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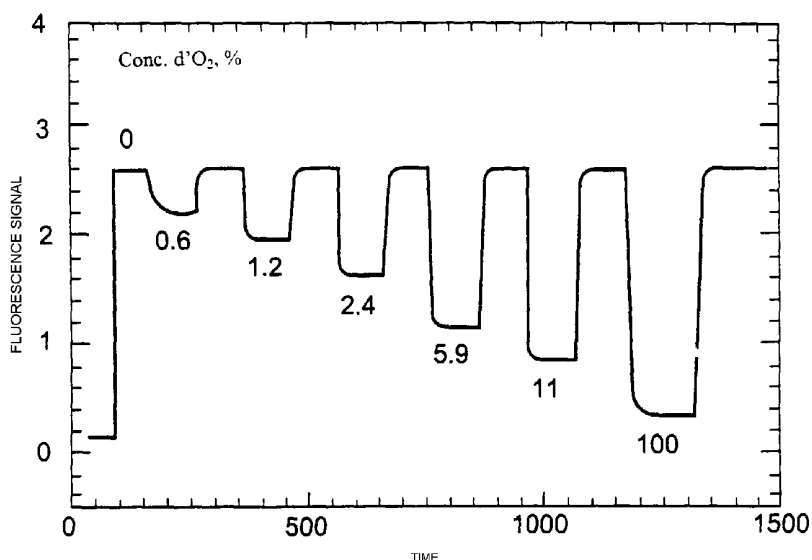
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(54) Title: METHODS FOR NONDESTRUCTIVE EVALUATION OF DEFECTS IN A TRANSPARENT COATING



(57) Abstract: A method for nondestructive evaluation of defects in a transparent coating (3) on polymers, comprising applying a sensor layer (2) comprising a fluorophore under the transparent coating (3) and exposing the transparent coating (3) to molecular oxygen, wherein the defects are identified by change in the fluorescence signature of the fluorophore in locations corresponding to the coating defects. The method can be used for nondestructive evaluation of defects in a library of transparent coatings (3) wherein a sensor layer (2) comprising a fluorophore is applied under a grid or an array of transparent coatings (3) and the transparent coatings (3) are exposed to different partial pressures of oxygen, to map and count defect density and to better understand the origins of defects in the coatings on a microscopic scale. Further, the method can be effectively used for a rapid screening of defects in a number of samples in a combinatorial array.



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METHODS FOR NONDESTRUCTIVE
EVALUATION OF DEFECTS IN A TRANSPARENT
COATING

BACKGROUND OF THE INVENTION

5 This invention was made with government support under Contract No. 70NANB9H3038 awarded by NIST. The government may have certain rights to the invention.

10 The present invention in general relates to a method for nondestructive evaluation of defects in a transparent coating, and more particularly to a method for nondestructive evaluation of defects in a transparent coating by applying a sensor layer comprising a fluorophore under the transparent coating. This method may be also used in combinatorial discovery of coating materials for applications as barrier, sensor, and other types of coatings.

15 Transparent coatings on polymers are increasingly being used as permeation barriers, and for various other functional uses such as protective coatings on spacecraft materials. Especially these transparent barrier coatings are the subject of increasing interest in the packaging, pharmaceutical, optical, aerospace and electronics industries.

20 Typically, transparent coatings applied by Plasma Enhanced Chemical Vapor Deposition (PECVD), reactive evaporation, sputtering, etc., such as silicon dioxide (SiO₂) or nitride (Si₃N₄), provide excellent barrier properties even when they are extremely thin. Despite the excellent barrier properties provided by these coatings, some residual permeation is observed, even when the barrier coatings are relatively thick. See, A.S. da Silva Sobrinho, M. Latreche, G. Czeremuszkina, J.E. Klemberg-Sapieha, M.R. Wertheimer, *J. Vac. Sci. Technol.* A16 (1998) 3190. The residual permeation is attributed to the presence of microscopic defects in the coating. A.S. da Silva Sobrinho, G. Czeremuszkina, M. Latreche, M.R. Wertheimer, *J. Vac. Sci.*

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Technol. 2000, *A18*, 129-157; and Jamieson, E. H. H. Windle, A. H., *J. Mater. Sci.* 1983, *18*, 64. These defects may result from dust particles on the substrate surface, from geometric shadowing, stress during film growth at sites of high surface roughness, or from other causes.

5 Thus, determination of defects in transparent coatings, especially transparent barrier coatings, is an important part in the evaluation of the coating quality.

 In an opaque coating, such as aluminized polyester (PET), even micrometer or submicrometer defects can be easily detected with transmission
10 electron microscopy or optical transmission microscopy using transmitted light. Jamieson, E. H. H. Windle, A. H., *J. Mater. Sci.* 1983, *18*, 64. However, when both coating and substrate are transparent, detection of defects, especially micrometer- or submicrometer-sized defects in a coating such as pinholes or microcracks are,
invisible in optical microscopy, are very difficult, if not impossible, to discern by
15 scanning electron microscopy (SEM). Reactive ion etching (RIE) in oxygen plasma has been used to visualize defects with submicrometer size in transparent barrier coatings on transparent polymers. A.S. da Silva Sobrinho; G. Czeremuszkina; M. Latreche; M.R. Wertheimer, *Appl. Phys. A: Mater. Sci. Process.* 1999, *68*, 1; and A.S. da Silva Sobrinho; G. Czeremuszkina; M. Latreche; G. Dennler; M.R. Wertheimer,
20 *Surf. Coat. Technol.* 1999, *116-119*, 1204. In the RIE treatment technique, the polymer underneath a defect region is etched by atomic oxygen (AO) creating a cavity that renders the defect visible by optical microscopy. To visualize defects in a large area (tens of square centimeters), after being exposed to AO, the transparent coating is coated with a thin layer of corn starch and the other side is exposed to
25 iodine vapor. The iodine that diffuses through the cavities underneath defects react with the corn starch giving a dark coloration and then a finger print of the defects in the sample. While this technique is effective in detecting defects in transparent coatings on transparent substrates, the RIE technique is destructive by nature rendering samples unsuitable for further analysis, it requires multiple steps in sample

preparation, utilizes a high-cost plasma system, and does not allow a real time monitoring of oxygen permeation through defects.

It is therefore desired to provide a method for detection of defects in transparent coatings without involving these problems.

5 Another advantages of the present invention is to use a method of nondestructive evaluation of defects in a combinatorial chemistry. The techniques of combinatorial synthesis of libraries of organic compounds are well known. For example, Pirrung *et al.* developed a technique for generating arrays of peptides and other molecules using, for example, light-directed, spatially-addressable synthesis
10 techniques (U.S. Pat. No. 5,143,854 and PCT Publication No. WO 90/15070). In addition, Fodor *et al.* have developed automated techniques for performing light-directed, spatially-addressable synthesis techniques, photosensitive protecting groups, masking techniques and methods for gathering fluorescence intensity data (Fodor *et al.*, PCT Publication No. WO 92/10092). Using these various methods of
15 combinatorial synthesis, arrays containing thousands or millions of different organic elements can be formed (see, U.S. Pat. No. 5,424,186). The solid phase synthesis techniques currently being used to prepare such libraries involve a stepwise process (i.e., sequential, coupling of building blocks to form the compounds of interest). In the Pirrung *et al.* method, for example, polypeptide arrays are synthesized on a
20 substrate by attaching photoremovable groups to the surface of the substrate, exposing selected regions of the substrate to light to activate those regions, attaching an amino acid monomer with a photoremovable group to the activated region, and repeating the steps of activation and attachment until polypeptides of the desired length and sequences are synthesized. The Pirrung *et al.* method is a sequential, step-wise
25 process utilizing attachment, masking, deprotecting, attachment, etc. Such techniques have been used to generate libraries of biological polymers and small organic molecules to screen for their ability to specifically bind and block biological receptors (i.e., protein, DNA, etc.). These solid phase synthesis techniques, which involve the sequential addition of building blocks (i.e., monomers, amino acids) to form the
30 compounds of interest, cannot readily be used to prepare many inorganic and organic

compounds. As a result of their relationship to semiconductor fabrication techniques, these methods have come to be referred to as "Very Large Scale Immobilized Polymer Synthesis," or "VLSIPS" technology.

Schultz *et al.* applied combinatorial chemistry techniques to the field of material science U.S. Pat. No. 5,985,356. More particularly, Schultz *et al.* disclose methods and apparatus for the preparation and use of a substrate having thereon an array of diverse materials in predefined regions. An appropriate array of materials is generally prepared by delivering components of materials to predefined regions on the substrate and simultaneously reacting the reactants to form different materials.

Once prepared, the array of materials can be screened in parallel for materials having useful properties. Properties which can be screened for include, for example, electrical, thermal, mechanical, morphological, optical, magnetic, chemical, etc. Either the entire array or, alternatively, a section thereof (e.g., a row of predefined regions) can be screened in parallel for materials having useful properties. Scanning detection systems suggested in Schultz *et al.* for use in screening method include scanning Raman spectroscopy; scanning NMR spectroscopy; scanning probe spectroscopy including, for example, surface potentialometry, tunnelling current, atomic force, acoustic microscopy, shearing-stress microscopy, ultra fast photo excitation, electrostatic force microscope, tunneling induced photo emission microscope, magnetic force microscope, microwave field-induced surface harmonic generation microscope, nonlinear alternating-current tunnelling microscopy, near-field scanning optical microscopy, inelastic electron tunneling spectrometer, etc.; optical microscopy at different wavelengths; scanning optical ellipsometry (for measuring dielectric constant and multilayer film thickness); scanning Eddy-current microscope; electron (diffraction) microscope, etc.

More particularly, to screen for conductivity and/or superconductivity, one of the following devices can be used: a Scanning RF Susceptibility Probe, a Scanning RF/Microwave Split-Ring Resonator Detector, or a Scanning Superconductors Quantum Interference Device (SQUID) Detection System. To screen for hardness, a nanoindenter (diamond tip) can, for example, be used. To

screen for magnetoresistance, a Scanning RF/Microwave Split-Ring Resonator Detector or a SQUID Detection System can be used. To screen for crystallinity, infrared or Raman spectroscopy can be used. To screen for magnetic strength and coercivity, a Scanning RF Susceptibility Probe, a Scanning RF/Microwave Split-Ring Resonator Detector, a SQUID Detection System or a Hall probe can be used. To screen for fluorescence, a photodetector can be used.

In combinatorial discovery of coating materials for applications as barrier, sensor, and other types of coatings, the rapid evaluation of defects of coatings is needed to estimate and determine their effects on the properties of the coating. Thus, it is apparent that there a need for a combinatorial method for detecting defects in coatings so as to greatly accelerate the rate discovering and optimizing new materials. Quite surprisingly, the instant invention provides such methods.

BRIEF SUMMARY OF THE INVENTION

The present invention provides a method for nondestructive evaluation of defects in transparent coatings, which is free from the limitations of known techniques for evaluation of defects in transparent coatings.

In accordance with one aspect of the present invention, there is provided a method for nondestructive evaluation of defects in a transparent coating, comprising applying a sensor layer comprising a fluorophore under the transparent coating, and exposing the transparent coating to molecular oxygen, wherein the defects are identified by change in the fluorescence signature of the fluorophore in locations corresponding to the coating defects.

It is another aspect of the present invention to provide a method for nondestructive evaluation of defects in a library of transparent coatings, comprising applying a sensor layer comprising a fluorophore under the transparent coating, and exposing the transparent coatings to molecular oxygen with varying concentrations, wherein change of fluorescence signal indicates defects in the transparent coatings.

The present invention can be also used to map and count defect density and to better understand the origins of defects in transparent coatings on a microscopic scale. Thus, it is yet another aspect of the present invention to provide a method for mapping and/or count defect density in transparent coatings, comprising
5 applying a sensor layer comprising a fluorophore under the transparent coatings, obtaining two fluorescence images of the grid of coating upon exposure of the transparent coatings to nitrogen and oxygen, respectively; and obtaining a ratio of the two fluorescence images.

The present invention also avails itself to use in rapidly screening a
10 number of samples in a combinatorial array.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 illustrates an absorption spectrum of platinum (II) octaethyl porphyrin in chloroform.

Fig. 2 illustrates fluorescence spectra of platinum (II)
15 octaethylporphyrin in a thin polycarbonate film in nitrogen and oxygen environment.

Fig. 3 illustrates a sensor response to different oxygen concentrations.

Fig. 4 illustrates reversibility of sensor response to oxygen and nitrogen.

Fig. 5 illustrates principle of spatial mapping of oxygen permeability
20 through a library of transparent coatings. A substrate 1; a sensor layer 2; library of transparent coatings 3; different partial pressures of oxygen 4.

Fig. 6 illustrates principle of spatial mapping of oxygen permeability
25 through a library of transparent coatings. A substrate 1; a sensor layer 2; library of transparent coatings 3; different partial pressures of oxygen 4; partial pressure of oxygen lower than on the other side of the substrate 5.

Fig. 7 illustrates principle of spatial mapping of oxygen permeability through a library of transparent coatings.

Fig. 8 illustrates fluorescence image of the coating grid when the grid of transparent coatings was exposed to air. Asterisks indicate the positions of deposited silicon nitride barrier coatings.

Fig. 9 illustrates fluorescence image of the coating grid when the grid of transparent coatings was exposed to nitrogen. Asterisks indicate the positions of deposited silicon nitride barrier coatings.

Fig. 10 illustrates oxygen-permeability map for the grid of silicon nitride barrier coatings produced as the ratio of two fluorescence images of the coating grid when the coating was exposed to nitrogen and oxygen.

Fig. 11 illustrates spatial mapping of defects in barrier coatings. Edge-induced diffusion of oxygen is also clearly visible.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is based on the understanding that fluorescence quenching of certain fluorophores upon their exposure to molecular oxygen can be used for detection of defects in coating layers. Certain types of fluorophores are known to provide an efficient quenching by molecular oxygen when dissolved in solvents or in a variety of polymer matrices. The absorption and fluorescence spectra of platinum (II) octaethylporphyrin fluorophore are illustrated in figures 1 and 2. Sensor response to different oxygen concentrations is presented in figure 3. Sensor reversibility upon changes the gas from nitrogen to oxygen at different concentrations is illustrated in figure 4. Fluorescence intensity and lifetime of such fluorophore decrease with increasing oxygen concentration. This fluorescence response can serve as a robust and predictable meter for the amount of oxygen around the fluorophore, which is caused by the defects in surface coating layers.

With fluorescence spectroscopy, the present invention provides advantages over the prior art techniques including the following:

- 5 (1) spatially resolved information about coating defects across the entire surface of the coating which can be limited only by the coating deposition technique and equipment;
- (2) noninvasive and/or nondestructive nature of detection of defects; and
- (3) dynamic measurements of oxygen diffusion at different time points.

10 The preferred embodiments of the present invention provide a method for nondestructive evaluation of defects in a barrier coating comprising applying a sensor layer comprising a fluorophore under a grid or an array of the barrier coatings; and exposing the barrier coating to molecular oxygen, wherein the defects are identified by change in the fluorescence signature of the fluorophore in locations
15 corresponding to the coating defects.

The invention is described herein primarily with regard to the detection of defects on barrier coatings, but readily be applied in the detection of other coatings.

In one embodiment, a sensor layer may be applied between a barrier coating and a substrate. In another embodiment, a sensor layer may be applied onto a
20 substrate such that a substrate is placed between the sensor layer and a barrier coating. It should be understood that in either of these embodiments, various types of other coating layers may be also applied under or onto a substrate, a sensor layer or a barrier coating.

A sensor layer comprises at least one class of fluorophores. One class
25 of fluorophores includes porphyrins. Examples of the porphyrins include but are not limited to platinum or palladium porphyrins, such as platinum(II) octaethylporphyrin (Pt-OEP) and palladium(II) octaethylporphyrin (Pd-OEP). P. Hartmann, W. Trettnak,

Effects of polymer matrices on calibration functions of luminescent oxygen sensors based on porphyrin ketone complexes, *Anal. Chem.* **1996**, *68*, 2615-2620; A. Mills, A. Lepre, Controlling the response characteristics of luminescent porphyrin plastic film sensors for oxygen, *Anal. Chem.* **1997**, *69*, 4653-4659.

5 Another class of fluorophores includes polycyclic aromatic hydrocarbons. Examples of this class of fluorophores are described in I. B. Berlman, Handbook of fluorescence spectra of aromatic molecules, Academic Press, New York, NY, 1971; O. S. Wolfbeis, In *Fiber Optic Chemical Sensors and Biosensors*; O. S. Wolfbeis, Ed.; CRC Press: Boca Raton, FL, 1991; Vol. 2; pp 19-53. Preferred
10 fluorophores of this class include pyrene, pyrenebutyric acid, fluoranthene, decacyclene, diphenylanthracene, and benzo(g,h,i)perylene.

 Another class of fluorophores includes a variety of long-wave absorbing dyes such as perylene dibutyrate, and heterocycles including fluorescent yellow, tryptaflavin and other heterocycle compounds as described in O. S. Wolfbeis,
15 In *Fiber Optic Chemical Sensors and Biosensors*; O. S. Wolfbeis, Ed.; CRC Press: Boca Raton, FL, 1991; Vol. 2; pp 19-53.

 Yet, another group of fluorophores includes metal-organic complexes of ruthenium, osmium, iridium, gold and platinum as described in O. S. Wolfbeis, In
20 *Fiber Optic Chemical Sensors and Biosensors*; O. S. Wolfbeis, Ed.; CRC Press: Boca Raton, FL, 1991; Vol. 2; pp 19-53, J. N. Demas, B. A. Degraff, P. B. Coleman, Oxygen sensors based on luminescence quenching, *Anal. Chem.* **1999**, *71*, 793A-800A, and J. N. Demas, B. A. DeGraff, Design and applications of highly luminescent transition metal complexes, *Anal. Chem.* **1991**, *63*, 829A-837A; A. Mills, A. Lepre, B. R. Theobald, E. Slade, B. A. Murrer, Use of luminescent gold
25 compounds in the design of thin-film oxygen sensors, *Anal. Chem.* **1997**, *69*, 2842-2847.

Fluorophores are incorporated into a sensor layer formed from film-forming polymeric material. The material for the sensor layer may affect the

properties of sensors such as selectivity, sensitivity, and limit of detection. Thus, suitable material for the sensor layer is selected from polymeric material capable of providing required response time, oxygen permeability, oxygen solubility, degree of transparency and hardness.

5 In general, polymers that can be used as matrices for oxygen sensors can be divided into several classes as described in S. A. Stern, B. Krishnakumar, S. M. Nadakatti, In *Physical Properties of Polymers Handbook*; J. E. Mark, Ed.; AIP Press: New York, 1996; pp 687-700. Such classes include polyolefins, vinyl and vinylidene polymers, natural and synthetic rubbers, polyesters, polycarbonates,
10 cellulose derivatives, fluoropolymers, polyorganosiloxanes, polynitriles, polyamides, polyimides, polyurethanes, polyoxides, polysulfones, polyacetylenes, polyacrylics. A variety of polymeric materials useful for incorporation of oxygen sensitive fluorophores are described in W. Xu, R. C. McDonough, B. Langsdorf, J. N. Demas, B. A. DeGraff, Oxygen sensors based on luminescence quenching: interactions of
15 metal complexes with the polymer supports, *Anal. Chem.* 1994, 66, 4133-4141; S. Draxler, M. E. Lippitsch, L. Klimant, H. Kraus, O. S. Wolfbeis, Effects of polymer matrices on the time-resolved luminescence of a ruthenium complex quenched by oxygen, *J. Phys. Chem.* 1995, 99, 3162-3167; W. Xu, R. Schmidt, M. Whaley, J. N. Demas, B. A. DeGraff, E. K. Karikari, B. L. Farmer, Oxygen sensors based on
20 luminescence quenching: interactions of pyrene with the polymer supports, *Anal. Chem.* 1995, 67, 3172-3180; P. Hartmann, W. Trettnak, Effects of polymer matrices on calibration functions of luminescent oxygen sensors based on porphyrin ketone complexes, *Anal. Chem.* 1996, 68, 2615-2620; A. Mills, Lepre, Controlling the response characteristics of luminescent porphyrin plastic film sensors for oxygen,
25 *Anal. Chem.* 1997, 69, 4653-4659.

Examples of such suitable polymeric materials include but are not limited to polyvinyl chloride (PVC), polystyrene (PS), poly(ethylene terephthalate) (PET), polycarbonate (PC), cellulose acetate butyrate (CAB), poly(methyl methacrylate) (PMMA), PMMA/CAB blends, fluoro-polymer such as poly(styrene-co-trifluoroethyl-methacrylate) (poly-styrene-co-TFEM) and other fluoropolymers,
30

silicones, silicone blends, silicone copolymers, cation exchange membranes such as Nafion, and others.

5 The sensor layer is made of thin film, suitably of a thickness from 0.05 to 1000 micrometers, particularly from 0.5 to 100 micrometers, and more particularly from 1 to 10 micrometers.

10 The sensor layer is formed by incorporating fluorophores into the polymeric material for the sensor layer. Incorporation of the fluorophores may be carried out by dissolving a fluorophore in a solution of polymeric material and then the resultant solution is applied to a substrate to form a sensor layer using various methods using thin-film deposition techniques that are explained below. Solvents can be either polar or non polar, including but not limited to water, ethanol, methanol, acetone, chloroform, toluene, benzene, and hexane.

15 Another method for incorporation of fluorophores includes dissolving a fluorophore in a suitable solvent and immersing a polymer film into the fluorophore solution. The polymer film swells in the solvent and some of the fluorophore molecules penetrate into the swollen polymer film. Upon drying, the solvent is removed while the fluorophore remains trapped in the polymer film.

20 The sensor layer is exposed to varying concentrations of oxygen. Oxygen concentrations range from 0 to 100 % by volume. Partial pressure of oxygen can range from 0 to 1 atmosphere. However, in order to accelerate penetration of oxygen, the partial pressure can be increased higher than 1 atmosphere and, depending on the equipment used, can be, for example 10, 100, or 1000 atmosphere or even higher.

25 The sensor layer may be exposed first to the atmosphere at which the coating deposition was performed, and then to nitrogen or oxygen. The change in fluorescence intensity or lifetime may be measured using a spectrometer such as Shimadzu F-5300PC, Hitachi F-4010, Edinburgh Analytical Instruments FL-900, SPEX Fluorog 2, Perkin Elmer LS50B, and others. Fluorescence of fluorophores is

excited using a light source from the spectrometer which typically a xenon arc lamp and/or xenon argon or discharge lamp with a power from 150W to 20kW.

Other equipment to measure fluorescence intensity and lifetime is available with other types of light sources. Other types of light sources are presented in Table 1.

5

Table 1. Light sources useful for excitation of luminescence.

Source	Spectral range of emission (nm)
Continuous wave sources:	200 – 1000
Xenon arc lamp	250 – 600
Mercury arc lamp	180 – 420
Deuterium lamp	320 – 2500
Tungsten lamp	different diodes cover range from 370 to 1500 nm
Light emitting diodes	different diode lasers cover range from about 400 to 1500 nm
Diode lasers	nm
Argon ion laser	several lines over 350 – 514 nm
Helium-neon laser	several lines over 543 – 633 nm
Krypton laser	several lines over 530 – 676 nm
Pulsed sources:	
Nitrogen laser	337 nm
Nd:YAG laser	fundamental – 1064, frequency doubled – 532, tripled – 355
Ti:Sapphire laser	355
Dye lasers	720–1000, frequency doubled 360–500 400 – 900

Oxygen sensitive materials, fluorophores, used in the present invention are excited at wavelengths ranging from about 300 to 650 nm. A comparison of fluorescence values is made for the coating library exposed to different concentrations of oxygen at different times.

10

The sensor response for different oxygen concentrations is shown in Table 2.

Table 2

Oxygen concentration (%)	Sensor response
0	1

0.621	1.26
2.44	2
11.1	4.79
100	25.3

A sensor response is defined as the ratio of fluorescence intensity of the fluorophore in nitrogen to fluorescence intensity of the fluorophore in a given oxygen-containing environment.

In one experimental configuration, fluorescence measurements were performed on a setup which included a white light source (450-W Xe arc lamp, SLM Instruments, Inc., Urbana, IL, Model FP-024), a monochromator for selection of the excitation wavelength (SLM Instruments, Inc., Model FP-092), and a portable spectrofluorometer (Ocean Optics, Inc., Dunedin, FL, Model ST2000). The spectrofluorometer was equipped with a 200- μm slit, 600-grooves/mm grating blazed at 400 nm and covering the spectral range from 250 to 800 nm with efficiency greater than 30%, and a linear CCD-array detector. Excitation light from the monochromator was focused into one of the arms of a "six-around-one" bifurcated fiber-optic reflection probe (Ocean Optics, Inc., Model R400-7-UV/VIS). Emission light was collected from a sample when the common end of the fiber-optic probe was positioned near the sample at a certain angle to minimize the amount of excitation light reflected from the sample back into the probe. The second arm of the probe was coupled to the spectrofluorometer.

A flow cell with transparent viewing windows was used to position samples of fluorescent material. Different oxygen concentrations were generated by diluting pure (100%) oxygen with a nitrogen carrier gas using flow mass controllers. Total flow was kept constant at 4 L/min. The gas was introduced into the flow cell. Fluorescent material was positioned in the flow cell. The fluorescent material was a thin film of polycarbonate (PC) material (Scientific Polymer Products, Inc, Ontario, NY) with immobilized fluorescent dye Pt(II)Octaethylporphyrin (Porphyrin Products, Inc., Logan, UT) used as a fluorophore. For film preparation, PC was dissolved in chloroform to about 10% by weight. The fluorophore was dissolved in chloroform.

Solutions of the PC and the fluorophore were mixed to produce about 10^{-6} M concentration of fluorophore. The film was cast using one of the techniques of spray coating, dip coating, or flow coating. The solvent was evaporated at room temperature for about 24 hours.

5 For steady state measurements of sensor response, the fluorescence was measured after about 3 min after the concentration had changed.

Materials for barrier coatings include, but are not limited to oxides, nitrides and oxinitrides of silicon, aluminum, zinc, boron and other metals, ceramics, polyvinyl alcohol, ethylene vinyl alcohol copolymers, polyvinyl dichloride, different
10 types of nylon, cellophane, polyethylene terephthalate, PVC, PCTFE, polypropylene, and others.

Barrier coatings are deposited either onto the sensor layer or onto the substrate. In the latter case, the sensor layer is deposited onto one side of the substrate wherein the barrier coating is applied onto an opposite site of the substrate
15 before or after the formation of the sensor layer. Fig. 5 details one embodiment where a library of transparent coatings 3 is deposited onto the sensor layer 2, which, in turn, is formed onto a substrate 1. Fig. 6 details another embodiment where a library of transparent coatings 3 is deposited onto one side of the substrate 1 while the sensor layer 2 is formed onto another side of the substrate 1.

20 Thin-film deposition techniques in combination with physical masking techniques or photolithographic techniques can be used to apply a barrier coating layer onto a sensor layer. Such thin-film deposition techniques can generally be broken down into the following four categories: evaporative methods, glow discharge processes, gas-phase chemical processes, and liquid-phase chemical techniques.
25 Included within these categories are, for example, sputtering techniques, spraying techniques, laser ablation techniques, electron beam or thermal evaporation techniques, ion implantation or doping techniques, chemical vapor deposition techniques, as well as other techniques used in the fabrication of integrated circuits.

All of these techniques can be applied to deposit highly uniform layers, i.e., thin-films, of the various coating materials on selected regions on the sensor layer. Moreover, by adjusting the relative geometries of the masks, the delivery source and/or the substrate, such thin-film deposition techniques can be used to generate
5 uniform gradients at each reaction region on the substrate or, alternatively, over all of the reaction regions on the substrate. For an overview of the various thin-film deposition techniques which can be used in the methods of the present invention, see, for example, Handbook of Thin-Film Deposition Processes and Techniques, Noyes Publication (1988), which is incorporated herein by reference for all purposes.

10 Thin-films of the various barrier coating materials can be deposited either onto the sensor layer or onto the substrate using evaporative methods in combination with physical masking techniques. Generally, in thermal evaporation or vacuum evaporation methods, the following sequential steps take place: (1) a vapor is generated by boiling or subliming a target material; (2) the vapor is transported from
15 the source to a substrate; and (3) the vapor is condensed to a solid film on the substrate surface. Evaporants, i.e., target materials, which can be used in the evaporative methods cover an extraordinary range of chemical reactivities and vapor pressures and, thus, a wide vary of sources can be used to vaporize the target materials. Such sources include, for example, resistance-heated filaments, electron
20 beams; crucible heated by conduction, radiation or rf-inductions; and arcs, exploding wires and lasers. In preferred embodiments of the present invention, thin-film deposition using evaporative methods is carried out using lasers, filaments, electron beams or ion beams as the source. Successive rounds of deposition, through different physical masks, using evaporative methods can be used to generate a library or grid of
25 barrier coatings on a sensory layer for detection of defects in the barrier coatings in combinatorial discovery of coating materials.

 Molecular Beam Epitaxy (MBE) is an evaporative method that can be used to grow epitaxial thin-films. In this method, the films are formed on single-crystal substrates by slowly evaporating the elemental or molecular constituents of the
30 film from separate Knudsen effusion source cells (deep crucibles in furnaces with

cooled shrouds) onto substrates held at temperatures appropriate for chemical reaction, epitaxy and re-evaporation of excess reactants. The Knudsen effusion source cells produce atomic or molecular beams of relatively small diameter which are directed at the heated substrate, usually silicon or gallium arsenide. Fast shutters
5 are interposed between the source cells and the substrates. By controlling these shutters, one can grow superlattices with precisely controlled uniformity, lattice match, composition, dopant concentrations, thickness and interfaces down to the level of atomic layers.

In addition to evaporative methods, thin-films of the various barrier coating materials can be deposited onto the sensor layer or onto the substrate using glow-discharge processes in combination with physical masking techniques. The most basic and well known of these processes is sputtering, i.e., the ejection of surface atoms from an electrode surface by momentum transfer from bombarding ions to surface atoms. Sputtering or sputter-deposition is a term used by those of skill in the art to cover a variety of processes, all of which can be used in the methods of the present invention. One such process is RF/DC Glow Discharge Plasma Sputtering. In this process, a plasma of energized ions is created by applying a high RF or DC voltage between a cathode and an anode. The energy ions from the plasma bombard the target and eject atoms which are then deposited on a substrate, a sensor layer.
15
20 Ion-Beam Sputtering is another example of a sputtering process which can be used to deposit thin-films of the various barrier coating materials on a substrate. Ion-Beam Sputtering is similar to the foregoing process except the ions are supplied by an ion source and not a plasma. It will be apparent to one of skill in the art that other sputtering techniques (e.g., diode sputtering, reactive sputtering, etc.) and other glow-discharge processes can be used in the methods of the present invention to deposit
25 thin-films on a substrate, a sensor layer. Successive rounds of deposition, through different physical masks, using sputtering or other glow-discharge techniques can be used to generate a grid or library of barrier coatings on a sensor layer for detection of defects in the barrier coating for use of combinatorial discovery of coating materials.

In addition to evaporative methods and sputtering techniques, thin-films of the various barrier coating materials can be deposited onto the sensor layer or onto the substrate using Chemical Vapor Deposition (CVD) techniques in combination with physical masking techniques. CVD involves the formation of stable solids by decomposition of gaseous chemicals using heat, plasma, ultraviolet, or other energy source, or a combination of energy sources. Photo-Enhanced CVD, based on activation of the reactants in the gas or vapor phase by electromagnetic radiation, usually short-wave ultraviolet radiation, and Plasma-Enhanced CVD, based on activation of the reactants in the gas or vapor phase using a plasma, are two particularly useful chemical vapor deposition techniques. Successive rounds of deposition, through different physical masks, using CVD technique can be used to generate a grid or library of barrier coatings on a sensor layer for detection of defects in the barrier coating in combinatorial discovery of coating materials.

In addition to evaporative methods, sputtering and CVD, thin-films of the various reactants can be deposited onto the sensor layer or onto the substrate using a number of different mechanical techniques in combination with physical masking techniques. Such mechanical techniques include, for example, spraying, spinning, dipping, draining, flow coating, roller coating, pressure-curtain coating, brushing, etc. Of these, the spray-on and spin-on techniques are particularly useful. Sprayers which can be used to deposit thin-films include, for example, ultrasonic nozzle sprayers, air atomizing nozzle sprayers and atomizing nozzle sprayer. In ultrasonic sprayers, disc-shaped ceramic piezoelectric transducers convert electrical energy into mechanical energy. The transducers receive electrical input in the form of a high-frequency signal from a power supply that acts as a combination oscillator/amplifier. In air atomizing sprayers, the nozzles intermix air and liquid streams to produce a completely atomized spray. In atomizing sprayers, the nozzles use the energy from a pressurized liquid to atomize the liquid and, in turn, produce a spray. Successive rounds of deposition, through different physical masks, using mechanical techniques, such as spraying, can be used to generate a grid or library of barrier coatings on a sensor layer for detection of defects in combinatorial discovery of coating materials.

The barrier coating suitably has a thickness from 0.1 nm to 100 micrometers, particularly from 1 nm to 10 micrometers, and more particularly from 10 nm to 1 micrometer.

5 A principle of spatial mapping of oxygen permeability through a library of barrier coatings is depicted in Fig. 5.

Fig. 7 illustrates an example of an instrumentation used for spatial mapping of oxygen permeability through a library of transparent coatings. A library of transparent coatings, sensor layer and substrate 11 is positioned in a gas cell 10. A light source 12 emits light through an excitation wavelength selection element 13. 10 The excitation radiation 14 illuminates the library of transparent coatings, sensor layer and substrate 11. The emission radiation 6 from the sensor layer is captured with an imaging detector 8 through an emission wavelength selection element 7. Data is collected at low partial pressure of oxygen 9 and at high partial pressure of oxygen 15. Results of mathematical image processing that includes division operation 16 are analyzed to produce oxygen distribution map 17 and to identify defects in transparent coating 18. 15

Fluorescence mapping measurements were performed using a setup which included a white light source (450-W Xe arc lamp, SLM Instruments, Inc., Urbana, IL, Model FP-024), a monochromator for selection of the excitation 20 wavelength (SLM Instruments, Inc., Model FP-092), and a CCD camera (Roper Scientific, Trenton, NJ, Model TE/CCD 1100 PF/UV). The excitation wavelength for the fluorophore was selected using the monochromator and was directed to the sample. Sample fluorescence was collected with the camera. The excitation light was filtered out from being captured by the camera with an integration time of 1 s 25 using a long pass optical filter that transmitted wavelengths above 610 nm.

Spatial maps of oxygen distribution in the barrier coatings were obtained by collecting fluorescence images of the sample with a grid of barrier coatings upon exposure of the sample to different oxygen concentrations (0 and

100%). Each image is represented in a digital two-dimensional format where each pixel in the image has its own recorded fluorescence intensity. Similar to the sensor signal which is defined as the ratio of fluorescence intensity of fluorophore in nitrogen to the fluorescence intensity of fluorophore in a given oxygen containing environment, the spatial map was obtained by dividing, pixel-by-pixel, the
5 fluorescence intensities of corresponding pixels. The result was a new two-dimensional array of relative fluorescence values which represent an oxygen distribution map.

The range of integration times can be selected ranging from about 10
10 ns to about 1000 s. The integration time depends on the available amount of fluorescence signal and the requirements for the signal-to-noise.

Fluorescence image map may be used to obtain density of defects on the library of coatings.

In a defect-free barrier coating deposited in oxygen-free environment,
15 the ratio of fluorescence intensity of fluorophore under the coating in nitrogen to the fluorescence intensity of fluorophore under the coating in a given oxygen containing environment should be unity because the coating does not transport oxygen through it. Oxygen permeation occurs in coating regions that have defects. This oxygen permeation is flagged by the fluorescence change of the fluorophore under the barrier
20 coating with a defect. Thus, the sections of the oxygen map of defect free regions will have a unity fluorescence ratio. The regions of barrier coating with defects will have an increased fluorescence ratio proportional to the amount of oxygen diffused down to the oxygen sensitive layer under the barrier coating. The density of defects is obtained by counting the regions with relative fluorescence intensity more than unity
25 over a unit area.

EXAMPLE 1

Barrier coatings were deposited on top of the sensor layer which, in turn, was deposited onto a polycarbonate or quartz substrate. Several 6-mm wide

stripes of silicon nitride barrier coatings were deposited in vacuum using a plasma-enhanced chemical vapor deposition onto the surface of the oxygen sensor.

The coating thickness was about 30 nm. Fluorescence mapping measurements were performed using a setup which included a white light source (450-W Xe arc lamp, SLM Instruments, Inc., Urbana, IL, Model FP-024), a monochromator for selection of the excitation wavelength (SLM Instruments, Inc., Model FP-092), and a CCD camera (Roper Scientific, Trenton, NJ, Model TE/CCD 1100 PF/UV). The excitation wavelength for the fluorophore was selected at 380 nm using the monochromator and was directed to the sample. Sample fluorescence was collected with the camera. The excitation light was filtered out from being captured by the camera using a long pass optical filter that transmitted wavelengths above 610 nm.

Fluorescence images of the coating grid upon exposure of the sensor to air and nitrogen are demonstrated in Figures 8 and 9, respectively. Fluorescence of the sensor region free from the deposited barrier coating is significantly quenched as indicated by the dark regions on the image. Upon exposure of the sensor to nitrogen, all sensor regions have the same fluorescence intensity indicating that no oxygen is present under the deposited coatings.

EXAMPLE 2

Spatial maps of oxygen distribution in the barrier coatings were obtained by collecting fluorescence images of the sample with a grid of barrier coatings upon exposure of the sample to different oxygen concentrations (0 and 100%), as illustrated in Fig. 7. Each image is represented in a digital two-dimensional format where each pixel in the image has its own recorded fluorescence intensity. Similar to the sensor signal which is defined as the ratio of fluorescence intensity of fluorophore in nitrogen to the fluorescence intensity of fluorophore in a given oxygen containing environment, spatial map was obtained by dividing pixel-by-pixel the fluorescence intensities of corresponding pixels. The result was a new two-

dimensional array of relative fluorescence values which represents an oxygen distribution map.

5 A ratio of two images when the sensor was exposed to nitrogen and oxygen represents an oxygen-permeability map for the grid of barrier coatings. See Fig. 10. The dark regions demonstrate that the fluorescence intensity under the barrier coatings was unchanged upon exposure of the grid to nitrogen and to oxygen. Bright regions free from the coating, which show high levels of signal, demonstrate that the fluorescence was efficiently quenched upon exposure to oxygen from its original high level in nitrogen atmosphere.

10 EXAMPLE 3

The region of interest was selected the middle stripe of the three coatings in Example 1 because measurements obtained in Example 1, as shown in Figs. 8 and 9, indicated that there are several defects of different shape that may induce the degradation of the barrier properties of the coating. The sequence of oxygen permeability maps was collected over 29 h after the exposure of the coating grid to oxygen. Results of spatial mapping of defects in barrier coatings at different times after the exposure of the coatings to oxygen are presented in Fig. 11. Edge-induced diffusion of oxygen is also clearly visible.

20 While the present invention has been described by way of an example and in terms of preferred embodiment, it is to be understood that the invention is not limited thereto. To the similar arrangements and procedures, and the scope of the appended claims therefore should be accorded the broadest interpretation so as to encompass all such modifications, similar arrangements and procedures.

I CLAIM:

1. A method for nondestructive evaluation of defects in a transparent coating (3) on a substrate (1), comprising applying a sensor layer (2) comprising a fluorophore under the transparent coating (3); and exposing the transparent coating (3) to molecular oxygen, wherein the defects are identified by change in the fluorescence signature of the fluorophore in locations corresponding to the coating defects.

2. A method of claim 1, wherein the transparent coating (3) is a permeation barrier coating or a protective coating.

3. A method of claim 2, wherein the transparent coating (3) is a permeation barrier coating.

4. A method of claim 1, wherein the transparent coating (3) comprises a material selected from a group consisting of oxides, nitrides and oxinitrides of silicon, aluminum, zinc, boron and other metals, ceramics, polyvinyl alcohol, ethylene vinyl alcohol copolymers, polyvinyl dichloride, different types of nylon, cellophane, polyethylene terephthalate, PVC, PCTFE, polypropylene, and others.

5. A method of claim 1, wherein the sensor layer (2) is applied between the substrate (1) and the transparent coating (3).

6. A method of claim 1, wherein the sensor layer (2) is applied such that the substrate (1) is placed between the sensor layer (2) and the transparent coating (3).

7. A method of claim 1, wherein the fluorophore is immobilized in the sensor layer (2).

8. A method of claim 1, wherein the fluorophore is selected from the class of porphyrins.

9. A method of claim 8, wherein the fluorophore is selected from a group consisting of platinum porphyrins and palladium porphyrins..

10. A method of claim 9, wherein the fluorophore is platinum (II) octaethylporphyrin (PtOEP) or palladium (II) octaethylporphyrin (PdOEP).

5 11. A method of claim 1, wherein the fluorophore is selected from a group consisting of polycyclic aromatic hydrocarbons.

12. A method of claim 11, wherein the polycyclic aromatic hydrocarbon is selected from a group consisting of pyrene, pyrenebutyric acid, fluoranthene, decacyclene, diphenylanthracene, and benzo(g,h,i)perylene.

10 13. A method of claim 1, wherein the fluorophore is selected from a group consisting of ruthenium-organic complex, osmium-organic complex, iridium-organic complex, platinum-organic complex and gold-organic complex.

15 14. A method of claim 1, wherein the sensor layer (2) comprises a film forming polymeric material capable of providing a required response time, oxygen permeability, oxygen solubility and degree of transparency and hardness, as a matrix.

20 15. A method of claim 14, wherein the film forming polymeric material is selected from a group consisting of polyolefins, vinyl and vinylidene polymers, natural and synthetic rubbers, polyesters, polycarbonates, cellulose derivatives, fluoropolymers, polyorganosiloxanes, polynitriles, polyamides, polyimides, polyurethanes, polyoxides, polysulfones, polyacetylenes, polyacrylics.

25 16. A method of claim 15, wherein the film forming polymeric material is selected from a group consisting of polyvinyl chloride (PVC), polystyrene (PS), poly(ethylene terephthalate) (PET), polycarbonate (PC), cellulose acetate butyrate (CAB), poly(methyl methacrylate) (PMMA), PMMA/CAB blends, silicones, silicone blends, silicone copolymers, and fluoro-polymers.

17. A method of claim 15, wherein the fluoropolymer is poly(styrene-co-trifluoroethyl-methacrylate) (poly-styrene-co TFEM).

18. A method of claim 1, wherein the sensor layer (2) is of a thickness from 0.05 to 1000 micrometers.

5 19. A method of claim 18, wherein the sensor layer (2) is of a thickness from 0.5 to 100 micrometers.

20. A method of claim 19, wherein the sensor layer (2) is of a thickness from 1 to 10 micrometers.

10 21. A method of claim 1, wherein the transparent coating (3) is formed by an evaporative method, a glow discharge process, a gas-phase chemical process, a liquid-phase chemical process, or a chemical vapor deposition.

22. A method of claim 21, wherein the transparent coating (3) is formed by a liquid-phase chemical process.

15 23. A method of claim 21, wherein the transparent coating (3) is formed by a chemical vapor deposition.

24. A method of claim 23, wherein the chemical vapor deposition is plasma-enhanced vapor deposition.

25. A method of claim 1, wherein the molecular oxygen is of concentration from about 0.1 % to 100%.

20 26. A method of claim 1, wherein the molecular oxygen is of partial pressure from about 0.01 to about 1000 atmospheres.

27. A method of claim 25, wherein the molecular oxygen is of partial pressure from about 0.1 to about 100 atmospheres.

28. A method of claim 26, wherein the molecular oxygen is of partial pressure from about 0.1 to about 10 atmospheres.

29. A method of claim 1, further comprising obtaining fluorescence images of the sensor layer (2) at different concentrations of oxygen, obtaining the ratio of the fluorescence image of sensor layer (2) at small oxygen concentration to the fluorescence image of sensor layer (2) at high oxygen concentration to detect defects and edges in the transparent coating (3).

30. A method of claim 1, further comprising obtaining fluorescence images of the sensor layer (2) at different partial pressures of oxygen, obtaining the ratio of the fluorescence image of sensor layer (2) at small oxygen partial pressure to the fluorescence image of sensor layer (2) at high oxygen partial pressure to detect defects and edges in the transparent coating (3).

31. A method for nondestructive evaluation of defects in a library of transparent coatings (3), comprising applying a sensor layer (2) comprising a fluorophore under the library of transparent coatings (3); and exposing the library of transparent coatings (3) to molecular oxygen with varying concentrations, wherein change of fluorescence signal indicates defects in the transparent coatings (3).

32. A method of claim 31, wherein the transparent coating (3) is a permeation barrier coating or a protective coating.

33. A method of claim 32, wherein the transparent coating (3) is a permeation barrier coating.

34. A method of claim 31, wherein the transparent coating (3) comprises a material selected from a group consisting of oxides, nitrides and oxinitrides of silicon, aluminum, zinc, boron and other metals; ceramics, polyvinyl alcohol, ethylene vinyl alcohol copolymers, polyvinyl dichloride, different types of nylon, cellophane, polyethylene terephthalate, PVC, PCTFE, polypropylene, and others.

35. A method of claim 31, wherein the sensor layer (2) is applied between the substrate (1) and the transparent coating (3).

5 36. A method of claim 31, wherein the sensor layer (2) is applied such that the substrate (1) is placed between the sensor layer (2) and the transparent coating (3).

37. A method of claim 31, wherein the fluorophore is immobilized in the sensor layer (2).

38. A method of claim 31, wherein the fluorophore is selected from the class of porphyrins.

10 39. A method of claim 38, wherein the fluorophore is selected from a group consisting of platinum porphyrins and palladium porphyrins..

40. A method of claim 39, wherein the fluorophore is platinum (II) octaethylporphyrin (PtOEP) or palladium (II) octaethylporphyrin (PdOEP).

15 41. A method of claim 31, wherein the fluorophore is selected from a group consisting of polycyclic aromatic hydrocarbons.

42. A method of claim 41, wherein the polycyclic aromatic hydrocarbon is selected from a group consisting of pyrene, pyrenebutyric acid, fluoranthene, decacyclene, diphenylanthracene, and benzo(g,h,i)perylene.

20 43. A method of claim 31, wherein the fluorophore is selected from a group consisting of ruthenium-organic complex, osmium-organic complex, iridium-organic complex, platinum-organic complex and gold-organic complex.

25 44. A method of claim 31, wherein the sensor layer (2) comprises a film forming polymeric material capable of providing a required response time, oxygen permeability, oxygen solubility, and degree of transparency and hardness, as a matrix

45. A method of claim 44, wherein the film forming polymeric material is selected from a group consisting of polyolefins, vinyl and vinylidene polymers, natural and synthetic rubbers, polyesters, polycarbonates, cellulose derivatives, fluoropolymers, polyorganosiloxanes, polynitriles, polyamides, polyimides, polyurethanes, polyoxides, polysulfones, polyacetylenes, polyacrylics.

46. A method of claim 45, wherein the film forming polymeric material is selected from a group consisting of polyvinyl chloride (PVC), polystyrene (PS), poly(ethylene terephthalate) (PET), polycarbonate (PC), cellulose acetate butyrate (CAB), poly(methyl methacrylate) (PMMA), PMMA/CAB blends, silicones, silicone blends, silicone copolymers, and fluoro-polymers.

47. A method of claim 46, wherein the fluoropolymer is poly(styrene-co-trifluoroethyl-methacrylate) (poly-styrene-co TFEM).

48. A method of claim 31, wherein the sensor layer (2) is of a thickness from 0.05 to 1000 micrometers.

49. A method of claim 48, wherein the sensor layer (2) is of a thickness from 0.5 to 100 micrometers.

50. A method of claim 49, wherein the sensor layer (2) is of a thickness from 1 to 10 micrometers.

51. A method of claim 31, wherein the transparent coating (3) is formed by an evaporative method, a glow discharge process, a gas-phase chemical process, a liquid-phase chemical process, or a chemical vapor deposition.

52. A method of claim 51, wherein the transparent coating (3) is formed by a liquid-phase chemical process.

53. A method of claim 51, wherein the transparent coating (3) is formed by a chemical vapor deposition.

54. A method of claim 53, wherein the chemical vapor deposition is plasma-enhanced vapor deposition.

55. A method of claim 31, wherein the molecular oxygen is of concentration from about 0.1 % to 100%.

5 56. A method of claim 55, wherein the molecular oxygen is of partial pressure from about 0.01 to about 1000 atmospheres.

57. A method of claim 56, wherein the molecular oxygen is of partial pressure from about 0.1 to about 100 atmospheres.

10 58. A method of claim 57, wherein the molecular oxygen is of partial pressure from about 0.1 to about 10 atmospheres.

59. A method of claim 31, further comprising obtaining fluorescence images of the sensor layer (2) at different concentrations of oxygen, obtaining the ratio of the fluorescence image of sensor layer (2) at small oxygen concentration to the fluorescence image of sensor layer (2) at high oxygen concentration to detect defects and edges in the transparent coating (3).

15

60. A method of claim 31, further comprising obtaining fluorescence images of the sensor layer (2) at different partial pressures of oxygen, obtaining the ratio of the fluorescence image of sensor layer (2) at small oxygen partial pressure to the fluorescence image of sensor layer (2) at high oxygen partial pressure to detect defects and edges in the transparent coating (3).

20

61. A method for mapping oxygen permeation in a grid of transparent coatings (3), comprising applying a sensor layer (2) comprising a fluorophore under the grid of the transparent coatings (3); exposing the grid of transparent coatings (3) to molecular oxygen, obtaining two fluorescence images of the grid of transparent coating (3) upon exposure to different partial pressures of oxygen; and obtaining a ratio of the two fluorescence images.

25

62. A method of claim 61, wherein the transparent coating (3) is a permeation barrier coating or a protective coating.

63. A method of claim 62, wherein the transparent coating (3) is a permeation barrier coating.

5 64. A method of claim 61, wherein the transparent coating (3) comprises a material selected from a group consisting of oxides, nitrides and oxinitrides of silicon, aluminum, zinc, boron and other metals, ceramics, polyvinyl alcohol, ethylene vinyl alcohol copolymers, polyvinyl dichloride, different types of nylon, cellophane, polyethylene terephthalate, PVC, PCTFE, polypropylene, and
10 others.

65. A method of claim 61, wherein the sensor layer (2) is applied between the substrate (1) and the transparent coating (3).

66. A method of claim 61, wherein the sensor layer (2) is applied such that the substrate (1) is placed between the sensor layer (2) and the transparent coating
15 (3).

67. A method of claim 61, wherein the fluorophore is immobilized in the sensor layer (2).

68. A method of claim 61, wherein the fluorophore is selected from the class of porphyrins.

20 69. A method of claim 68, wherein the fluorophore is selected from a group consisting of platinum porphyrins and palladium porphyrins.

70. A method of claim 69, wherein the fluorophore is platinum (II) octaethylporphyrin (PtOEP) or palladium (II) octaethylporphyrin (PdOEP).

25 71. A method of claim 61, wherein the fluorophore is selected from a group consisting of polycyclic aromatic hydrocarbons.

72. A method of claim 71, wherein the polycyclic aromatic hydrocarbon is selected from a group consisting of pyrene, pyrenebutyric acid, fluoranthene, decacyclene, diphenylanthracene, and benzo(g,h,i)perylene.

5 73. A method of claim 61, wherein the fluorophore is selected from a group consisting of ruthenium-organic complex, osmium-organic complex, iridium-organic complex, platinum-organic complex and gold-organic complex.

10 74. A method of claim 61, wherein the sensor layer (2) comprises a film forming polymeric material capable of providing a required response time, oxygen permeability, oxygen solubility, and degree of transparency and hardness, as a matrix.

15 75. A method of claim 74, wherein the film forming polymeric material is selected from a group consisting of polyolefins, vinyl and vinylidene polymers, natural and synthetic rubbers, polyesters, polycarbonates, cellulose derivatives, fluoropolymers, polyorganosiloxanes, polynitriles, polyamides, polyimides, polyurethanes, polyoxides, polysulfones, polyacetylenes, polyacrylics.

20 76. A method of claim 75, wherein the film forming polymeric material is selected from a group consisting of polyvinyl chloride (PVC), polystyrene (PS), poly(ethylene terephthalate) (PET), polycarbonate (PC), cellulose acetate butyrate (CAB), poly(methyl methacrylate) (PMMA), PMMA/CAB blends, silicones, silicone blends, silicone copolymers, and fluoro-polymers.

77. A method of claim 76, wherein the fluoropolymer is poly(styrene-co-trifluoroethyl-methacrylate) (poly-styrene-co TFEM).

78. A method of claim 61, wherein the sensor layer (2) is of a thickness from 0.05 to 1000 micrometers

25 79. A method of claim 61, wherein the sensor layer (2) is of a thickness from 0.5 to 100 micrometers.

80. A method of claim 79, wherein the sensor layer (2) is of a thickness from 1 to 10 micrometers

81. A method of claim 61, wherein the transparent coating (3) is formed by an evaporative method, a glow discharge process, a gas-phase chemical process, a liquid-phase chemical process, or a chemical vapor deposition.

82. A method of claim 81, wherein the transparent coating (3) is formed by a liquid-phase chemical process.

83. A method of claim 81, wherein the transparent coating (3) is formed by a chemical vapor deposition.

84. A method of claim 83, wherein the chemical vapor deposition is plasma-enhanced vapor deposition.

85. A method of claim 61, wherein the molecular oxygen is of concentration from about 0.1 % to 100%.

86. A method of claim 61, wherein the molecular oxygen is of partial pressure from about 0.01 to about 1000 atmospheres.

87. A method of claim 86, wherein the molecular oxygen is of partial pressure from about 0.1 to about 100 atmospheres.

88. A method of claim 87, wherein the molecular oxygen is of partial pressure from about 0.1 to about 10 atmospheres.

89. A method of claim 61, wherein the ratio of the fluorescence images is obtained at small oxygen partial pressure to the fluorescence image of sensor layer (2) at high oxygen partial pressure.

90. A method of claim 61, wherein fluorescence images of the grid of transparent coating (3) are obtained upon exposure to different concentrations of oxygen and by obtaining the ratio of the fluorescence images at small oxygen

concentration to the fluorescence image of sensor layer (2) at high oxygen concentration.

5 91. A method for a rapid screening of defects in transparent coating (3) samples in a combinatorial array, comprising applying a sensor layer (2) comprising a fluorophore under the transparent coating (3) samples; and exposing the transparent coatings (3) to molecular oxygen with varying concentrations, wherein the defects are identified by change in the fluorescence signature of the fluorophore in locations corresponding to the coating defects.

10 92. A method of claim 91, wherein the transparent coating (3) is a permeation barrier coating or a protective coating.

93. A method of claim 92, wherein the transparent coating (3) is a permeation barrier coating.

15 94. A method of claim 91, wherein the transparent coating (3) comprises a material selected from a group consisting of oxides, nitrides and oxinitrides of silicon, aluminum, zinc, boron and other metals, ceramics, polyvinyl alcohol, ethylene vinyl alcohol copolymers, polyvinyl dichloride, different types of nylon, cellophane, polyethylene terephthalate, PVC, PCTFE, polypropylene, and others.

20 95. A method of claim 91, wherein the sensor layer (2) is applied between the substrate (1) and the transparent coating (3).

96. A method of claim 91, wherein the sensor layer (2) is applied such that the substrate (1) is placed between the sensor layer (2) and the transparent coating (3).

25 97. A method of claim 91, wherein the fluorophore is immobilized in the sensor layer (2).

98. A method of claim 91, wherein the fluorophore is selected from the class of porphyrins.

99. A method of claim 98, wherein the fluorophore is selected from a group consisting of platinum porphyrins and palladium porphyrins..

5 100. A method of claim 99, wherein the fluorophore is platinum (II) octaethylporphyrin (PtOEP) or palladium (II) octaethylporphyrin (PdOEP).

101. A method of claim 91, wherein the fluorophore is selected from a group consisting of polycyclic aromatic hydrocarbons.

10 102. A method of claim 101, wherein the polycyclic aromatic hydrocarbon is selected from a group consisting of pyrene, pyrenebutyric acid, fluoranthene, decacyclene, diphenylanthracene, and benzo(g,h,i)perylene.

103. A method of claim 91, wherein the fluorophore is selected from a group consisting of ruthenium-organic complex, osmium-organic complex, iridium-organic complex, platinum-organic complex and gold-organic complex.

15 104. A method of claim 91, wherein the sensor layer (2) comprises a film forming polymeric material capable of providing a required response time, oxygen permeability, oxygen solubility and degree of transparency and hardness, as a matrix.

20 105. A method of claim 104, wherein the film forming polymeric material is selected from a group consisting of polyolefins, vinyl and vinylidene polymers, natural and synthetic rubbers, polyesters, polycarbonates, cellulose derivatives, fluoropolymers, polyorganosiloxanes, polynitriles, polyamides, polyimides, polyurethanes, polyoxides, polysulfones, polyacetylenes, polyacrylics.

25 106. A method of claim 105, wherein the film forming polymeric material is selected from a group consisting of polyvinyl chloride (PVC), polystyrene (PS), poly(ethylene terephthalate) (PET), polycarbonate (PC), cellulose acetate

butyrate (CAB), poly(methyl methacrylate) (PMMA), PMMA/CAB blends, silicones, silicone blends, silicone copolymers, and fluoro-polymers.

107. A method of claim 106, wherein the fluoropolymer is poly(styrene-co-trifluoroethyl-methacrylate) (poly-styrene-co TFEM).

5 108. A method of claim 91, wherein the sensor layer (2) is of a thickness from 0.05 to 1000 micrometers

109. A method of claim 108, wherein the sensor layer (2) is of a thickness from 0.5 to 100 micrometers.

10 110. A method of claim 109, wherein the sensor layer (2) is of a thickness from 1 to 10 micrometers

111. A method of claim 91, wherein the transparent coating (3) is formed by an evaporative method, a glow discharge process, a gas-phase chemical process, a liquid-phase chemical process, or a chemical vapor deposition.

15 112. A method of claim 111, wherein the transparent coating (3) is formed by a liquid-phase chemical process.

113. A method of claim 111, wherein the transparent coating (3) is formed by a chemical vapor deposition.

114. A method of claim 113, wherein the chemical vapor deposition is plasma-enhanced vapor deposition.

20 115. A method of claim 91, wherein the molecular oxygen is of concentration from about 0.1 % to 100%.

116. A method of claim 91, wherein the molecular oxygen is of partial pressure from about 0.01 to about 1000 atmospheres.

117. A method of claim 116, wherein the molecular oxygen is of partial pressure from about 0.1 to about 100 atmospheres.

118. A method of claim 117, wherein the molecular oxygen is of partial pressure from about 0.1 to about 10 atmospheres.

5 119. A method of claim 91, further comprising obtaining fluorescence images of the sensor layer (2) at different concentrations of oxygen, obtaining the ratio of the fluorescence image of sensor layer (2) at small oxygen concentration to the fluorescence image of sensor layer (2) at high oxygen concentration to detect defects and edges in the transparent coating (3).

10 120. A method of claim 91, further comprising obtaining fluorescence images of the sensor layer at different partial pressures of oxygen, obtaining the ratio of the fluorescence image of sensor layer at small oxygen partial pressure to the fluorescence image of sensor layer at high oxygen partial pressure to detect defects and edges in the transparent coating.

15

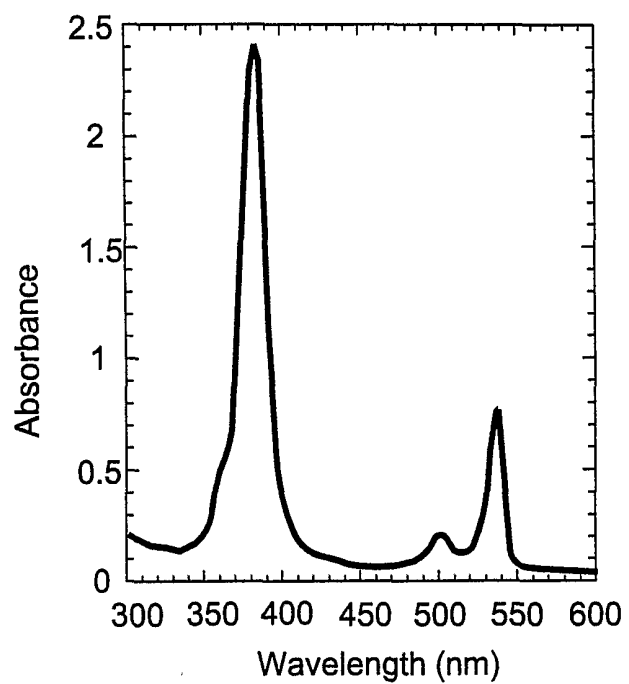


fig. 1

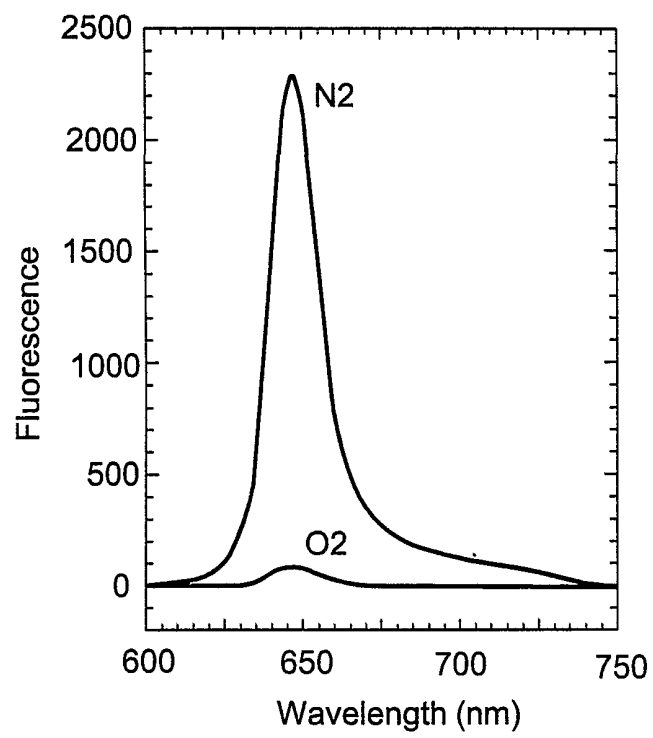


fig. 2

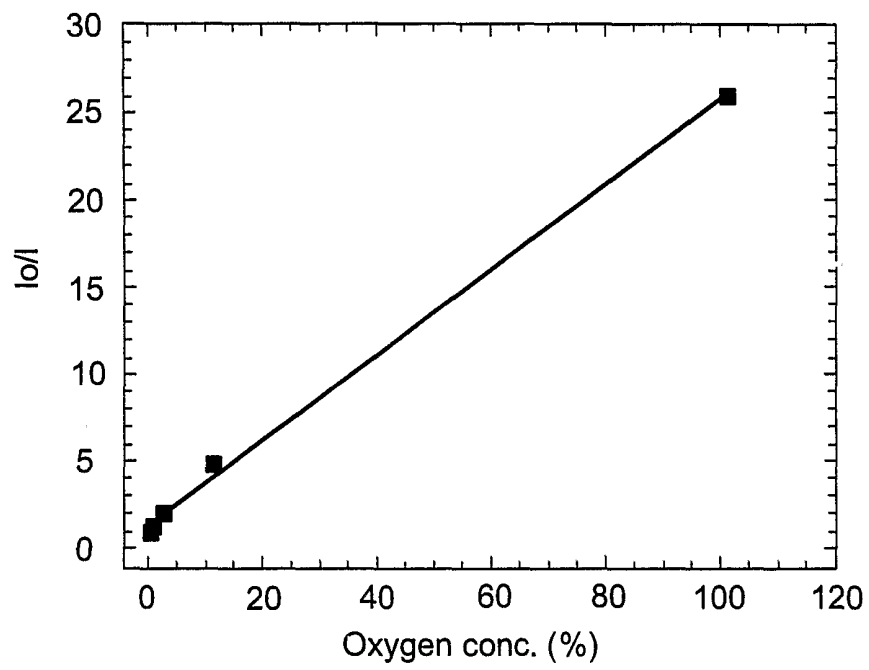


fig. 3

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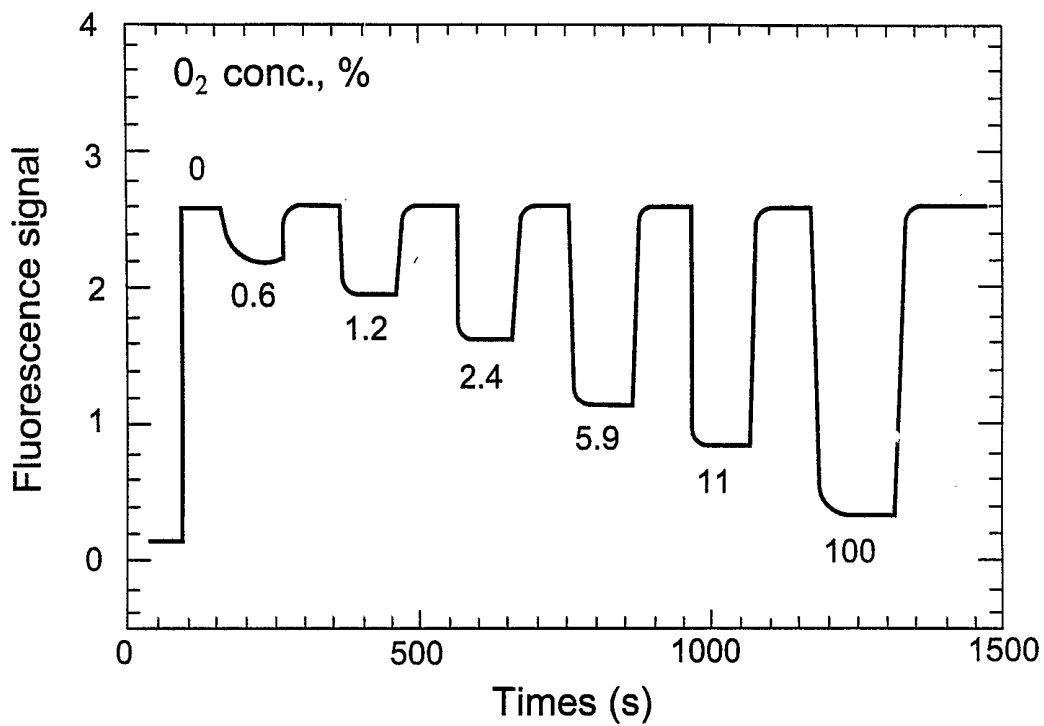


fig. 4

5/11

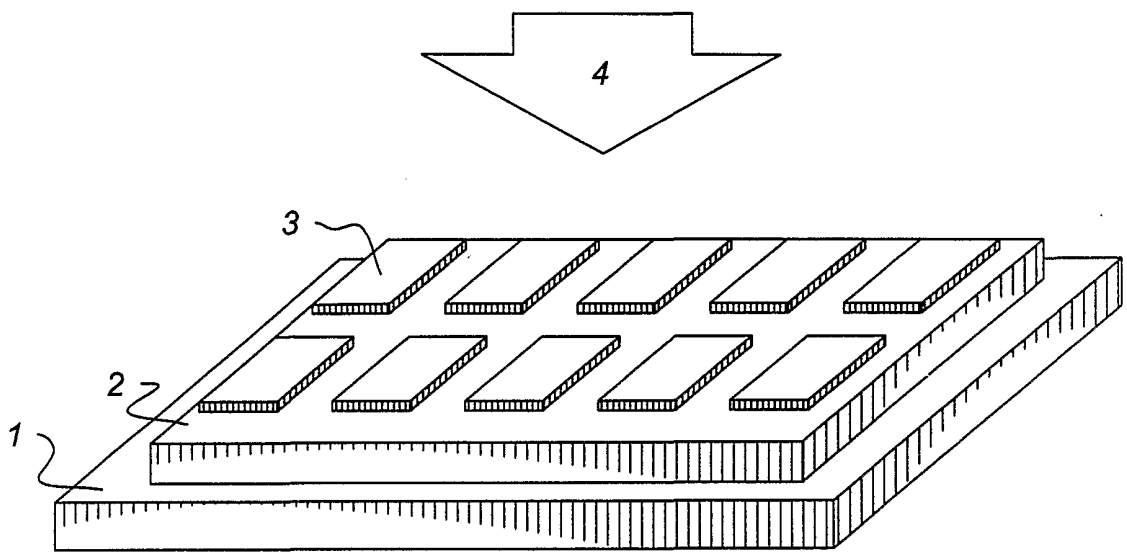


fig. 5

6/11

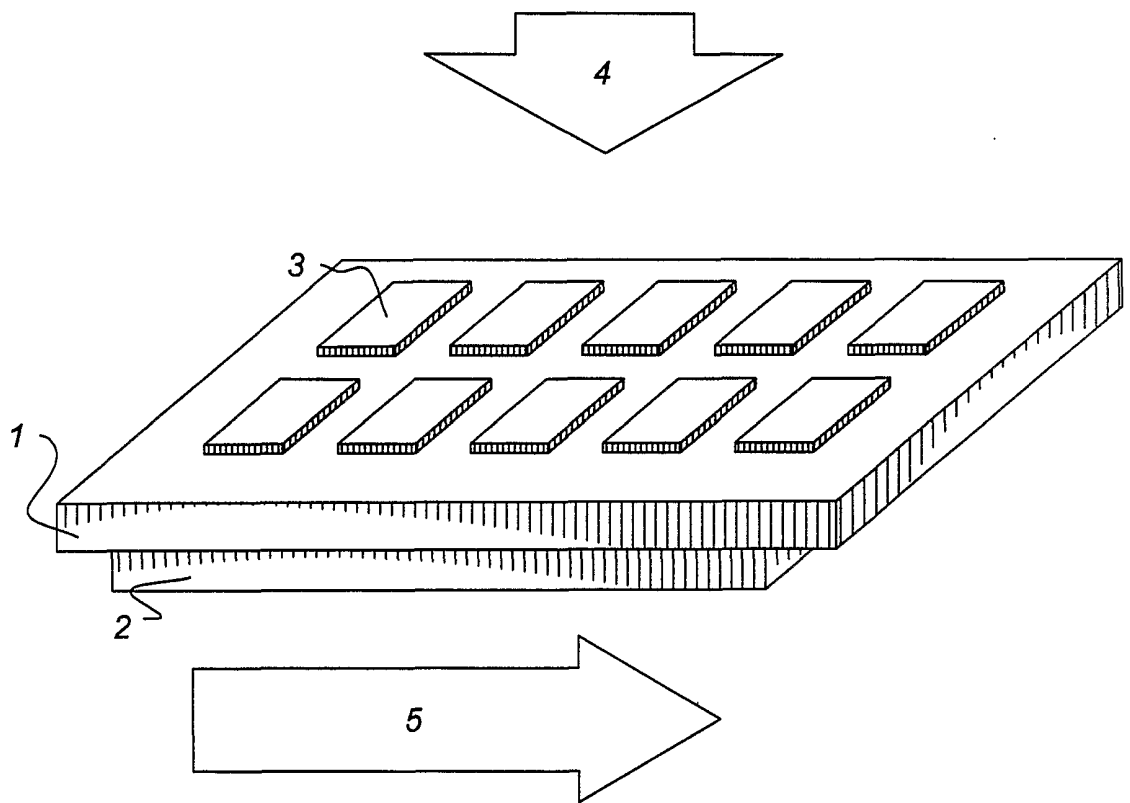


fig. 6

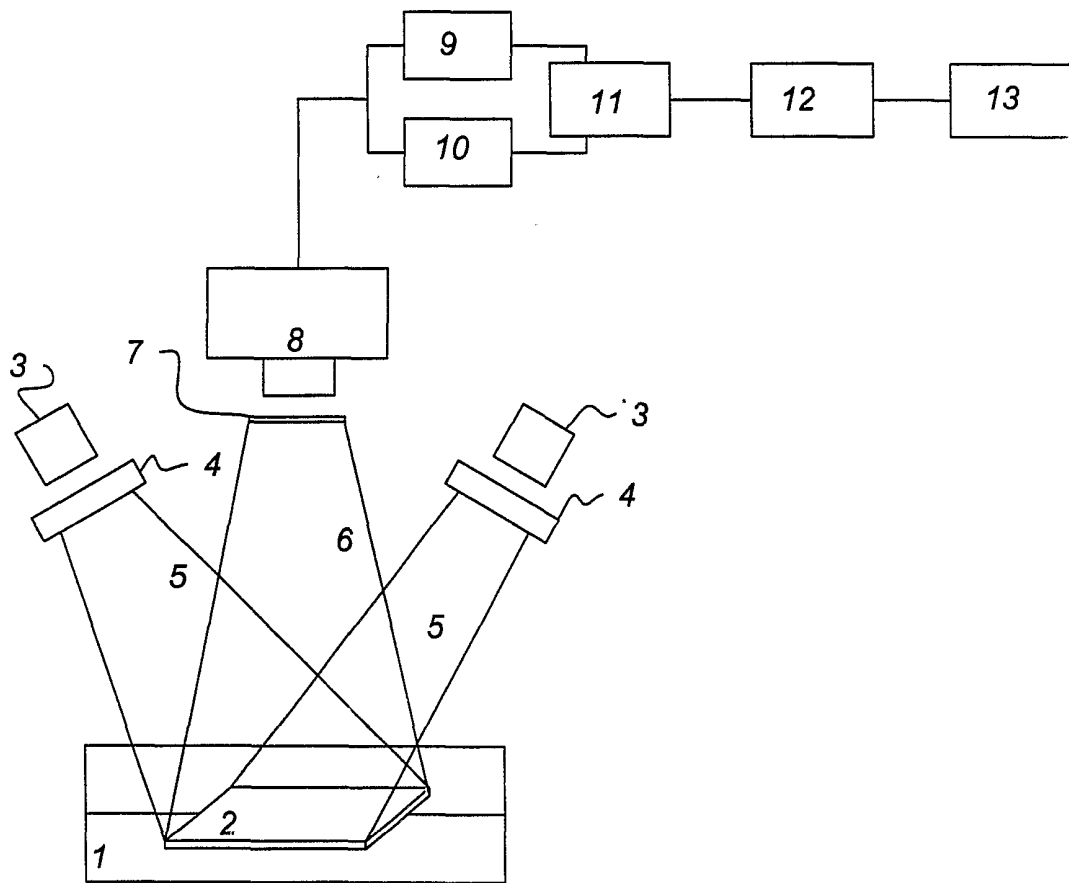


fig. 7

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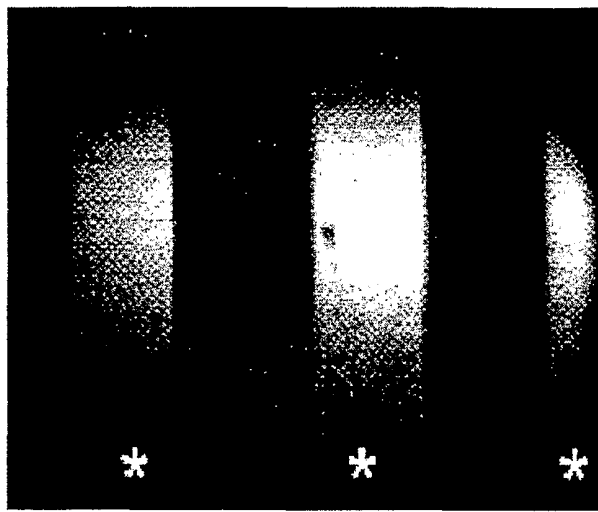


fig. 8

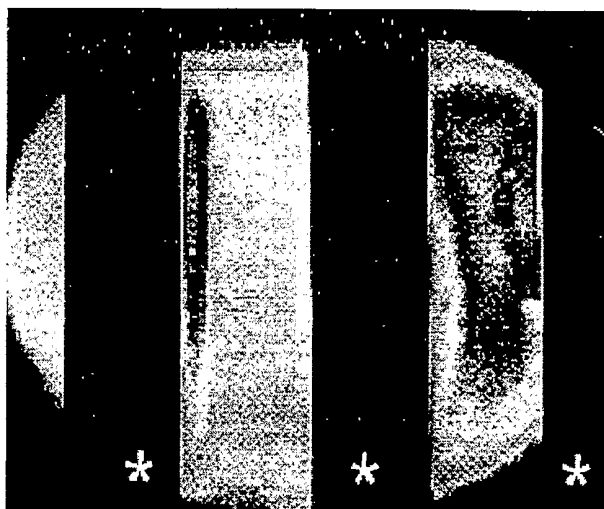


fig. 10

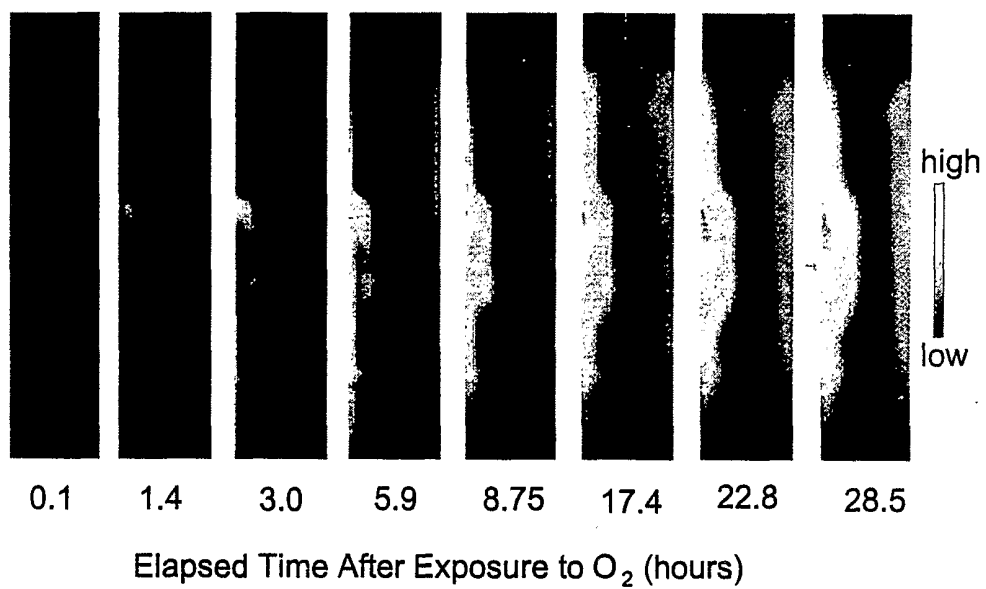


fig. 11

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/20375

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G01N21/84 G01N31/22

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)

IPC 7 G01N G01B

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 practical, search terms used)

EPO-Internal, COMPENDEX, INSPEC, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category ^o	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 5 583 047 A (BLINKA THOMAS A ET AL) 10 December 1996 (1996-12-10) column 1, line 13 - line 15 column 1, line 34 - line 42 column 5, line 43 - line 59 column 6, line 45 - line 57 column 9, line 22 - last line -/-	1-5,7, 14-16 18,19, 31-35, 37, 44-46, 48,49, 61-65, 67, 74-76, 78,79, 91-95, 97, 104-106, 108,109



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

31 January 2002

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/US 01/20375

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