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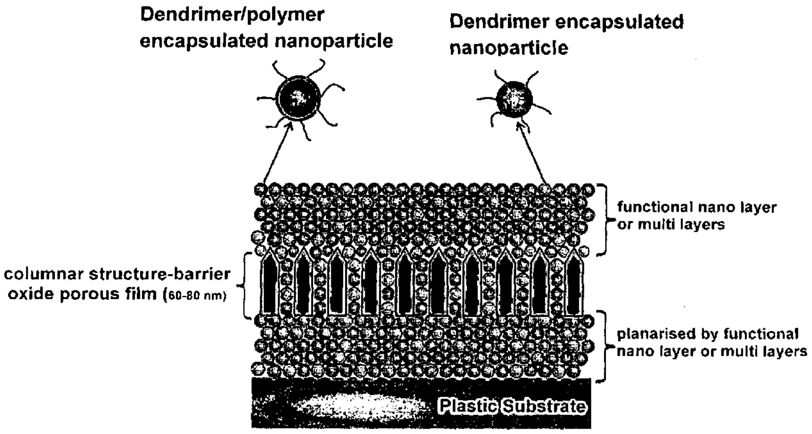

Fig. 3C

(57) **Abstract**: Disclosed is an encapsulation barrier stack, capable of encapsulating a moisture and/or oxygen sensitive article and comprising a multilayer film, wherein the multilayer film comprises: - one or more barrier layer(s) having low moisture and/or oxygen permeability, and - one or more sealing layer(s) arranged to be in contact with a surface of the at least one barrier layer, thereby covering defects present in the barrier layer, wherein the one or more sealing layer(s) comprise(s) a plurality of dendrimer encapsulated nanoparticles, the nanoparticles being reactive in that they are capable of interacting with moisture and/or oxygen to retard the permeation of moisture and/or oxygen through the defects present in the barrier layer.

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ENCAPSULATION BARRIER STACK COMPRISING DENDRIMER ENCAPSULATED NANOP ARTICLES

FIELD OF THE INVENTION

[0001] The present invention relates to the field of barrier stacks, and more particularly to a barrier stack that includes encapsulated nanoparticles. The encapsulation of the particles can be obtained by partially or fully encapsulating the nanoparticles with dendrimers and/or dendrons. Encapsulating the nanoparticles may include forming directly a dendrimer compound in the presence of the nanoparticle and linking the obtained dendrimer on the surface of nanoparticle or, adding the dendrimer compound to the nanoparticle and linking the dendrimer on the surface of the reactive nanoparticles or coating the nanoparticles with dendrons wherein the focal groups of the Dendron is able to bind (ionically or covalently) with the nanoparticle surface. The encapsulated nanoparticles may be deposited on to inorganic thin oxide (barrier) films. A respective barrier stack can be arranged on a substrate, for example in an electronic device.

[0002] Dendrimers are complex monodisperse macromolecules with a regular and highly branched three-dimensional architecture. Dendrimers are produced in iterative sequences of reaction steps, in which each additional iteration leads to a higher generation dendrimer. The construction of dendrimers can be carried out in two major ways: by a divergent approach where the molecule grows from the center to the periphery, and a convergent approach where the dendrimer molecule is built starting from the periphery fragments. The choice of the divergent or convergent synthetic methods is determined by the available chemical reactions, requirements toward the dendrimer molecules, or the type of the “building blocks” used in the dendrimer construction. Commercially available dendrimers, such as poly(propyleneimine) (PPI) and poly(amidoamine) (PAMAM), are synthesized by a divergent approach. Oppositely, the convergent approach permits better structural control due to a low number of coupling reactions at each growth step. In addition, the convergent approach provides targeted functionalization of the core and the dendron exterior, allowing for further chemical reactions with high yields and dendritic products of high purity and functional versatility. Examples of commercially available dendrimers synthesized by a convergent method are polyether dendrimers (Frechet dendrimers). It is noteworthy that the majority of dendrimers can be synthesized by a combination of both methods. (See Bronstein rt al. Dendrimers as Encapsulating, Stabilizing, or Directing Agents for Inorganic Nonopaticles”. Inorganic nanoparticle (metal, metal oxide, metal halide) can be either encapsulated by the dendrimer molecule or surrounded by dendrimers. The nanoparticle may be also the core after the attachment of dendron to its surface.

[0003] Flexible solar cells and flexible plastic or printed electronics are considered as a next generation display technology. However, like many new technologies of the future, many technical questions have to be resolved such as those related to the high gas barrier performance and the cost of the polymeric substrates. Polymer films do not typically show high barrier performance (as compared to the requirement of less than 10-5 to 10-6g/m2/day permeability of water vapour at 39°C and 95% relative humidity) even if they are coated with a metal-oxide coating to improve their barrier properties. It is well known that high barrier thin film oxides, coated onto plastic films, have imperfections such as pinholes, cracks, grain boundaries, etc. which vastly affect the performance of barrier films. The integrity of deposited coatings is a critical factor in determining the overall gas barrier performance and the control of defects within the oxide layers is a most important. Indeed, the performance of the metal-oxide-coated polymer films and the cost is a major technological hurdle towards a breakthrough in flexible solar cells, flexible OLED displays and plastic electronics applications. It is well known that multi-layer inorganic and organic barrier films decouple the defects of the barrier oxide films. These barrier films can only enhance the barrier properties, but don't address other properties such as mechanical, optical and weatherability.

[0004] The global solar cell industry has seen a significant growth in recent years, with a compound annual growth rate above 50% for the last 10 years. The downside of this rapid expansion has been an oversupply of solar cell modules leading to a dramatic price decrease of more than 50% over the last 2 years. The target price of US$ 1/Watt has been broken already for solar cells.

[0005] The price structure for a module with 12% efficiency and a price target of US$ 0.7/W would mean a module price of US$ 84/m^2. Out of this encapsulation and barrier films comprise 30% to 35%, i.e. US$ 25 - 30. This would include substrates (top and bottom) as well as sealants and other protective laminates. Since the base substrate generally is a lower cost metal film, the barrier film share would be in the range of US$ 15-20/m^2 maximum. If the PV module price continues to decline (as expected by many industry analysts), the barrier film share of the total PV module product cost would be in the range of US$ 10/m^2. Similarly for OLED lighting applications, the cost expectation is similar to the PV applications. This invention proposes to reduce the production cost of the barrier stack and provide additional cost benefits by enhancing the UV blocking and anti-reflection properties. Therefore, the proposed barrier stack design can provide barrier and optical properties at lower cost for PV and OLED lighting applications.

[0006] Manufacturers of flexible solar cells have set their target at less than US$ 1/Watt, since their flexible rolls of solar modules are easily transported and installed. Currently, CIGS manufacturers have achieved more than 12% efficiency on their regular roll-to-roll production lines, with champion efficiencies of more than 16%.

[0007] Most of the barrier coating technologies are based on the use of oxide barrier films in their barrier stack in order to get high barrier properties. These oxide barrier films are deposited on the plastic substrates by Sputtering (Physical Vapour Deposition) processes and PECVD methods. However, the most preferred method is the sputtering process, which can provide high packing density of oxide films, which has lower density of defects such as pinholes, cracks and other defects such as grain boundary. The atomic layer deposition can also provide high packing density barrier films with lower number of defects, but the production throughput is currently lower than sputtering The Roll-to-Roll production systems and efforts in increasing production throughput are under development stage. However, efforts have been taken to increase the production speed by Roll-to-Roll processes, which are currently being developed. The typical barrier properties which can be achieved by Sputtering and ALD techniques are in the order of 0.02 $g/m^2 \cdot day$ to 0.006 $g/m^2 \cdot day$ at 38 °C and 90% relative humidity. Nevertheless, the sputtering technology has already reached a matured stage, and Roll-to-Roll coating manufacturing plants are commercially available. However, with sputtering, the coating throughput is still very low, in the range of 2.5 meters/min to 4.9 meters/min. Therefore, the production cost of the barrier oxide films such as aluminium oxide by a sputtering process would be considerably high, typically S$2.00 to S$5.00/m^2 depending on coating plant specification and configuration. Most barrier stack designs require at least 3-barrier oxide layers and 3 polymer-decoupling layers. Therefore, the 3 layer-system production costs would dramatically increase up to S$18 to S$28/m^2. In addition to the base substrate cost, further cost factors are UV filter costs and anti-reflection coating costs as well as operational costs which would turn out to be uneconomical for PV and OLED lighting manufacturers.

[0008] The high speed manufacturing process (500 - 1000 meters/min) of Electron Beam and Plasma enhanced evaporation methods provide flexibility for the use of different coatings with the high robustness, high adhesion and extremely good transmittance/transparency. Electron beam evaporation or plasma enhanced evaporation methods could achieve a throughput in the range of 400 meters/min to 900 meters/min.

However, the metal oxide film integrity is poor when compared to the sputtering/plasma-enhanced chemical vapor deposition (PECVD) processes. The evaporation processes such as plasma-enhanced physical vapor deposition (PEPVD) methods could only provide lower packing density oxide films and the film properties are columnar structure and high porous films. The barrier properties typically show 1.5g/m^2·day to 0.5 g/m^2·day at 38 °C and 90% relative humidity. The barrier oxide production cost by high speed manufacturing process typically is in the range of S$0.20¢ to 0.40¢/m^2. PECVD, which can achieve a throughput of 50 meters/min to 100 meters/min, was proposed by many researchers since PECVD provides better barrier properties than PEPVD methods. The production cost of PECVD barrier films are however comparatively higher than PEPVD methods since capital cost and consumable cost is higher than for PEPVD methods. In addition, metal oxide films produced by a high speed manufacturing process in the art (500m/min to 1000m/min) exhibit a porous microstructure and have numerous defects.

[0009] It is therefore an object of the present invention to provide a barrier stack system that overcomes at least some of the above drawbacks. In this regard it is also an object of the invention to provide a barrier stack system with improved flexibility, gas barrier properties, weatherability, optical, mechanical properties and reliability of flexible high barrier substrate system and also to provide cost effective solutions. This object is solved by the subject matter of the independent claims.

SUMMARY OF THE INVENTION

[0010] The present inventors have surprisingly found that a sealing layer comprising dendrimer encapsulated nanoparticles may provide an advantage when used in barrier stack for one of the following functions or properties or any combination thereof:

a) the high molecularly designed high packing density of dendrimer-nanoparticle film (sealing layer) reduces the porosity of the nanoparticle film, which enables to block the moisture oxygen diffusion through the dendrimer encapsulated nanoparticle sealing layer;

b) the cross-linking with other components of the sealing layer (such as nanoparticles, oligomers, polymers) gives mechanical stability and increasing the bond strength between the nanoparticles;

c) the chemical nature of the composite material and, thereby, the chemical selectivity of the intended barrier stack utilizes the chemical properties of the dendrimer's interior and/or of its surface;

d) the surface of the dendrimer encapsulated nanoparticle sealing layer of the invention has "a ball rug" conformation that provides the sealing layer with a greater contact surface if compared with the sealing layer with embedded nanoparticle (e.g. those disclosed in WO 2005/0249901 A1 and WO2008/057045). A greater contact surface allows a better blocking of the moisture and renders the sealing layer more efficient.

[0011] The present inventors have also surprisingly found that dendrimer encapsulated nanoparticles are capable of sealing or plugging defects.

[0012] This provide an encapsulated barrier stack according to the invention that is a low-cost device that has multi-functional properties including UV light blocking and has excellent anti-reflection properties.

[0013] Hence, in one aspect, the invention provides an encapsulation barrier stack, capable of encapsulating a moisture and/or oxygen sensitive article and comprising a multilayer film, wherein the multilayer film comprises:

one or more barrier layer(s) having low moisture and/or oxygen permeability, and

one or more sealing layer(s) arranged to be in contact with a surface of the at least one barrier layer, thereby covering and/ or plugging defects present in the barrier layer, wherein the one or more sealing layer(s) comprise(s)

a plurality of dendrimer encapsulated nanoparticles, the nanoparticles being reactive in that they are capable of interacting with moisture and/or oxygen to retard the permeation of moisture and/or oxygen and wherein the nanoparticle are totally or partially encapsulated in dendrimers and/or dendrons.

Prefererably, the dendrimer encapsulated nanoparticles are crosslinked to each other i.e. are "crosslinked dendrimer encapsulated nanoparticles".

[0014] In another aspect, the invention provides an electronic module comprising an electronic device that is sensitive to moisture and/or oxygen, wherein the electronic device is arranged within an encapsulation barrier stack according to invention.

[0015] In yet another aspect, the invention provides a method of manufacturing an encapsulation barrier stack having one or more sealing layer(s) that comprises dendrimer encapsulated nanoparticles.

[0016] In an embodiment of the method of manufacturing an encapsulation barrier stack, the method comprises:

providing one or more barrier layer(s), and

forming one or more sealing layer(s), wherein forming the one or more sealing layer(s) comprises

(i) mixing an encapsulation material consisting of or comprising of dendrimers or precursors thereof, dendrons or precursors thereof, optionally in the presence of a polymerizable compound and/or a cross-linkable compound, with a plurality of nanoparticles, the nanoparticles being reactive in that they are capable of interacting with moisture and/or oxygen, thereby forming a sealing mixture,

(ii) applying the sealing mixture onto the barrier layer under conditions that allow the nanoparticles to be encapsulated by or in the dendrimers, thereby forming the sealing layer.

A polymerization step of the polymerizable compound or a crosslinking of the cross-linkable compound is performed when the polymerizable compound or a crosslinking of the cross-linkable compounds are present in the encapsulation material.

[0017] Preferably, the polymerizable compound of the encapsulating material is a monomer. The encapsulation material may further comprises organic material such silane, surfactant and other additives. Additionally, it may comprise suitable solvent.

Preferably, “crosslinked dendrimer encapsulated nanoparticles” are formed.

[0018] Alternatively, in a second embodiment of the method of manufacturing an encapsulation barrier stack, the method comprises:

providing one or more barrier layer(s), and

forming one or more sealing layer(s), wherein forming the one or more sealing layer(s) comprises

(i) providing an encapsulation material consisting of or comprising dendrimer encapsulated nanoparticle, the nanoparticles being reactive in that they are capable of interacting with moisture and/or oxygen,

(ii) optionally mixing the encapsulation material with a polymerizable compound or with a cross-linkable compound, thereby forming a sealing mixture,

(iii) applying the sealing mixture onto the barrier layer under conditions allowing the nanoparticles to form a sealing layer.

[0019] Preferably, the encapsulation material comprises a dendrimer and a polymerizable compound.

[0020] Preferably, the polymerizable compound of the encapsulating material is a monomer. The encapsulation material may further comprises organic material such silane, surfactant and other additives. Additionally, it may comprise suitable solvent.

Preferably, "crosslinked dendrimer encapsulated nanoparticles" are formed.

[0021] An encapsulation barrier stack according to the invention has encapsulated nanoparticles. Dendrimers, dendrons and precursors thereof, optionally in combination with the polymerizable compounds and cross linkers are used as an encapsulation material or for the functionalization of nanoparticles. Dendrimers, dendrons or precursor thereof, optionally in combination with the polymerizable compounds and cross linker of the encapsulation material are reacted with the nanoparticles to form the "encapsulating material". Hence in the present context "encapsulation material" is the material before the reaction(s) that lead(s) to the encapsulation and the sealing layer formation. The "encapsulating material" is the material that encapsulates the nanoparticles once the reaction(s) that lead(s) to the encapsulation is occurred.

[0022] In the present context, the "dendrimer encapsulated nanoparticle" is either encapsulated by the dendrimer molecule, or surrounded by dendrimers, or is a dendrimer core after attachment of dendrons on to its surface.

[0023] Further, in this context, it is noted that the term "encapsulated" does not necessarily mean that the entire surface of the reactive nanoparticle is coated/encapsulated with the encapsulation material of the invention. Rather than the surface of the nanoparticle being 100% encapsulated, it is also encompassed in the present invention that only about 50% or more, or about 60% or more, or about 75% or more, or about 80 % or more, or about 85% or more, or about 90% or more or about 95%

or more of the surface of the reactive nanoparticles are encapsulated, or in other words, passivated by the encapsulation material after forming the encapsulation, by for example linking each other the dendrimers or the dendrons or curing or cross-linking of the polymerizable compound. The present inventors have also surprisingly found that dendrimer encapsulated nanoparticles are capable of sealing or plugging defects and that they also enhance gas barrier properties. In addition an encapsulated barrier stack according to the invention is a low-cost device that has multi-functional properties including UV light blocking and has excellent anti-reflection properties.

[0024] An encapsulated barrier stack of the invention may have a porous barrier layer, which may be an oxide film, as well as a sealing layer. The sealing layer may contain functionalized nanoparticles, which are either encapsulated or passivated by dendrimer or by dendrimer/polymer mixture.

[0025] The sealing layer may in some embodiments be a single layer. In some embodiments the encapsulated barrier stack has a single sealing layer. In some embodiments the encapsulated barrier stack includes multiple sealing layers. Examples of embodiments of the general build-up of a barrier stack according to the invention are depicted in **Fig. 3**.

[0026] The present disclosure provides a barrier stack with improved flexibility, gas barrier, weatherability, optical, mechanical properties and reliability, and also provides a cost effective solution.

[0027] According to a first aspect, the present invention provides an encapsulation barrier stack. The encapsulation barrier stack is capable of encapsulating a moisture and/or oxygen sensitive article. The encapsulation barrier stack includes a multilayer film. The multilayer film includes one or more barrier layer(s) and one or more sealing layers comprising dendrimer encapsulated nanoparticles that provide low moisture and/or oxygen permeability. The multilayer film further includes one or more sealing layer(s). The one or more sealing layer(s) are arranged to be in contact with a surface of the at least one barrier layer. Thereby the one or more sealing layer(s) cover defects present in the barrier layer. The one or more sealing layer(s) include(s) a plurality of dendrimers and/or dendrons and organic species, for example, dendrimers encapsulated nanoparticles. The nanoparticles are reactive in that they are capable of interacting with moisture and/or oxygen to retard the permeation of moisture and/or oxygen through the defects present in the barrier layer.

[0028] According to a second aspect, the invention provides an electronic device. The electronic device includes an active component that is sensitive to moisture and/or oxygen. The active component is arranged within an encapsulation barrier stack according to the first aspect.

[0029] According to a third aspect, the invention provides a method of manufacturing an encapsulation barrier stack according to the first aspect. The method includes providing one or more barrier layer(s). The method also includes forming one or more sealing layer(s). In a first embodiment of the third aspect, forming the one or more sealing layer(s) includes mixing an encapsulation material according to the invention which consists of or comprises one of the following: dendrimer or precursor thereof, dendron or precursor thereof, a dendrimer/polymerizable compound mixture, dendron/polymerizable compound mixture, dendrimer/crosslinkable compound mixture, dendron/crosslinkable compound mixture with a plurality of nanoparticles or functionalized nanoparticles. The polymerizable or cross-linkable species include monomers, polymer and/or oligomer or combinations thereof.

[0030] Alternatively in a second embodiment of the third aspect forming the one or more sealing layer(s) includes optionally mixing an encapsulating material which consists of or comprises dendrimer encapsulated nanoparticle with a polymerizable or a cross-linkable compound. The polymerizable or cross-linkable species include monomers, polymer and/or oligomer or combinations thereof.

[0031] According to a fourth aspect, the invention relates to the use of dendrimer encapsulated reactive nanoparticles for preparing a sealing layer of a barrier stack. The nanoparticles are reactive in that they are capable of interacting with moisture and/or oxygen to retard the permeation of moisture and/or oxygen through the defects present in the barrier layer.

[0032] According to a fifth aspect, the invention relates to the use of dendrimer encapsulated reactive nanoparticles for encapsulating an electronic device, or use in food packaging, or pharmaceutical packaging or medical packaging.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033] **Figure 1** depicts a known barrier stack device, in which the barrier oxide coating defects are decoupled by an intermediate polymer layer. The tortuous path, i.e. the permeation path for fluid or the time taken to diffuse through the barrier depends on the number of inorganic/organic pairs used. If a higher number of the pairs are used, the path is longer and therefore, higher barrier properties can be achieved. Using multiple barrier layers, the overall performance will vary depending on whether the pinholes in one barrier layer are lined up with the defects in the other barrier layers or not. In addition, if the numbers of defects are higher, the decoupling concept will not work. In the sense, the defects of the barrier layer may be lined up with the defects in the second barrier layer. This invention requires very high packing density (lower number of pin holes) barrier oxide films, which are produced either by sputtering methods or PECVD methods.

[0034] Figure 2 depicts a further known barrier stack device disclosed in WO 2008/057045 and WO2010/140980, in which nanoparticles are distributed in the polymer matrix to improve the barrier properties. These disclosures are not concerned with sealing barrier oxide film defects. A drawback of the device shown in Fig. 2 is that water vapor will be released through the pinholes of the barrier oxide films once the reactive nanoparticles are saturated with water vapor. Further, there is a limitation in loading the nanoparticles in the thermoplastics (the base film normally formed by extrusion process where in the thermoplastic melts, the films are drawn and then cooled down), it is a complex process and a higher number of getter nanoparticles loading in the film would affect the transmittance.

[0035] Figure 3A depicts an embodiment of a barrier stack according to the invention.

[0036] Figure 3B depicts a further embodiment of a barrier stack according to the invention.

[0037] Figure 3C depicts yet another embodiment of a barrier stack according to the invention, deposited onto a planarized or non-planarized substrate that is of plastic material.

[0038] Figure 4 illustrates a qualitative test on barrier stack performance, analysing whether calcium degradation can occur (Type A).

[0039] Figure 5 illustrates a quantitative test on barrier stack performance, analysing calcium degradation (Type B).

[0040] Figure 6 depicts a nanogetter layer coated polycarbonate substrate.

[0041] Figure 7 shows an illustration of dendrimer encapsulated nanoparticles and with dendrimer passivated particles as used in the invention, with Figures 7A and 7B showing a partially encapsulated (i.e. a passivated) nanoparticle and Figure 7C showing a completely encapsulated nanoparticle.

[0042] Figure 8 shows illustrative examples of dendrimers that can be used in the present invention, with **Figure 8A** showing a polyamidoamine (PAMAM) dendrimer that consists of an alkyl-diamine core and tertiary amine branches and that has a variety of surface groups available, for example, for crosslinking, with **Figure 8B** showing a Polypropylenimine hexadecaamine Dendrimer (PEI), Generation 3.0, (linear Formula [-$CH_2CH_2N[(CH_2)_3N[(CH_2)_3N[(CH_2)_3NH_2]_2]_2]_2$, aminopropyl surface groups, 1,4-diaminobutane core (4-carbon core)) and **Figure 8C** showing aphosphorous-based dendrimer such as a cyclotriphosphazene dendrimers based on hexachlorocyclotriphosphazene and **Figure 8D** showing a Polyester-16-hydroxyl-1-acetylene bis-MPA dendron, generation 4.

DETAILED DESCRIPTION OF THE INVENTION

Dendrimers

[0043] As used herein, the terms "dendrimer encapsulated nanoparticle" and "DENs" refer generally to a nanostructure where one dendrimer molecule entraps one or more nanoparticles. Dendrimer encapsulated nanoparticle as used herein refers to nanoparticle of metal, metal oxide, metal halide as disclosed herein which are either encapsulated by the dendrimeric molecule or surrounded by dendrimer or the nanoparticle is a dendrimer core after attachment of dendrons on its surface.

[0044] "Dendrimer" or "dendritic structure" means a macromolecule having a branched structure which can be obtained by polymerization (or co-polymerization) of organic monomer units having a functionality greater than 2. The chemical functions present at the ends of the branches of such a structure are referred to by the expression "terminal functions". By definition, the number of terminal functions on a dendritic polymer is greater than 2. Dendrimers are macromolecules composed of monomers which combine with each other in accordance with an arborescent process. Dendrimers, also called "cascade molecules", are highly branched functional polymers of defined structure. These macromolecules are in fact polymers since they are based on the association of repeating units. However, dendrimers differ fundamentally from conventional polymers in as much as they have their own properties owing to their arborescent construction. The molecular weight and the architecture of dendrimers can be precisely controlled. Dendrimers are constructed step by step by the iteration of a reaction sequence allowing the multiplication of each repeating unit and terminal functions. Each reaction sequence forms a so-called "new generation". The arborescent construction is effected by repeating a reaction sequence, which enables a new generation and an increasing number of identical branches and therefore of terminal functions to be obtained at the end of each reaction cycle. After a few generations, the dendrimer generally assumes a globular form which is highly branched and multi-functionalized owing to the large number of "terminal functions" present at the periphery.

In the context of the present description, "modified dendritic structure" means structures in which all or some of the functions, especially terminal functions, are bonded, in a covalent or non-covalent manner, by ionic or Van der Waals interactions, to molecules or macromolecules, which may be hydrophilic or hydrophobic. These modified dendritic structures therefore comprise a "core" formed from the initial dendrimer or hyper-branched polymer and a "cortex" formed by the hydrophilic or hydrophobic molecules, including, especially, fluorinated molecules.

[0045] Preferably, the dendrimer structures according to the invention are dendrimers or hyper-branched polymers comprising secondary amine (--NH--) or primary amine (-NH.$_2$) functions, hydroxyl functions (--OH), carboxylic acid functions (--COOH), halogen functions (Hal), such as Cl, Br or I, thiol functions (SH), more preferably amine or hydroxyl functions.

[0046] For these amine or hydroxyl functions may advantageously be coupled to molecules comprising functions of the carbonyl (CO) type, such as (--COOH); (--COHal); or ester, for example (--COOAlk) in order to lead to the production of modified dendrimers.

[0047] The hydrophilic or hydrophobic molecules that can be used according to the invention also comprise at least one function capable of reacting with at least one of the functions of the dendritic structure, especially with the terminal functions, which are generally readily accessible. For example, the hydrophilic or hydrophobic molecules can react with either a nanoparticle as used here or with metal cations as explained further below.

[0048] Dendrimers are known in the art. For example dendrimers according to the invention may be selected from poly(amidoamines) (PAMAM), polyethylene imines (PEI), poly(propyleneimines) (PPI), andpolypropyleneimine dotriacontaamine dendrimers (DAB) and Frechet dendrimers. Those dendrimer molecules are available in different sizes depending on the generation of the dendrimer (e.g. generation-1 to generation-8 or even

10). Examples of dendrimers or hyperbranched polymers are especially poly(amidoamines) (PAMAM), polyethylene imines (PEI), poly(propyleneimines) (PPI), and polypropyleneimine dotriacontaamine dendrimers (DAB), which are commercially available, for example, from Sigma Aldrich. Other examples of hyperbranched polymers are especially the polyphenylenes described by Y. H. Kim and O. W. Webster, the polyamides or the polyesters having a dendritic structure which are, for example, described in the International patent applications WO 92/08749 or WO 97/26294, the polyglycerols or also the polymers described in the International patent applications WO 93/09162, WO 95/06080 or WO95/06081.

[0049] As mentioned dendrimers may have different “terminal groups”, terminal group are functional groups present on the outer shell of the dendrimer. They are also known as “surface groups”. “Surface group” is for example the term used by Sigma Aldrich to identify the terminal group of a dendrimer. The dendrimer can have various surface groups such as Amidoethanol Surface Groups, Amidoethylethanolamine Surface Groups -Amino Surface Groups (such Dendrimer-($NHCH_2CH_2$)$_Z$) (Z is the average number of surface groups $NHCH_2CH_2$), Mixed (bi-functional) Surface Groups, Sodium Carboxylate Surface Groups, Succinamic Acid Surface Groups, Trimethoxysilyl Surface Groups, Tris(hydroxymethyl)amidomethane Surface Groups, 3-Carbomethoxypyrrolidinone Surface Groups. Additional surface groups may be PEG molecules having different length, or other crosslinker compounds. The surface group may allow the formation of crosslink between dendrimer encapsulated nanoparticles, additionally they confer different properties to the dendrimer. For example, an amido-ethanol surface group is a neutral alcohol surface group. PAMAM dendrimers, with surfaces fully derivatized with externally presented amidoethanol groups, have higher solubility in less polar organic solvents. The neutral alcohol surface groups render e.g. PAMAM dendrimer having amidoethanol surface group useful in applications where more neutral pH conditions are necessary. To mention another example, the “amino surface group” consists of polar, highly reactive primary amine surface groups. The surfaces of the amino-functional PAMAM dendrimers (i.e. with amino surface groups) are cationic and can be derivatized, either through ionic interactions with negatively charged molecules, or using many well-known reagents for covalent functionalization of primary amines. The sodium carboxylate is an anionic surface group. PAMAM dendrimers with sodium carboxylate surfaces exhibit higher solubility in polar and aqueous solvents. Dendrimer functionalized with different functional groups are commercially available. For example Sigma Aldrich provides a wide variety of

PAMAM dendrimers having different core type and/or surface group or having different "generation".

[0050] The number of surface groups present in the outer shell may vary for example in dependence of the "generation" of the dendrimer. Typically, the number of surface group is higher for higher generation.

[0051] As an illustrative example: Polyamidoamine (PAMAM) dendrimers are the most common class of dendrimers suitable for many materials science and biotechnology applications. PAMAM dendrimers consist of alkyl-diamine core and tertiary amine branches. They are available in generations G 0 - 10 with 5 different core types and 10 functional surface groups. Typically PAMAM dendrimer core types are Ethylendiamine (2 carbon core), 1,4 dibutane amine (4 carbon core), 1,6 diaminohexane (6-carbon core), 1,12 diaminodecane (12-carbone core) and cystamine core (cleavable core). As already mentioned PAMAM dendrimers exist with different surface groups. PAMAM dendrimer having surface group selected from Amidoethanol Surface Groups, Amidoethylethanolamine Surface Groups -Amino Surface Groups (such Dendrimer-$(NHCH_2CH_2)_Z$), Mixed (bi-functional) Surface Groups, Sodium Carboxylate Surface Groups, Succinamic Acid Surface Groups, Trimethoxysilyl Surface Groups, Tris(hydroxymethyl)amidomethane Surface Groups 3-Carbomethoxypyrrolidinone Surface Groups are commercially available (Sigma Aldrich).

[0052] Other commercially available dendrimers which may be used for preparing the dendrimer encapsulated nanoparticle of the invention are: "DAB-Am-4, Polypropylenimine tetramine dendrimer, generation 1", Hyperbranched bis-MPA polyester-16-hydroxyl, generation 2 (having hydroxyl surface group), Hyperbranched bis-MPA polyester-64-hydroxyl, generation 4 (having hydroxyl surface group-average number 64), DAB-Am-32, Polypropylenimine dotriacontaamine Dendrimer, Generation 4.0, Cyclotriphosphazene-PMMH-12 dendrimer, generation 1.5 (with aldehyde surface group), Cyclotriphosphazene-PMMH-6 dendrimer, generation 1.0 (with dichlorophosphinothioyl surface groups).

[0053] "Dendrons" may be defined as are monodisperse wedge-shaped dendrimer sections with multiple terminal groups and a single reactive function at the focal point. They also have surface groups as disclosed above for the dendrimers. They are commercially available e.g., by Sigma Aldrich. As illustrative examples of commercially available dendrons: Polyester-8-hydroxyl-1-acetylene bis-MPA dendron, generation 3; Polyester-16-hydroxyl-1-acetylene bis-MPA dendron, generation 4; Polyester-32-hydroxyl-1-carboxyl bis-MPA dendron, generation 5; Polyester-8-hydroxyl-1-carboxyl bis-MPA dendron, generation 3; Polyester-16-hydroxyl-1-carboxyl bis-MPA dendron, generation 4; Poly(ethylene glycol), 16 hydroxyl dendron, generation 3; Poly(ethylene glycol), 4 acetylene dendron, generation 1; Polyester bis-MPA dendron, 16 hydroxyl, 1 allyl; Polyester bis-MPA dendron, 32 hydroxyl, 1 thiol; Polyester bis-MPA dendron, 2 hydroxyl, 1 azide; Polyester bis-MPA dendron, 2 hydroxyl, 1 acetylene may be mentioned. Several other dendrons are commercially available. The dendrons are characterized by having a reactive focal point that allows the binding of the dendron to the surface of the nanoparticle (conveniently functionalized). Amine group, thiol, azide, allyl, acetylene, hydroxyl, carboxylic group are suitable and known groups for the focal point of dendrons.

[0054] It is further noted that "dendrimer" are typically considered polymeric macromolecules composed of multiple perfectly-branched monomers radially emanating from a central core, while hyper-branched polymers are polydisperse dendritic macromolecules that possess dendrimer-like properties but are prepared in a single synthetic polymerization step. They are imperfectly branched and have an average (rather than precise) number of terminal functional groups. For the purpose of the present invention hyper-branched polymers fall under the term "dendrimer".

Sealing layer

[0055] More in detail, there are many approaches that can be undertaken to form a sealing layer with dendrimer encapsulates nanoparticles which may include, but is not limited to "ligand exchange" and "cross-linked" approaches.

[0056] The nanoparticles are usually present in the sealing mixture in a rather high amount, and typically make up more than 80%, more than 85 % or more than 90% of the total mass of the sealing layer, meaning that the weight of the encapsulating material of the first aspect of the invention is 20 % or less of the total weight of the total weight of the sealing layer. In some embodiments, the weight of the nanoparticles is 90% to 95%, including 91 %, 92 %, 93 % and 94 % (w/w). In other embodiments, the weight of the nanoparticles is 96, 97 or 98 % (w/w) of the weight of the sealing layer. In typical embodiments most or ideally each nanoparticle is encapsulated with the encapsulating material of the invention.

[0057] Therefore, the nanoparticle layer has a high packing density and provides strong bonding between the particles due the encapsulated dendrimer and the organic material such as polymer, silane, surfactant and other additives.

[0058] The ratio of nanoparticles to encapsulation material (and thereby the encapsulating material) is important for the high packing density and desired properties. A preferable ratio of nanoparticles to encapsulation material is 19:1 (weight by weight). In certain embodiments and depending on the desired properties the weight ratio of nanoparticles to encapsulation material may be 9:1 or 12:1 or 15:1. The invention focuses to reduce the amount of organic component content of the encapsulating material or to reduce the amount of encapsulation material as such to the minimum such that the encapsulation can even be only partial. In one embodiment, the encapsulation material used enhances the bond strength between adjacent particles and enhances oxygen and barrier properties. The encapsulating material may cover only 50 to 90%, or 95% or up to 100% of the surface area of the nanoparticle (cf. Fig. 7). And therefore, the moisture or oxygen permeates through the encapsulating material, and the nanoparticle can react with the oxygen and moisture. Therefore, the overall permeation through the sealing layer is minimised. In one of the embodiment the encapsulation material may be reactive or non-reactive.

[0059] In one embodiment forming the one or more sealing layer(s) also includes applying the sealing mixture onto the barrier layer.

[0060] The encapsulation material comprising the dendrimer or the dendron may be directly combined with the nanoparticles and let them react in the presence of a suitable reagent (e.g. reducing agent) to form the dendrimer encapsulated nanoparticles. For example the focal group of the dendrons is let to react with a suitable functionalized surface of a nanoparticle to produce a dendrimer encapsulated nanoparticle. Thereby, the sealing layer is formed.

[0061] Alternatively, the dendrimer and precursors such as a silane, acrylate, or imidazole compound (or mixtures thereof) are polymerized or formed on the nanoparticle surface. In order to ensure that the dendrimers start from the particle surface, the dendrimers are chosen with functional groups that can adsorb on the particle surface and dendrimer encapsulation is performed in a controlled manner.

[0062] In order to enhance the selective interaction with certain compounds the repeating units may also be functionalized with terminating structural units. The valences of the structural units, which are not involved in linking these units to the dendrimer structure may carry a hydrogen atom or a small alkyl group, e.g. a methyl or an ethyl group, a small alkoxy group, e.g. methoxy, ethoxy, or may be deprotonated to form an ionic unit.

[0063] The dendrimer preferably cross-links other components of the encapsulation material such as polymerisable monomeric or oligomeric compounds (for example, acrylic monomers or a silane such as (3-acryloxypropyl)methyldimethoxysilane) or methacryloxypropyltrimethoxysilane) through covalent bonds or coordinative bonds (e.g. metal-ligands). To this end the outer shell of the dendrimers/dendrons comprises a terminal functionalized group (also known as surface groups) that may form covalent bonds with the other components of the encapsulating material (e.g. cross linker compound or linker unit, polymerizable compound such as monomer, etc.). A linking between single dendrimer encapsulated nanoparticles may be thereby advantageously achieved and crosslinked dendrimer encapsulated nanoparticles are formed. Linking between dendrimer encapsulated nanoparticles may be also achieved via cross linkers that are cross-linkable compounds that form a "linker unit" with the surface group of the dendrimer/dendron. Cross-linkable compounds are for example monomer or oligomer or compounds comprising linker unit as defined below. For example linking or cross linking between dendrimer encapsulated nanoparticles can be obtained by reacting the surface group of the dendrimer or dendron with crosslinking compounds. The crosslinking compound (such as PEG or a silane such as (3-acryloxypropyl)methyldimethoxysilane) or methacryloxypropyltrimethoxysilane) can be bonded to the outer shell of the dendrimer/dendron (e.g. via the surface group of the dendrimer/dendron) before the encapsulation step. Hence, the crosslinking (after the cross-linking reaction) between dendrimer encapsulated nanoparticles is a direct link between the surface groups of distinct dendrimer encapsulated nanoparticle or the crosslinking is "mediated" by a crosslinker compounds (e.g. bi-functionalized compounds, monomer, or PEG, to name only a few examples. The dendrimer might also be photocurable. An example of such a dendrimer is a PAMAM dendrimer G3.0 to which polyethylene glycol (PEG) chains of various lengths (MW=1500, 6000, or 12000 gmol^{-1}) can be coupled and the resulting PEGylated PAMAM dendrimers can be further coupled with acrylate groups to yield photoreactive dendrimer macromonomers (cf. in respect Desai et al., Biomacromolecules 2010 March 8; 11(3): 666–673.=Another example of photocurable dendrimers are photo cross-linkable poly(glycerol-succinic acid)-*co*-poly-(ethylene glycol) dendrimers (first-generation (G1) dendritic polymer, ([G1]-PGLSA-MA)2-PEG) described in Degoricija et al. Investigative Ophthalmology & Visual Science, May 2007, Vol. 48, No. 5, pages 2037-2042).

[0064] Linking of the dendrimer molecules may also be obtained through non-covalent bonding, such as ionic or dipole-dipole interactions or metal-ion complexation.

[0065] The "**linker units**" or "**cross linker units**" may be coupled to the dendrimer molecule by appropriate spacer units (e.g. cross linking compounds). Preferably the "linker units" are selected from the group formed of thiol groups, disulphide groups, amino groups, isocyanide groups, thiocarbamate groups, dithiocarbamate groups, chelating polyether, and carboxyl groups. Within the dendrimer molecule the linker units may be of the same or of different type.

[0066] The structure of the dendrimer (especially the repeating units, the spacer units, and/or the linker units) may comprise or may be formed from amino acids, e.g. glycine (GLY), alanine (Ala), valine (Val), leucine (Leu), isoleucine (Ile), methionine (Met), proline (Pro), phenylalanine (Phe), tryptophan (Trp), serine (Ser), threonine (Thr), cysteine (Cys), tyrosine (Tyr), asparagine (Asn), glutamine, (Gln), aspartic acid (Asp), glutamic acid (Glu), lysine (Lys), arginine (Art), histidine (His), or nucleotides, or nucleotide building blocks, e.g. cytosine, uracil, thymine, adenine, guanine, ribose, 2-deoxyribose, or derivatives of such compounds.

[0067] The structure of the "dendrimer core" and the "repeating units" may comprise electron-donating groups, e.g. amino groups, imino groups, aromatic groups comprising hetero atoms (N, S, O), carbonyl groups, carboxy groups, ether groups, thio groups, etc., which may be used for complexing metal cations that can be used to further stabilize the dendrimer encapsulated nanoparticles.

[0068] Suitable metal cations that can be used for stabilizing the dendrimer encapsulation may be main group metals, such as Mg2+, Ca2+,Pb2+, etc., transition metals, such as Mn2+, Co2+, Ru2+, Fe2+, Fe3+, Cu2+, Ag+, Zn2+, Cd2+,Hg2+, Cr3+, Pt2+, Au3+, Pd2+, etc., rare earth metals, such as Ce3+, Eu3+, etc., which themselves can serve, if wanted, to form selective interaction sites for analytes, e.g. O2, CO, NH3, SOx, NOx. Examples of metallodendrimers are given in G.R. Newkome, E. He, C.N. Moorefield, Chem. Rev. 1999, 99, 1689 – 1746.

[0069] Both PAMAM- and PPI- dendrimers can incorporate (complex) metal cations (e.g. Ag+, Au3+, Pt2+, Pd2+, Cu2+). Furthermore the metal cations can be reduced by UV-irradiation or by wet-chemical methods to form dendrimer stabilized metal nanoparticles. Also semiconductor materials can form clusters with such dendrimer molecules, e.g. PAMAM stabilized CdS clusters. Nanoparticles might therefore be used as second component of the sensor medium. Stabilization of the nanoparticles by dendrimers is achieved by adsorption of the dendrimers on the nanoparticle's surface. The amino groups on the dendrimer's outer sphere serve as linker units to bind to the surface of the nanoparticles. Since the amino groups have a high affinity for many metal surfaces PAMAM-dendrimers form monolayers on metal substrates (e.g. Au substrates). Further the primary amino groups of PPI and PAMAM dendrimers can be used to covalently attach the dendrimer to self-assembled monolayers of organic thiols, as described by Wells and Crooks (M. Wells, R.M. Crooks, J. Am. Chem. Soc.1996, 118, 3988 – 3989

[0070] The chemical nature of the outer sphere of PPI- and PAMAM-dendrimers can be controlled by coupling various organic residues to the primary amino groups via amide coupling. This can be utilized to tune the chemical selectivity (to react or not react with moisture and oxygen) of dendrimer based to improve the coupling of the dendrimer molecules e.g. to the surface of a nanoparticle. This might be achieved by providing e.g. a thiol group or a disulfide group on the surface of the dendrimer molecule by coupling such linker units to the terminal amino groups through an appropriate spacer unit by an amide bond. An example, which demonstrates how PAMAM-dendrimers can be functionalized with terminal thiol groups has been described by V. Chechik et al., Langmuir 1999, 15, 6364 –6369. Nanoparticles are nanoscopic objects that are confined in at least one dimension to the nanometer scale (< 1000 nm, preferably < 100 nm). Thus, nanoparticles may resemble spheres (3-dimensional confinement), fibers or tubes (2-dimensional confinement) or sheets (1-dimensional confinement). Examples for 3-dimensionally confined nanoparticles are surfactant-stabilized metal and semiconductor nanoparticles, and fullerenes such as C60.

[0071] Examples for 2-dimensionally confined nanoparticles are carbon nanotubes, and semiconductor nanofibers, such as V2O5-nanofibers. Examples for 1-dimensionally confined nanoparticles are sheets made from ZnS or titania. Preferred is the use of three dimensionally confined nanoparticles in the size regime between 0.8 to 100 nm.

[0072] The preparation of dendrimer/polymer composites has already been described by M. Zhao, Y. Liu, R.M. Crooks, D.E. Bergbreiter, J. Am. Chem. Soc. 1999, 121, 923 - 930 W0/9858970 . Hence, in one embodiment forming the one or more sealing layer(s) also includes applying the sealing mixture onto the barrier layer and polymerising the polymerizable compound of the encapsulation material to form a polymer and/or linkage between the nanoparticle. The polymer forming monomer precursors such as a silane, acrylate, or imidazole compound (or mixtures thereof) are polymerized. (Semi)conducting polymers or oligomers, which are useful to provide useful electronic properties to the dendrimer composite material are for example polypyrrole, polyaniline, polythiophene, or any derivatives of these polymers. Other examples of semiconducting polymers are described in G. Hadziioannou, P.F. van Hutten (Eds.): "Semiconducting Polymers - Chemistry, Physics and Engineering", Wiley-VCH, Weinheim, Germany.

[0073] The problem of the invention can be resolved by producing encapsulated nanoparticle with maximum particle - particle linkage by a sealing layer comprising dendrimer encapsulated nanoparticle (preferably cross linked) having an optimal ratio encapsulating material/ nanoparticle. This purposed is also achieved by optimization of mixing and reaction conditions. The thickness of encapsulation shell can be controlled by varying the experimental conditions such as method of mixing, time or methods, reaction time, reaction medium or by selecting right dendrimer/dendron.

[0074] In some embodiments, the preferred nanoparticle thickness is about 20nm without dendrimer encapsulation. The preferred encapsulation or shell thickness may be in the range of about 5 angstrom to about 100 angstrom. Therefore, the dendrimer is formed under conditions that allow the nanoparticles to be encapsulated by the formed dendrimer. In this context, it is noted that conditions that allow the nanoparticles to be encapsulated are for example, conditions in which the dendrimer compound is present in the sealing mixture in such a concentration that the dendrimer compound will interact with the nanoparticles. Such conditions may include using a low concentration of the dendrimer, dendron or mixture thereof with optionally polymerizable or crosslinkable compound/units in the sealing mixture. For example, in such a liquid sealing solution the encapsulation material may be present in a concentration of about 5 % (w/v) or less, or 10 % /w/v) of the sealing mixture or of 3 % (w/v) or of 5% (w/v) of the sealing mixture. Expressed differently, such conditions might also be achieved by using less than 10 wt.-% or less that 25 wt.-% or less (dry form-without solvent) of encapsulation material of the weight of the reactive nanoparticles (that means a weight ratio of 1:9 or of 1:4). The weight ratio of encapsulation material to reactive nanoparticles weight also is 1: 9, or 1:12, or 1:15, or 1:19 or less. Under such conditions, a sealing solution contains such low concentrations of the dendrimers or dendrons that the dendrimer or dendron is adsorbed on the reactive nanoparticle, thereby coating the reactive nanoparticles with the dendrimer or dendron.

[0075] In order to facilitate conditions that allow the nanoparticles to be encapsulated, the sealing solution may also be sonificated such that the encapsulation material is mixed with the nanoparticles and the freely moving reactive nanoparticles are coated with the dendrimer or dendron during the sonification treatment. If such a sealing solution is then applied onto a barrier layer and exposed to suitable conditions, dendrimer are formed on the surface of reactive nanoparticles and, possibly bonds are also formed between different nanoparticles. In some embodiments, heating may be required before or after the encapsulation process. The mixing may be undertaken under inert environment if reactive nanoparticles are used.

[0076] However, if crosslinking between different nanoparticles occurs during the encapsulation step the sealing layer as described here does not form a polymer matrix as described in US Patent 8,039,739 or the international patent applications WO 2005/0249901 A1 and WO2008/057045 in which the nanoparticles are distributed and embedded. Rather a "ball rug" like surface is created by the modulation of the ratio encapsulation material (in particular dendrimer or dendron)/nanoparticle. The sealing layer is formed substantially (say to about at least 80%, or 90%, or 95% or 100% of the surface of nanoparticle covered by encapsulation material) or entirely by the individually encapsulated nanoparticles. As said a variety of chemical functionalities (linker) such as amine, carboxylate, polyethylene glycol (PEG) can be introduced either as terminal functionality of the dendrimer/dendron or in the encapsulation material which may additionally provide a "cross linked encapsulation" (i.e. dendrimer encapsulated nanoparticle cross linked each other). It has been seen that these cross-linked encapsulations provide an excellent colloidal stability without affecting the properties or functionalities of the core nanoparticle.

[0077] In some embodiments a surface-modifying compound such as a silane is added to the sealing mixture.

Encapsulated barrier stack

[0078] In typical embodiments an encapsulated barrier stack according to the invention has a porous barrier oxide layer, which may for example have been deposited by a Physical Vapor Deposition method and/or by a Chemical Vapor Depositions method. An encapsulated barrier stack according to the invention comprises a sealing layer comprising dendrimer encapsulated nanoparticle and optionally further have surface functionalized nanoparticles and/or polymer/monomer encapsulated nanoparticles. These nanoparticles may serve in defining a single layer or multi-layers such as two, three, four or more layers. An encapsulated barrier stack according to the invention has multi-functional properties. The layer(s) of functionalized nanoparticle serve in plugging the defects, increase the tortious path that is available for a fluid (e.g. gas or moisture), block the UV rays, act as thermal barrier, improve anti-reflection and anti-static properties of the barrier stack. In addition, the nanoparticles serve in enhancing thermal barrier properties of the barrier stack.

[0079] The one or more nanoparticulate multi-layer(s), e.g. three layers, may be deposited by a slot die coating process in single pass coating (simultaneous multilayer coating method), in some embodiments using a triple slot die or by sequential coating. The nanoparticulate layer, such as a multi-layer, is capable of planarizing the plastic substrates and conformably covering the defects of the plastic films. In addition, it may serve in enhancing the barrier, optical and mechanical properties of the barrier films.

[0080] The present invention provides a barrier stack that, being completely or at least substantially devoid of a polymer matrix in which reactive nanoparticles are embedded, comprises an amount of dendrimer encapsulated nanoparticle layer optionally linked each other that is lower than in known barrier stacks. Known barrier stacks have a polymer interlayer in which the nanoparticles are distributed in the polymer layer/matrix. The polymer may become porous, thereby leading to a pathway for oxygen and moisture and reducing the life time of the devices that are encapsulated by the barrier stack (Fig. 1 and Fig. 2).

[0081] "Defects" in the barrier layer refer to structural defects, such as pits, pinholes, microcracks and grain boundaries. Such structural defects are known to exist in all types of barrier layers that are fabricated using deposition processes with which barrier layers are typically produced, such as chemical vapour deposition, as well as roll-to-roll processes. Gases can permeate these defects, thereby leading to poor barrier properties (see Mat. Res. Soc. Symp. Proc. Vol. 763, 2003, B6.10.1-B610.6).

Nanoparticles

[0082] "Reactive" nanoparticles refer to nanoparticles capable of interacting with moisture and/or oxygen, either by way of chemical reaction (e.g. hydrolysis or oxidation), or through physical or physico-chemical interaction (e.g. capillary action, adsorption, hydrophilic attraction, or any other non-covalent interaction between the nanoparticles and water/oxygen). Reactive nanoparticles may comprise or consist of metals which are reactive towards water and/or oxygen, i.e. metals which are above hydrogen in the reactivity series, including metals from Group 2 to 14 (IUPAC) may be used. Some preferred metals include those from Groups 2, 4, 10, 12, 13 and 14. For example, these metals may be selected from Al, Mg, Ba and Ca. Reactive transition metals may also be used, including Ti, Zn, Sn, Ni, and Fe for example.

[0083] Other than metals, reactive nanoparticles may also include or consist of certain metal oxides which are capable of interacting with moisture and/or oxygen, such as TiO_2, Al_2O_3, ZrO_2, ZnO, BaO, SrO, CaO and MgO, VO_2, CrO_2, MoO_2, and $LiMn_2O_4$. In certain embodiments, the metal oxide may comprise a transparent conductive metal oxide selected from the group consisting of cadmium stannate (Cd_2SnO_4), cadmium indate ($CdIn_2O_4$), zinc stannate (Zn_2SnO_4 and $ZnSnO_2$), and zinc indium oxide ($Zn_2In_2O_5$). In some embodiments a reactive nanoparticle may comprise or consist of a metal, a metal oxide, a metal nitride, a metal sulfite, a metal phosphate, a metal carbide and/or a metal oxynitride. Examples of metal nitrides that can be used include, but are not limited to TiN, AlN, ZrN, Zn_3N_2, Ba_3N_2, Sr_3N_2, Ca_3N_2 and Mg_3N_2, VN, CrN or MoN. Examples of metal oxynitrides that can be used include, but are not limited to TiO_xN_y such as TiON, AlON, ZrON, $Zn_3(N_{1-x}O_x)_{2-y}$, SrON, VON, CrON, MoON and stoichiometric equivalents thereof. Examples of metal carbides include, but are not limited to, hafnium carbide, tantalum carbide or silicon carbide.

[0084] The nanoparticles may consist of metal. Such nanoparticles can be prepared by various methods, ranging from gas-phase techniques to wet-chemical synthesis, which have been described by numerous papers in the literature. The wet-chemical preparation methods usually provide ligand-stabilized and/or charge-stabilized nanoparticle solutions. Such preparation methods are well known to persons skilled in the art. Metals suited for the fabrication of a nanoparticle sensor film are preferably selected from the group consisting of Au, Ag, Pt, Pd, Cu, Co, Ni, Cr, Mo, Zr, Nb, and Fe. It is also possible to use nanoparticles comprising combinations (e.g. alloys) of these metals.

[0085] It is also possible to use semiconductor nanoparticles (e.g. II/VI semiconductors such as CdS, CdSe, CdTe, ZnO, ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe, or III/V semiconductors such as GaAs, InAsInP, or others such as PbS, Cd3P2, Ti02, V2O5, SnO and other transition metal oxides, or combinations of these materials, including core/shell structures, e.g. CdS/CdSe or CdSe/ZnS. These particles can be doped with As Sb, Al, B, P, In Lanthanides, transition metals. In this case the dendrimers serve to interlink the nanoparticles. Further, also combinations of metals, semiconductors, and/or insulators may be used as nanoparticles. As insulator materials may be used as SiO2, Al2O3 or MgO.

[0086] As to the size of the particles, the person skilled in the art understands that reactivity may depend on the size of the material used (see J. Phys. Chem. Solids 66 (2005) 546-550). For example, Al_2O_3 and TiO_2 are reactive towards moisture in the form of nanoparticles but are unreactive (or reactive only to a very small extent) in the (continuous) bulk phase, such as a microscale or millimeter scale barrier layer which is beyond the nanoscale dimension of several nanometers to several hundred nanometers typically associated with nanoparticles. Accordingly, using Al_2O_3 and TiO_2 as illustrative examples, Al_2O_3 and TiO_2 nanoparticles are considered to be reactive towards moisture, whereas Al_2O_3 and TiO_2 bulk layers are passive barrier layers having low reactivity towards moisture. In general, reactive metal or metal oxide nanoparticles, for example Al_2O_3, TiO_2 or ZnO nanoparticles, may be present in suitable colloidal dispersions for the preservation of reactivity and may be synthesized via any conventional or proprietary method such as the NanoArc® method from Nanophase Technologies Corporation.

[0087] Apart from metals and metal oxides, reactive nanoparticles in the sealing layer may also comprise or consist of carbon nanoparticles, such as carbon nanotubes, which are hollow, or nanowires, which are solid. The reactive nanoparticles may also comprise or consist of carbon nanoribbons, nanofibres and any regular or irregular shaped carbon particles with nanoscale dimensions. For carbon nanotubes, single-walled or multi-walled carbon nanotubes may be used. In a study carried out by the present inventors, it was found that carbon nanotubes (CNTs) can serve as a desiccant. Carbon nanotubes can be wetted by low surface tension liquids via capillary action, particularly liquids whose surface tension does not exceed about 200 Nm^{-1} (Nature, page 801, Vol. 412, 2001). In principle, this would mean that water molecules can be drawn into open-ended carbon nanotubes by capillary suction. It is suggested that water molecules may form quasi-one-dimensional structures within carbon nanotubes, thereby helping to absorb and retain a small volume of oxygen and water molecules. While the quantity of carbon nanotubes may be maximized for maximum moisture and/or oxygen absorption, the inventors have found that in practice lower amounts are also suitable. For example, carbon nanotubes may be used in low quantities of about 0.01% to 10% by weight of the nanoparticles present. Higher concentrations of carbon nanotubes may also be used, but with a corresponding decrease in the transparency of the encapsulation barrier stack.

[0088] Hence, in another embodiment, graphene nano-sheets or flakes can be encapsulated according to the invention. Graphene appears to bond well to the polymers or monomers or dendrimer or dendron or precursor thereof, allowing a more effective coupling of the graphene. A consideration for creating a graphene suspension is overcoming the enormous van der Waals-like forces between graphite layers to yield a complete exfoliation of graphite flakes and dispersing the resulted graphene sheets stably in a liquid media. Sonication has been extensively used as an exfoliation and dispersion strategy to produce colloidal suspensions of graphene sheets in a liquid phase. This procedure has been successful in various solvents with a surface tension value 40–50 mJ m^{-2} which are good media for graphite exfoliation especially with the aid of a third, dispersant phase, such as surfactants and polymers. Herein, ball-milling can be used to exfoliate graphite in a wide variety of organic solvents including ethanol, formamide, acetone, tetrahydrofuran (THF), tetramethyluren (TMU), N,N-dimethylformamide (DMF), and N-methylpyrrolidone (NMP) to create colloidal dispersions of unfunctionalized graphene sheets.

[0089] As further example, the reactive nanoparticles may also be nanofilaments, for example a metal (e.g. a gold or a silver nanowire), a semiconductor (e.g. a silicon or a gallium nitride nanowire) or a polymeric nanoparticle. A further illustrative example is a nanofilament of a metal compound, such as indium phosphide (InP), molybdenum ditelluride ($MoTe_2$) or Zinc-doped indium phosphide nanowires, molybdenum ditelluride nanotubes. Further examples of nanofilaments of a metal compound include, but are not limited to nanotubes of MoS_2, WS_2, WSe_2, NbS_2, TaS_2, $NiCl_2$, SnS_2/SnS, HfS_2, V_2O_5, CdS/CdSe and TiO_2. Examples of metal phosphates include, but are not limited to InP and GaP. In one embodiment of a sealing layer, the nanoparticulate metal compound is made of a metal oxide, such as ZnO_2.

[0090] The nanoparticles in the sealing layer may also be obtained using a combination of conventional coating methods for the deposition of a seed layer of a metal compound and a solvent thermal method for growing a nanostructure based on the metal compound seeds. The nanostructures obtained by using those methods can be a nanowire, a single-crystal nanostructure, a double-crystal nanostructure, a polycrystalline nanostructure and an amorphous nanostructure.

[0091] The nanoparticle, such as a nanowire in the sealing layer may comprise at least one dimension in the range from about 10 nm to 1 μm, e.g. from about 20 nm to about 1 μm, from about 50 nm to about 600 nm, from about 100 nm to about 1 μm, from about 200 nm to about 1 μm, from about 75 nm to about 500 nm, from about 100 nm to about 500 nm, or from about 150 nm to about 750 nm, while another dimension may be in the range from about 200 nm to about 1 μm. Any suitable thickness can be chosen for the nanoparticle sealing layer, for example a thickness of between about 50 nm (for example, when using nanoparticles with a size of about 10 to about 20 nm) to about 1000 nm or even higher (if transparency of the sealing layer is not of concern). The sealing layer may thus have a thickness from about 200 nm to about 10 μm. In another embodiment, the thickness may be from about 200 nm to about 5 μm, or from about 200 nm to about 2 μm or from about 200 nm to about 1 μm, or at least 200 nm.In other embodiments, the nanoparticle sealing layer may have a thickness of about 250 nm to about 850 nm or of about 350 nm to about 750 nm.

[0092] In one embodiment, inert nanoparticles are included in the sealing layer and used in conjunction with reactive nanoparticles. As used herein, "inert nanoparticles" refer to nanoparticles which do not interact at all with moisture and/or oxygen, or which react to a small extent as compared to reactive nanoparticles. Such nanoparticles may be included into the sealing layer to obstruct the permeation of oxygen and/or moisture through the sealing layer. Examples of inert particles include nanoclays as described in US Patent No. 5,916,685. Such nanoparticles serve to plug the defects in the barrier layer, thereby obstructing the path through which permeation takes place, or at least reducing the defect cross-sectional area, thus rendering permeation pathways by which water vapor or oxygen diffuses through the defect much more tortuous, thus leading to longer permeation time before the barrier layer is breached and thereby improving barrier properties.

[0093] Other suitable materials for inert nanoparticles may also include unreactive metals such as copper, platinum, gold and silver; minerals or clays such as silica, wollastonite, mullite, monmorillonite; rare earth elements, silicate glass, fluorosilicate glass, fluoroborosilicate glass, aluminosilicate glass, calcium silicate glass, calcium aluminum silicate glass, calcium aluminum fluorosilicate glass, titanium carbide, zirconium carbide, zirconium nitride, silicon carbide, or silicon nitride, metal sulfides, and a mixture or combination thereof.

[0094] Encapsulation barrier stacks which comprise sealing layers having only inert nanoparticles, such as nanoclay particles, do not belong to the invention.

[0095] In addition the barrier stack may have a terminal layer, which defines a surface of the barrier stack in that it is in contact with the ambience. This terminal layer may comprise or consist of an acrylic polymer. The acrylic polymer may encompass metal halogenide particles. An illustrative example of a metal halogenide is a metal fluoride such as LiF and/or MgF_2.

[0096] Without wishing to be bound by theory, the inventors believe that strong barrier properties can be achieved by using a combination of different types of nanoparticles. By studying the absorption/reaction characteristics of different types of nanoparticles, it is possible to select a combination of nanoparticles which complement each other to achieve stronger barrier effects than with a single type of material. For example, different types of reactive nanoparticles may be used in the sealing layer, or a combination of reactive and inert nanoparticles may be used.

[0097] In accordance with the above, the sealing layer may include a combination of carbon nanotubes and metal and/or metal oxide nanoparticles. One exemplary embodiment would be the combination of TiO_2/Al_2O_3 nanoparticles with carbon nanotubes. Any range of quantitative ratios may be used and optimized accordingly using regular experimentation. In an exemplary embodiment, the quantity of metal oxide nanoparticles present is between 500 to 15000 times (by weight) the quantity of carbon nanotubes. For oxides of metals having low atomic weight, lower ratios can be used. For example, TiO_2 nanoparticles can be used in combination with carbon nanotubes, with the weight ratio of carbon nanotubes to TiO_2 being between about 1 : 10 to about 1 : 5, but not limited thereto.

[0098] The encapsulation barrier stack of the invention may be used to encapsulate any type of moisture and/or oxygen sensitive article, such as an electronic component, an electronic devices, drugs, foods, and reactive materials, for example. For encapsulating electroluminescent devices, the quality of light transmitted through the encapsulation barrier stack is particularly important. Thus, when the encapsulation barrier stack is used as a cover substrate over a top-emitting OLED, or when the encapsulation layer is designed for transparent OLED or see-through displays, the encapsulation barrier stack should not cause the quality of light transmitted by the electroluminescent device to be substantially degraded.

[0099] Based on the above requirement, the size of the particles may be chosen in such a way that optical transparency is maintained. In one embodiment, the sealing layer comprises nanoparticles having an average size of less than 1/2, or more preferably less than 1/5, the characteristic wavelength of light produced by the electroluminescent electronic component. In this context, the characteristic wavelength is defined as the wavelength at which the peak intensity of the light spectrum that is produced by the electroluminescent device. For electroluminescent devices emitting visible light, this design requirement translates into nanoparticles having a dimension of less than about 350 nm, or more preferably less than 200 nm.

[00100] As the random packing density of nanoparticles in the defects of the barrier layer is determined by the shape and size distribution of the nanoparticles, it is advantageous to use nanoparticles of different shapes and sizes to precisely control the sealing of defects of the barrier oxide layer. The nanoparticles may be present in one uniform shape or it may be formed in two or more shapes. Possible shapes that the nanoparticles can assume include spherical shapes, rod shapes, elliptical shapes or any irregular shapes. In the case of rod shaped nanoparticles, they may have a diameter of between about 10 nm to 50 nm, a length of 50 to 400 nm, and an aspect ratio of more than 5, but not limited thereto.

[00101] In order to provide efficient interaction between the reactive nanoparticles and the water vapour/oxygen permeating the barrier layer, the nanoparticles occupying the defects may have suitable shapes that would maximize the surface area that can come into contact with the water vapour and oxygen. This means that the nanoparticles may be designed to have a large surface area to volume, or surface area to weight ratio. In one embodiment, the nanoparticles have a surface area to weight ratio of between about 1 m^2/g to about 200 m^2/g. This requirement can be achieved by using nanoparticles with different shapes, such as two, three, four or more different shapes as described above.

[00102] A binder in which the nanoparticles are distributed may optionally be used in the sealing layer. Materials suitable for use as the binder include polymers, such as polymers derivable from monomers having at least one polymerizable group, and which can be readily polymerized. Examples of polymeric materials suitable for this purpose include polyacrylate, polyacrylamide, polyepoxide, parylene, polysiloxanes and polyurethane or any other polymer. For strong adhesion between two successive barrier layers, or to adhere the multilayer film onto a substrate, the polymers with good adhesive quality may be chosen. The sealing layer containing the nanoparticles is typically formed by coating the barrier with a dispersion containing nanoparticles mixed with a monomer solution, e.g. an unsaturated organic compound having at least one polymerisable group. The thickness of the sealing layer comprising binder with distributed nanoparticles therein can be in the range of about 2 nm to about several micrometers.

[00103] A sealing layer of a multilayer film in a barrier stack of the invention is designed to be capable of contacting at least a portion of the surface of a barrier layer. A sealing layer may for example be capable of contacting at least 50 %, at least 60 %, at least 70 %, at least 75 %, at least 80 %, at least 85 %, at least 90 %, at least 92 %, at least 95 %, at least 96 %, at least 97 %, at least 98 %, at least 99 %, at least 99.5 % or 100 % of the surface of the barrier layer.

[00104] In some embodiments, the sealing layer is arranged to be in close proximate contact with the entire surface of the barrier layer. For example, the sealing layer may be formed over the barrier layer in such a manner that it conforms to the shape of defects present on the surface of the barrier layer, i.e. either occupying or filling up entirely the pits present in the at least one barrier layer, or levelling rough protrusions over the surface of the barrier layer. In this manner, defects giving rise to the permeation of corrosive gases through the encapsulation barrier stack are "plugged", while protrusions which would otherwise give rise to poor interfacial contact between barrier layers are levelled. Any conformal coating or deposition method can be used, e.g. chemical vapour deposition or spin coating. Atomic layer deposition and pulsed laser deposition may also be used to form the sealing layer.

[00105] The barrier material used for forming the barrier layer of the multilayer film may comprise any typical barrier material with low permeability to water vapour and/or oxygen in the bulk phase. For example, the barrier material may comprise metals, metal oxides, ceramics, inorganic polymers, organic polymers and combinations thereof. In one embodiment, the barrier material is selected from indium tin oxide (ITO), TiAlN, SiO_2, SiC, Si_3N_4, TiO_2, HfO_2, Y_2O_3, Ta_2O_5, and Al_2O_3. The thickness of a barrier layer may be between 20 nm to 80 nm. In this respect, materials for reactive nanoparticles can be used as the barrier layer since the reactivity of the material depends on its size. For example, although nanoparticulate Al_2O_3 is reactive towards water, a bulk layer of Al_2O_3 which has larger than nanoscale dimensions does not display the same level of reactivity with water, and can thus be used for the barrier layer.

[00106] For certain applications which require the encapsulation barrier stack to have good mechanical strength, a substrate may be provided to support the multilayer film. The substrate may be flexible or rigid. The substrate may comprise any suitable variety of materials such as polyacetate, polypropylene, polyimide, cellophane, poly(1-trimethylsilyl-1-propyne, poly(4-methyl-2-pentyne), polyimide, polycarbonate, polyethylene, polyethersulfone, epoxy resins, polyethylene terephthalate, polystyrene, polyurethane, polyacrylate, polyacrylamide, polydimethylphenylene oxide, styrene-divinylbenzene copolymers, polyvinylidene fluoride (PVDF), nylon, nitrocellulose, cellulose, glass, indium tin oxide, nano-clays, silicones, polydimethylsiloxanes, biscyclopentadienyl iron, or polyphosphazenes, to name some illustrative examples. The base substrate may be arranged to face the external environment or it may face the encapsulated environment. In food packaging, the substrate may face the internal surface that is in contact with food while the encapsulation barrier stack forms the external surface in contact with atmospheric conditions.

[00107] Although it may be possible to form a multilayer film directly on a substrate, a substrate with a rough surface may be undesirable for direct contact with the barrier layer of the multilayer film. An interface layer between the multilayer film and the substrate may be provided to improve the contact between them. In one embodiment, a planarising layer is interposed between the substrate and the multilayer film so that the interface between the substrate and the multilayer film is improved. The planarising layer may include any suitable type of polymeric adhesive material such as epoxy. In one embodiment, the planarising layer comprises polyacrylate (acrylic polymer), as polyacrylate is known for having strong water absorption properties. In the absence of a planarising layer, the multilayer film may be orientated such that the sealing layer is in contact with the surface of the substrate, for example.

[00108] Typically an encapsulation barrier stack according to the invention has a water vapor transmission rate of less than about 10^{-3} g/m^2/day, less than about 10^{-4} g/m^2/day, less than about 1 x 10^{-5} g/m^2/day such as less than about 0.5 x 10^{-5} g/m^2/day, less than about 1 x 10^{-6} g/m^2/day or less than about 0.5 x 10^{-6} g/m^2/day.

[00109] The barrier effect of a single barrier layer coupled with a sealing layer, i.e. a single 'paired layer', is additive, meaning that the number of pairs of barrier/sealing layers coupled together is proportional to the overall barrier property of the multilayer film. Accordingly, for applications requiring high barrier properties, a plurality of paired layers may be used. In one embodiment, a barrier layer is arranged, e.g. stacked, on top of a sealing layer in alternating sequence. In other words, each sealing layer acts as an interface layer between 2 barrier layers. In some embodiments, 1, 2, 3, 4, or 5 paired layers are present in the multilayer film. For general purpose applications in which water vapour and oxygen transmission rates are less stringent (e.g. less than 10^{-3} g/m^2/day), the multilayer film may include only 1 or 2 barrier layers (1, 2 or 3 sealing layers would correspondingly be present), whereas for more stringent applications, 3, 4, 5 or more barrier layers may be included in the multilayer film to achieve water vapour transmission rates of less than 10^{-5} g/m^2/day or preferably less than 10^{-6} g/m^2/day. Where more than 2 paired layers are used, any combination of paired layers may be formed on opposing sides of the substrate to provide a double-laminated or deposited on to the substrate, or they be formed on the same side of the substrate.

[00110] In order to protect the multilayer film from mechanical damage, the multilayer film may be capped or overlaid with a terminal protective layer. The terminal layer may comprise any material having good mechanical strength and is scratch resistant. In one embodiment, the terminal layer comprises an acrylic film having distributed therein LiF and/or MgF_2 particles. In another embodiment, the terminal layer comprises an oxide film such as Al_2O_3 or any inorganic oxide layers.

[00111] The encapsulation barrier stack according to the invention may be used for any suitable barrier application, such as in the construction of a casing or housing, or a barrier foil for blister packs, or it may be used as an encapsulating layer over an electronic component. The encapsulation barrier stack may also be laminated or deposited over any existing barrier material, such as packaging materials for food and drinks, to improve their existing barrier properties. In a preferred embodiment, the encapsulation barrier stack is used to form an encapsulation for protecting electroluminescent electronic components comprising moisture and/or oxygen sensitive reactive layers, wherein the electroluminescent component is encapsulated within the encapsulation. Examples of such devices include, but are not limited to, reactive components comprised in Organic Light Emitting Devices (OLEDs), flexible solar cells, thin film batteries, charged-coupled devices (CCDs), or micro-electromechanical sensors (MEMS).

[00112] In OLED applications, the encapsulation barrier stack may be used to form any part of an encapsulation for isolating the active component of the OLED device. In one embodiment, the encapsulation barrier stack is used to form a base substrate for supporting the reactive layers of the electroluminescent component. In a rim-sealing structure, the encapsulation barrier stack may be used to form a rigid cover that is arranged over the reactive layers of the electroluminescent component. The rigid cover may be attached to the base substrate by means of an adhesive layer, the adhesive layer being arranged at least substantially along the edge of the cover substrate for forming an enclosure around the reactive component. In order to minimize lateral diffusion of oxygen/moisture into the enclosure containing the reactive component, the width of the covering layer or the adhesive layer may be made larger than the thickness of the encapsulation barrier stack. The term “covering layer” used herein refers to any layer that covers the barrier stack, meaning the cover layer is different from the sealing layer. The cover layer can, for example, be a protection layer that provides protection for the barrier stack from mechanical wear and tear (abrasion) or chemical or physical-chemical environmental influences (humidity, sunlight etc.).

[00113] In another embodiment, the encapsulation barrier stack is used to form a flexible encapsulating layer which seals the electroluminescent component against the base substrate. In this case, such an encapsulating layer may wrap around the surface of the electroluminescent component to form a 'proximal encapsulation'. The shape of the encapsulating layer thus conforms to the shape of the reactive component, leaving no gap between the electroluminescent component to be encapsulated and the encapsulating layer.

[00114] The present invention is further directed to a method of forming an encapsulation barrier stack according to the invention. The method comprises forming at least one barrier layer and at least one sealing layer. As the sealing layer contains reactive nanoparticles, steps involving the preparation and the use of the sealing layer are preferably carried out under vacuum to preserve the reactivity of the nanoparticles towards the moisture and/or oxygen. The step of forming the sealing layer may comprise mixing a polymerisable compound with a nanoparticle dispersion to form a sealing mixture, and polymerising the sealing mixture after being applied on the barrier layer under vacuum to form a sealing layer. The nanoparticle dispersion may comprise nanoparticles dispersed in at least one organic solvent. The at least one organic solvent may include any suitable solvent, such as ethers, ketones, aldehydes and glycols for example.

[00115] Nanoparticles may be synthesized by any conventional method known in the art, including vapor phase synthesis (Swihart, Current Opinion in Colloid and Interface Science 8 (2003) 127-133), sol-gel processing, sonochemical processing, cavitation processing, microemulsion processing, and high-energy ball milling, for instance. Nanoparticles are also commercially available either as nanoparticle powders or in a ready-made dispersion from Nanophase Technologies Corporation, for example. Proprietary methods may be used to synthesize commercially obtained nanoparticles such as NanoArc® synthesis.

[00116] In one embodiment, surface-activation of the nanoparticles is carried out in order to remove contaminants from the surface of the nanoparticles that may interfere with their ability to react with moisture and/or oxygen. Surface activation may comprise treating the nanoparticles with an acid, including a mineral acid such as hydrochloric acid or sulphuric acid. In some embodiments the acid used for said treatment is a dilute acid. Treatment comprises immersing the nanoparticles in the acid for a period of about 1 hour. It is to be noted that nanoparticles which can be easily contaminated such as carbon nanotubes and carbon nanofibres may require surface activation. On the other hand, nanoparticles such as aluminium oxide and titanium oxide may not require surface activation since these nanoparticles have high surface energy.

[00117] A polymerisable compound can additionally be used as a binder. This compound may be any readily polymerisable monomer or pre-polymer. Suitable monomers are preferably readily polymerisable via UV curing or heat curing or any other convenient curing method.

[00118] In one embodiment, polyacrylamide is used as polymer for binding the nanoparticles. Acrylic acid monomer powder may be dissolved in polar organic solvents such as 2-methoxyethanol (2MOE) and ethylene glycol (EG) or isopropyl alcohol and ethyl acetate. In order to obtain a uniform distribution of the nanoparticles in the sealing mixture, sonification of the sealing mixture may additionally be carried out. For instance, sonification may be carried out for at least about 30 minutes prior to polymerisation.

[00119] A substrate may be a part of the device to be encapsulated, such as a part of a circuit board, or it may be an additional structure that is included as part of the encapsulation, such as a flexible substrate. It is also possible that the substrate is part of the encapsulation barrier stack, comprising a thick barrier layer on which further sealing layers arid barrier layers are subsequently deposited. Otherwise, the substrate may be the surface of a worktop for fabricating the multilayer film and as such does not form part of the encapsulation barrier stack.

[00120] Once the substrate has been provided, it can be coated with barrier layers and the sealing solution. The barrier layer can be formed via physical vapor deposition (e.g. magnetron sputtering, thermal evaporation or electron beam evaporation), plasma polymerization, CVD, printing, spinning or any conventional coating processes including tip or dip coating processes.

[00121] The sealing solution may be formed on the barrier layer via any wet process method such as spin coating, screen printing, WebFlight method, tip coating, CVD methods or any other conventional (conformational) coating methods. Metal oxide and metal nano-particles, as well as carbon nanotubes, can be co-deposited through the wet-coating process or co-evaporated along with monomer or dimers of parylene based polymer films. Any type of parylene dimers including parylene C or D or any other grades can be evaporated along with nano particles.

[00122] If multiple barrier/sealing layers, i.e. paired layers, are to be formed, a substrate can be repetitively coated with the barrier material and sealing mixture (see also below). In order to establish an alternating arrangement comprising one or more successive barrier layers and sealing layers, the substrate may be successively coated first with the barrier material and then the sealing solution repeating over several times until the intended number of layers is formed. Each time the sealing solution is applied, it is cured, for example UV cured prior to the formation of the next barrier layer over it. In this context, it is noted that a barrier layer can be coated with two or more functional sealing layers. Therefore, a barrier stack of the invention may not be an alternating order of one barrier layer coated with one sealing layer. Rather, a barrier stack might consist of only one barrier layer on which one, two, three, four or even more functional sealing layers are deposited. Alternatively, if the barrier stack comprises more than one barrier layer, each barrier layer might be coated with one or more sealing layers. For example, one barrier layer might have only one sealing layer coated thereon, whereas a second or third barrier layer of the barrier stack might have two or more sealing layers arranged on the respective barrier layer.

[00123] After the sealing and barrier layers have been formed, optional steps may be taken to complete the construction of the encapsulation barrier stack, such as the formation of a glass cover, ITO lines and ITO coating. For example, Passive Matrix displays may require ITO lines to be formed on the encapsulation barrier stack. After the cover has been formed, the exposed surface of the cover may be further protected with a protective coating via deposition of a capping layer (MgF/LiF coating).

[00124] With reference to the figures, **FIG. 3C** shows one embodiment of an encapsulation barrier stack according to the invention, which is, in addition arranged on a plastic substrate. The encapsulation barrier stack comprises a multilayer film. The multilayer film comprises one or more barrier layers and one or more sealing layers. The multilayer film may for example include one, two, three, four, five, six, seven, eight nine or ten barrier layers. The multilayer film may for example include one, two, three, four, five, six, seven, eight nine or ten sealing layers. In embodiments with a plurality of barrier layers and sealing layers individual barrier layers and sealing layers may be in contact with other barrier layers and/or sealing layers. In some embodiments an individual barrier layer is in contact with two further barrier layers. In some embodiments an individual barrier layer is in contact with two sealing layers. In some embodiments an individual barrier layer is in contact with one further barrier layer and one sealing layer. In some embodiments an individual sealing layer is in contact with two further sealing layers. In some embodiments an individual sealing layer is in contact with two barrier layers. In some embodiments an individual sealing layer is in contact with one further sealing layer and one barrier layer. In some embodiments two or more sealing layers and one or more barrier layer(s) of the multilayer film are arranged in an alternating manner. In some embodiments the multilayer film includes a plurality of sealing layers and barrier layers arranged in an alternating sequence. In the embodiment depicted in **Fig. 3C** one barrier layer is present, denominated the barrier oxide. In the embodiment depicted in **Fig. 3C** two sealing layers are present, each denominated a functional nano layer. As noted above, it is also the scope of the present invention that each barrier layer has a different number of sealing layers arranged thereon. In it also in the scope of the invention that in case of a barrier stack with more than one sealing layers, only the sealing layer that directly contacts the barrier layer comprises or consists of dendrimer encapsulated nanoparticles of the invention and that other layers can be a sealing layer of the prior art, for example, a sealing layer as described in WO 2008/057045 in which reactive nanoparticles are distributed in a polymer matrix. The barrier layers have low permeability to oxygen and/or moisture. It will be noted that barrier layers contain pinhole defects which extend through the thickness of the barrier layer. Pinhole defects along with other types of structural defects limit the barrier performance of barrier layers as oxygen and water vapour can permeate into the barrier layer via these defects, eventually traversing the encapsulation barrier stack and coming into contact with the oxygen/moisture sensitive device.

[00125] The sealing layer(s) comprise(s) reactive nanoparticles, in particular dendrimer encapsulated nanoparticles, capable of interacting with water vapour and/or oxygen, thereby retarding the permeation of oxygen/moisture through the encapsulation barrier stack. In accordance with the present invention, these defects are at least partially covered up, or in some embodiments, entirely filled up by the nanoparticles in the sealing layer. As can be appreciated from **Fig. 3C**, the sealing layer preferably has a “ball rug” like surface. In other word, the encapsulated nanoparticle are not embedded in layer as disclosed in WO2008/057045 but rather the profile of the nanoparticles is clearly identifiable on the surface.

[00126] The encapsulated nanoparticles are dendrimer encapsulated nanoparticle. Dendrimer encapsulated nanoparticles are nanoparticles of metal, metal oxide, metal halide as disclosed herein which are either encapsulated by the dendrimeric molecule or surrounded by dendrimer or the nanoparticle is a dendrimer core after attachment of dendrons on its surface.

[00127] Optionally, the terminal group of the dendrimers or of the dendrons of the encapsulated nanoparticle may be a reactive group that allows a crosslinking between the single encapsulated nanoparticle. The terminal groups of the dendrimer or dendron is preferably such that no charge repulsion is created.

[00128] Optionally polymerizable compound or crosslinkable compound are added as linker/binder. The amount of linker is such that does not create a layer within which the dendrimer encapsulate nanoparticle are embedded. As stressed, in one embodiment, an important feature of the present invention is that the surface of the sealing layer as a “ball rug” like surface as schematically disclosed in Fig. 3C.

[00129] A sealing layer is prepared by providing a sealing mixture comprising an encapsulation material and the nanoparticles. As seen above, the encapsulation material and hence the sealing mixture may comprises in addition to dendrimer or precursor thereof, dendrons or precursor thereof, additional components such as linker units (cross linker), polymerizable compounds (such monomer or oligomer), solvents, surfactant, surface modifier and other reagents and additive suitable for the preparation of dendrimer encapsulated nanoparticle.

[00130] In a preferred embodiment, the encapsulation material comprised dendrimers or dendrons already formed and optionally other components such as linker unit, polymer, surfactant. Preferably, the dendrimers or the dendrons have the terminal groups at least partially modified to allow to have cross linked dendrimer encapsulated nanoparticles by reacting e.g. with the linker unity of the linker spacer (cross linker compound). Polymerizable compound after polymerization can crate as well cross linked dendrimer polymerizable nanoparticles. In some embodiments at least 50%, or 60 % or 70 or 73, or 75 % of the dendrimer encapsulated nanoparticles are crosslinked (see in this context Lemcoff et al, J. Am. Chem. Soc. Vol. 26, No. 37, 2004, pages 11420-11421 for the determination of the cross-linking degree)

[00131] The sealing mixture is then applied onto the barrier layer and the dendrimer encapsulated nanoparticles are formed under suitable conditions. Preferably, cross linked dendrimer encapsulated nanoparticles are formed.

[00132] Optionally, the sealing layer is prepared by providing a sealing mixture comprising the nanoparticle and the dendrimer or dendron, optionally in the presence of cross-linker reagent or a polymerizable reagent that act as binder/linker. Once the sealing mixture is applied to the barrier layer the dendrimer encapsulated nanoparticle is let be formed. Optionally, a curing/polymerization/linking reaction occurs to provide a crosslinking between the dendrimer encapsulated particles. Optionally curing/polymerization/linking is contemporaneous or subsequent the formation of the dendrimer encapsulated nanoparticle. For example the dendrimer encapsulated nanoparticle can be formed via a chemical reaction, while the polymerization may be UV induced e.g. in the presence of photo initiator) so that the two reactions (dendrimer encapsulated nanoparticle formation and polymerization of the binder) do not interfere each-other.

[00133] Examples of suitable polymers include, but are not limited to, polypropylene, polyisoprene, polystyrene, polyvinyl chloride, polyisobutylene, polyethylene terephthalate (PET), polyacrylates (e.g. polymethyl-methacrylate (PMMA)), ethylene-vinyl acetate (EVA) copolymers, phenol formaldehyde resins, epoxy resins, poly(N-propargylamides), poly(O-propargylesters), and polysiloxanes.

[00134] The monomer or the pre-polymer that may be present in the encapsulation material (and that is typically included in a non-aqueous based discontinuous phase solution for the preparation of the sealing layer) may be selected from any suitable hydrophobic material. Illustrative examples of hydrophobic monomers include, but are not limited to, styrenes (e.g., styrene, methylstyrene, vinylstyrene, dimethylstyrene, chlorostryene, dichlorostyrene, tert-butylstyrene, bromostyrene, and p-chloromethylstyrene), monofunctional acrylic esters (e.g., methyl acrylate, ethyl acrylate, isopropyl acrylate, n-butyl acrylate, butoxyethyl acrylate, isobutyl acrylate, n-amyl acrylate, isoamyl acrylate, n-hexyl acrylate, octyl acrylate, decyl acrylate, dodecyl acrylate, octadecyl acrylate, benzyl acrylate, phenyl acrylate, phenoxyethyl acrylate, cyclohexyl acrylate, dicyclopentanyl acrylate, dicyclopentenyl acrylate, dicyclopentenyloxyethyl acrylate, tetrahydrofurfuryl acrylate, isobornyl acrylate, isoamyl acrylate, lauryl acrylate, stearyl acrylate, benhenyl acrylate, ethoxydiethylene glycol acrylate, methoxytriethylene glycol acrylate, methoxydipropylene glycol acrylate, phenoxypolyethylene glycol acrylate, nonylphenol EO adduct acrylate, isooctyl acrylate, isomyristyl acrylate, isostearyl acrylate, 2-ethylhexyl diglycol acrylate, and oxtoxypolyethylene glycol polypropylene glycol monoacrylate), monofunctional methacrylic esters (e.g., methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, i-butyl methacrylate, tert-butyl methacrylate, n-amyl methacrylate, isoamyl methacrylate, n-hexyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate, tridecyl methacrylate, stearyl methacrylate, isodecyl methacrylate, octyl methacrylate, decyl methacrylate, dodecyl methacrylate, octadecyl methacrylate, methoxydiethylene glycol methacrylate, polypropylene glycol monomethacrylate, benzyl methacrylate, phenyl methacrylate, phenoxyethyl methacrylate, cyclohexyl methacrylate, tetrahydrofurfuryl methacrylate, tert-butylcyclohexyl methacrylate, behenyl methacrylate, dicyclopentanyl methacrylate, dicyclopentenyloxyethyl methacrylate, and polypropylene glycol monomethacrylate), allyl compounds (e.g., allylbenzene, allyl-3-cyclohexane propionate, 1-allyl-3,4-dimethoxybenzene, allyl phenoxyacetate, allyl phenylacetate, allylcyclohexane, and allyl polyvalent carboxylate), unsaturated esters of fumaric acid, maleic acid, itaconic acid, etc., and radical polymerizable group-containing monomers (e.g., N-substitued maleimide and cyclic olefins).

[00135] In some embodiments the one or more sealing layer(s) at least essentially consist(s) of the dendrimer encapsulated reactive nanoparticles.

DEFINITIONS

[00136] To facilitate an understanding of the present invention, a number of terms and phrases are defined below:

[00137] As used herein, the terms "dendrimer encapsulated nanoparticle" and "DENP" refer generally to a nanostructure where one dendrimer molecule entraps one or more nanoparticles. Dendrimer encapsulated nanoparticle as used herein refers to nanoparticle of metal, metal oxide, metal halide as disclosed herein which are either encapsulated by the dendrimeric molecule or surrounded by dendrimer or the nanoparticle is a dendrimer core after attachment of dendrons on its surface. "Dendrimer" or "dendritic structure" means a macromolecule having a branched structure which can be obtained by polymerization (or co-polymerization) of organic monomer units having a functionality greater than 2. The chemical functions present at the ends of the branches of such a structure are referred to by the expression "terminal functions". By definition, the number of terminal functions on a dendritic polymer is greater than 2. Dendrimers are macromolecules composed of monomers which combine with each other in accordance with an arborescent process. Dendrimers, also called "cascade molecules", are highly branched functional polymers of defined structure. These macromolecules are in fact polymers since they are based on the association of repeating units. However, dendrimers differ fundamentally from conventional polymers in as much as they have their own properties owing to their arborescent construction. The molecular weight and the architecture of dendrimers can be precisely controlled. Dendrimers are constructed step by step by the iteration of a reaction sequence allowing the multiplication of each repeating unit and terminal functions. Each reaction sequence forms a so-called "new generation". The arborescent construction is effected by repeating a reaction sequence, which enables a new generation and an increasing number of identical branches and therefore of terminal functions to be obtained at the end of each reaction cycle. After a few generations, the dendrimer generally assumes a globular form which is highly branched and multi-functionalized owing to the large number of terminal functions present at the periphery.

In the context of the present description, "modified dendritic structure" means structures in which all or some of the functions, especially terminal functions, are bonded, in a covalent or non-covalent manner, by ionic or Van der Waals interactions, to molecules or macromolecules, which may be hydrophilic or hydrophobic. These modified dendritic structures therefore comprise a "core" formed from the initial dendrimer or hyper-branched polymer and a "cortex" formed by the hydrophilic or hydrophobic molecules, including, especially, fluorinated molecules.

[00138] Preferably, the dendrimer structures according to the invention are dendrimers or hyperbranched polymers comprising secondary amine (--NH--) or primary amine (-NH.sub.2) functions, hydroxyl functions (--OH), carboxylic acid functions (--COOH), halogen functions (Hal), such as Cl, Br or I, thiol functions (SH), more preferably amine or hydroxyl functions.

[00139] For these amine or hydroxyl functions may advantageously be coupled to molecules comprising functions of the carbonyl (CO) type, such as (--COOH); (--COHal); or ester, for example (--COOAlk); in order to lead to the production of modified dendrimers.

[00140] The hydrophilic or hydrophobic molecules that can be used according to the invention also comprise at least one function capable of reacting with at least one of the functions of the dendritic structure, especially with the terminal functions, which are generally readily accessible.

[00141] As used herein, the terms "functionalized dendrimer encapsulated nanoparticle" and "functionalized DENP" refer generally to a dendrimer encapsulated nanoparticle wherein functional group (e.g., acetamide and hydroxyl) have been substituted for terminal groups present within the dendrimer component of the dendrimer encapsulated nanoparticle. The present invention is not limited to acetamide and hydroxyl groups. Indeed, any molecule that can be substituted for terminal groups and that reduces the overall net charge of the dendrimer encapsulated nanoparticle or create possibility of cross binding with other dendrimer encapsulated nanoparticle finds use in the present invention.

[00142] "Hydrophilic molecules or macromolecules "means molecules that are soluble in water and polar solvents. They typically comprise one or more polar functions, such as OH, NH_2, OAlk, COOH. Examples of hydrophilic molecules that can be used according to the invention are especially oligo- or polysaccharides, for example cellulose or dextran, polyethers (polyethylene glycol), polyalcohols (polyvinyl alcohol), polyacrylates (polycarboxylates) and molecules having anionic or cationic functions, such as sulphate, phosphate or ammonium functions.

[00143] "Fluorinated molecule" means a hydrophobic compound comprising one or more poly- or perfluorinated, saturated or unsaturated, linear or branched aliphatic chains, especially aliphatic chains having two or more carbon atoms, especially C_5-C_{20} aliphatic chains.

[00144] As used herein "at least essentially consisting of" means that the respective layer is generally free of other matter, as judged by standard analytical techniques. The layer may contain minor amounts of other matter, but it may also be entirely free of other matter, at least as judged by known analytical techniques. Thus, the one or more sealing layer(s) may consist(s) only of the dendrimer encapsulated reactive nanoparticles. A portion of the plurality of dendrimer encapsulated nanoparticles or all polymer encapsulated nanoparticles may have an aliphatic, alicyclic, aromatic or arylaliphatic compound immobilized thereon. The aliphatic, alicyclic, aromatic or arylaliphatic compounds have a polar group. The polar group may, for example, be a hydroxyl group, a carboxyl group, a carbonyl group, an amino group, an amido group, a thio group, a seleno group, and a telluro group.

[00145] The term "aliphatic" means, unless otherwise stated, a straight or branched hydrocarbon chain, which may be saturated or mono- or poly-unsaturated and include heteroatoms (see below). An unsaturated aliphatic group contains one or more double and/or triple bonds (alkenyl or alkinyl moieties). The branches of the hydrocarbon chain may include linear chains as well as non-aromatic cyclic elements. The hydrocarbon chain, which may, unless otherwise stated, be of any length, and contain any number of branches. Typically, the hydrocarbon (main) chain includes 1 to 5, to 10, to 15 or to 20 carbon atoms. Examples of alkenyl radicals are straight-chain or branched hydrocarbon radicals which contain one or more double bonds. Alkenyl radicals normally contain about two to about twenty carbon atoms and one or more, for instance two, double bonds, such as about two to about ten carbon atoms, and one double bond. Alkynyl radicals normally contain about two to about twenty carbon atoms and one or more, for example two, triple bonds, such as two to ten carbon atoms, and one triple bond. Examples of alkynyl radicals are straight-chain or branched hydrocarbon radicals which contain one or more triple bonds. Examples of alkyl groups are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, the n isomers of these radicals, isopropyl, isobutyl, isopentyl, sec-butyl, tert-butyl, neopentyl, 3,3-dimethylbutyl. Both the main chain as well as the branches may furthermore contain heteroatoms as for instance N, O, S, Se or Si or carbon atoms may be replaced by these heteroatoms.

[00146] The term "alicyclic" means, unless otherwise stated, a non-aromatic cyclic moiety (e.g. hydrocarbon moiety), which may be saturated or mono-or poly-unsaturated. The cyclic hydrocarbon moiety may also include fused cyclic ring systems such as decalin and may also be substituted with non-aromatic cyclic as well as chain elements. The main chain of the cyclic hydrocarbon moiety may, unless otherwise stated, be of any length and contain any number of non-aromatic cyclic and chain elements. Typically, the hydrocarbon (main) chain includes 3, 4, 5, 6, 7 or 8 main chain atoms in one cycle. Examples of such moieties include, but are not limited to, cylcopentyl, cyclohexyl, cycloheptyl, or cyclooctyl. Both the cyclic hydrocarbon moiety and, if present, any cyclic and chain substituents may furthermore contain heteroatoms, as for instance N, O, S, Se or Si, or a carbon atom may be replaced by these heteroatoms. The term "alicyclic" also includes cycloalkenyl moieties that are unsaturated cyclic hydrocarbons, which generally contain about three to about eight ring carbon atoms, for example five or six ring carbon atoms. Cycloalkenyl radicals typically have a double bond in the respective ring system. Cycloalkenyl radicals may in turn be substituted.

[00147] The term "aromatic" means, unless otherwise stated, a planar cyclic hydrocarbon moiety of conjugated double bonds, which may be a single ring or include multiple fused or covalently linked rings, for example, 2, 3 or 4 fused rings. The term aromatic also includes alkylaryl. Typically, the hydrocarbon (main) chain includes 5, 6, 7 or 8 main chain atoms in one cycle. Examples of such moieties include, but are not limited to, cylcopentadienyl, phenyl, napthalenyl-, [10]annulenyl-(1,3,5,7,9-cyclodecapentaenyl-), [12]annulenyl-, [8]annulenyl-, phenalene (perinaphthene), 1,9-dihydropyrene, chrysene (1,2-benzophenanthrene). An example of an alkylaryl moiety is benzyl. The main chain of the cyclic hydrocarbon moiety may, unless otherwise stated, be of any length and contain any number of heteroatoms, as for instance N, O and S. Examples of such heteroarom containing moieties (which are known to the person skilled in the art) include, but are not limited to, furanyl-, thiophenyl-, naphtyl-, naphthofuranyl-, anthraxthiophenyl-, pyridinyl-, pyrrolyl-, quinolinyl, naphthoquinolinyl-, quinoxalinyl-, indolyl-, benzindolyl-, imidazolyl-, oxazolyl-, oxoninyl-, oxepinyl-, benzoxepinyl-, azepinyl-, thiepinyl-, selenepinyl-, thioninyl-, azecinyl- (azacyclodecapentaenyl-), diazecinyl-, azacyclododeca-1,3,5,7,9,11-hexaene-5,9-diyl-, azozinyl-, diazocinyl-, benzazocinyl-, azecinyl-, azaundecinyl-, thia[11]annulenyl-, oxacyclotrideca-2,4,6,8,10,12-hexaenyl- or triazaanthracenyl-moieties.

[00148] By the term "arylaliphatic" is meant a hydrocarbon moiety, in which one or more aromatic moieties are substituted with one or more aliphatic groups. Thus the term "arylaliphatic" also includes hydrocarbon moieties, in which two or more aryl groups are connected via one or more aliphatic chain or chains of any length, for instance a methylene group. Typically, the hydrocarbon (main) chain includes 5, 6, 7 or 8 main chain atoms in each ring of the aromatic moiety. Examples of arylaliphatic moieties include, but are not limited, to 1-ethyl-naphthalene, 1,1'-methylenebis-benzene, 9-isopropylanthraxcene, 1,2,3-trimethyl-benzene, 4-phenyl-2-buten-1-ol, 7-chloro-3-(1-methylethyl)-quinoline, 3-heptyl-furan, 6-[2-(2,5-diethylphenyl)ethyl]-4-ethyl-quinazoline or, 7,8-dibutyl-5,6-diethyl-isoquinoline.

[00149] Each of the terms "aliphatic", "alicyclic", "aromatic" and "arylaliphatic" as used herein is meant to include both substituted and unsubstituted forms of the respective moiety. Substituents my be any functional group, as for example, but not limited to, amino, amido, azido, carbonyl, carboxyl, cyano, isocyano, dithiane, halogen, hydroxyl, nitro, organometal, organoboron, seleno, silyl, silano, sulfonyl, thio, thiocyano, trifluoromethyl sulfonyl, p-toluenesulfonyl, bromobenzenesulfonyl, nitrobenzenesulfonyl, and methane-sulfonyl.

[00150] According to the present invention, the alkyl or "Alk" groups represent straight-chain or branched-chain saturated hydrocarbon groups comprising from 1 to 30 carbon atoms, preferably from 5 to 20 carbon atoms. When they are linear, special mention may be made of the groups methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, hexadecyl and octadecyl. When they are branched or substituted by one or more alkyl radicals, special mention may be made of the radicals isopropyl, tert-butyl, 2-ethylhexyl, 2-methylbutyl, 2-methylpentyl, 1- methylpentyl and 3- methylheptyl.

[00151] In some embodiments the at least one sealing layer conforms substantially to the shape of the defects present on the surface of the at least one barrier layer. The sealing layer may act as a planarising material that smoothens the surface of the substrate, thereby covering defects on the substrate which could provide pathways for the infiltration of moisture/oxygen. In this regard, application of a sealing layer above a barrier layer may further allow smoothening the surface in case further barrier layers are intended to be deposited on the barrier film.

[00152] The preceding embodiments relate to, an encapsulation barrier stack in which the multilayer film is immobilized, e.g. laminated onto only one side of a substrate. In some embodiments a barrier stack is immobilized on a double-laminated substrate in which a multilayer film is laminated or deposited on to two sides, which may be opposing sides, of a base substrate. An encapsulation barrier stack may for instance include a substrate that is sandwiched between two multilayer films.

[00153] As will be apparent from the above, a multilayer film according to the invention has at least two layers, a barrier layer and a sealing layer, each of which has an upper face and a lower face, defining a plane. Each layer further has a circumferential wall defining a thickness of the layer. Typically each layer is of at least essentially uniform thickness. In some embodiments the circumference of each layer is of at least essentially the same dimensions as the circumference of any other layer. A multilayer film according to the invention has two (upper and lower) outer surfaces defined by the upper face of a first layer and the lower face of a second layer. These two surfaces are arranged on at least essentially opposing sides of the multilayer film. Each of these two surfaces defines a plane. In typical embodiments these two planes are essentially parallel to each other. Furthermore these two surfaces are exposed to the ambience. Typically one or both of these planes is/are adapted for being contacted with the surface of a substrate, including for being immobilized thereon. In some embodiments the surface topology of the respective surface of the multilayer film is at least essentially matching, e.g. at least essentially congruent to, the surface topology of the plane of the substrate.

[00154] The encapsulation barrier stack of the invention can be used in several ways for encapsulating a moisture and oxygen sensitive device. Any device may be encapsulated by an encapsulation barrier stack of the invention, such as an OLED, pharmaceutical drugs, jewellery, reactive metals, electronic components or food substances. For example, it can be arranged, for example laminated or deposited, onto a conventional polymer substrate that is used to support the OLED. As explained above, pinhole defects in the barrier layer are sealed by the dendrimer encapsulated nanoparticulate material of the sealing layer. The OLED may be arranged directly on the multilayer film, and for instance encapsulated under a cover such as a glass cover, for instance using rim sealing or thin-film encapsulation comprising the attachment of an encapsulation barrier stack over the OLED, hereinafter referred to as 'proximal encapsulation', is also possible. Proximal encapsulation is in particular suitable for flexible OLED devices. In such an embodiment the multilayer film of the encapsulation barrier stack conforms to the external shape of the OLED device.

[00155] An encapsulation barrier stack according to the invention may be produced by forming on one or more barrier layer(s), on a substrate or on a (further) sealing layer, a sealing layer. In some embodiments the sealing layer may be formed on a substrate. The sealing layer may be formed as disclosed above. The plurality of nanoparticles may in some embodiments be a colloidal dispersion comprising nanoparticles dispersed in a suitable liquid such as an organic solvent. In some embodiments a polar solvent such as e.g. ethanol, acetone, N,N-dimethyl-formamide, isopropanol, ethyl acetate or nitromethane, or a non-polar organic solvent such as e.g. benzene, hexane, dioxane, tetrahydrofuran or diethyl ether (cf. also below). As explained above, in order to allow for encapsulation of the reactive nanoparticles, the dendrimer, the dendron, the polymerizable compound (which might be a monomeric compound) and the crosslinked compound are present in such a low concentration in the sealing mixture that coating the particles is achieved and the formation of a (bulk) matrix that incorporates the entire reactive particles is avoided.

[00156] The sealing mixture according to the invention may further contain a solvent. Often liquids are classified into polar and non-polar liquids in order to characterize properties such as solubility and miscibility with other liquids. Polar liquids typically contain molecules with an uneven distribution of electron density. The same classification may be applied to gases. The polarity of a molecule is reflected by its dielectric constant or its dipole moment. Polar molecules are typically further classified into protic and non-protic (or aprotic) molecules. A fluid, e.g. a liquid, that contains to a large extent polar protic molecules may therefore be termed a polar protic fluid. A fluid, e.g. a liquid, that contains to a large extent polar non-protic molecules may be termed a polar non-protic fluid. Protic molecules contain a hydrogen atom which may be an acidic hydrogen when the molecule is dissolved for instance in water or an alcohol. Aprotic molecules do not contain such hydrogen atoms.

[00157] Examples of non-polar liquids include, but are not limited to, hexane, heptane, cyclohexane, benzene, toluene, dichloromethane, carbon tetrachloride, carbon disulfide, dioxane, diethyl ether, or diisopropylether. Examples of dipolar aprotic liquids are methyl ethyl ketone, chloroform, tetrahydrofuran, ethylene glycol monobutyl ether, pyridine, methyl isobutyl ketone, acetone, cyclohexanone, ethyl acetate, isobutyl isobutyrate, ethylene glycol diacetate, dimethylformamide, acetonitrile, N,N-dimethyl acetamide, nitromethane, acetonitrile, N-methylpyrrolidone, methanol, ethanol, propanol, isopropanol, butanol, N,N-diisopropylethylamine, and dimethylsulfoxide. Examples of polar protic liquids are water, methanol, isopropanol, tert.-butyl alcohol, formic acid, hydrochloric acid, sulfuric acid, acetic acid, trifluoroacetic acid, dimethylarsinic acid [$(CH_3)_2AsO(OH)$], acetonitrile, phenol or chlorophenol. Ionic liquids typically have an organic cation and an anion that may be either organic or inorganic. The polarity of ionic liquids (cf. below for examples) is known to be largely determined by the associated anion. While e.g. halides, pseudohalides, BF_4^-, methyl sulphate, NO_3^-, or ClO_4^- are polar liquids, hexafluorophosphates, AsF_6^-, bis(perfluoroalkyl)-imides, and $[C_4F_6SO_3]^-$ are non-polar liquids.

[00158] The mixing of the dendrimer, dendron or precursor compound with the plurality of nanoparticles may in some embodiments be carried out in a polar organic solvent such as defined above. In one embodiment the polar organic solvent includes a mixture of isopropanol and ethyl acetate, for example in a molar ratio from about 2 : 1 to about 1 : 10, e.g. about 1 : 1, about 1 : 2, about 1 : 3, about 1 : 5 or about 1 : 10. The mixture of the dendrimer, dendron or precursor compound compound and the reactive nanoparticles may be applied onto the barrier layer, and the polymerisable compound may be polymerised to form a polymer. Polymerisation is allowed to occur under conditions that allow the nanoparticles to be encapsulated by the polymer formed, i.e. using a low concentration of the polymerisable compound and, for example, additionally subjecting the sealing mixture to sonification. The sealing solution may be web flight coated onto the barrier layer, for example, via a roll-to-roll process. The coating of barrier layer and sealing layer is repeated for a predetermined number of times to obtain a multilayer film with a desired barrier property. For example, a multilayer film comprising 5 paired layers may be obtained by oxide coating and web flight coating to be repeated 5 times to form 5 paired layer.

[00159] In some embodiments a surfactant is added to the mixture of the polymerisable compound and the plurality of nanoparticles. Numerous surfactants, which are partly hydrophilic and partly lipophilic, are used in the art, such as for instance alkyl benzene sulfonates, alkyl phenoxy polyethoxy ethanols, alkyl glucosides, secondary and tertiary amines such as diethanolamine, Tween, Triton 100 and triethanolamine, or e.g. fluorosurfactants such as ZONYL® FSO-100 (DuPont). A surfactant may for instance be a hydrocarbon compound, a hydroperfluoro carbon compound or a perfluorocarbon compound. It may for example be substituted by a sulfonic acid, a sulphonamide, a carboxylic acid, a carboxylic acid amide, a phosphate, or a hydroxyl group. Examples of a hydrocarbon based surfactant include, but are not limted to, sodium dodecyl sulfate, cetyl trimethyl-ammonium bromide, an alkylpolyethylene ether, dodecyldimethyl (3-sulfopropyl) ammonium hydroxide ($C_{12}N_3SO_3$), hexadecyldimethyl (3-sulfopropyl) ammonium hydroxide ($C_{16}N_3SO_3$), coco (amidopropyl)hydroxyl dimethylsulfobetaine

$(RCONH(CH_2)_3N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$ with $R=C_8–C_{18}$), cholic acid, deoxycholic acid, octyl glucoside, dodecyl maltoside, sodium taurocholate, or a polymer surfactant such as e.g. Supelcoat PS2 (Supelco, Bellefonte, PA, USA), methylcellulose, hydroxypropylcellulose, hydroxyethylcellulose, or hydroxypropylmethylcellulose. The surfactant may for instance be a hydrocarbon compound, a hydroperfluoro carbon compound or a perfluorocarbon compound (supra), which is substituted by a moiety selected from the group consisting of a sulfonic acid, a sulphonamide, a carboxylic acid, a carboxylic acid amide, a phosphate, or a hydroxyl group.

[00160] Examples of perfluorocarbon-surfactants include, but are not limited to, pentadecafluorooctanoic acid, heptadecafluorononanoic acid, tridecafluoroheptanoic acid, undecafluorohexanoic acid, 1,1,1,2,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heneicosafluoro-3-oxo-2-undecanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluoro-1-hexanesulfonic acid, 2,2,3,3,4,4,5,5-octafluoro-5-[(tridecafluorohexyl)oxy]-pentanoic acid, 2,2,3,3-tetrafluoro-3-[(tridecafluorohexyl)oxy]-propanoic acid], N,N'-[phosphinicobis(oxy-2,1-ethanediyl)]bis[1,1,2,2, 3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-N-propyl-1-octanesulfonamide, 1,1,2,2,3,3,4,4,5,5,6, 6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonyl fluoride, 2-[(□-D-galactopyranosyloxy)methyl]-2-[(1-oxo-2-propenyl)amino]-1,3-propanediyl carbamic acid (3,3,4,4,5,5,6,6,7,7,8, 8,8-tridecafluorooctyl)-ester, 6-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl hydrogen phosphate)-D-glucose, 3-(3,3,4,4,5,5, 6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl hydrogen phosphate)-D-glucose, 2-(perfluorohexyl)ethyl isocyanate, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-N-phenyl-octanamide, 1,1,2,2,3, 3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-pentacosafluoro-N-(2-hydroxyethyl)-N-propyl-1-dodecanesulfonamide, 2-methyl-,2-[[(heptadecafluorooctyl)sulfonyl]methylamino]-2-propenoic acid ethyl ester, 3-(2,2,3,3,4,4, 5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctyl)-benzenesulfonic acid, 3-(heptadecafluorooctyl)-benzenesulfonic acid, 4-[(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-oxooctyl)amino]-benzenesulfonic acid, 3-[(o-perfluorooctanoyl)phenoxy]propanesulfonic acid, N-ethyl-1,1,2,2,2-pentafluoro-N-(26-hydroxy-3,6,9,12,15,18,21,24-octaoxahexacos-1-yl)-ethanesulfonamide, 3-[ethyl[(heptadecafluorooctyl)sulfonyl]amino]-1-propanesulfonic acid, 1,2,2,3,3, 4,5,5,6,6-decafluoro-4-(pentafluoroethyl)-cyclohexanesulfonic acid, 2-[1-[difluoro(pentafluoroethoxy)methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro-ethanesulfonic acid, N-[3-(dimethyloxidoamino)propyl]-2,2,3,3,4,4-hexafluoro-4-(heptafluoropropoxy)-butanamide, N-ethyl-N-[(heptadecafluorooctyl)sulfonyl]-glycine, or 2,3,3,3-tetrafluoro-2-[1,1,2,3,3,3-hexafluoro-2-

[(tridecafluorohexyl)oxy]propoxy]-1-propanol, to name a few.

[00161] Examples of perfluorocarbon-surfactants also include polymeric compounds such as α-[2-[bis(heptafluoropropyl)amino]-2-fluoro-1-(trifluoromethyl)-ethenyl]-ω-[[2-[bis(heptafluoropropyl)amino]-2-fluoro-1-(trifluoromethyl)ethenyl]oxy]-poly-(oxy-1,2-ethanediyl), α-[2-[[(nonacosafluorotetradecyl)sulfonyl]propylamino]ethyl]-ω-hydroxy-poly(oxy-1,2-ethanediyl), polyethylene glycol diperfluorodecyl ether, α-[2-[ethyl-[(heptadecafluorooctyl)sulfonyl]amino]ethyl]-ω-hydroxy-poly(oxy-1,2-ethanediyl), α-[2-[ethyl[(pentacosafluorododecyl)sulfonyl]amino]ethyl]-ω-hydroxy-poly(oxy-1,2-ethanediyl), α-[2-[[(heptadecafluorooctyl)sulfonyl]propylamino]ethyl]- α-hydroxy-poly(oxy-1,2-ethanediyl), N-(2,3-dihydroxypropyl)-2,2-difluoro-2-[1,1,2,2-tetrafluoro-2-[(tridecafluorohexyl)oxy]ethoxy]-acetamide, α-(2-carboxyethyl)-ω-[[(tridecafluorohexyl)oxy]methoxy]-poly(oxy-1,2-ethanediyl),α-[2,3,3,3-tetrafluoro-2-[1,1,2, 3,3,3-hexafluoro-2-(heptafluoropropoxy)propoxy]-1-oxopropyl]-ω-hydroxy-poly(oxy-1,2-ethanediyl), and 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)-propionic acid polymer.

[00162] In some embodiments a surface modifying compound such as a silane is added to the sealing mixture. Examples of suitable silanes include acetoxy, alkyl, amino, amino/alkyl, aryl, diamino, epoxy, fluroalkyl, glycol, mercapto, methacryl, silicic acid ester, silyl, ureido, yinyl, and vinyl/alkyl silanes.

[00163] Illustrative examples of such silanes include, but are not limited to, di-tert-butoxydiacet-oxysilane, hexadecyltrimeth-oxysilane, alkylsiloxane, Bis(3-triethoxysilyl-propyl) amine, 3-aminopropyl-methyldiethoxysilane, triamino-functional propyltrimethoxy-silane, phenyltrimethoxysilane, phenyltriethoxysilane, 2-aminoethyl-3-amino-propylmethyl, dimethoxysilane, 2-aminoethyl-3-amino-propyl, trimethoxysilane, proprietary aminosilane composition, 3-glycidyloxy, propyltriethoxysilane, tridecafluoroocty-ltriethoxysilane, polyether-functional trimethoxysilane, 3-mercaptopropyltri-methoxysilane, 3-methacryloxypropyl-trimethoxysilane, ethyl polysilicate, tetra-n-propyl orthosilicate, hexamethyl-disilazane, vinyltrichlorosilane, vinyltrimethoxysilane, vinyl-functional oligosiloxane, 3-methacryloxypropyltrimethoxysilane and combinations thereof.

[00164] In some embodiments forming the sealing layer is carried out under an inert atmosphere, which may for example include or consist of nitrogen, argon, neon, helium, and/or sulfur hexafluoride (SF_6).

[00165] Forming the one or more barrier layer(s) may be achieved by any suitable deposition method such as spin coating, flame hydrolysis deposition (FHD), slot die coating, curtain gravure coating, knife coating, dip coating, plasma polymerization or a chemical vapor deposition (CVD) method. Examples of CVD methods include, but are not limited to plasma enhanced chemical vapor deposition (PECVD) or inductive coupled plasma enhanced chemical vapor deposition (ICP-CVD).

[00166] In one embodiment the barrier layer is deposited onto a further layer such as a sealing layer or onto a substrate using sputtering techniques known in the art. Sputtering is a physical process of depositing a thin film by controllably transferring atoms from a source to a substrate, which is known in the art. The substrate is placed in a vacuum chamber (reaction chamber) with the source material, named a target, and an inert working gas (such as argon) is introduced at low pressure. A gas plasma is struck in radio frequency (RF) or direct current (DC) glow (ejection of secondary electrons) discharged in the inter gas, which causes the gas to become ionized. The ions formed during this process are accelerated towards the surface of the target, causing atoms of the source material to break off from the target in vapour form and condense on the substrate. Besides RF and DC sputtering, magnetron sputtering is known as third sputtering technique. For magnetron sputtering, DC, pulsed DC, AC and RF power supplies can be used, depending upon target material, if reactive sputtering is desired and other factors. Plasma confinement on the target surface is achieved by locating a permanent magnet structure behind the target surface. The resulting magnetic field forms a closed-loop annular path acting as an electron trap that reshapes the trajectories of the secondary electrons ejected from target into a cycloidal path, greatly increasing the probability of ionization of the sputtering gas within the confinement zone. Positively charged argon ions from this plasma are accelerated toward the negatively biased target (cathode), resulting in material being sputtered from the target surface.

[0166] Magnetron sputtering differentiates between balanced and unbalanced magnetron sputtering. An "unbalanced" magnetron is simply a design where the magnetic flux from one pole of the magnets located behind the target is greatly unequal to the other while in a "balanced" magnetron the magnetic flux between the poles of the magnet are equal. Compared to balanced magnetron sputtering, unbalanced magnetron sputtering increases the substrate ion current and thus the density of the substrate coating. In one embodiment a sputtering technique such as RF sputtering, DC sputtering or magnetron sputtering is used to deposit the barrier layer onto the substrate layer. The magnetron sputtering can include balanced or unbalanced magnetron sputtering. In one embodiment, the barrier layer is a sputtered barrier layer.

[0167] The barrier stack may be applied onto a substrate, such as a polycarbonate or a PET substrate. In some embodiments a barrier layer may be formed with the aid of a respective substrate. The substrate may be plasma treated and coated with alumina barrier material via magnetron sputtering, thereby forming a barrier layer.

[0168] In some embodiments a further material such as ITO may be deposited, e.g. magnetron sputtered, over the multilayer film to form an ITO coating after the multilayer film has been formed. If the encapsulation barrier stack is to be used in Passive Matrix displays, only ITO lines are required instead of a complete coat of ITO. A protective liner is subsequently formed on the ITO coating. Any suitable material may be used, depending on the intended purpose, e.g. scratch resistant films or glare reduction films, such as MgF/LiF films. After forming the protective film, the encapsulation barrier stack is packed in aluminium foil packaging or slit into predetermined dimensions for assembly with other components.

[0169] As one of ordinary skill in the art will readily appreciate from the disclosure of the present invention, other compositions of matter, means, uses, methods, or steps, presently existing or later to be developed that perform substantially the same function or achieve substantially the same result as the corresponding exemplary embodiments described herein may likewise be utilized according to the present invention.

EXEMPLARY EMBODIMENTS

[0170] Typical embodiments of a multi-layer barrier stack design of the present invention include a barrier oxide film deposited onto planarized or non-planarized plastic substrate (stretchable or non-stretchable). Dendrimer encapsulated nano-materials are deposited on to barrier oxide films. For example, functionalized nano-particles consist of dendrimer-encapsulated nanoparticles and optionally functionalized nanoparticle with organic species may be deposited on to a barrier oxide film as a functionalized nanoparticle layer. The dendrimer-encapsulated nanoparticles can penetrate into the pores of the barrier oxide film and enhance the barrier properties. The combination of mutually chemically interconnected organic and inorganic nanoparticles results in coatings with very low permeability of gases. If the dendrimer is encapsulated on to the nanoparticle, the ratio of dendrimer and nanoparticles by weight are preferably 1:4 or less, 1:5 or less, or 1:6 or less.

[0171] In one embodiment, the defect-sealing layer(s) consist of dendrimer encapsulated titanium nanoparticles, zinc nanoparticles, silica or hollow silica particles. These particles may be used to enhance the barrier properties of the stack, to block the UV light and have anti-reflection properties in the visible region.

Functionalization Nanoparticles Layer or Multi-Nano layers

Substrate Materials

[0172] Polymers that may be used in the base substrate in the present invention include both organic and inorganic polymers. Examples of organic polymers which are suitable for forming the base substrate include both high and low permeability polymers such as cellophane, poly(1-trimethylsilyl-1-propyne, poly(4-methyl-2-pentyne), polyimide, polycarbonate, polyethylene, polyethersulfone, epoxy resins, polyethylene terephthalate (PET), polystyrene, polyurethane, polyacrylate, and polydimethylphenylene oxide. Microporous and macroporous polymers such as styrene-divinylbenzene copolymers, polyvinylidene fluoride (PVDF), nylon, nitrocellulose, cellulose or acetate may also be used. Examples of inorganic polymers which are suitable in the present invention include silica (glass), nano-clays, silicones, polydimethylsiloxanes, biscyclopentadienyl iron, polyphosphazenes and derivatives thereof. The base substrate may also include or consist of a mixture or a combination of organic and/or inorganic polymers. These polymers can be transparent, semi-transparent or completely opaque.

Surface Preparation

[0173] The barrier stacks or glass substrates are rinsed with isopropyl alcohol (IPA) and blow-dried with nitrogen. These processes help to remove macro scale adsorbed particles on the surface. Acetone and methanol cleaning or rinsing is not recommended. After nitrogen blow-dry, the substrates are placed in the vacuum oven, with the pressure of 10-1 mbar, for degassing absorbed moisture or oxygen. The vacuum oven is equipped with fore line traps to prevent hydrocarbon oil back migrating from vacuum pump to the vacuum oven. Immediately after the degassing process, the barrier stacks are transferred to the plasma treatment chamber (e.g. ULVAC SOLCIET Cluster Tool). RF argon plasma is used to bombard the surface of the barrier film with low energy ions in order to remove surface contaminants. The base pressure in the chamber was maintained below 4 x 10-6 mbar. The argon flow rate is 70sccm. The RF power is set at 200 W and an optimal treatment time usually 5 to 8 minutes is used depending on the surface condition.

Inorganic barrier oxide films fabrication

[0174] The sputtering technique, EB evaporation and Plasma Enhanced Physical Vapor deposition methods were used to deposit the metal oxide barrier layer. The unbalanced magnetron sputter system is used to develop high-density oxide barrier films. In this sputtering technique, a metal layer of typically a few mono-layers will be deposited from an unbalanced magnetron and then oxygen will be introduced to the system to create oxygen plasma, directed towards the substrate to provide argon and oxygen ion bombardment for a high packing-density oxide film. This plasma will also increase the reactivity of the oxygen directed onto the growing film surface and provides for more desirable structures. In order to deposit dense films without introducing excessive intrinsic stresses, a high flux (greater than 2 mA/cm^2) of low energy (~25 eV) oxygen and argon ions to bombard the growing barrier oxide films.

[0175] The continuous feedback control unit is used to control the reactive sputtering processes. The light emitted by the sputtering metal in the intense plasma of the magnetron racetrack is one indicator of the metal sputtering rate and the oxygen partial pressure. This indication can be used to control the process and hence achieve an accurate oxide film stoichiometry. By using a continuous feedback control unit from a plasma emission monitor, reproducible films and desirable barrier properties were obtained. Various barrier layers including SiN, Al_2O_3, and Indium tin oxide were prepared by conventional and unbalanced magnetron sputtering techniques and tested the single barrier layer properties.

[0176] In addition, barrier oxide films (SiO_x & Al_2O_3) were produced by EB evaporation and Plasma enhanced physical vapor deposition methods at the speed of 500 meters/min. Coating thickness is 60nm to 70nm.

Functionalized Nanoparticle Layer

[0177] The surface modification is a key aspect in the use of nanosized materials (also referred to as nanomaterials here). It is the surface that makes the nanosized materials significantly more useful than conventional non-nanomaterials. As the size of the material decreases, its surface-to-volume ratio increases. This presents considerable advantage to modify properties of nanomaterials through surface functionalization techniques. The functionalized nanoparticles are inclusive of dendrimer encapsulation on to the nanoparticle or on to organic species (which includes polymers) passivated nanoparticles. The functionalization techniques, which includes non-covalent (physical) bond and covalent bond (chemical) that can be applied to the nanoparticles. There are several methods available. Ultrasonic cavitation can be used to disperse nano-sized particles into solvent.

[0178] Covalent functionalization has been widely investigated and has produced an array of modified nanomaterial bearing small molecules, polymers and inorganic/organic species. Since nanomaterials, although quite small, are much larger than molecules, organic molecules can be used to modify the surfaces of these small particles. In addition to controlling the shape and size of the nanoparticles, controlling the surface of nanomaterial with organic chemistry has played a key role in the barrier stack design.

[0179] Surfactants, polymeric surfactants or dendrimers are employed to passivate or encapsulate the surface of the nanoparticles during or after the synthesis to avoid agglomeration before formation of the film (encapsulation layer) on the substrate or the barrier layer. Generally electrostatic repulsion or steric repulsion can be used to disperse nanoparticles and keep them in a stable colloidal state before the formation of the encapsulation material. Also, surfactants or silane can be chemically anchored or physically adsorbed on nanomaterials to form a layer stabilization and specific functionalization, i.e. naturally charged dendrimer have repelling charge. Functionalization is also used to avoid repulsion. However, once the dendrimer containing encapsulation has been formed, no repulsion between the encapsulated nanoparticles occurs.

Dendrimer encapsulated nanoparticles

[0180] The commercially available surface functionalized nanoparticles can be selected according to the desired application. Illustrative examples of surface functionalized nanoparticles include, but are not limited, to 1-Mercapto-(triethylene glycol) methyl ether functionalized Zinc nanoparticles ethanol, colloidal dispersion w/ dispersant, Aluminum oxide, NanoDur™ X1130PMA, 50% in 1,2-propanediol monomethyl ether acetate, colloidal dispersion, Zinc oxide, NanoArc® ZN-2225, 40% in 1,2-propanediol monomethyl ether acetate, colloidal dispersion with dispersant, Zinc oxide, NanoTek® Z1102PMA, 50% in 1,2-propanediol monomethyl ether acetate, colloidal dispersion with dispersant. Examples of silane compounds are inclusive of but limited to alkali, amino, epoxy, methacryl silanes.

[0181] A dendrimer coating can be established on the nanoparticle core via covalent bonding or physical bonding, for example, by means of in situ dendrimer in a discontinuous phase of an inverse mixture. A so obtained dendrimer-encapsulated nanoparticle may have a size ranging from about 20 nm to about 1000 nm.

[0182] Dendrimer encapsulated nanoparticles are prepared as follows:

[0183] Mixture A: Commercially available Dendrimer poly(amidoamines) (PAMAM) (2.3g to 5g) is mixed with anhydrous methanol (20ml) and (3-acryloxypropyl)methyldimethoxysilane (6.2ml) is added. The mixture is sonicated under nitrogen at room temperature for the entire duration of the reaction time.

[0184] Mixture B: The surface functionalized aluminium oxide (NanoDur) nanoparticles (20ml) are mixed in the Ethyl acetate (10ml), 3-Methacryloxypropyltrimethoxysilane (10ml) and surfactant (0.5% by weight). THINKY ARE-250 Mixer can undertake the mixing of the above mentioned solution. Sonication time is 2 hours at 28 °C.

[0185] After sonication, a UV curable acrylic monomer (Addision Clear Wave) is added to mixture B by 4% to 6% (2 to 3 ml) by weight of the total solution. The sonication is typically undertaken for 2 hours to 12 hours. The UV curable acrylic monomer is diluted in the solvent and adsorbed and chemically anchored on the nanoparticles during the Sonication process. Then mixture A is added to mixture B and sonicated.

[0186] The coating process can be undertaken by spin coating, inkjet printing, slot die coating, gravure printing or any wet coating processes. Then the resultant solution is cured under UV or heat curing or EB curing processes. By so doing, a layer of dendrimer/polymer encapsulated nanoparticles is obtained, in which the encapsulation material that encapsulates the nanoparticles contain both dendrimer and polymerised acrylate. Without being bound by theory, it is believed that the structure of the encapsulation material might be such that the nanoparticles are coated with a first layer of polymerised acrylate and a second layer of dendrimer. It is noted here that it is of course also possible to use an encapsulation material that only comprise dendrimers, for example, photo or UV-crosslinkable dendrimers. Photoreactive groups can be introduced, for example, into a dendrimer used in the present invention such as a PAMAM dendrimer; a polyethylene imine (PEI) dendrimer, a poly(propyleneimines) (PPI) dendrimer, a polypropyleneimine dotriacontaamine dendrimer (DAB) or a Frechet dendrimer by, for example, the method described in Desai et al., Biomacromolecules 2010 March 8; 11(3): 666–673. To introduce photoreactive acrylate groups to PEGylated PAMAM dendrimer, reactive groups of the dendrimer such as –OH groups can be reacted as described by Desai et al. with, acryloyl chloride with a base such as triethylamine in an organic solvent such as THF.

[0187] The functionalized nano-particles can penetrate effectively in to pores or the defects of barrier oxide layer and plug the defects. And also, improves the bond strength between barrier oxide layer and functionalized nano-particle layer. The high packing density of the nanoparticle coating can be obtained by the suitable functionalization techniques (coating thickness in the range of 50nm to few hundred nanometers) on to barrier oxide films. The functionalized nano-particles thickness may be determined based on barrier oxide film coating thickness.

[0188] In a preferred embodiment, the majority of the dendrimer/polymer or only dendrimer coated nano-particles of metal or metal oxide particles and organic species passivated nanoparticles, which include metal and metal oxide, are rod like with a diameter of 10 to 50 nm and length up to 200nm. The diameter and size of the particles are chosen in such a way that they do not influence the transparency of the eventual coatings. The packing density of the nano-particle is determined by the shape and size distribution of the nano-particles. Therefore, it may be advantageous to use nano particles of different shapes and sizes to precisely control the surface nano-structure for the effective sealing of defects of barrier oxide layer.

[0189] Polymer encapsulated Carbon nanotubes (CNTs)/carbon particles can be also used to seal the defects of the pinholes. Typically it is advantageous to employ the maximum amount of absorbent particles in order to increase the ability of the sealing layer to seal the barrier oxide films defects and also absorb and retain water and oxygen molecules. The characteristic wavelength is defined as the wavelength at which the peak intensity of OLED or any other displays output light spectrum occurs. When the encapsulation layer designed for Transparent OLED or see-through displays, the size of the particles may be typically less than ½ and preferably less than 1/5 of the characteristic wavelength. Typically these ratios correspond to particle sizes of less than 200nm and preferably less than 100nm. In some barrier designs, larger particles may be desirable, for example where it is required to have scattering of the emitted light.

Calcium degradation test method

[0190] After the plasma treatment process, the barrier stacks are transferred to the vacuum evaporation chamber (thermal evaporation) under vacuum where the two metal tracks that are used as electrodes has dimension 2 cm by 2 cm. The sensing element is fabricated in between the two electrodes and designed with 1 cm long, 2 cm wide and 150 nm thick. The measured resistivity of the sensor element is 0.37Ω-cm. After the deposition process, a load lock system is used to transfer the sample to a glove box under dry nitrogen at atmospheric pressure. After the calcium deposition, a 100 nm silver protection layer were deposited for the qualitative analysis (test cell type A), cf. Fig. 4.

[0191] To accelerate the permeation a silver protection layer was deposited for the qualitative analysis (test cell type A). In the case of the quantitative resistance measurement method (test cell type B), cf. Fig. 5, 300 nm silver was used for the conductive track, 150 nm calcium was used as the sensor and 150 nm lithium fluoride was used as a protection layer. After the deposition processes, a UV curable epoxy was applied on the rim of the substrate and then the whole substrate was sealed with a 35mm x 35mm glass slide. The getter material was attached to the 35mm x 35mm cover glass slide in order to absorb any water vapour due to out gassing or permeation through the epoxy sealing. A load lock system was used for the entire process and the test cells were encapsulated in the glove box under dry nitrogen at atmospheric pressure. For the testing, the samples were placed into a humidity chamber at constant temperature and humidity of 80°C & 90% RH respectively. These were viewed optically at regular intervals for a qualitative degradation test and analysis of the defects, and measured electrically for the quantitative analysis of the Calcium degradation.

[0192] The Calcium test cell's conductive track terminals are connected to a constant current source (Keithey source meter), which is interfaced with a computer. Resistance of the calcium sensor / silver track is monitored every second and plotted automatically by the computer using lab view software. A Dynamic Signal Analyzer with a FFT analysis is proposed to take the noise spectrum measurement automatically at periodic intervals of one second.

Experimental Details & Results

Embodiment 1

1. Plastic substrate - PET
2. Dendrimer encapsulated nanoparticle coating
3. SiN layer –CVD method
4. Dendrimer encapsulated nanoparticle coating
5. SiN layer –CVD method

[0193] Nano Solution Preparation: The generation 5 PAMAM dendrimers, (2.3g mixed with 20ml of methanol) were obtained from Sigma Aldrich. The aluminum oxide nanoparticles "Aluminum oxide, NanoDur™ X1130PMA (50% by weight concentration in 1,2-propanediol monomethyl ether acetate, average particle size 45 nm according to the product bulletin of the supplier) were obtained from Alfa Aeser (a Johnson and Mathey Company). The solvents IPA:Ethylactate (5:15 ml ratio) were mixed and 3-Methacryloxypropyltrimethoxysilane (10ml) added and then surfactant Dow corning FZ 2110 was further added by 0.5% by total weight of the solution and mixed. The UV curable acrylate monomer (Addision Clear Wave) – (3ml) was then added to the above mixture for subsequent formation of a dendrimer/polymer encapsulated nanoparticle. The mixture was kept in sonication for 2 hours. PAMAM dendrimers (2.3 g) was added to the mixture after sonication. The surface functionalized nanoparticle "Aluminum oxide, NanoDur™ X1130PMA, 50% in 1,2-propanediol monomethyl ether acetate"- 20ml was added to the solvent/monomer mixture and sonicated for a few hours. The above mixture was then spin coated and cured. The formulation was undertaken under inert gas environment. The set of experiments were carried out with different mixture of nanoparticles and spin coated onto the plain polymer substrate, barrier coated plastic substrates and aluminum oxide anodisk®. The entire deposition/coating process was carried out by a batch process. The Water Vapour Transmission Rate (WVTR) at 60°C & 90% RH (relative humidity) and the calcium oxidation was measured and is shown together with the results of the following experimental examples in Table 1 below.

Embodiment 2

[0194] Nano Solution Preparation: The generation 5 PAMAM dendrimers, (2.3g mixed with 20ml of methanol) were obtained from Sigma Aldrich. The aluminum oxide nanoparticles "Aluminum oxide, NanoDur™ X1130PMA (50% by weight concentration in 1,2-propanediol monomethyl ether acetate, average particle size 45 nm according to the product bulletin of the supplier) was obtained from Alfa Aeser (Johnson and Mathey Company). The solvents IPA:Ethyleactate (5:15 ml ratio) were mixed, and 3-Methacryloxypropyltrimethoxysilane (10ml) added and then surfactant Dow corning FZ 2110 was further added by 0.5% by total weight of the solution and mixed. The UV curable acrylate monomer (Addision Clear Wave) – (3ml) was then added to the above mixture for subsequent formation a dendrimer/polymer encapsulated nanoparticle. The mixture was kept in sonication for 2 hours. PAMAM dendrimers (2.3 g) was added to the mixture after sonication. The surface functionalized nanoparticle "Aluminum oxide, NanoDur™ X1130PMA, 50% in 1,2-propanediol monomethyl ether acetate"- 20ml was added to the solvent/monomer mixture and sonicated for a few hours. The above mixture was then spin coated and cured. The formulation was undertaken under inert gas environment. The set of experiments were carried out and spin coated onto the plain polymer substrate and barrier coated plastic substrates.

Embodiment 3

[0195] The aluminum oxide nanoparticles (37% by weight concentration in 2-methoxypropyl acetate) were obtained from BYK Chemicals (NANOBYK 3610) and mixed with cyclohexanone in the ratio of 1:0.5 (60ml). The cyclohexanone included 0.1% by weight of Dow 56 additive (obtained from Dow Corning). Then 3-methacryloxypropyltrimethoxysilane (5ml) was added to the mixture and sonicated. After sonication, fourth generation (G4) poly(amidoamine) (PAMAM) dendrimers (1,2) 3g mixed with 20ml of methanol (obtained from Sigma Aldrich) was then added and further sonicated. 1,6-hexanediol ethoxylate diacrylate 5% by weight was added to the above mixture and sonicated for one hour. The above mixture was then spin coated and cured. The formulation was undertaken under inert gas environment. The set of experiments were carried out and spin coated onto the plain polymer substrate and barrier coated plastic substrates.

Embodiment 4

[0196] The aluminum oxide nanoparticles (37% by weight concentration in 2-methoxypropyl acetate) were obtained from BYK Chemicals (NANOBYK 3610) and mixed with cyclohexanone in the ratio of 1:0.5 (60ml). The cyclohexanone included 0.1% by weight of Dow 56 additive (obtained from Dow Corning). Then 3-methacryloxypropyltrimethoxysilane (5ml) was added to the mixture and sonicated. After sonication, fourth generation (G4) poly(amidoamine) (PAMAM) dendrimers (1,2) 3g mixed with 20ml of methanol (obtained from Sigma Aldrich) is then added and further sonicated. 1,6-hexanediol diacrylate (obtained from Sigma Aldrich) 5% by weight added to the above mixture and sonicated for one hour. The above mixture was then spin coated and cured. The formulation was undertaken under inert gas environment. The set of experiments were carried out and spin coated onto the plain polymer substrate, and Al_2O_3 barrier oxide coated plastic substrates.

Embodiment 5

[0197] The zinc oxide nanoparticles NanoTek® Z1102PMA (50% by weight concentration in 1,2-propanediol monomethyl ether acetate, average particle size 70 nm according to the product bulletin of the supplier) was mixed with cyclohexanone in the ratio of 1:0.5 (60ml). The cyclohexanone included 0.1% by weight of Dow 56 additive (obtained from Dow Corning). 3-methacryloxypropyltrimethoxysilane (10ml) was added and sonicated. After sonication, generation 5 PAMAM dendrimers, 2.3g mixed with 20ml of methanol (obtained from Sigma Aldrich) was then added and further sonicated. The 1,6-hexanediol ethoxylate diacrylate – 5% by weight was then further added to the above mixture. The mixture is kept in sonication for 2 hours. The formulation was undertaken under inert gas environment. Titanium in isopropanol to produce 5% of titanium oxide and 3-Methacryloxypropyltrimethoxysilane was added and then doped surfactant Dow corning FZ 2110. This mixture was sonicated for 2 hours. Barium titanium ethylhexano-isopropoxide in isopropanol was used to produce 5% $BaTiO_3$ and then 3-methacryloxypropyltrimethoxysilane was added after which surfactant Dow corning FZ 2110 was further added and sonicated for 2 hours. A Thinky ARE 250 mixer was used to mix the above Zinc oxide, Titanium oxide, $BaTiO_3$ mixture before the coating process. The formulation was undertaken under inert gas environment. The set of experiments were carried out and spin coated onto the plain polymer substrate, barrier coated plastic substrates.

Table 1

Structure	Water Vapour Transmission Rate (WVTR) at 60°C & 90% RH (relative humidity)	Transmittance	UV filter	Reduction of reflectance in UV-visible range
Comparative test PET/SiOx alone (by high speed manufacturing process)	no calcium oxidation up to 2 hours > 2g/m^2·day	88%	-	-
Embodiment 1 PET/SiOx/ dendrimer encapsulated nanolayer/SiOx	no calcium oxidation up to **500** hours. Less than 2 x 10^{-4} g/m^2·day	85%	-	-
Embodiment 2 PET/SiOx/ dendrimer encapsulated nanolayer/SiOx	no calcium oxidation up to **500** hours. Less than 2 x 10^{-4} g/m^2·day	85%	-	-
Embodiment 3 PET/SiOx/ dendrimer encapsulated nanolayer/SiOx	no calcium oxidation up to **300** hours. Less than 1 x 10^{-3} g/m^2·day	85%	-	-
Embodiment 4 PET/SiOx/ dendrimer encapsulated nanolayer/SiOx	no calcium oxidation up to **500** hours. Less than 2 x 10^{-4} g/m^2·day	85%	-	-
Embodiment 5 PET/SiOx/ dendrimer encapsulated nanolayer/SiOx	no calcium oxidation up to **500** hours. Less than 2 x 10^{-4} g/m^2·day	85%	30 to 40% at 350nm	5 to 10%

[0198] The polymer-encapsulated nanolayer used in the comparative test was deposited onto aluminum oxide coated PET substrate. The adhesion test was performed as per the ASTM STD 3359. The cross-cut tool from BYK was used to make a perpendicular cut on the coatings. The permacel tape was used to peel the coating and the peeled area was inspected using optical microscope.

[0199] It can be appreciated form the result above that the dendrimer encapsulated nanoparticles according to the invention provide an excellent water vapour transmission rate as well as an outstanding resistance to the calcium oxidation with respect to the comparative test when tested with the calcium degradation test method described herein.

[0200] The listing or discussion of a previously published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

[0201] The invention illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including," containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by exemplary embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0202] The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein. Other embodiments are within the following claims. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

CLAIMS

What is claimed is:

1. An encapsulation barrier stack, capable of encapsulating a moisture and/or oxygen sensitive article and comprising a multilayer film, wherein the multilayer film comprises:
   - one or more barrier layer(s) having low moisture and/or oxygen permeability, and
   - one or more sealing layer(s) arranged to be in contact with a surface of the at least one barrier layer, thereby covering and/ or plugging defects present in the barrier layer,

   wherein the one or more sealing layer(s) comprise(s) a plurality of dendrimer encapsulated nanoparticles, the nanoparticles being reactive in that they are capable of interacting with moisture and/or oxygen to retard the permeation of moisture and/or oxygen.

2. An encapsulation barrier stack according to claim 1 wherein the dendrimer encapsulated nanoparticle are nanoparticles which are either encapsulated by dendrimeric molecule or surrounded by dendrimer or the nanoparticle is a dendrimer core after attachment of dendrons on its surface.

3. The encapsulation barrier stack according to claim 1 or 2 wherein the dendrimer encapsulated nanoparticles are crosslinked.

4. The encapsulation barrier stack of any of claims 1 to 3, wherein the one or more sealing layer(s) at least essentially consist(s) of the dendrimer encapsulated reactive nanoparticles.

5. The encapsulation barrier stack according to any of claims 1 to 4, wherein the nanoparticles are encapsulated by a encapsulating material which comprises or consists of dendrimer or dendron.

6. The encapsulation barrier stack of any of claims 1 to 5, wherein the encapsulating material further comprises one or more of the following: an organic polymer, inorganic polymer, a water soluble polymer, organic solvent soluble polymer,

biological polymer, synthetic polymer, oligomer, surfactant, organic compounds or crosslinker compounds.

7. The encapsulation barrier stack according to claim 6 wherein the organic compounds include any of a mercapto group, an epoxy group, an acrylic group, a methacrylate group, an allyl group, a vinyl group, a halogen and an amino group and the crosslinker compound includes a linker unit selected from the group of thiol groups, disulphide groups, amino groups, isocyanide groups, thiocarbamate groups, dithiocarbamate groups, chelating polyether, and carboxy groups.

8. The encapsulation barrier stack of any of claims 1 to 7, wherein the encapsulating material comprises, prior to the encapsulation, cross-linked or cross-linkable compounds, a UV curable group, electron beam curable or heat curable material.

9. The encapsulation barrier stack of any of claims 1 to 8, wherein the nanoparticles are selected from pigment particles, quantum dots, colloidal particles, and combinations thereof.

10. The encapsulation barrier stack of any one of claims 1 to 9, being adapted to be arranged on a substrate.

11. The encapsulation barrier stack of any one of the foregoing claims, wherein one of the one or more sealing layers conforms substantially to the shape of the defects present on the surface of one of the one or more barrier layers.

12. The encapsulation barrier stack of claim 11, wherein the sealing layer is formed by conformal deposition.

13. The barrier stack of any one of claims 1 to 12, wherein the multilayer film comprises a plurality of sealing layers and barrier layers arranged in an alternating sequence.

14. The barrier stack of any one of claims 1 to 14, wherein the multilayer film comprises a single sealing layer.

15. The barrier stack of any one of the preceding claims, wherein the multilayer film comprises a single barrier layer.

16. The barrier stack of any one of the preceding claims, wherein the nanoparticles are capable of interacting with moisture and/or oxygen through chemical reaction.

17. The barrier stack of any one of the preceding claims, wherein the nanoparticles comprise a material selected from the group consisting of a metal, a metal oxide and a combination thereof.

18. The barrier stack of any one of the preceding claims, comprising a plurality of sealing layers, wherein each of the plurality of sealing layers comprises a different material.

19. The barrier stack of claims 17 or 18, wherein the nanoparticles comprise a metal selected from the group consisting of Al, Ti, Mg, Ba, Ca and alloys thereof.

20. The barrier stack of any one of claims 17 to 19, wherein the nanoparticles comprise a metal oxide selected from the group consisting of TiO_2, AbO_3, ZrO_2, ZnO, BaO, SrO, CaO, MgO, VO_2, CrO_2, MoO_2, and $LiMn_2O_4$.

21. The barrier stack of any one of claims 17 to 20, wherein the nanoparticles comprise a transparent conductive oxide selected from the group consisting of cadmium stannate (Cd_2SnO_4), cadmium indate ($CdIn_2O_4$), zinc stannate (Zn_2SnO_4 and $ZnSnO_3$), and zinc indium oxide ($Zn_2In_2O_5$), barium titanate and barium strontium titanate.

22. The barrier stack of any one of claims 1 to 21, wherein the nanoparticles are capable of interacting with moisture and/or oxygen through adsorption.

23. The barrier stack of claim 22, wherein the nanoparticles comprise carbon nanotubes and or graphene nano-sheets or nanoflakes.

24. The barrier stack of any one of the preceding claims, wherein at least one of the one or more sealing layers further comprises a plurality of inert nanoparticles, the inert nanoparticles being capable of obstructing the permeation of moisture and/or oxygen through the defects present in the barrier layer.

25. The barrier stack of claim 24, wherein the inert nanoparticles comprise a material selected from the group consisting of gold, copper, silver, platinum, silica, wollastonite, mullite, monmorillonite, silicate glass, fluorosilicate glass, fluoroborosilicate glass, aluminosilicate glass, calcium silicate glass, calcium aluminium silicate glass, calcium aluminium fluorosilicate glass, titanium carbide, zirconium carbide, zirconium nitride, silicon carbide, silicon nitride, a metal sulfide, and a mixture or combination thereof.

26. The barrier stack of any one of the preceding claims, wherein the nanoparticles comprised in the one or more sealing layers have a size that is smaller than the average diameter of defects present in the one or more barrier layers.

27. The barrier stack of any one of the preceding claims, wherein the oxygen and/or moisture sensitive article comprises an electroluminescent electronic component or a solar device, and wherein the average size of the nanoparticles is less than one-half the characteristic wavelength of light produced by the electroluminescent electronic component or absorbed by the solar device.

28. The barrier stack of any one of claims 1 to 27, wherein the barrier layer comprises a material selected from indium tin oxide (ITO), TiAlN, SiO_2, SiC, Si3N_4, TiO_2, HfO_2, Y_2O_3, Ta_2O_5, and Al_2O_3.

29. The barrier stack of any one of the preceding claims, further comprising a substrate for supporting the multilayer film.

30. The barrier stack of claim 29, wherein the multilayer film is orientated such that the sealing layer is arranged on the substrate.

31. The barrier stack of claim 30, wherein the multilayer film is orientated such that the barrier layer is arranged on the substrate.

32. The barrier stack of any of claims 28 to 31, wherein the substrate comprises a material selected from polyacetate, polypropylene, polyimide, cellophane, poly(1-trimethylsilyl-1-propyne, poly(4-methyl-2-pentyne), polyimide, polycarbonate, polyethylene, polyethersulfone, epoxy resins, polyethylene terepthalate, polystyrene, polyurethane, polyacrylate, and polydimethylphenylene oxide, styrene-divinylbenzene copolymers, polyvinylidene fluoride (PVDF), nylon, nitrocellulose, cellulose, glass, indium tin oxide, nano-clays, silicones, polydimethylsiloxanes, biscyclopentadienyl iron, and polyphosphazenes.

33. The barrier stack of any of claims 28 to 32 wherein the substrate is flexible.

34. The barrier stack of any of claims 28 to 32, wherein the substrate is rigid.

35. The barrier stack of any one of claims 28 to 34, further comprising a planarising layer, wherein the planarising layer is arranged between the substrate and the multilayer film.

36. The barrier stack of any one of claims 1 to 35, further comprising a terminal layer for protecting the multilayer film, wherein the terminal layer is facing the ambience.

37. The barrier stack of claim 36, wherein the terminal layer comprises an acrylic film or wherein the terminal layer is an oxide layer.

38. The barrier stack of claim 37, wherein the acrylic film has distributed therein LiF and/or MgF_2 particles.

39. The barrier stack of any one of the preceding claims, wherein the encapsulation barrier stack has a water vapour permeation rate of less than about 10^{-3} g/m^2/day, less than about 10^{-4} g/m^2/day, 10^{-5} g/m^2/day or less than about 10^{-6} g/m^2/day.

40. The barrier stack of any one of the preceding claims, wherein the one or more sealing layers provide moisture and oxygen barrier properties and at least one property selected from the group consisting of a UV filter property, an antireflection property, a light extraction property and an anti-static property.

41. The barrier stack of any one of the preceding claims further comprising arranged on the at least one sealing layer a further layer.

42. The barrier stack of claim 41, wherein the further layer is a polymer layer containing no reactive nanoparticles or a polymer layer in which reactive nanoparticles are distributed in a polymeric matrix.

43. An electronic module comprising an electronic device that is sensitive to moisture and/or oxygen, said electronic device being arranged within an encapsulation barrier stack according to any one of claims 1 to 42.

44. The electronic module of claim 43, wherein the electronic device is selected from the group consisting of an Organic Light Emitting Device (OLED), a charged-coupled device (CCD), a Liquid Crystal Display (LCD), a solar cell, a thin-film battery, an Organic Thin Film Transistor (OTFT), an organic Integrated Circuit (IC), an organic sensor, and a micro-electro-mechanical sensor (MEMS).

45. The electronic module of claim 43 or 44, wherein the barrier stack defines a base substrate for supporting the electronic device.

46. The electronic module of claim 43 or 44, wherein the encapsulation barrier stack further comprises a covering layer arranged proximally above the electronic device, thereby defining a proximal encapsulation, the electronic device being sandwiched between the covering layer and the encapsulation barrier stack.

47. The electronic module of claim 46, wherein the shape of the covering layer conforms to the external shape of the electronic device.

48. The electronic module of claim 443 or 444, wherein the electronic device is arranged on a base substrate, and the encapsulation barrier stack forms an encapsulation layer over the electronic device that seals the electronic device against the base substrate.

49. A method of manufacturing an encapsulation barrier stack according to any one of claims 1 to 42, the method comprising:

- providing one or more barrier layer(s), and
- forming one or more sealing layer(s), wherein forming the one or more sealing layer(s) comprises
    - (i) mixing an encapsulation material consisting of or comprising of dendrimers or precursors thereof, dendrons or precursors thereof, optionally in the presence of a polymerizable compound and/or a cross-linkable compound, with a plurality of nanoparticles, the nanoparticles being reactive in that they are capable of interacting with moisture and/or oxygen, thereby forming a sealing mixture,

(ii) applying the sealing mixture onto the barrier layer under conditions that allow the nanoparticles to be encapsulated by or in the dendrimers, thereby forming the sealing layer.

50. The method of claim 49, wherein the dendrimers are dendrimers or hyper-branched polymers comprising one or more of the following: secondary amine (--NH--) or primary amine (-NH_2) groups, hydroxyl group (--OH), carboxylic acid (--COOH), -COONH2, -COCl, Cl, Br or I or F, thiols (SH), more preferably amine or hydroxyl group.

51. The method according to claim 50, wherein the amine or hydroxyl group are coupled to molecules comprising one or more of the following; (--COOH), (--COHal); or (--$COOC_1$-C_{20} alkyl) to provide modified dendrimers and wherein Hal is selected from I, Br, Cl and F.

52. The method according to any one of claims 49 to 51, wherein the dendrimers are selected from poly(amidoamines) (PAMAM), polyethylene imines (PEI), poly(propyleneimines) (PPI), and polypropyleneimine dotriacontaamine dendrimers (DAB) and Frechet dendrimers.

53. The method according to any one of claims 49 to 52, wherein the encapsulation material further comprises one or more of the following: an organic polymerizable compound, inorganic polymerizable compound, a water soluble polymerizable compound , organic solvent soluble polymerizable compound, biological polymer, synthetic polymerizable compound, monomer, oligomer, surfactant, organic compounds that are cross linkable compounds, a solvent or mixture of solvents and wherein preferably the organic polymerizable compound is selected from acrylic acid, methyl acrylate, ethyl acrylate and butyl acrylate.

54. The method according to claim 53 wherein the cross linkable compound includes a mercapto group, an epoxy group, an acrylic group, a methacrylate group, an allyl group, a vinyl group, and an amino group.

55. The method of any one of claims 49 to 54, further comprising adding a surface modifying compound to the sealing mixture.

56. The method of claim 54, wherein the surface modifying compound is a silane.

57. The method of any one of claims 49 to 56, wherein providing the one or more barrier layer(s) comprises forming the one or more barrier layer(s).

58. The method of any one of claims 49 to 57 wherein the conditions and/or the concentration of the polymerizable compound is chosen such that the polymerizable compound is immobilized on the surface of the reactive nanoparticles.

59. The method of any one of claims 49 to 58 wherein the sealing mixture is applied onto the barrier layer via conformal deposition.

60. The method of claims 59, wherein the sealing mixture is applied onto the barrier layer by means of spin coating, screen printing, a WebFlight method, slot die, curtain gravure, knife coating, ink jet printing, screen printing, dip coating, plasma polymerisation or a chemical vapour deposition (CVD) method.

61. The method of any one of claims 49 to 60, wherein after being deposited onto the barrier layer the sealing mixture is exposed to conditions that initiate polymerization of the polymerisable compound or cross-linking the cross-linkable compound.

62. The method of claim 61, wherein the conditions that initiate polymerization comprise UV radiation or IR radiation, electron beam curing, plasma polymerisation (for curing of the polymerisable compound or crosslinking the cross-linkable compound).

63. The method of any of claims 49 to 62, wherein the one or more sealing layer(s) formed at least essentially consist(s) of the dendrimer encapsulated reactive nanoparticles.

64. The method of any of claims 49 to 63, further comprising carrying out sonication of the sealing mixture prior to polymerisation.

65. The method of claim 64, wherein sonication is carried out for at least about 30 minutes.

66. The method of any one of claims 49 to 65, the method further comprising providing a substrate for supporting the barrier stack.

67. The method of claim 67, wherein the substrate comprises the barrier layer.

68. The method of any one of claims 49 to 67, wherein the substrate comprises a polymer.

69. The method of any one of claims 49 to 68, wherein the plurality of nanoparticles is a colloidal dispersion comprising nanoparticles dispersed in an organic solvent.

70. The method of any one of claims 49 to 69, wherein the encapsulation compound comprises a polar organic solvent and/or the plurality of nanoparticle are suspended in a solvent, preferably a polar organic solvent

71. The method of claim 70, wherein the polar organic solvent comprises a mixture of isopropanol and ethyl acetate in 1 : 3 molar ratio.

72. The method of any one of claims 49 to 71, wherein the polymerizable or cross-linkable compound is curable by ultraviolet light, infrared light, electron beam curing, plasma polymerisation and or heat curing.

73. The method of any one of claims 49 to 72 wherein mixing of the encapsulation material with the plurality of nanoparticles in step (i) comprises mixing about 20 wt.-% dry form or less of the encapsulation material to 80 wt.-% dry form of the nanoparticles (weight ratio 1:4 or less).

74. The method of claim 73, wherein the encapsulation material is mixed with the nanoparticle at a weight ratio of 1: 5 or less.

75. The method of any of claims 49 to 74, wherein the sealing mixture obtained in step (i) comprises 10 % (w/v) or less of the encapsulation material.

76. The method of claim 75, wherein the sealing mixture comprises about 5 % (w/v) of the encapsulation material.

77. The method of claims 49 to 76 wherein crosslinked dendrimer encapsulated nanoparticles are formed.

78. Use of dendrimer encapsulated reactive nanoparticles as defined in any of the preceding claims for preparing a sealing layer of a barrier stack, wherein the nanoparticles are reactive in that they are capable of interacting with moisture and/or oxygen to retard the permeation of moisture and/or oxygen through the defects present in the barrier layer.

79. Use of an encapsulation barrier stack defined in any of the preceding claims 1-42 for encapsulating an electronic device, or for food packaging, pharmaceutical packaging or medical packaging.

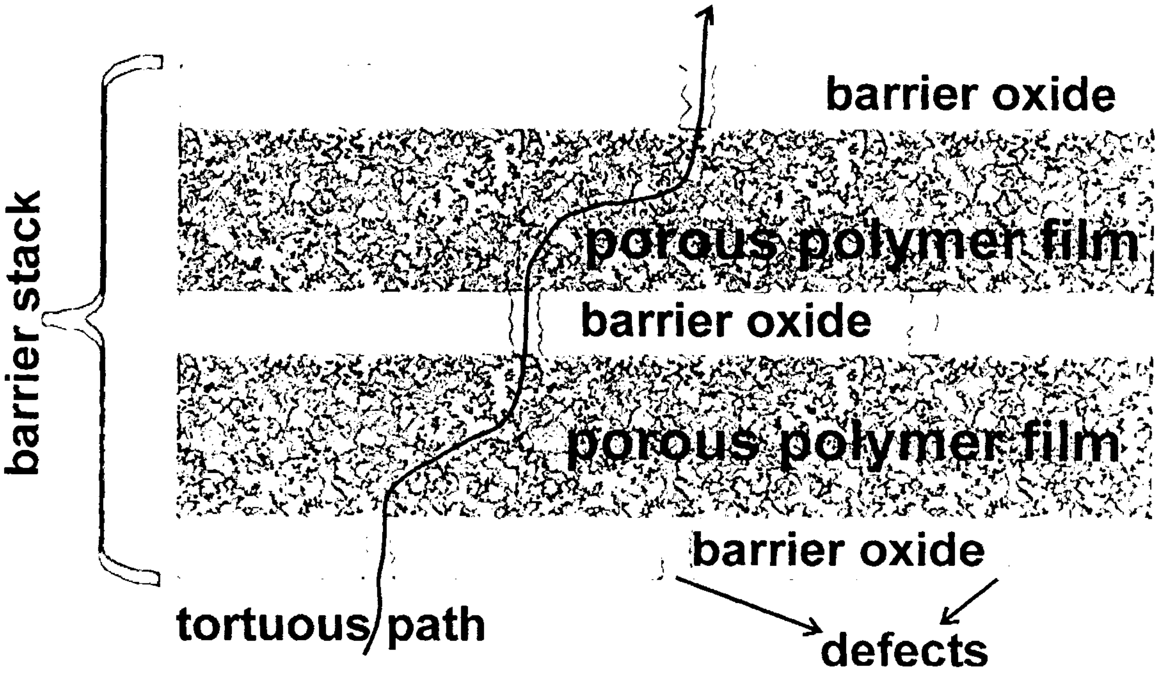


Fig. 1 (prior art)

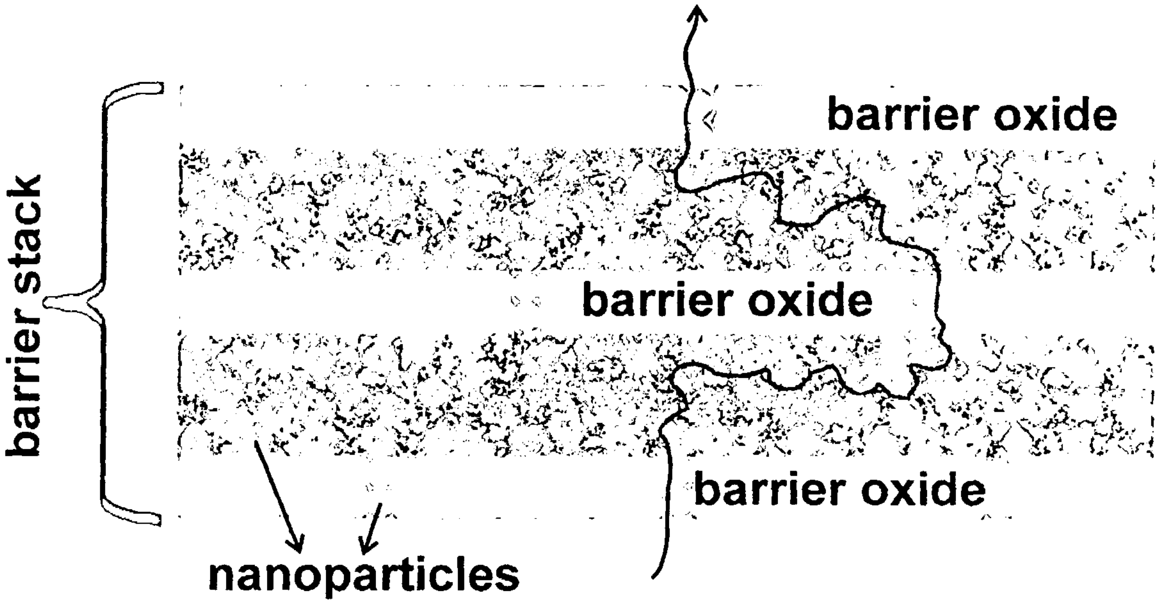


Fig. 2 (prior art)

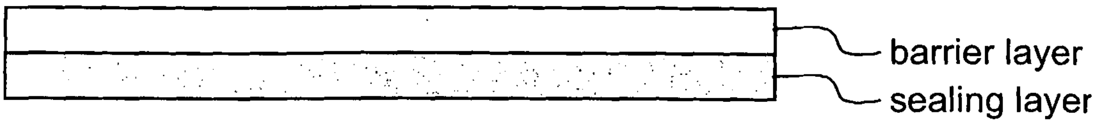


Fig. 3A

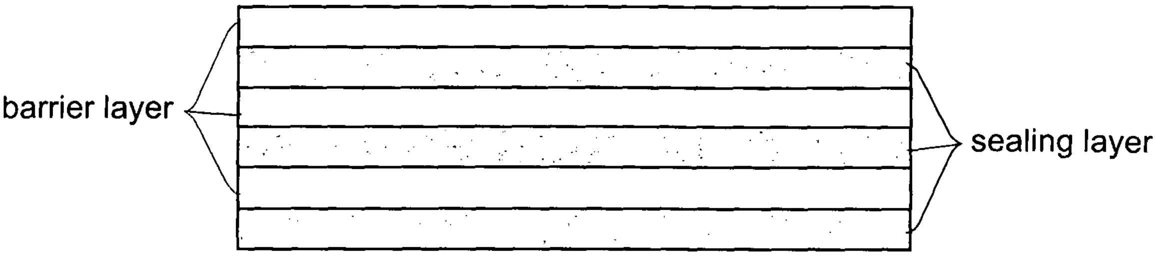


Fig. 3B

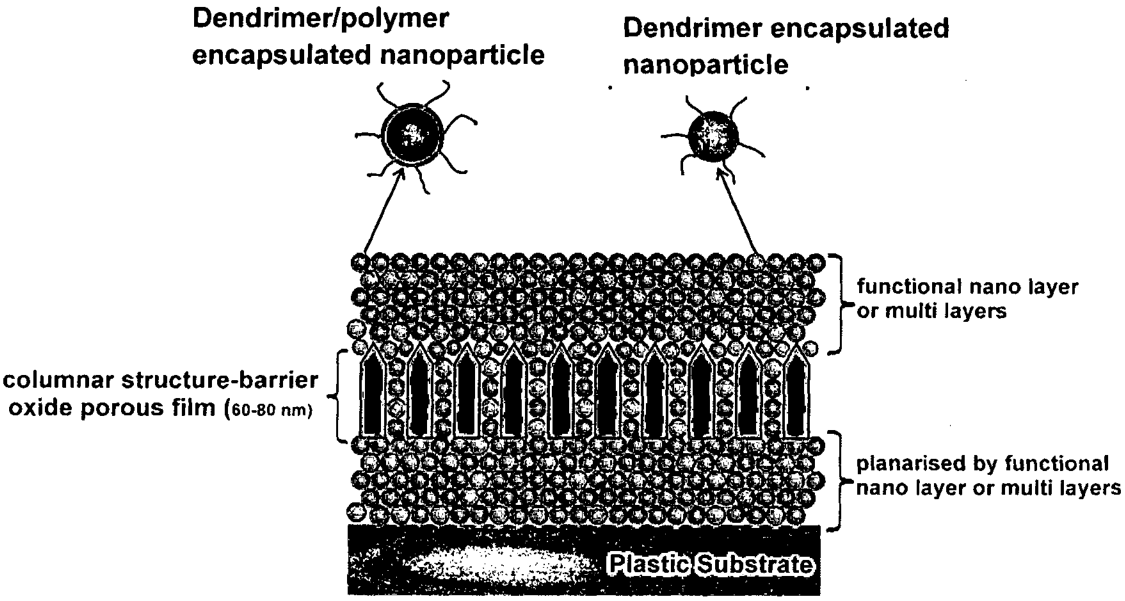


Fig. 3C

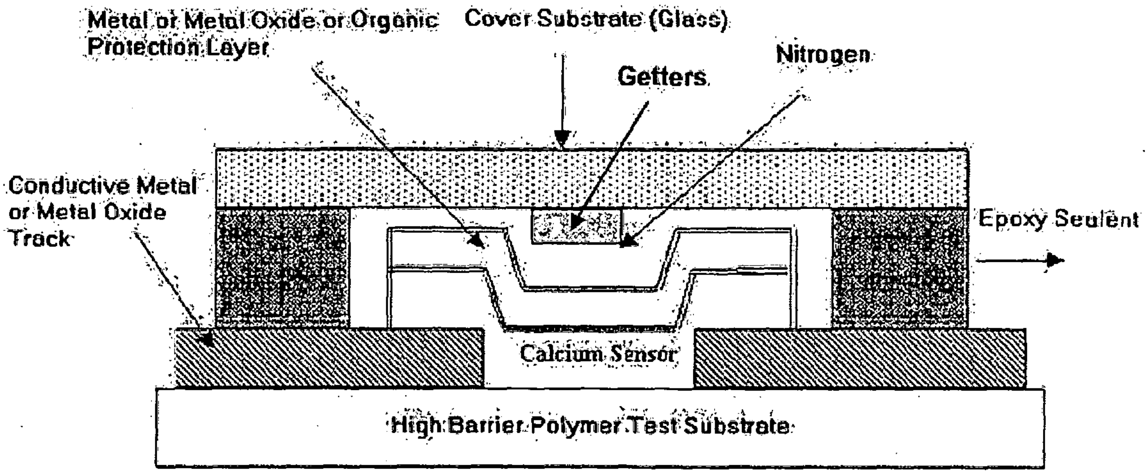


Fig. 4

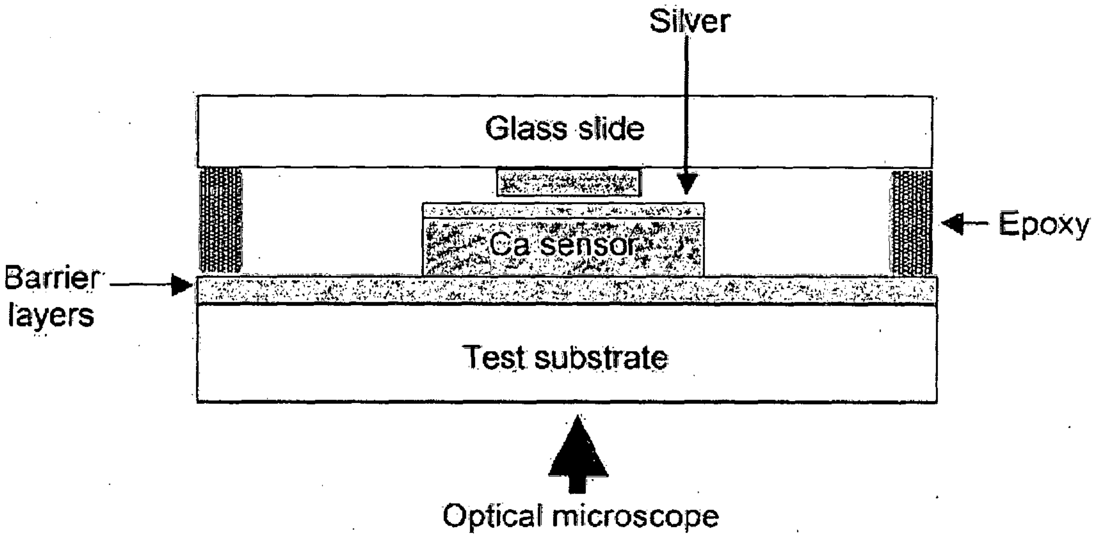


Fig. 5

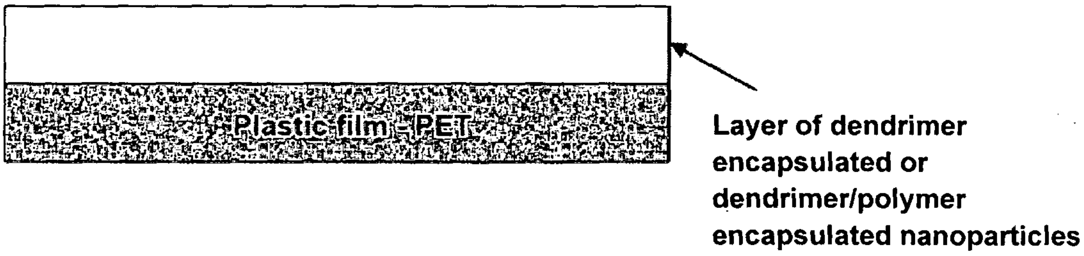


Fig. 6

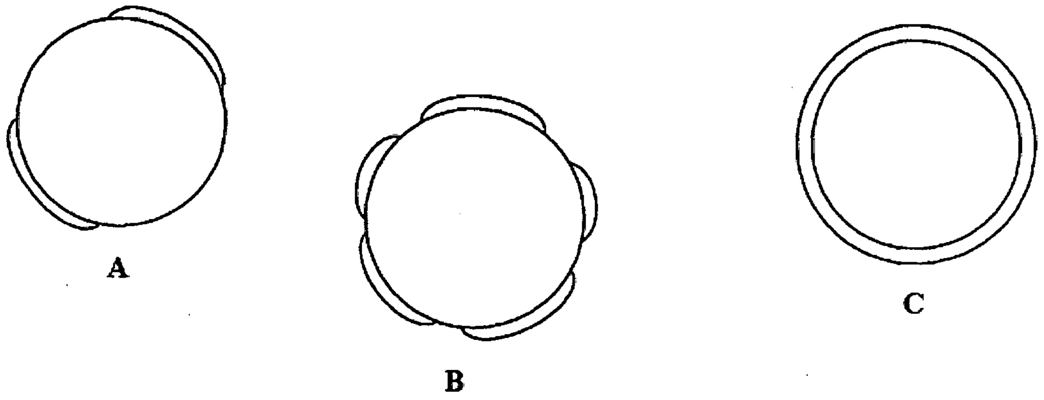

A
B
C

Fig. 7

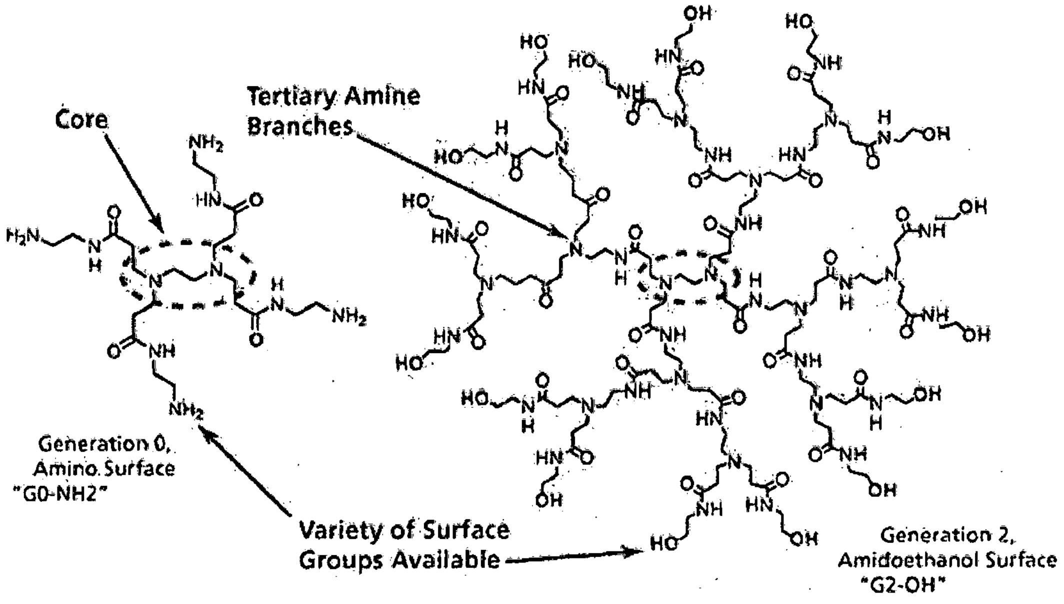

Core
Tertiary Amine Branches
Generation 0, Amino Surface "G0-NH2"
Variety of Surface Groups Available
Generation 2, Amidoethanol Surface "G2-OH"

Fig. 8A

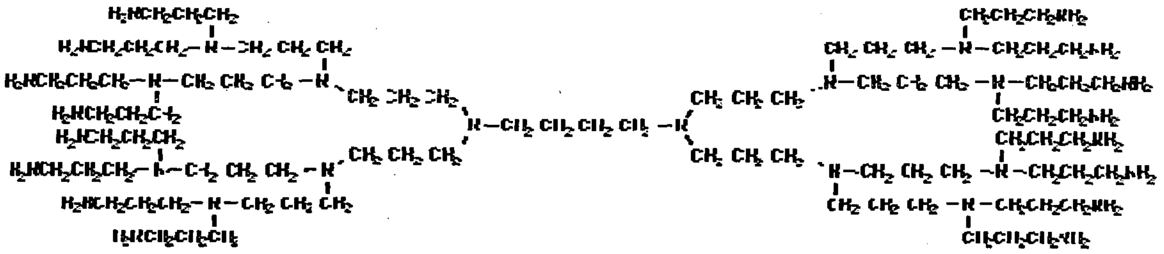
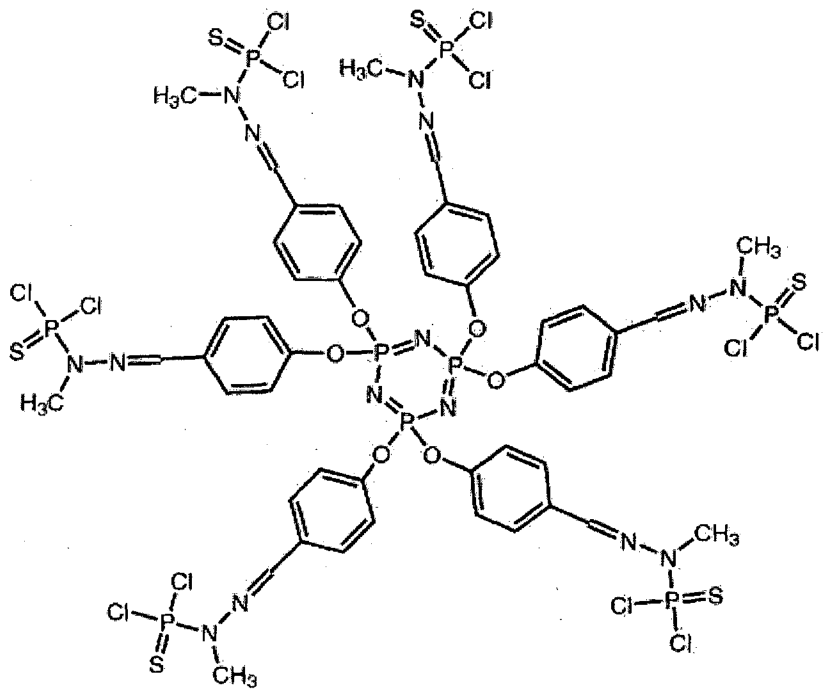


Fig. 8B

Phosphorous Dendrimer Structure



Cyclotriphosphazene core,
Dichlorophosphinothioyl Surface
G = 1.0

Fig. 8C

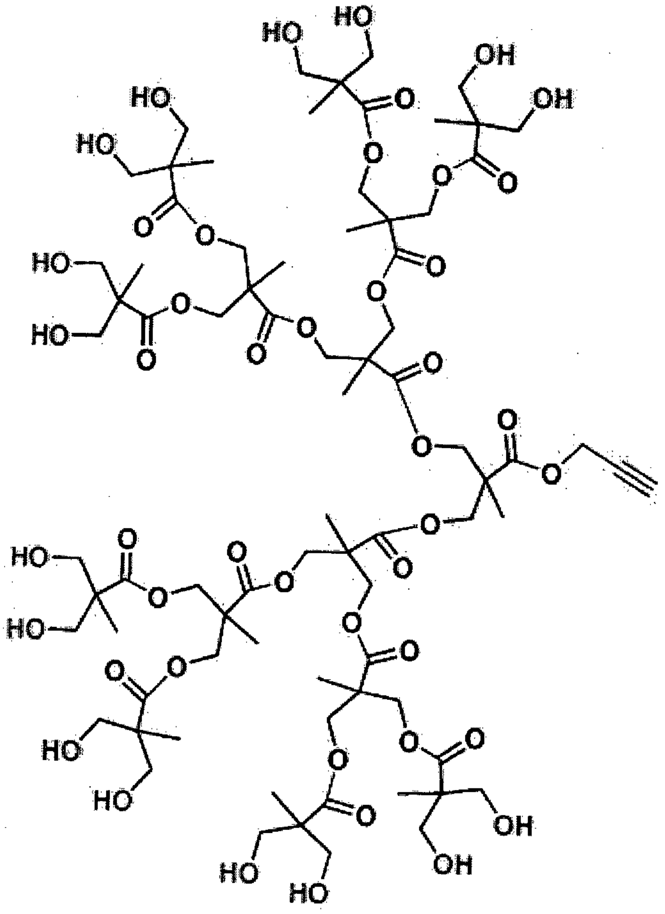

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Fig. 8D

INTERNATIONAL SEARCH REPORT	International application No. **PCT/SG2014/000196**

A. CLASSIFICATION OF SUBJECT MATTER

B32B 7/02 (2006.01) B32B 27/14 (2006.01) H05B 33/04 (2006.01) H01L 51/52 (2006.01) B82Y 30/00 (2011.01)

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)

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)

WPI, EPODOC, CAPLUS, TXTUS5, TXTUS4, TXTUS3, TXTUS2, TXTUS1, TXTUS0, TXTEP1, TXTGB1, TXTWO1, TXTAU1, TXTCA1, TXTSG1, GOOGLE SCHOLAR, GOOGLE PATENTS, ESPACENET: Keywords (layer, stack, barrier, nanoparticle, film, impermeable, permeability, sealant, moisture, water, oxygen, air, dendrimer, OLED, LED, encapsulated) and variations thereon

ESPACENET: Applicant/Inventor name search

GOOGLE SCHOLAR: Inventor name search

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

☒ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
5 August 2014	05 August 2014
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Alan Criddle AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832846

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT	International application No. **PCT/SG2014/000196**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/057045 A1 (AGENCY FOR SCIENCE, TECHNOLOGY AND RESEARCH) 15 May 2008 Abstract; [020]–[027]	1–79
A	WO 2005/108215 A2 (SIGMA LABORATORIES OF ARIZONA INC) 17 November 2005 Abstract; Claims	1–79
A	WO 2005/092986 A1 (TOYO BOSEKI KABUSHIKI KAISHA) 06 October 2005 Abstract	1–79
A	EP 1344794 A1 (EASTMAN KODAK COMPANY) 17 September 2003 Abstract; Examples	1–79
P,A	WO 2013/062486 A1 (TERA-BARRIER FILMS PTE LTD et al) 02 May 2013 Abstract; [0019]–[0026], Claims	1–79
P,A	WO 2014/062135 A1 (TERA-BARRIER FILMS PTE LTD) 24 April 2014 Abstract; [0019]; Examples; Figures 4A–4D; Claims	1–79

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2014/000196

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
WO 2008/057045 A1	15 May 2008	AU 2006350626 A1	15 May 2008
		AU 2006350626 B2	19 Sep 2013
		CN 101518151 A	26 Aug 2009
		EP 2082619 A1	29 Jul 2009
		JP 2010511267 A	08 Apr 2010
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WO 2005/108215 A2	17 November 2005	EP 1753662 A2	21 Feb 2007
		JP 2007536169 A	13 Dec 2007
		US 2005249901 A1	10 Nov 2005
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		JP 2003292804 A	15 Oct 2003
		US 2003203989 A1	30 Oct 2003
		US 7166657 B2	23 Jan 2007
WO 2013/062486 A1	02 May 2013	AU 2012329403 A1	10 Apr 2014
		CA 2852879 A1	02 May 2013
WO 2014/062135 A1	24 April 2014	None	

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.