(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 818 110 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
15.08.2007 Bulletin 2007/33

(51) Int Cl.:
B05D 7/24 *(2006.01)*

(21) Application number: **06101672.1**

(22) Date of filing: **14.02.2006**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK YU

(71) Applicants:
- **The European Community, represented by the European Commission**
  1049 Brussels (BE)
- **Tethis S.r.l.**
  20121 Milano (IT)

(72) Inventors:
- **Rossi, François**
  21033 Cittiglio (VA) (IT)
- **Colpo, Pascal**
  74000 Annecy (FR)
- **Piseri, Paolo**
  20127 Milano (IT)
- **Milani, Paolo**
  27100 Pavia (IT)

(74) Representative: **Ocvirk, Philippe et al**
Office Ernest T. Freylinger S.A.
P.O. Box 48
8001 Strassen (LU)

(54) **Functionalised material and production thereof**

(57) A Polymer-cluster composite comprising nanoclusters embedded in a polymer matrix is proposed, wherein the polymer-cluster composite comprises an at least partially functionalised surface. A process and apparatus for producing such a cluster-polymer composite are also presented. The composite is formed by concurrent plasma-assisted polymerisation from polymer precursors and deposition of clusters onto a substrate. The plasma assisted polymerisation is controlled so as to achieve at least partial functionalisation of a surface of the composite.

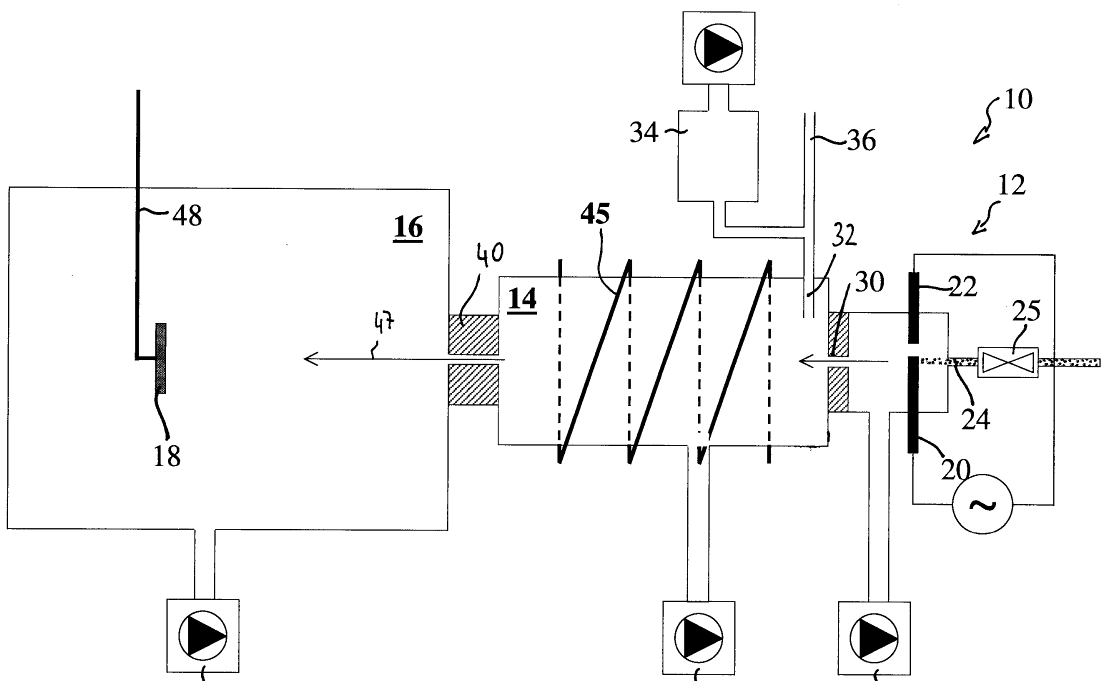

Fig. 1

EP 1 818 110 A1

Description

TECHNICAL FIELD

[0001] The present invention generally relates to a functionalised material as well as to its production process. More particularly, the invention relates to the production of a functionalised material by a process involving plasma-assisted polymerisation.

BACKGROUND ART

[0002] Recently, one of the major trends in the material research has been the functionalisation of material surfaces to control their interfacial properties, namely in nanostructured materials. For this purpose, low pressure plasma processes have been widely recognised as a technology of choice. One of the advantages that plasma techniques offer is the possibility to modify the very first layers of the surface, keeping the bulk material properties unchanged. Plasma treatments and plasma deposition of films are easily controllable by choosing suitable precursors and appropriate plasma conditions. Moreover, in case of polymers, the selectivity (or density) and the mobility of the functional groups on the surface can be varied to some extent by changing the degree of crosslinking. Thus materials can be engineered with different surface properties in order to improve and control for instance their electronic, magnetic and/or optical properties.

[0003] Such technique finds particular application in the biotech area, where it permits the production of biomaterials having functionalised surfaces to control the response of the host (human body) to improve the biocompatibility (typically with biological fluids).

[0004] Among the wide spectrum of possible treatments, plasma polymerisation of acrylic acid (PPAA) has proven to provide highly functionalised surfaces, with a high retention of the monomer structure and high density of -COOH groups. This kind of surface modification is suitable for biomedical application to control protein adsorption and surface immobilization of bioactive molecules. Such a process for PPAA has been described by P. Rossini et al., Materials Science and Engineering: C, Volume 23, Issue 3, 3 March 2003, Pages 353-358.

[0005] In order to vary the possible applications of such functionalised polymer materials, it would be good to be capable of further tailoring the properties of functionalised materials.

GENERAL DESCRIPTION OF THE INVENTION

[0006] While working on plasma assisted polymerisation processes for the developments of functionalised polymer materials, the present inventors thought of combining nanoparticles such as clusters with functionalised polymers in order to increase the adaptability of the polymer material to the aimed application. Accordingly, one aspect of the present invention relates to a polymer-cluster composite that comprises clusters embedded in a polymer matrix and that has an at least partially functionalised surface.

[0007] The term "functionalised", as used herein, means that the composite is capable of binding to a target substance, for instance a bioactive molecule, a protein or a cell. Generally, it implies that the polymer in the composite has at least one pendant functional group capable of attaching the target substance.

[0008] The term "cluster", as used herein, refers to tiny aggregates of atoms, molecules or ions that are held together by van der Waals forces, by ionic or covalent bonds or by metallic bonds. The clusters may comprise up to a few hundred thousands atoms. Preferably, clusters to be used in the present invention shall contain between 100 and 10 000 atoms.

[0009] The choice of the cluster type or nature will generally depend on the aimed application. The composite may also comprise a mixture of clusters of different types. The clusters can be made from a variety of materials, such as e.g. pure metals, alloys (e.g. binary alloys) or ceramics.

[0010] In one preferred embodiment, the clusters are made from electrically conductive material, e.g. a metal, an alloy or carbon. This permits to provide a composite with adaptable-and thus controlled-electrical conductivity, depending on the amount and distribution of electrically conductive clusters in the polymer matrix. More specifically, an appropriate choice and distribution of the clusters in the polymer matrix can provide semi-conducting properties to the composite.

[0011] Such a composite may especially find application in the biotech area, where the composite may be used in the manufacture of biosensors. Conventionally, a biosensor is composed of a biochemical receptor, which uses receptors such as enzymes, antibodies or microbes to detect an analyte, and a transducer, which transforms changes in physical or chemical value accompanying the reaction into a measurable response, most often an electrical signal. The biochemical receptor, depending on its design, determines the sensitivity or the biosensor to one or more specific biomolecules or cells. A well known type of biosensor is the ISFET (Ion Sensitive Field Effect Transistor), which comprises such a biochemical receptor layer over its gate oxide.

[0012] It will be appreciated that an enhanced ISFET-like biosensor can be obtained with the composite of the present invention. Indeed, a layer of the present composite with biocompatible functionality can be applied in the gate region of a Field Effect Transistor (FET). The biocompatible composite layer will then preferentially adsorb target substances present in the solution to be analysed, whereby the adsorbed target substances will alter the electric potential of the composite layer and therefore induce a change of gate potential, thus giving rise to a measurable change in current flowing through the transistor. As a result, whereas the functionalised surface of the composite permits to bind the target substances (biomolecules or cells in the solution to be analysed and in contact with the composite's surface), the enhanced electrical behaviour of the present composite improves control and response of the biosensor.

[0013] In another embodiment, the clusters are made from ceramic material, such as SiC (electronic material), or $LiSn_xP_yO_z$ (e.g. for electronic or optronic applications). This is of particular interest for the manufacture of electronic components, such as ceramic capacitors, electrostrictive actuators, electromechanical transducers, etc.

[0014] Furthermore, the clusters may be made from magnetic material. In such a case, the functionalized coverage of the clusters allows some specific interactions (anchorage, protection...) with the medium without modification of the properties of the magnetic core. Such material can be used for bio-magnetic storage, hybrid devices, tracking particles (e.g. FeCo, CoPt...), detection or tissue therapy, as described for example by Bansmann and al. in Surface Science Reports 56 (2005) 189-275 J.

[0015] Hence, the clusters consist of material different from the matrix polymer material and may comprise clusters from electrically conductive material and/or clusters from ceramic material and/or clusters from magnetic material.

[0016] Without willing to be bound by theory, it is to be noted that the properties of clusters may vary with the cluster size. In other words, whereas the physico-chemical properties of a given material are generally well known and established for bulk material and atomic vapours, at the atomic scale, a cluster of that material might instead have different properties depending on its size. Nevertheless, as used herein, a cluster is considered as electrically conductive if the material it is made of is electrically conductive at the macroscopic scale. This convention is used herein for any other physical property of the materials that are to be used as clusters, in particular regarding magnetic and ceramic materials

[0017] Depending on its manufacturing process, the composite of the invention may be obtained in the form of a film or membrane, but also in powder or grain form. This further broadens the scope of application of the present composite.

[0018] The present invention thus provides a polymer-cluster composite that has not only an engineered surface with an enhanced chemical affinity to specific biological or chemical target molecules, but also other controlled properties, such as conductivity or magnetism. Compared to known functionalised polymers, the present composite offers a wider range of obtainable physical, chemical or biological properties. The present invention especially provides a polymer-cluster composite having enhanced biocompatibility with body fluids.

[0019] A particular aspect of the invention also concerns a biosensor comprising a layer of the present cluster-polymer composite provided in the gate region of a FET and acting as gate electrode.

[0020] According to another aspect of the invention a process for producing a cluster-polymer composite is proposed, wherein the cluster-polymer composite is formed by concurrent plasma-assisted polymerisation from polymer precursors and deposition of clusters onto a substrate. The plasma assisted polymerisation is controlled so as to achieve at least partial functionalisation of a surface of the composite.

[0021] More specifically, the process may generally comprise the steps of:

- providing a gas phase mixture comprising clusters and polymer precursors in a plasma chamber;
- generating a plasma from the mixture in the plasma chamber, thereby forming a plasma activated mixture;
- depositing the plasma-activated mixture onto a substrate in a deposition region to form the cluster-polymer composite.

[0022] A merit of the present invention is thus to have thought of introducing clusters in a plasma chamber to simultaneously deposit the polymer and the cluster, while controlling the plasma deposition so as to provide polymer functionalisation, and thereby form functionalised polymer-cluster composites. Plasma-assisted polymerisation techniques are well known, and so is the control of the process to functionalise the deposited polymer. Besides, various methods can be used to produce clusters.

[0023] Depending on the aimed application of the composite, the clusters to be used in the present process may comprise clusters of electrically conductive material and/or clusters of ceramic material and/or clusters of magnetic material.

[0024] The functionalisation is preferably controlled by adjusting at least one of the following parameters: the dwell time of the polymer precursors and/or clusters in the plasma, the power provided to the plasma, the amount of gas introduced into the plasma chamber and its possible dilution with a noble gas such as e.g. Ar or He, or an active gas e.g. O_2, H_2, or NH_3. Adjusting these parameters allows controlling the plasma generation so that at least a part of the polymer precursors is fragmented, thereby controlling the degree of functionality of the composite. The dwell time of the polymer precursors in the plasma chamber can be adjusted by injecting the polymer precursors at different locations in the plasma chamber. The dwell time influences the degree of fragmentation, the amount of fragmented polymer precursors and thus the obtainable functionalities. These mixture properties are also dependent on the power provided to the plasma and on the pumping conditions.

[0025] Preferably, a neutral or reactive gas or vapour is introduced into the plasma chamber, so that the mixture formed in the plasma chamber also comprises such gas or vapour. The gas or vapour can act as a catalyst or react with the fragmented polymer precursors in order to achieve the desired functionalisation. In case of a neutral gas or vapour, the deposition rate can be, as indicated above, influenced by the amount of that gas or vapour.

[0026] It will be appreciated that the above parameters can be modified during the production cycle of a given cluster-polymer composite, which allows a complex configuration and design of the end product. In case of composite film deposition, a layered composition may be obtained, by varying some of the above parameters or by changing the composition of the mixture.

[0027] Without willing to be bound by theory, it is believed that in the course of the present process, the plasma-activated mixture comprises aggregates formed by clusters having reacted with fragmented polymer precursors. These aggregates may be of different sizes and can comprise a cluster core to which polymer precursors are attached and/or on the surface of which polymerisation may occur. The formation of aggregates mainly depends on the cluster and plasma density and on dwell time of the clusters and the polymer precursors in the plasma. The above parameters therefore can also be used to control the formation of these aggregates.

[0028] In a preferred embodiment of the process, the deposition step comprises forming a particle beam with the plasma-activated mixture and directing the particle beam towards the substrate so that it impinges thereon. Such a beam can e.g. be produced by forming a pressure gradient or pressure difference between the plasma chamber and the evacuated deposition region.

[0029] The substrate may be arranged at a certain distance from the plasma source, so that the incident angle of the particles of the mixture on the substrate is substantially the same. By using a collimated narrow particle beam or a mask, the high beam directionality enables depositing very fine pattern structures with high precision. With regard to other techniques, this has the important advantage that no post-deposition treatment (e.g. etching) of the composite is necessary. Especially etching might affect the functionality of the composite surface, giving rise to undesired response of e.g. a biosensor.

[0030] In the case of charged particles, the particle beam may be a result of electric attraction to the substrate and by magnetically guiding that beam. Advantageously, however, the substrate is arranged in the deposition region, and the particle beam results from a pressure gradient or pressure difference between the plasma and the deposition region. A lower pressure in the deposition region than in the plasma may be obtained by differential pumping. Consequently, the particles in the plasma chamber are dragged to the deposition region, where they impact on the substrate which is arranged at a suitable location. The particle beam may be formed or shaped by causing the plasma-activated mixture to flow from the plasma chamber into the deposition region through a narrow orifice, e.g. a nozzle. In this case, the plasma deposition region is preferably physically separated from the plasma chamber and the gaseous, activated mixture is lead towards the substrate via appropriate nozzle (and ducting) means.

[0031] The substrate and the particle beam may be moved relative to each other for controlling the deposition, so that e.g. a cluster-polymer composite film having a certain thickness profile and width may be formed. The skilled person will understand that this can be done by moving the substrate and/or by changing the direction of the particle beam.

[0032] As will be appreciated by those skilled in the art, the compactness and cohesion of the deposits may vary depending on the manufacturing conditions. Accordingly, one may control the process to obtain a rather compact and cohesive film of composite, wherein the clusters are embedded in the polymer matrix with functionalised surface. Alternatively, one may adjust the process parameters to form a relatively porous deposit having low cohesion, whereby powder-like deposits of composite aggregates (aggregates of clusters coated by polymer precursors and/or functionalised polymers) can be obtained. The compactness and cohesion of the deposits may be controlled by adjusting for example the following parameters: temperature of the substrate receiving the deposits (the compactness of the films increasing with temperature); stagnation temperature of the gas-particle mixture, (the increase of which will increase the particle kinetic energy and thus increase the compactness of the film); pressure in the deposition region (increasing the pressure reduces the particle energy and compactness of the film); dwell time of the cluster in the plasma (the increase of which increases the polymer fraction in the film obtained).

[0033] Regarding more specifically the cluster production, it may be carried out by cathodic discharge (also called sputtering) arc, electron beam or thermal evaporation as well as laser ablation. Furthermore, the clusters introduced into the plasma chamber may be produced by a single cluster source or by a plurality thereof. In the latter case, clusters of different species can be present in the mixture.

[0034] In a preferred embodiment, the clusters are produced by a pulsed DC diode discharge process, fed with a buffer gas compatible with the synthesis of the clusters of interest, such as described e.g. in EP 1 031 639.

[0035] A variety of polymer precursors can be used depending on the desired properties of the end product, in particular: acrylic acid, any polymerizable amine precursors (such as alkylamines), alcohols, alkylaldehydes, acetone, or alkylthiols. For biology related applications, the polymer precursor is advantageously selected for its capability-as a result of plasma assisted polymerization-of providing OH, COOH, SH, CO or NH2 functionalities.

[0036] These polymer precursors above can be used with different gases such as e.g. nitrogen, oxygen, Ar or He.

[0037] As for the clusters, for the above described applications they may e.g. consist of C, B, of any metallic material such as e.g. Ti, Co, Ta, Zr, or of an alloy of these or other metals.

[0038] According to a further aspect of the invention, a plasma-assisted polymerisation apparatus for producing a cluster-polymer composite is proposed, which comprises:

- a plasma chamber with means for providing a gaseous mixture of polymer precursors and clusters therein;
- means for generating a plasma in the plasma chamber by providing energy to at least a part of the mixture, thereby forming a plasma activated mixture;
- a substrate holder arranged in a deposition region for holding a substrate on which the plasma activated mixture is to be deposited;
- means for controlling the plasma-assisted polymerisation so as to achieve at least partial functionalisation of a surface of the composite.

[0039] Such apparatus is designed to allow simultaneous plasma assisted polymerisation and cluster deposition onto a substrate, while controlling the plasma process to achieve at least partial surface functionalisation, in order to obtain the composites of the present invention.

[0040] In a preferred embodiment of the apparatus, the means for controlling the plasma-assisted polymerization is designed to allow adjusting at least one of the following parameters: dwell time of the polymer precursors in the plasma, power provided to the plasma, amount of gas introduced into the plasma chamber. This permits to control the proportion of polymer precursors being fragmented by interaction with the plasma. The dwell time of the polymer precursors in the plasma can be adjusted by different means. A direct and simple means for this is by controlling the throughput of the plasma chamber outlet and thus the precursor stream velocity in the plasma chamber. Another way to control the dwell time is to inject the polymer precursors at different locations in the plasma chamber. This can be done either by means of a moveable nozzle or by providing a plurality of polymer precursor inlets added to an inlet for some inert buffer gas. The apparatus may further comprise more inlets for neutral or reactive gas or vapour, which can act as a catalyst or react with the fragmented polymer precursors in order to achieve the desired functionalisation. Alternatively these can be pre-mixed with the polymer precursor. Finally, at the apparatus design stage, it may be kept in mind that the length of the reaction zone (distance on which the nanoclusters can react with the plasma) is also directly related to dwell time at given flow velocity.

[0041] The substrate holder is preferably arranged in a deposition chamber separated from the plasma chamber by a partition wall, a narrow orifice being arranged in this partition wall to allow passage of the plasma activated mixture.

[0042] The apparatus can comprise at least one vacuum pump for creating a pressure gradient between the plasma chamber and the deposition chamber. In use, this allows forming of a particle beam with the plasma activated mixture.

[0043] The apparatus preferably includes a vapour delivery system for producing vapours of organic monomers that are fed into the plasma chamber.

[0044] The cluster generation may be achieved by any appropriate means. In particular, the clusters can be generated by cathodic discharge (also known as sputtering) arc, electron beam or thermal evaporation as well as laser ablation, e.g. in a heated boat. More preferably, the clusters are generated in a pulsed DC diode discharge unit, as described in EP 1 031 639.

[0045] The plasma generation means may comprise any appropriate energy source. High frequency (10 MHz and above) RF plasma sources can for example be used, with adequate coupling devices (electrode, inductor, or launcher).

BRIEF DESCRIPTION OF THE DRAWINGS

[0046] The present invention will now be described, by way of example, with reference to the accompanying drawing, in which:

FIG.1: shows a preferred embodiment of an apparatus for producing a cluster-polymer composite according to the invention; and

FIG.2: is a principle diagram of a biosensor featuring a layer of a composite according to the present invention.

DETAILED DESCRIPTION WITH RESPECT TO THE DRAWINGS

[0047] The present invention concerns a cluster-polymer composite having a functionalised surface (at least in part) and comprising clusters embedded in a polymer matrix.

[0048] A preferred embodiment of the production process of such a cluster-polymer composite will now be explained in more detail with reference to Fig.1, which shows a preferred embodiment of an apparatus 10 for carrying out the process.

[0049] The apparatus 10 comprises a cluster source 12, a plasma chamber 14 and a deposition chamber 16. According to the present process, the plasma chamber 14 is provided with a mixture comprising clusters from the cluster source 12 and with polymer precursors, and the mixture is ignited to form a plasma. The present process involves simultaneous plasma assisted polymerisation of the polymer precursor and cluster deposition, so as to form a polymer with embedded clusters. In fact, the plasma generation produces an activated mixture which is caused to flow to the deposition chamber 16, wherein a substrate 18 is arranged, the mixture depositing (condensing) onto this substrate 18 to form the cluster-polymer composite. It is to be noted that the plasma assisted polymerization is controlled so as to achieve at least partial functionalisation of a surface of the composite.

[0050] In the present embodiment, the cluster source

12 is preferably of the pulsed DC diode discharge type fed with a buffer gas similar to that described in EP 1 031 639. Accordingly, an electric discharge is created between a cathode 20 and an anode 22 separated by a reduced gap, and a gas flow 24 is directed to strike onto the cathode 20 below the gap. The buffer gas flow 24 is dispensed by a valve 25 and drawn by means of a duct from a gas source (not shown), e.g. a storage bottle. Due to this narrow gap and to the fact that in the region surrounding the point where the buffer gas flow 24 strikes the cathode 20, the gas pressure is higher than in the adjoining regions, the electrical discharge closes between the anode 22 and the region of the cathode 20 struck by the buffer gas flow 24, instead of closing inside the gap between the two electrodes . The electrical discharge ionises the buffer gas and cathode material is ablated from the region struck by the buffer gas 24. The evaporated material ablated from the cathode 20 cools in contact with the buffer gas 24 and condenses into nanosized neutral or ionised clusters.

[0051] In the present embodiment, the cathode 20 may be made from any conductive material such as metal, alloy, cermet, or electrically conductive ceramic, carbon or a mixture of those. In particular, the cathode material can have magnetic properties. The cathode 20 may rotate and/or be translated, in order to allow homogeneous ablation. If oxygen is present in the cluster synthesis stage, also oxide clusters can be formed.

[0052] The buffer gas can be any gas compatible with the synthesis of the clusters of interest, e.g. He, Ar, NH_3 or N_2. If He is chosen, the DC discharge can produce metastable excited He atoms suitable for the activation of chemical reactions in the plasma chamber 14.

[0053] The so-formed clusters and the buffer gas are caused to flow to the plasma chamber 14 by means of a pressure gradient between the cluster source 12 and the plasma chamber 14 created by vacuum pumps 26 and 28. The plasma chamber 14 is maintained at a lower pressure than the cluster source 12 by means of differential pumping, and the clusters carried by the buffer gas flow into the plasma chamber 14 via a passage 30 defining a narrow orifice .

[0054] The plasma chamber 14 is also fed with polymer precursors that are introduced into the plasma chamber 14 via an inlet duct 32. The inlet duct 32 is therefore connected, outside the plasma chamber 12, to a vapor delivery system 34 to vaporize the liquid precursor, for example a solution comprising one or more types of monomers. A valve and flow meter (not shown) allow controlling the amount of monomer flowing into the plasma chamber 14.

[0055] The mixture of clusters, buffer gas and vapours of polymer precursors is thus provided in the plasma chamber 14, and the mixture is ignited to form a plasma. If desired, other buffer gases or vapors may be introduced by a gas duct 36 also connecting inlet duct 32 outside the plasma chamber 14. In particular, other gases such as He or mixtures of He and other reactive gases such as nitrogen, hydrogen ammonia or any gas compatible with the plasma generation can be used.

[0056] By interaction with the plasma, at least a part of the polymer precursors are fragmented, ionised and excited. In the plasma various species react with each other and with the clusters to produce aggregates of different sizes. Without willing to be bound by any theory, these aggregates are believed to comprise a core consisting of a cluster extracted from the cathode with selected electric and/or magnetic properties and an outer shell formed by attached polymer precursors, fragments thereof and pendant functional groups induced by the above interaction. These polymer precursors attached at the surface of the cluster may partially react to form a partially polymerised shell, with pendant functional groups.

[0057] The degree of fragmentation of the polymer precursor can be controlled via the dwell time of the polymer precursor in the plasma, by the power provided to the plasma energy source, by the evacuation throughput (pumping level) and by the amount of gas in the mixture. Injecting the polymer precursor further downstream with respect to the cluster source 12 and adding a buffer gas flow injected upstream close to the cluster source outlet will also result in a shorter dwell time and thus in less fragmentation. Furthermore, the amount of aggregates in the plasma-activated mixture may thereby be lower.

[0058] The additional gas provided by duct 36 and injected via inlet 32 is chosen depending on the desired degree of functionalisation of the cluster-polymer composite. The amount of buffer gas present in the mixture also influences the deposition rate in the following step. In other words, the concentration of neutral/reactive gas in the mixture may be adapted depending on the deposition rate aimed and the properties of the composite that are required.

[0059] Although not shown in Fig.1, the plasma generation is preferably based on the classical inductive coupling plasma technology, that can work in continuous or pulsed mode. In the latter case, the plasma pulse frequency is typically adjusted to match the frequency of production of the clusters, that is: the plasma pulse frequency is equal or larger than the cluster production frequency. The plasma chamber 14, wherein the inductive plasma is produced, may typically comprise a quartz tube surrounded by a metallic inductive coil (45) connected to an HF generator through a matching unit (not shown). Such a technique is known in the art and need not be explained in detail herein.

[0060] The plasma-activated mixture formed in the plasma chamber 14 is caused to flow to the deposition chamber 16 by means of a pressure difference. More specifically, the plasma-activated mixture flows through a nozzle 40 into the deposition chamber 16, where a lower pressure is maintained by means of pump 44. Thereby the activated mixture expands so as to form a supersonic particle beam (illustrated by arrow 46), which impinges and condenses on the substrate 18 attached to a substrate holder 48. The substrate holder 48 can be moved in the deposition chamber 16, which allows moving the substrate 18 relative to the particle beam 46 to form a film of desired area or configuration. Again, without willing to be bound by theory, it is believed that as the beam of the functionalised clusters in the beam condenses onto the substrate 18, neighbouring clusters are linked to each-other via partial sintering and/or polymerisation of their polymeric shell-also with potentially free polymer precursors in the beam condensing on the substrate-whereby a cohesive film of clusters embedded in a polymer matrix is obtained, the outer surface of the matrix however having pendant functional group providing the desired functionalities.

[0061] If desired, a mask (not shown) may be used to shield given areas of the substrate so as to form a composite with a predetermined pattern on the substrate 18.

[0062] It will be understood that the choice of polymer precursors and clusters will depend on the desired specification of the composite to be manufactured.

[0063] A variety of polymer precursors can be used depending on the desired properties of the end product, in particular: acrylic acid, any polymerizable amine precursors (such as alkylamines), alcohols, alkylaldehydes, acetone, or alkylthiols. For biology related applications, the polymer precursor is advantageously selected for its capability-as a result of plasma assisted polymerization-of providing OH, COOH, SH, CO or NH2 functionalities.

[0064] These polymer precursors can be used with different gases such as nitrogen, oxygen, NH_3, CF_4 or other reactive gases, but also noble gases such as Ar or He.

[0065] As for the clusters, for the above described applications they may e.g. consist of C, B or any metallic material such as Ti, Co, Ta, Zr. For the manufacture of functionalised polymers with enhanced electric conductivity, the clusters are preferably made from electrically conductive material, in particular metals such as Ti, Fe, Zr, Ag or Cu. For magnetic clusters, metals chosen can be Co, Fe, or metallic magnetic alloys.

Example 1

[0066] In order to illustrate the present process, different sets of experiments have been performed with an apparatus of the type described hereabove, using same inductive plasma conditions and different couples of cathodes and precursors: Carbon and acrylic acid; Carbon and allylamine; Tantalum and allylamine. With the following experimental conditions, functionalized composite films comprising a polymeric matrix with embedded clusters of Ta, rep. Carbon were obtained.

[0067] The parameters of cluster source were kept constant (the following parameters may be better understood by referring to EP 1 031 639, since the cluster source in the present apparatus is similar): opening time of the gas valve 200μs, delay time before arc ignition 650μs, discharge delay 80μs, frequency 1 Hz, power 70% and He pressure 25 bar). After starting the discharge, the beam focalisation was checked and adjusted. The vapour from the vapour source was then introduced in the plasma tube with a work pressure for the plasma discharge equal to 10^{-1}mbar.

[0068] The inductive plasma was then put on and stabilised using a RF tuner (13.56 MHz, forward power 1-120W, with a reflected power lower than 2W). The substrate holder was then placed in front of the focused cluster beam in the deposition chamber, and the deposition started.

[0069] Different composite films have been successfully produced with different plasma powers varying from 3W to 70W. Several composites have been deposited with different cathodes (carbon, titanium) and different plasma gases (acrylic acid (AAC), Argon (Ar) and nitrogen (N_2)).

Example 2

[0070] As a further illustration of the present invention, Fig.2 shows a sketch of biosensor featuring a layer of the present composite as species sensitive gate layer in a FET structure.

[0071] The biosensor 110 shown in FIG.2 has a structure similar to an ISFET, however the conventional biosensitive layer is replaced by a layer of the present composite. As can be seen, the transistor basically consists of a p-type silicon substrate 112 with source 114 and drain 116 diffusion regions separated by a conducting channel 118. The channel 118 is overlaid by a layer of a composite 120 according to the present invention, forming a sensitive gate layer. In the present embodiment, the composite layer 120 is arranged directly on the substrate 112 above the channel 118; alternatively, the composite layer may be formed on top of an intermediate gate oxide insulating the former from the substrate. The solution (analyte) 122 is in direct contact with the composite gate layer 120 and a reference electrode 124 replaces the metal gate used conventionally in ISFETs. The typical electrical connection of such biosensor is also illustrated in FIG.2.

[0072] Depending on the functionalization of the composite gate layer 12, targeted molecules such as antibody fragments or enzymes can be immobilized on the composite gate layer (illustrated by the "Y" symbols in Fig.2). Hence, upon reaction with the analyte, the properties of the circuit are changed and the current circulating in the FET varies. This variation is related to the quantity of analyte reacting with the surface of the composite gate layer and thus the system functions as a biosensor. The advantage of this configuration lies in the adjustment of the physico-chemical properties of the sensing layer by the combination of a chemically active layer (plasma polymer) and electrically conductive or magnetic nanoparticles (clusters).

Claims

1. Cluster-polymer composite comprising clusters embedded in a polymer matrix, wherein said polymer-cluster composite comprises an at least partially functionalised surface.

2. Cluster-polymer composite according to claim 1, wherein said clusters comprise clusters of electrically conductive material and/or clusters of ceramic material and/or clusters of magnetic material.

3. Cluster-polymer composite according claim 1 or 2, wherein said composite is in the form of a film.

4. Cluster-polymer composite according claim 1 or 2, wherein said composite is in powder or grain form.

5. A process for producing a cluster-polymer composite, wherein said composite is formed by concurrent plasma-assisted polymerisation from polymer precursors and deposition of clusters onto a substrate, and wherein said plasma assisted polymerisation is controlled so as to achieve at least partial functionalisation of a surface of said composite.

6. Process according to claim 5, comprising the steps of:

   providing a gaseous mixture comprising clusters and polymer precursors in a plasma chamber;
   generating a plasma from said mixture in said plasma chamber, thereby forming a plasma activated mixture;
   depositing the plasma-activated mixture onto a substrate in a deposition region to form said cluster-polymer composite.

7. Process according to claim 6, wherein the degree of functionalisation is controlled by adjusting at least one of the following parameters: dwell time of said polymer precursors and/or clusters in said plasma, power provided to said plasma, amount of gas introduced into said plasma chamber.

8. Process according to claim 6 or 7, wherein plasma generation is controlled so that at least part of said polymer precursors are fragmented.

9. Process according to any one of claims 6 to 8, wherein said polymer precursors comprise one or more monomer species.

10. Process according to any one of claims 6 to 9, wherein said mixture comprises a neutral or reactive gas or vapour.

11. Process according to any one of claims 5 to 10, wherein said deposition is carried out by forming a particle beam with said mixture, said particle beam being directed towards said substrate in said deposition region so that it impinges thereon.

12. Process according to claim 11, wherein said particle beam is formed by causing said plasma activated mixture to flow from said plasma chamber into said deposition region through a narrow orifice, while maintaining a pressure gradient between said plasma chamber and said deposition region.

13. Process according to claims 11 or 12, wherein said substrate and said particle beam are moved relative to each other for controlling said deposition.

14. Process according to any one of claims 5 to 13, comprising the step of producing clusters by a pulsed DC diode discharge process.

15. Process according to any one of claims 5 to 14, wherein said clusters comprise clusters of electrically conductive material and/or clusters of ceramic material and/or clusters of magnetic material.

16. Process according to any one of claims 5 to 15, wherein the compactness and cohesion of the deposits are adjusted by adapting at least one of the following parameters: temperature of the substrate receiving the deposits; pressure in the deposition region; dwell time of the cluster in the plasma and kinetic energy of the aggregates upon landing.

17. Apparatus for producing a cluster-polymer composite, comprising
   a plasma chamber comprising means for providing a gaseous mixture of polymer precursors and clusters therein;
   means for generating a plasma in said plasma chamber by providing energy to at least a part of said mixture, thereby forming a plasma activated mixture;
   a substrate holder arranged in a deposition region for holding a substrate on which the plasma activated mixture is to be deposited;
   said apparatus further comprising means for controlling said plasma-assisted polymerisation so as to achieve at least partial functionalisation of a surface of said composite.

18. Apparatus according to claim 17, wherein said means for controlling said plasma-assisted polymerisation is able to adjust at least one of the following parameters: dwell time of said polymer precursors and/or clusters in said plasma, power provided to said plasma, amount of gas introduced into said plasma chamber; thereby controlling an amount of polymer precursors being fragmented by interaction with said plasma.

19. Apparatus according to claim 17 or 18, wherein said substrate holder is arranged in a deposition chamber separated from said plasma chamber by a partition wall, said wall having a narrow orifice arranged therein for allowing passage of said plasma activated mixture.

20. Apparatus according to claim 19, comprising at least one vacuum pump for creating a pressure gradient between said plasma chamber and said deposition chamber so as to enable forming of a particle beam comprising said plasma activated mixture.

21. Apparatus according to any one of claims 17 to 20, wherein said cluster source comprises a pulsed DC diode discharge.

22. A biosensor comprising a field effect transistor substructure, wherein a layer of cluster-polymer composite according to any one of claims 1 to 3 is arranged in the gate region.

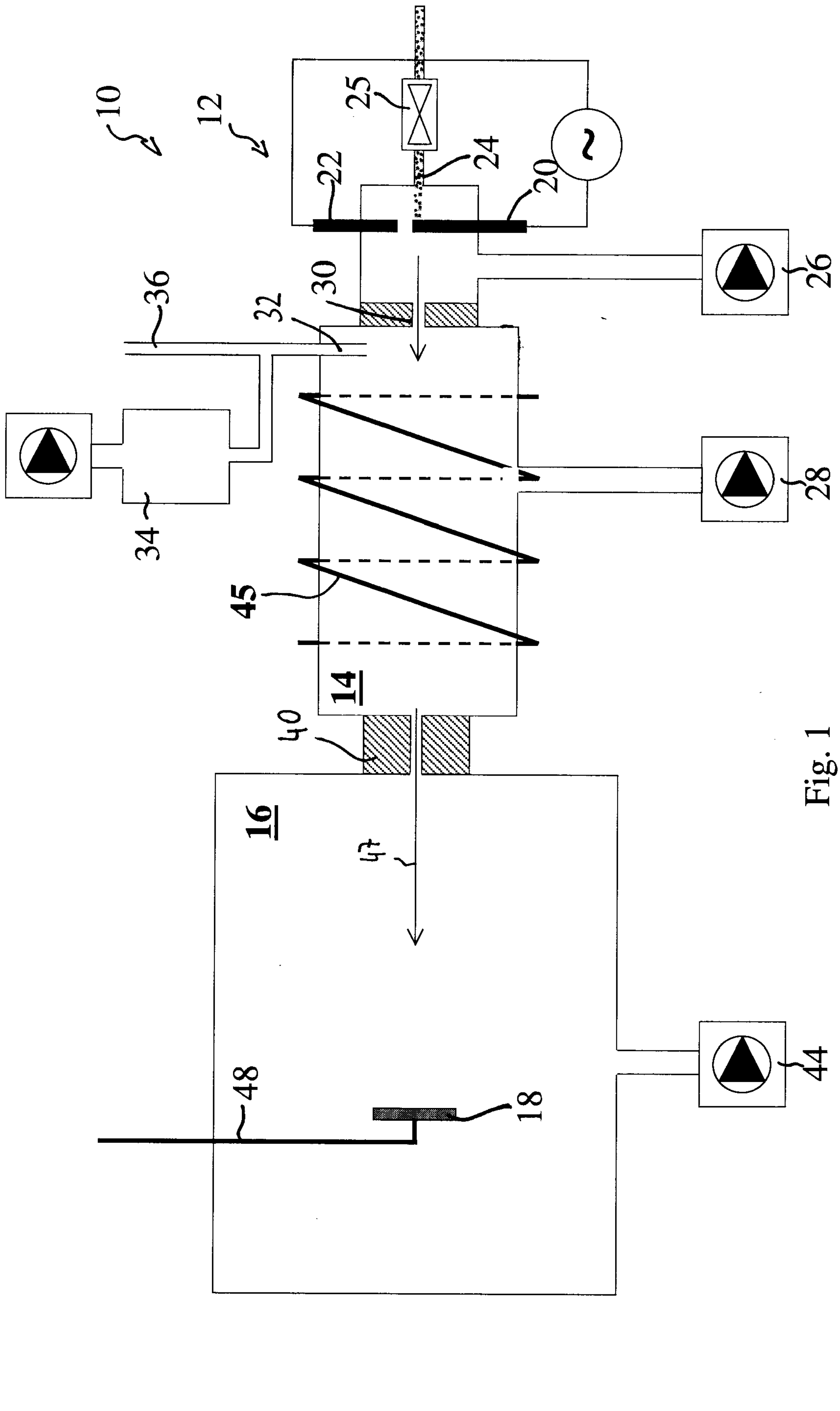

Fig. 1

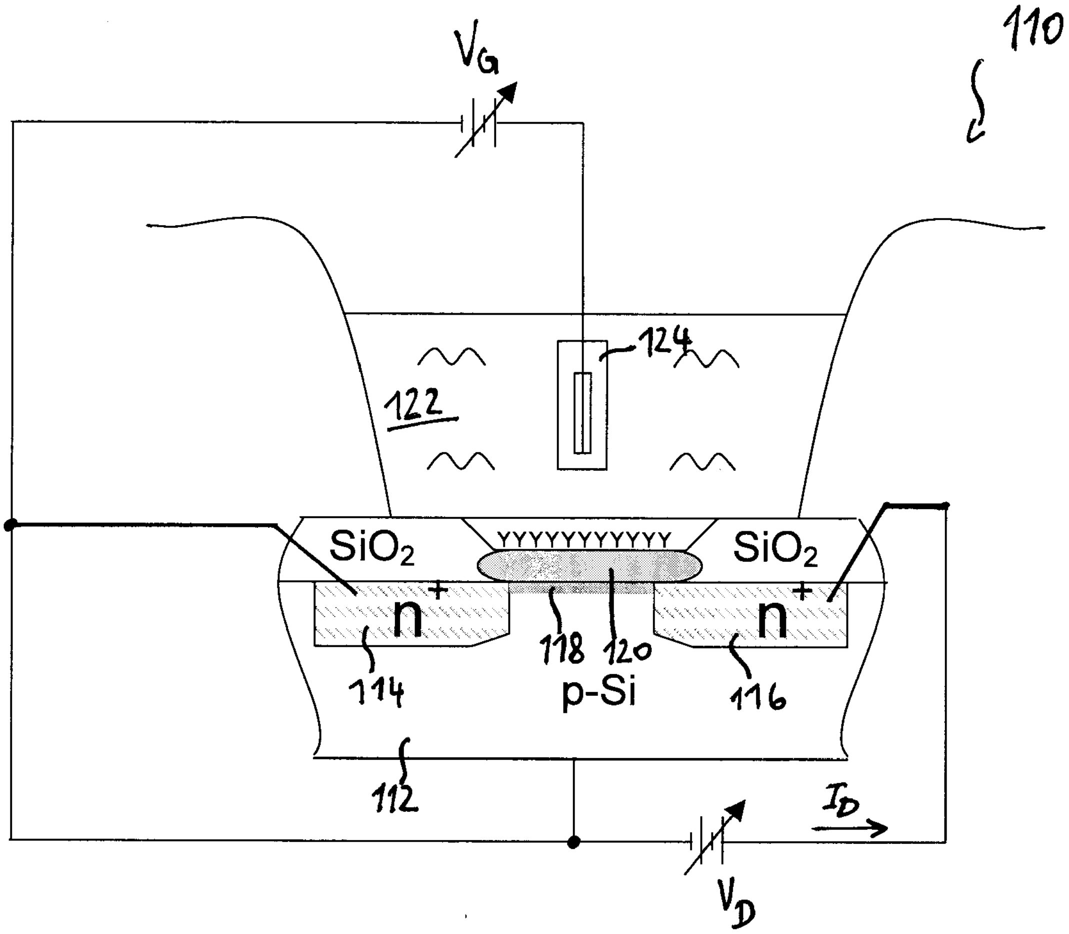

Fig. 2

European Patent Office

PARTIAL EUROPEAN SEARCH REPORT

which under Rule 45 of the European Patent Convention shall be considered, for the purposes of subsequent proceedings, as the European search report

Application Number
EP 06 10 1672

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2003/148139 A1 (MOSER EVA MARIA) 7 August 2003 (2003-08-07) * paragraphs [0006], [0011], [0025], [0026], [0048] *	1-7, 9-14,16, 22	INV. B05D7/24
X	US 6 613 393 B1 (RAUSCHNABEL JOHANNES ET AL) 2 September 2003 (2003-09-02) * column 1, line 57 - column 2, line 5 * * column 3, line 24 - line 35 * * column 6, line 21 - line 34 * * figure 1 *	1-7, 9-14,16, 22	
D,X	EP 1 031 639 A (ISTITUTO NAZIONALE PER LA FISICA DELLA MATERIA) 30 August 2000 (2000-08-30) * the whole document *	17-21	
A	EP 0 801 146 A (CE.TE.V. CENTRO TECNOLOGIE DEL VUOTO) 15 October 1997 (1997-10-15) * the whole document *	1,5,17	
	-/--		

TECHNICAL FIELDS SEARCHED (IPC)

B05D
C23C

INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:

see sheet C

1

Place of search	Date of completion of the search	Examiner
The Hague	5 July 2006	Slembrouck, I

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C07)

European Patent Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number
EP 06 10 1672

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (IPC)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	US 5 786 068 A (DORFMAN ET AL) 28 July 1998 (1998-07-28) * claims; examples * -----	1,5,17	
			TECHNICAL FIELDS SEARCHED (IPC)

1

EPO FORM 1503 03.82 (P04C10)

European Patent Office

INCOMPLETE SEARCH SHEET C

Application Number
EP 06 10 1672

Claim(s) searched completely:
17-21

Claim(s) searched incompletely:
1-7, 9-14, 16, 22

Claim(s) not searched:
8 15

Reason for the limitation of the search:

(1) Present claim 5 relates to a method which has a given desired property or effect, namely "said plasma assisted polymerisation is controlled soa as to achieve at least partial functionalisation of a surface of said composite". However, the description does not provide support and disclosure in the sense of Article 84 and 83 EPC for any such method having the said property or effect and there is no common general knowledge of this kind available to the person skilled in the art. This non-compliance with the substantive provisions is to such an extent, that a meaningful search of the whole claimed subject-matter of the claim could not be carried out (Rule 45 EPC and Guidelines B-VIII, 3).

(2) The present claims 1-4, 5-16 and 22 relate to an extremely large number of possible products and methods. Support and disclosure in the sense of Article 84 and 83 EPC is to be found however for only a very small proportion of the products and methods claimed, see [examples 1 and 2, p. 16-17 in the description). The non-compliance with the substantive provisions is to such an extent, that a meaningful search of the whole claimed subject-matter of the claim could not be carried out (Rule 45 EPC and Guidelines B-VIII, 3). The extent of the search was consequently limited.

The search of claims 1 was restricted to those claimed products which appear to be supported and a generalisation of their structural formulae, i.e.:

a cluster-polymer composite comprising clusters selected from the group consisting of Carbon and Tantalum, embedded in a polymer matrix formed from plasma polymerisation of a precursor selected from the group consisting of allylamine and acrylic acid, wherein said polymer-cluster composite comprises an at least partially functionnalised surface.

Claims 2-4 and 22, which are dependant from claim 1 have been restricted accordingly.

The search of claims 5 was restricted to those claimed processes which appear to be supported and a generalisation of their structural formulae and in accordance with the remark raised under point (1) hereabove, i.e.

a process for producing a cluster-polymer composite, wherein said composite is formed by concurrent plasma assisted polymerisation from a polymer precurson selected from the group consisting of allylamine and acrylic acid, and deposition of clusters selected from the group

European Patent Office

INCOMPLETE SEARCH SHEET C

Application Number
EP 06 10 1672

consisting of Carbon and Tantalum, onto a substrate.

Claims 6, 7, 9-14 and 16, which are dependant from claim 5 have been restricted accordingly.
With due consideration to the restriction on claim 5, dependant claim 15 has not been searched.

(3) Present claim 8 relates to a method which has a given desired property or effect, namely "said plasma generation is contgrolled so that at least part of said polymer precursors are fragmented". However, the description does not provide support and disclosure in the sense of Article 84 and 83 EPC for any such method having the said property or effect and there is no common general knowledge of this kind available to the person skilled in the art. This non-compliance with the substantive provisions is to such an extent, that a meaningful search of the whole claimed subject-matter of the claim could not be carried out (Rule 45 EPC and Guidelines B-VIII, 3).

Claim 8 has therefore not been searched.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 06 10 1672

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

05-07-2006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2003148139 A1	07-08-2003	AT 269172 T	15-07-2004
		AU 2660701 A	07-08-2001
		WO 0155489 A2	02-08-2001
		DE 50102589 D1	22-07-2004
		EP 1251975 A2	30-10-2002
US 6613393 B1	02-09-2003	WO 9963129 A1	09-12-1999
		DE 19824364 A1	02-12-1999
		EP 1088116 A1	04-04-2001
		JP 2002517611 T	18-06-2002
EP 1031639 A	30-08-2000	IT GE990020 A1	28-08-2000
		US 6392188 B1	21-05-2002
EP 0801146 A	15-10-1997	IT RM960240 A1	17-10-1997
US 5786068 A	28-07-1998	US 5728465 A	17-03-1998
		US 5718976 A	17-02-1998

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 1031639 A **[0034] [0044] [0050] [0067]**

Non-patent literature cited in the description

- **P. ROSSINI et al.** *Materials Science and Engineering: C,* 03 March 2003, vol. 23 (3), 353-358 **[0004]**
- **BANSMANN.** *Surface Science Reports,* 2005, vol. 56, 189-275 **[0014]**