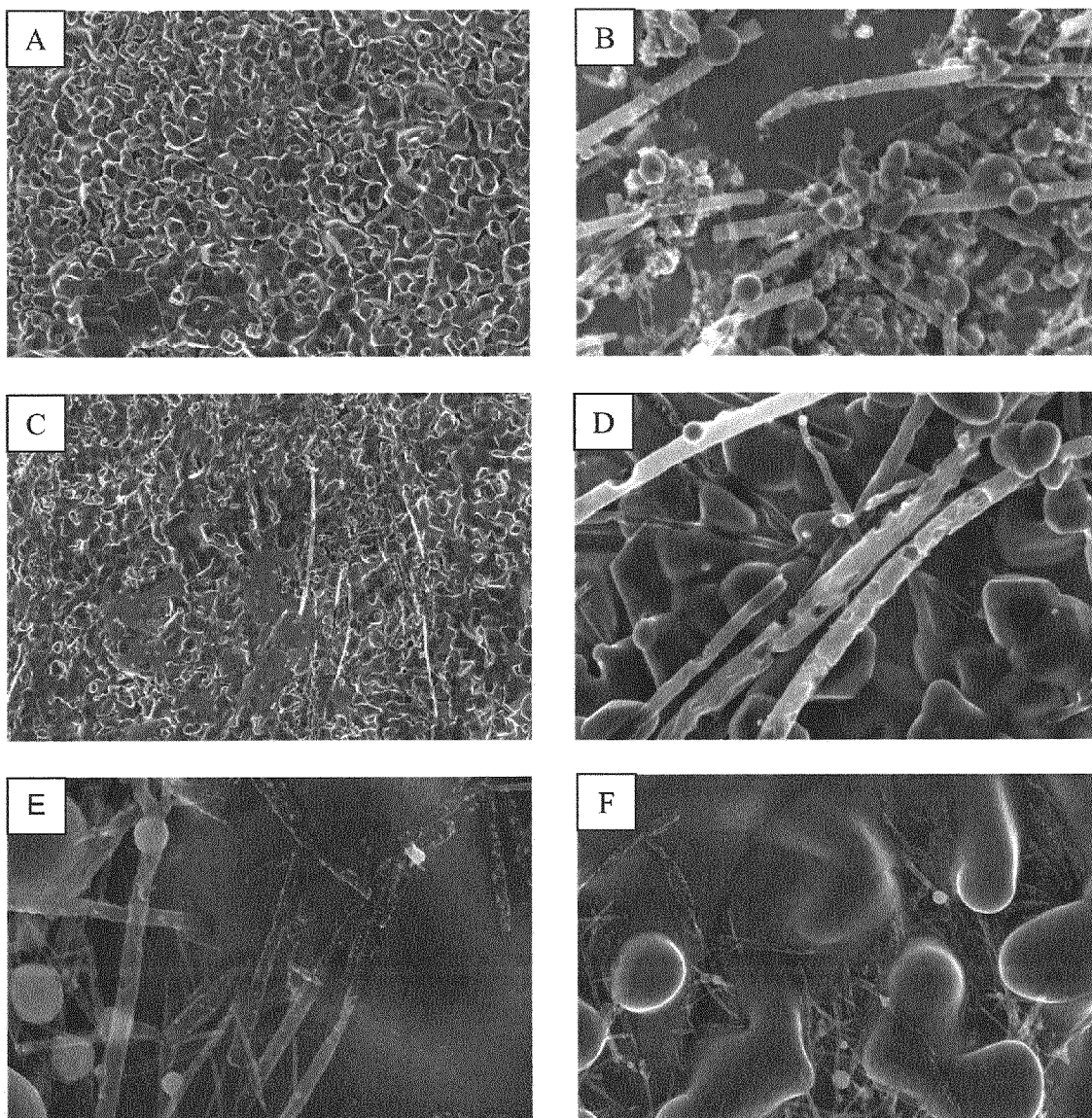


Fig. 12D

**Fig. 13**



Figs. 14A-14F

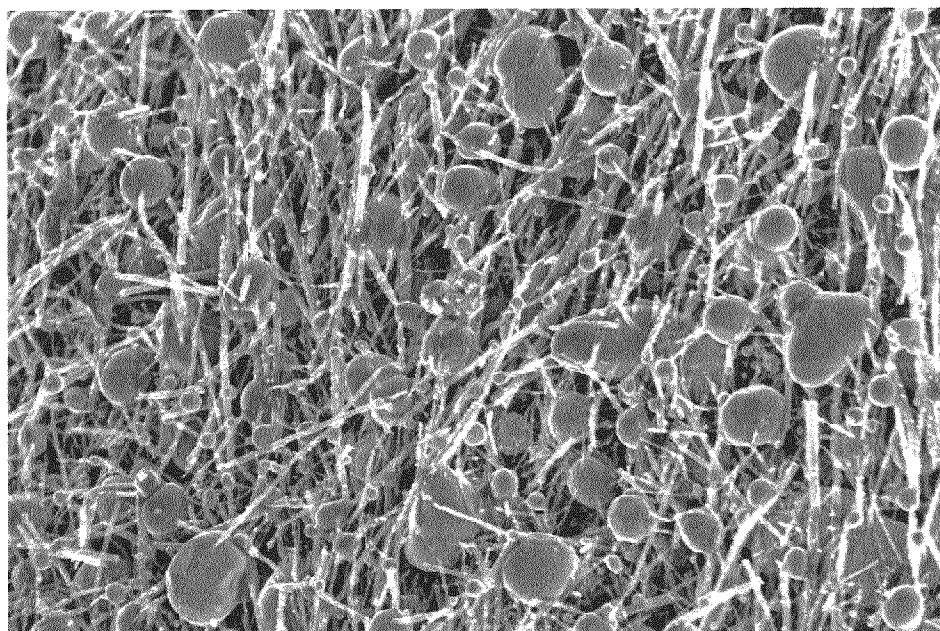


Fig. 15A

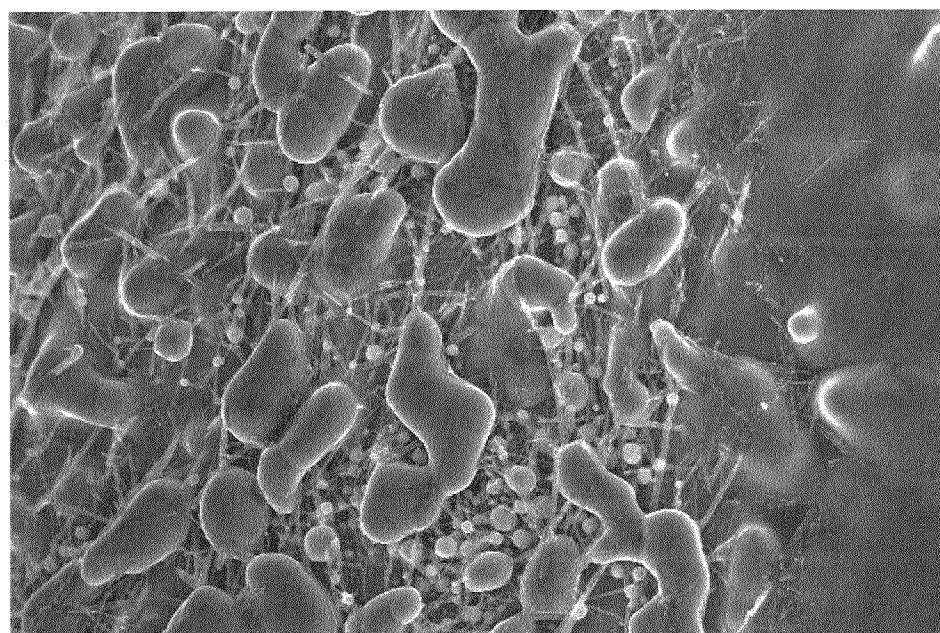
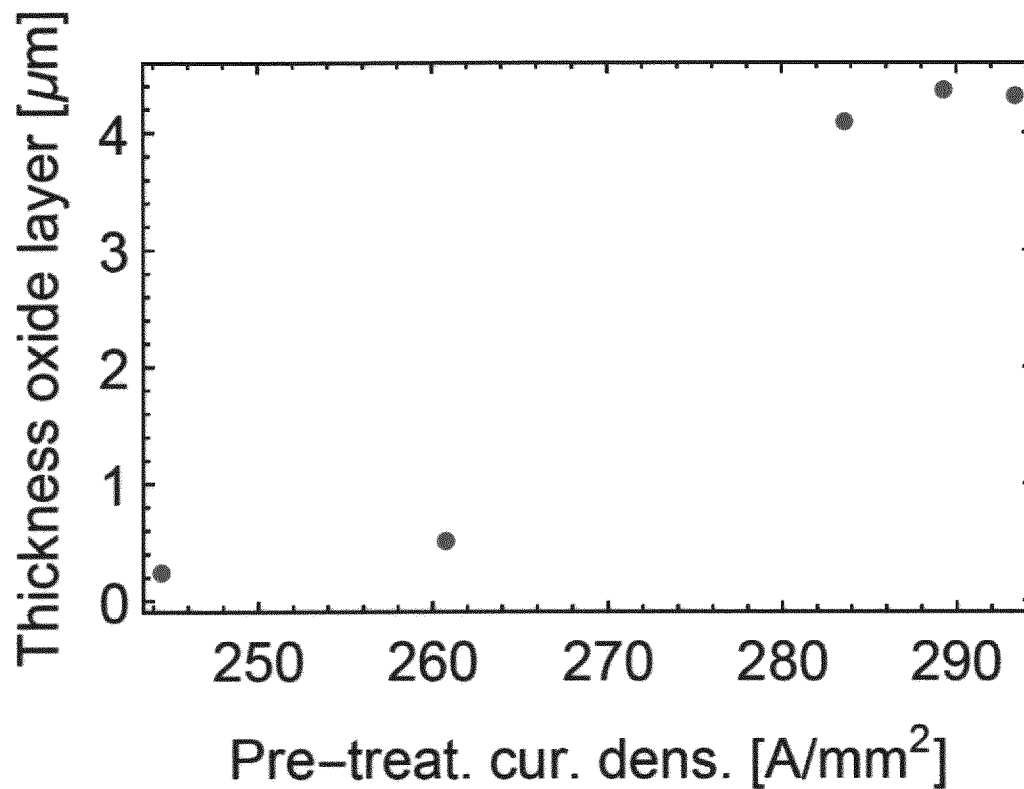
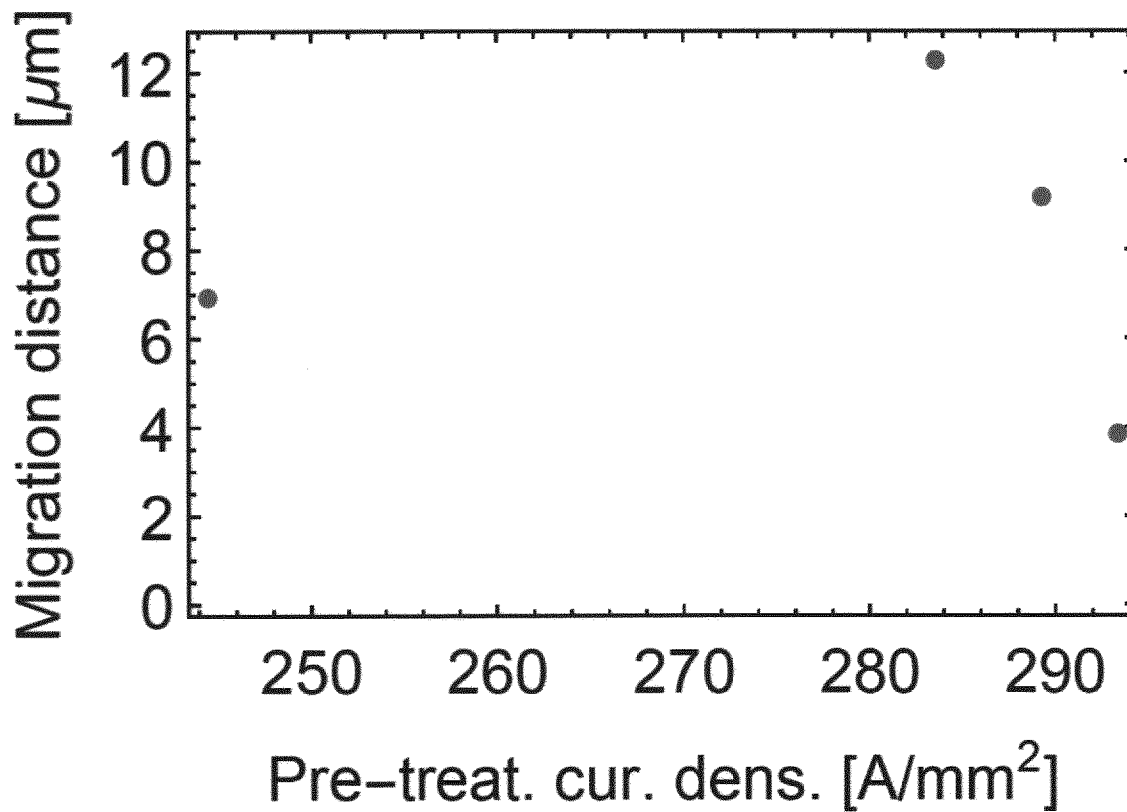
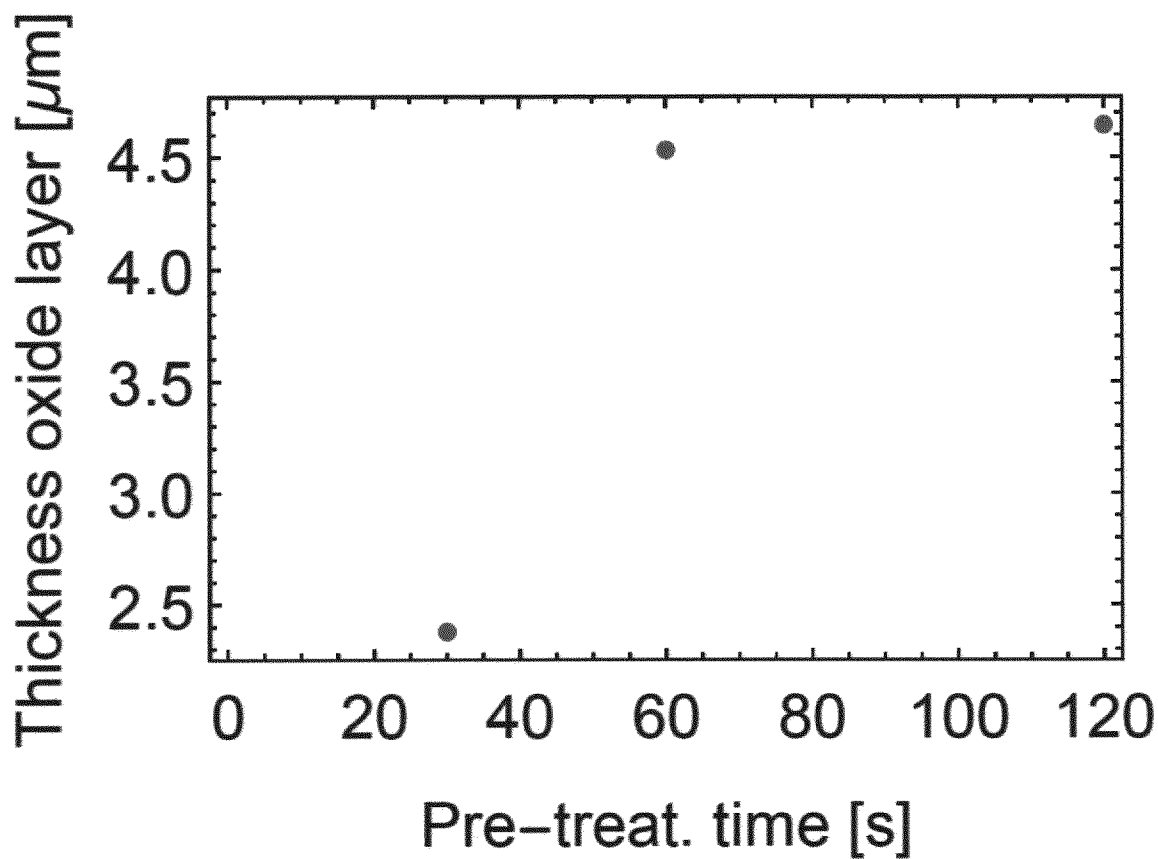
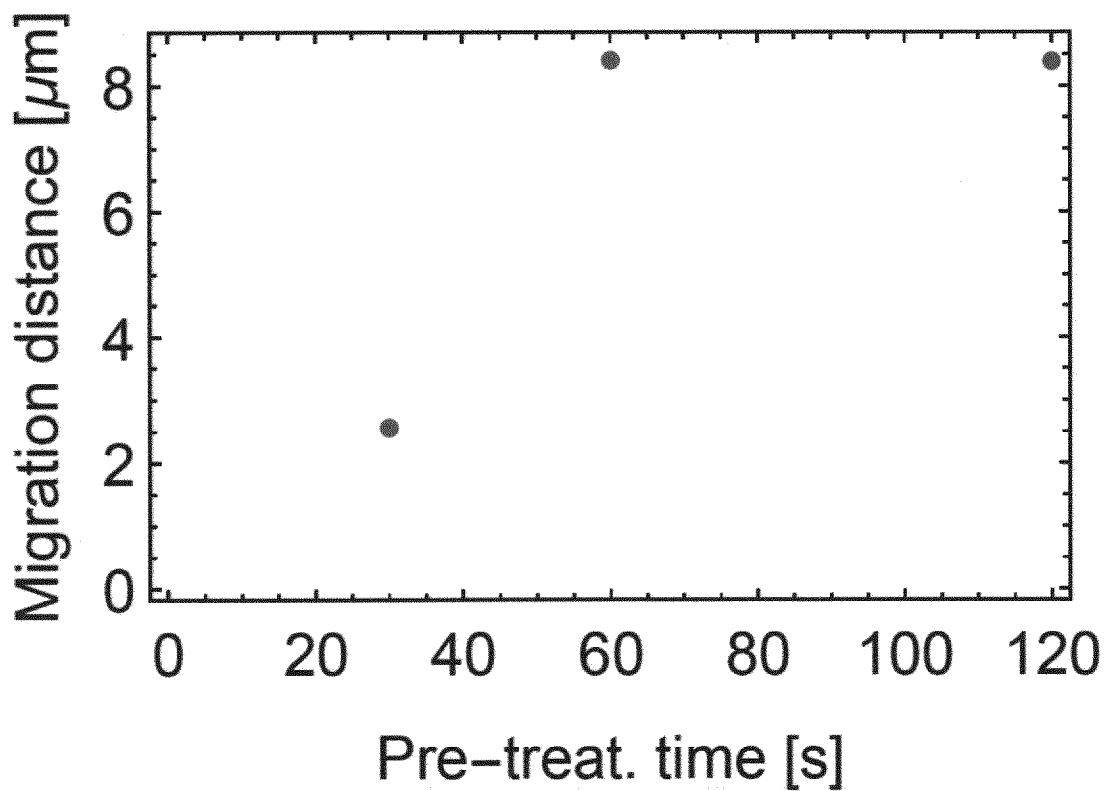


Fig. 15B

**Fig. 16A****Fig. 16B**

**Fig. 17A****Fig. 17B**

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/071472

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01B1/02 H01B1/04
ADD.

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)
H01B

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

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

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HANSUNG LEE ET AL: "High-current field emission of point-type carbon nanotube emitters on Ni-coated metal wires", CARBON, ELSEVIER, OXFORD, GB, vol. 50, no. 6, 30 December 2011 (2011-12-30), pages 2126-2133, XP028403526, ISSN: 0008-6223, DOI: 10.1016/J.CARBON.2011.12.064 [retrieved on 2012-01-11]	1-10
A	Section Experimental	11-13
A	US 2013/140059 A1 (KOLJONEN PETTERI [FI] ET AL) 6 June 2013 (2013-06-06) the whole document	1-13
	----- -/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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Date of the actual completion of the international search

22 November 2016

Date of mailing of the international search report

30/11/2016

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Mehdaoui, Imed

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/071472

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2014/189549 A2 (LOS ALAMOS NAT SECURITY LLC [US]) 27 November 2014 (2014-11-27) the whole document -----	1-13
A	US 2005/238810 A1 (SCARINGE ROBERT P [US] ET AL) 27 October 2005 (2005-10-27) the whole document -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2016/071472

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013140059	A1	06-06-2013	CN 103069501 A 24-04-2013
			EA 201390216 A1 30-07-2013
			EP 2603919 A1 19-06-2013
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			WO 2012020167 A1 16-02-2012

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			WO 2014189549 A2 27-11-2014

US 2005238810	A1	27-10-2005	NONE
