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(54) COLORIMETRIC SENSOR

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(57) **ABSTRACT**

Disclosed herein are calorimetric sensor films comprising a reflective layer, polymeric detection layer, and semi-reflective layer. Also disclosed are devices comprising the colorimetric sensor films and methods of making the films and devices.
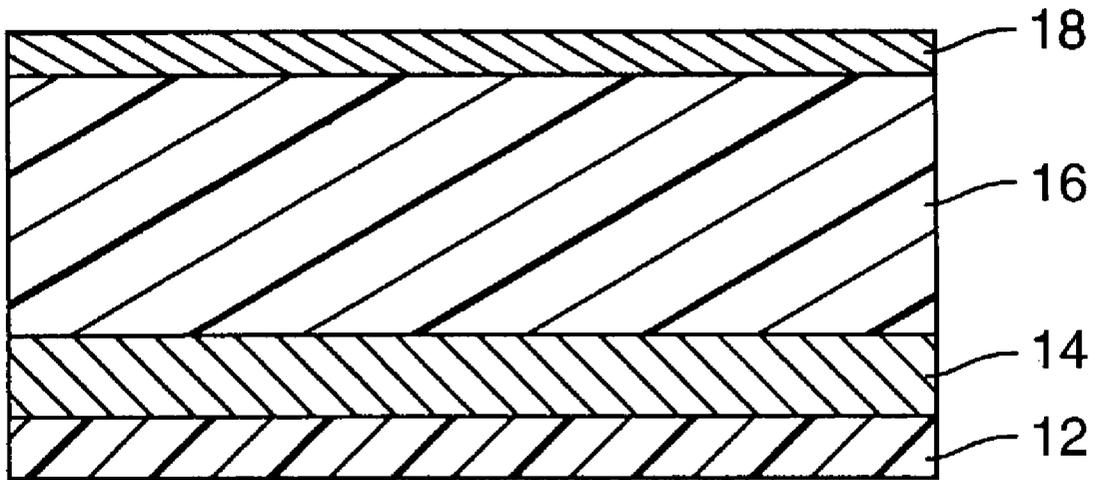
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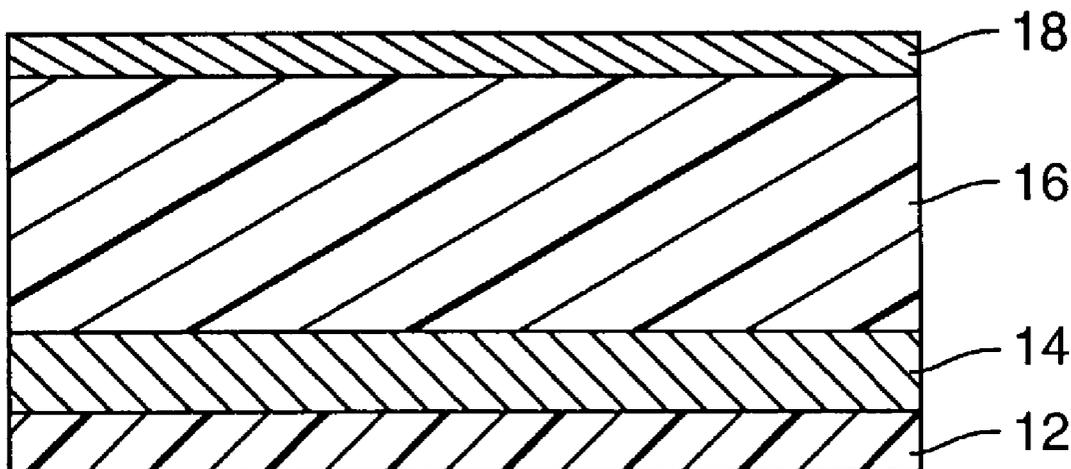
Fig. 1

COLORIMETRIC SENSOR

TECHNICAL FIELD

[0001] This disclosure relates to colorimetric sensor films.

BACKGROUND

[0002] The development of robust chemical sensors for a range of analytes remains an important endeavor for applications such as environmental monitoring, product quality control, and chemical dosimetry. Among the many methods available for chemical sensing, calorimetric techniques remain advantageous in that the human eye can be used for signal transduction, rather than extensive instrumentation.

[0003] Though calorimetric sensors currently exist for a range of analytes, most are based upon employing dyes or colored chemical indicators for detection. Such compounds are typically selective, meaning arrays are necessary to enable detection of various classes of compounds. Moreover, many of these systems have lifetime limitation issues, due to photo-bleaching or undesirable side reactions. Other optical sensing techniques, such as surface plasmon resonance and spectral interferometry, require substantial signal transduction hardware to provide response, and thus are not useful for simple visual indication.

SUMMARY OF INVENTION

[0004] The present invention features novel multi-layered colorimetric sensor films. The films typically constitute a highly colored multi-layered interference filter whose hue shifts upon analyte exposure. The multi-layered structure provides a versatile platform for incorporating a variety of chemistries that can detect a range of species. The films are flexible and robust, and can be designed to provide fast, reversible (or, in some cases, permanent) responses. As such, they are well-suited for application to the areas mentioned above.

[0005] One aspect of the invention is a colorimetric sensor for measuring one or both of the presence and concentration of an analyte comprising a substantially continuous reflective layer; a detection layer over the reflective layer, the detection layer comprising at least one polymer component, said layer being capable of a change in optical thickness upon exposure to said analyte; and a substantially continuous semi-reflective layer over the detection layer, the semi-reflective layer having an index of refraction different from the index of refraction of the detection layer.

[0006] Another aspect of the invention is a device comprising the colorimetric sensor and a light source. Another aspect of the invention is a calorimetric sensor for measuring one or both of the presence and concentration of an analyte comprising a substantially continuous reflective layer; a detection layer over the reflective layer, the detection layer comprising at least one polymer component; and a substantially continuous semi-reflective layer over the detection layer, the semi-reflective layer having an index of refraction different from the index of refraction of the detection layer, said sensor being capable of a change in color upon exposure to said analyte.

[0007] Another aspect of the invention is a method of detecting the presence or absence of an analyte comprising providing a calorimetric sensor as described above, providing a light source, contacting the sensor with a medium that may contain an analyte, and monitoring the sensor for a change in optical properties.

[0008] As used in this invention:

[0009] "analyte" means the specific component that is being detected in a chemical analysis;

[0010] "dimensional change" means a change of distance in a direction normal to the surface of the detection layer surface;

[0011] "porous material" means a material containing a continuous network of pores throughout its volume;

[0012] "reflective" means semi-reflective or fully reflective;

[0013] "semi-reflective" means neither fully reflective nor fully transmissive, preferably about 30 to about 70% reflective, more preferably about 40 to about 60%.

[0014] "substantially continuous" means a layer of material is non-porous, but may have cracks, grain boundaries, or other structures that create pathways through the layer of material.

[0015] An advantage of at least one embodiment of the present invention is that the multi-layer sensor films can be constructed so that water vapor does not create a change in the optical properties.

[0016] Another advantage of at least one embodiment of the present invention is that the films can be readily processed. The reflective layers can be deposited via evaporative or sputter coating, while the detection layer can be deposited via solvent coating, plasma deposition, and vapor coating (as described in U.S. Pat. No. 5,877,895).

[0017] Another advantage of at least one embodiment of the present invention is that the change in appearance of the sensor can be designed to be reversible or permanent.

[0018] Other features and advantages of the invention will be apparent from the following drawings, detailed description, and claims.

BRIEF DESCRIPTION OF DRAWINGS

[0019] FIG. 1 depicts a multi-layered film of the present invention.

DETAILED DESCRIPTION

[0020] The multi-layered colorimetric sensor films of the present invention may comprise colored films containing at least one polymeric detection layer between a reflective and a semi-reflective layer, which may both be metal layers. These multi-layered films provide a general means for visual signal transduction. The films function as interference filters, and thus can be highly colored due to reflection of particular wavelengths within the visible range. The coloration of the sensor films is highly dependent upon the thickness of each layer within the stack.

[0021] A general depiction of a multi-layered sensor film of the present invention is shown in FIG. 1. In general, the

films comprise (optional) substrate layer **12**, reflective layer **14**, detection layer **16**, and semi-reflective layer **18**.

[0022] The sensor films can be used for detecting the presence and/or concentration of an analyte. The analyte may be a gas or a liquid. The analyte may be present in a gaseous medium (such as air) or liquid medium (such as water or other fluids). Typically the analyte is an organic material.

[0023] In at least one embodiment, the analyte is detected by a change in optical thickness of a polymer comprising a detection layer upon exposure to the analyte. The analyte passes through an outer semi-reflective layer and changes the optical thickness of the detection layer. In one embodiment the analyte is absorbed into at least a portion of the detection layer. Upon absorption, color changes (often vivid) can indicate the presence of the analyte.

[0024] The change in optical thickness is typically observable in the visible light range and can be detected by the unaided human eye. However, sensors can be designed to show a change in optical thickness when subjected to other light sources such as UV, infrared, or near infra-red. Various detection mechanisms can also be used. Examples of suitable detection mechanisms include photo-detectors, e.g., charge coupled devices (ccd), digital cameras, etc.

[0025] In another embodiment, the analyte is detected when its presence causes the delamination of the detection layer from an adjacent layer. Typically, delamination occurs when the analyte wets the interface of the detection layer and an adjacent layer, thereby reducing the interface adhesion. When delamination occurs, optical interference is destroyed and the sensor loses perceptible color. The presence of the analyte may also cause dewetting of one or more polymers within the detection layer from an adjacent layer. This process, which involves changes in the shape of the detection layer that reduce the interfacial area with adjacent layers, causes defects within the material which permanently change the optical properties of the sensor film.

[0026] Substrate

[0027] The substrate is optional, but when present it may comprise any suitable material capable of providing support for the colorimetric sensor. It may be flexible or non-flexible. The substrate material can be tailored to the application. Preferably, it is suitable to use in a vacuum deposition process.

[0028] Reflective Layer

[0029] The reflective layer may comprise any material that can form a fully reflective or semi-reflective layer. It is preferable that the material is fully reflective at a thickness of about 20 to about 200 nm. Thinner layers can typically be used to make the reflective layer semi-reflective. Although the reflective layer is typically made to be more reflective than the semi-reflective layer, sometimes it is desirable to have the reflectivity of the reflective layer and semi-reflective layer be the same so a response to the presence of an analyte can be seen from either side of the sensor film.

[0030] Suitable materials for the reflective layer include metals such as aluminum, chromium, gold, nickel, silicon, and silver. Other suitable materials include metal oxides such as chrome oxide and titanium oxide.

[0031] In some embodiments, the reflective layer also acts as the substrate, providing support for the sensor.

[0032] Detection Layer

[0033] The detection layer may comprise one or more polymers or copolymers. In most embodiments, the detection layer comprises at least one polymer whose optical thickness changes upon exposure to an analyte. The change in optical thickness can be caused by a dimensional change such as a change in physical thickness of the polymer due to swelling or shrinkage or a change in refractive index of the detection layer due to the presence or chemical reaction of the analyte. The detection layer may change from one color to another, from a color to no color, or from no color to a color.

[0034] The detection layer may comprise two or more sub-layers. One or more of the sub-layers may be discontinuous or patterned. The sub-layers typically comprise different polymeric materials and may absorb different analytes and/or may have different degrees of sensitivity to one or more analytes. The sub-layers may have a variety of configurations. For example, they may be stacked or may be side by side.

[0035] The detection layer may comprise a pattern so as to create colored images, words, or messages upon exposure to an analyte. A sublayer may be patterned by having one or more portions that are reactive to a particular analyte and one or more portions that are non-reactive to the same analyte. Alternatively, a pattern of reactive material may be deposited on a larger non-reactive sublayer. In this case, it is preferable to make the patterned layer very thin so that no difference in optical thickness is apparent until an analyte is absorbed. The patterning can provide easily identifiable warnings for a user upon exposure to an analyte.

[0036] The thickness of the detection layer may be patterned, for example as described in U.S. Pat. No. 6,010,751. This may be desirable when the sensor is designed so that the presence of an analyte causes the detection layer to swell or shrink, thereby making a pattern disappear (for example when a thinner portion swells to the same thickness as a thicker portion) or a appear (for example, when an portion shrinks to a thinner thickness than an adjacent portion).

[0037] The detection layer may comprise a blend of polymer components. The blend may be homogeneous or heterogeneous. A blend of polymer components in the detection layer can allow for large number of analytes to be detected with the use of a relatively small sensor.

[0038] The detection layer may be porous. This can boost the sensitivity of detection due to the increase in surface area exposed to an analyte. Porosity can be obtained by using porous materials such as foams made from high internal phase emulsions, such as those described in WO 01/21693, to form the detection layer. Porosity may also be obtained via carbon dioxide foaming to create bi-continuous, nanoporous material (see "Macromolecules", 2001, vol. 34, pp. 8792-8801), or by nanophase separation of polymer blends (see "Science", 1999, vol. 283, p. 520). In general, the pore diameters need to be smaller than the wavelength of the light source used in the detection process. Nano-sized pores are preferred.

[0039] One or more polymers comprising the detection layer may be at least partially crosslinked. Crosslinking may

be desirable in some embodiments because it can increase mechanical stability and sensitivity to certain analytes. Crosslinking can be achieved by incorporating one or more multi-functional monomers into the detection layer, or by subjecting the detection layer to, e.g., electron beam or gamma ray treatment.

[0040] For many applications, it is desirable that the polymer or copolymer be hydrophobic. This will reduce the chance that water vapor (or liquid water) will cause a change in optical thickness of the polymer and interfere with the detection of an analyte, for example, in the detection of organic solvent vapors.

[0041] For the detection of organic solvent vapors, polymeric materials suitable for the detection layer include, but are not limited to, polymers and copolymers prepared from classes of monomers including hydrophobic acrylates and methacrylates, difunctional monomers, vinyl monomers, hydrocarbon monomers (olefins), silane monomers, and fluorinated monomers.

[0042] Examples of hydrophobic acrylates and methacrylates include methyl(meth)acrylate, isodecyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, cyclohexyl(meth)acrylate, n-decyl(meth)acrylate, n-butyl(meth)acrylate, isopropyl-(meth)acrylate, lauryl(meth)acrylate, ethyl(meth)acrylate, adamantyl(meth)acrylate, t-butyl(meth)acrylate, 2-phenoxyethyl acrylate, isobornyl acrylate

[0043] Examples of multi-functional monomers include ethyleneglycol di(meth)acrylate, diethyleneglycol di(meth)acrylate, triethyleneglycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate 1,6-hexanedioldi(meth)acrylate, trimethylol propane di(meth)acrylate, neopentyl glycol di(meth)acrylate, N,N-methylenebis(meth)acrylamide, diacrylates such as IRR-214 (UCB Chemicals), pentaerythritol tri- and tetra-acrylate, and trimethylol propane tri(meth)acrylate.

[0044] Examples of vinyl monomers include styrene, α-methylstyrene, vinylacetate, vinylbutyrate, vinylstearate, vinylchloride, and vinyl norbornene.

[0045] Examples of hydrocarbon monomers (olefins) include isobutylene, ethylene, propylene, and norbornene.

[0046] Examples of silane monomers include organohydrosilanes, alkoxysilanes, phenoxysilanes, and fluoroalkoxysilanes.

[0047] Examples of fluorinated monomers include tetrafluoroethylene, vinylidene fluoride, and hexafluoropropylene.

[0048] For detection in solution, detection of highly polar analytes, and/or use in sensor arrays polymeric materials suitable for the detection layer include, but are not limited to, polymers and copolymers prepared from classes of monomers including hydroxylated monomers, acrylamides, anhydrides, aldehyde-functionalized monomers, amine or amine salt functionalized monomers, acid functionalized monomers, epoxide functionalized monomers, vinyl monomers, and other polymers.

[0049] Examples of hydroxylated monomers include hydroxyalkyl(meth)acrylates.

[0050] Examples of acrylamides include (meth)acrylamide, N-isopropyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide.

[0051] Examples of anhydrides include (meth)acrylic anhydride.

[0052] Examples of aldehyde-functionalized monomers include acrolein.

[0053] Examples of amine or amine salt functionalized monomers include tbutylaminoethyl (meth)acrylate, diisopropylaminoethyl (meth)acrylate, dimethylaminoethyl (meth)acrylate, vinylpyridine, dimethylaminoethyl-(meth)acrylate-methyl chloride salt, 4-aminostyrene, and vinylimidazole.

[0054] Examples of acid functionalized monomers include (meth)acrylic acid, carboxyethyl(meth)acrylate, (meth)acrylic acid-metal salts, and styrene sulfonic acid.

[0055] Examples of epoxide functionalized monomers include glycidyl(meth)acrylate.

[0056] Examples of vinyl monomers include N-vinylpyrolidone, vinyldimethylazalactone (VDM) and vinylidene chloride.

[0057] Examples of other polymers include poly(ethyleneoxide), poly(caprolactone), poly(sulfone), poly(ethyleneglycol), poly(urethanes), poly(carbonate), ethyl cellulose, fluoropolyol, polyesters, polyamides, polyimides, and polyacetals. The polymer component(s) of the detection layer may also have appropriate functional groups or molecular receptors incorporated to detect specific analytes. For example, acid-functionalized polymers, such as poly-(acrylic acid), enable detection of organic bases such as ammonia gas. Incorporation of metal complexes, such as metalloporphyrins, within the detection layer enables detection of ligating species such as phosphines or mercaptans. Suitable molecular receptors include calixarenes, cyclodextrins, azacrowns, crown ethers, porphyrins, metalloporphyrins, peptides, proteins, oligonucleotides, and nucleic acids.

[0058] By incorporating the appropriate chemistries within the detection layer, it should be feasible to create sensors for a wide range of analytes in solution. Either by initial deposition or by post-functionalization of deposited materials, receptor molecules, such as peptides or antibodies, may potentially be covalently linked to the polymer. In such fashion, biosensors for selective detection of bacteria, proteins, ions, etc. could be fabricated.

[0059] The detection layer can have a thickness of more than about 50 nm, preferably in the range of about 100 to about 1000 nm.

[0060] Semi-Reflective Layer

[0061] The semi-reflective layer may comprise any material that can form a permeable, substantially continuous, semi-reflective layer and has a different index of refraction than the detection layer. In most embodiments, it is preferable that the material is semi-reflective at a thickness of about 5 nm because at this thickness most analytes will be able to permeate through this layer to the detection layer. Desired thicknesses will depend on the material used to form the layer, the analyte to be detected, and the medium that will carry the analyte.

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[0062] Suitable materials include metals such as aluminum, chromium, gold, nickel, silicon, and silver. Other suitable materials include oxides such as aluminum oxide, titanium oxide, and chromium oxide.

[0063] Additional Layers

[0064] The sensor film may comprise additional layers between any of the previously described layers, as long as an additional layer does not interfere with the optics of the sensor film. Additional layers could include tie layers, structural layers, etc.

[0065] Method of Making

[0066] The multi-layered films of the present invention can be created via methods such as the process described, e.g., in U.S. Pat. No. 5,877,895. The detection layers may also be made by spin-coating, solution coating, extrusion coating, or other suitable techniques known in the art. The detection layer may also be made by plasma deposition processes such as plasma polymerization. The reflective and semi-reflective layers may also be made by standard vapor coating techniques such as evaporation, sputtering, chemical vapor deposition (CVD), plasma deposition, or flame deposition. Another method for making the reflective and semi-reflective layers is plating out of solution.

[0067] Uses

[0068] The film sensors may be used in a system comprising the sensor, a light source, and, optionally, a means of monitoring the sensor for a change of color. The light source could be a natural or artificial light source. The monitoring could be done in a variety of ways. It could be done visually, with a photo-detector, or by other suitable means.

[0069] The analyte may be present in a vapor or liquid medium. For example, an analyte may be present in the atmosphere or in a liquid solvent.

[0070] Two or more film sensors may be used together to form an array. The array may be in any suitable configuration. For example an array may comprise two or more sensors side by side, or sensors may be attached to, or constructed on, opposite sides of a substrate. The sensors may be of the same type or may be different. Arrays of multi-layered film sensors would be useful for identification of analytes, as opposed to only detecting the presence of a chemical agent.

[0071] The film sensors of the present invention have many useful applications. They can be used, e.g., to detect a wide range of organic vapors.

EXAMPLES

[0072] This invention may be illustrated by way of the following examples.

[0073] Unless otherwise stated, the sensor film samples were viewed from an angle normal to the surface of the film. Other viewing angles may be used. The color observed can vary depending on the angle of observation.

Example 1

[0074] A multi-layered calorimetric sensor film was produced via the deposition method described in U.S. Pat. No. 5,877,895.

[0075] An aluminum reflective layer (100 nm) and polymeric detection layer (500 nm) were sequentially deposited upon a polyester substrate layer (50 μm) in a single pass (15.24 m/min) through a vacuum web system. The aluminum reflective layer was thermally evaporated by feeding 0.1587 cm diameter aluminum wire (Alcoa stock number 1199, Pittsburgh, Pa.) onto an electrically heated (7V, 1250 amp) evaporation bar at a feed rate of 225 mm/min. The polymeric detection layer (500 nm) was deposited followed by an electron beam cure of 6.9 W-Sec. The monomer composition was a 48.5/48.5/3 by weight mixture of lauryl acrylate (available from Sartomer, Exton, Pa.)/IRR214 (a proprietary hydrocarbon diacrylate, available from UCB Chemicals, Drogenbos, Belgium)/Ebecryl170 (a phosphoric acid monoacrylate compound also available from UCB Chemicals). Chromium (Academy Precision Materials, Albuquerque, N. Mex.) was then sputtered (2.95 W/cm2 DC power at 2 mTorr Argon pressure), in a subsequent pass (15.24 m/min) through the vacuum web system, onto the cured detection layer, to give a 5 nm thick outer layer. The multi-layer sensor film had a green hue.

[0076] Sections of the multi-layered film (2.54 cm square) were affixed on glass slides and exposed for one minute to saturated vapors of various organic solvents in sealed jars. Within each jar, the multi-layered film was suspended within the headspace above the neat liquid analyte. As shown in Table 1, the exposures resulted in vivid, visually detectable color changes. In each case, the color changes were reversible upon removal from the solvent vapor within tens of seconds, restoring the original green hue. Responses were qualitatively reproducible, as repeat exposures produced the same color changes.

TABLE 1

Color Changes on Exposure to Various Compounds		
Solvent	Initial Color	Color After Exposure
Chloroform	Green	Red/Pink
Toluene	Green	Red/Pink
Pyridine	Green	Red/Pink
Ethanol	Green	Yellow
Acetone	Green	Red/Pink
Water	Green	Green

Example 2

[0077] Visible reflectance spectra were taken of the multi-layered films before and after exposure to a range of solvent vapors. Film sections (2.54 cm square, from Example 1) were affixed on glass slides and exposed to saturated organic vapors within sealed jars. Once equilibrated, the exposed films were removed and covered immediately with glass cover slides to prevent vapor desorption. Reflectance spectra of the exposed materials were then taken using a diffuse reflectance UV-VIS spectrometer. For all organic vapors tested, substantial red-shifting of the reflectance maxima were observed upon analyte exposure. The reflectance maximum centered at 524 nm (before exposure), for instance, exhibits shifts to higher wavelengths (red shifts). The magnitudes of the shifts ranged from 22 nm (acetonitrile) to 116 nm (methylene chloride), as shown in Table 2. This example shows that the multi-layered calorimetric sensor films respond to organic vapors, exhibiting calorimetric shifts for

halocarbons, arenes, alcohols, ketones, nitrites, and ethers. No shift was observed in the reflectance spectra on exposure to saturated water vapor. Even upon submerging films in liquid water, no color change was observed.

TABLE 2

Reflectance Maxima Wavelength Shifts Upon Exposure to Solvent Vapors

Solvent	Wavelength Shift (nm)
Chloroform	65
Toluene	62
Methylene Chloride	116
Acetonitrile	22
Acetone	28.5
Ethanol	29
Diethyl Ether	35
Bromobenzene	81
3-pentanol	51
3-pentanone	46
Methyl Ethyl Ketone	62
Water	0

Example 3

[0078]   In an effort to gauge the response sensitivity to different analyte vapors, sensor film, made as described in Example 1, was exposed to analytes at a range of concentrations using a simple flow-through setup. Concentrations (as determined by partial pressures) were controlled by bath temperatures. Air was bubbled through neat liquid analytes, which were chilled using cold temperature baths to control the vapor pressure. Mixtures of solid carbon dioxide (dry ice) and 3-heptanone or ethylene glycol gave bath temperatures of –38° C. and –15° C. respectively. An ice water bath was used to give temperatures of 0° C. Vapor pressures for each analyte were calculated at these temperatures using data from the *Handbook of Vapor Pressure* (Yaws, C. L. Gulf Publishing: Houston, 1994). Each air/vapor stream was then flowed via a stainless steel cannula into a septum-sealed vial containing the multi-layered film. The color changes of each film on exposure were monitored visually, and multiple observations were taken to ensure equilibrium. Table 3 presents the responses as a function of concentration, with "green" indicating the unexposed film color, "pink" indicating response for saturated vapors, and "yellow" indicating an intermediate response. The results indicate the ability to determine analyte concentration as well as the qualitative presence of the vapor using the calorimetric sensor films of this invention.

TABLE 3

Film Colors as a Function of Solvent Vapor Concentration

Analyte	Concentration (torr)	Film Color (visual)
Chloroform	5.1	Green/Yellow
	25	Yellow/Yellow-pink
	59	Pink
	196	Pink
Acetone	6.4	Green
	30	Green/Yellow
	69	Yellow/Yellow-pink
	230	Pink
Methylene Chloride	15	Green/Yellow
	63	Yellow-pink
	141	Pink
	430	Pink

TABLE 3-continued

Film Colors as a Function of Solvent Vapor Concentration

Analyte	Concentration (torr)	Film Color (visual)
Toluene	0.37	Green
	2.4	Yellow-pink
	6.7	Pink
	28	Pink
Bromobenzene	0.028	Green/Green-yellow
	0.24	Yellow-pink
	0.79	Pink
	4.2	Pink

Example 4

[0079]   Sensor film (from Example 1) was used to detect organic compounds in water. Submersion of the film within solution of tetrahydrofuran (THF) in water (5% by volume) yielded a visual change in color from green to yellow. Submersion into a solution of acetone in water (25% by volume) produced a visible change in color from green to yellow-green. This example shows that the multi-layer calorimetric sensor films of this invention can detect the presence of organic compounds in water. No change in color was observed upon exposure of the film to plain water.

Example 5

[0080]   Two multi-layered sensor films were prepared via spin-coating of the detection layers. The structures were the same, except for the polymer detection layers. To make each sensor film, an aluminum reflective layer (100 nm) was deposited by electron beam evaporation (2.5 nm/sec evaporation rate) in a batch system vacuum coater onto a 50 μm polyester substrate layer. Poly(styrene) and poly(methylmethacrylate) detection layers were each deposited onto one of the aluminum-coated substrates via spin-coating. The polymers were coated via toluene solutions at concentrations of 5% (w/w) and 9.4% (w/w) respectively. The spin-coating was carried out at 3500 rpm for 25 seconds. The resulting polymer thicknesses were 260 nm (poly(styrene)) and 500 nm (poly(methylmethacrylate)). Chromium layers (5 nm) were then deposited onto each polymeric surface via sputtering conditions identical to those in Example 1, to complete the multi-layered sensor film constructions. Exposure of the sensor films to saturated chloroform vapor yielded reversible color shifts from purple to blue (poly(styrene)) and from pink to light green (poly(methylmethacrylate)). Exposure of the films to toluene vapor caused a permanent loss of interference-based color, as indicated by the failure of the film to recover its original color upon removal from the analyte. Transmission electron microscopy (TEM) studies indicate that this irreversible change was caused by delamination of the aluminum layer from the rest of the stack. This example demonstrates the ability to create multi-layered colorimetric sensors by spin-coating. It also demonstrates that a permanent change in the appearance of a sensor of the invention can be realized by the appropriate selection of materials and processes used to make the sensors.

Example 6

[0081]   Two different multi-layered films were constructed having the same general structure and composition as that

described in Example 1 except that the detection layer thickness for Sample 6A was 500 nm, while the thickness was 650 nm for Sample 6B. Both films contained detection layers made via polymerization of lauryl acrylate/IRR214/ EB 170 mixtures, as in Example 1. Responses of the two films to a series of vapors are shown in Table 4. While neither individual sensor can identify every analyte (i.e., 6A does not distinguish between toluene and acetone and 6B does not distinguish between acetonitrile and acetone), the combined responses from both sensors are unique to each species tested. The utility of sensor arrays containing more than one unique multi-layered film for analyte identification is demonstrated by this example.

TABLE 4

Color Changes Upon Exposure to Various Solvents

	6A (500 nm thick detection layer)		6B (650 nm thick detection layer)	
Solvent	Initial	After Exposure	Initial	After Exposure
Acetonitrile	Green	Yellow	Red	Green
Toluene	Green	Red/Pink	Red	Brown/Red
Acetone	Green	Red/Pink	Red	Green

[0082] Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

What is claimed is:

1. A colorimetric sensor for measuring one or both of the presence and concentration of an analyte comprising:

a substantially continuous reflective layer;

a detection layer over the reflective layer, the detection layer comprising at least one polymer component, said layer being capable of a change in optical thickness upon exposure to said analyte; and

a substantially continuous semi-reflective layer over the detection layer, the semi-reflective layer having an index of refraction different from the index of refraction of the detection layer.

2. The calorimetric sensor of claim 1 further comprising a substrate layer under the reflective layer.

3. The calorimetric sensor of claim 1 wherein the detection layer comprises a porous material.

4. The colorimetric sensor of claim 1 wherein the change in optical thickness of the detection layer is due to a dimensional change of said detection layer.

5. The colorimetric sensor of claim 1 wherein the change in optical thickness of the detection layer is due to a change in the index of refraction of said detection layer.

6. The calorimetric sensor of claim 1 wherein the change in optical thickness of the detection layer is permanent.

7. The colorimetric sensor of claim 1 wherein the change in optical thickness of the detection layer is reversible.

8. The colorimetric sensor of claim 1 wherein the detection layer comprises two or more polymer components and wherein the optical thickness of each polymer component will change in the presence of a different analyte.

9. The sensor of claim 8 wherein the polymer components are blended.

10. The sensor of claim 8 wherein different polymer components comprise different areas of the detection layer.

11. The colorimetric sensor of claim 1 wherein the detection layer comprises at least two polymers and wherein the optical thickness of only one polymer will change in the presence of an analyte.

12. The colorimetric sensor of claim 11 wherein the at least two polymers are arranged such that a visible pattern will form when the sensor is exposed to the analyte.

13. The colorimetric sensor of claim 1 wherein at least one polymer in the detection layer is at least partially crosslinked.

14. The colorimetric sensor of claim 1 wherein at least one polymer in the detection layer is selected from the group consisting of polymers or copolymers comprising acrylates and methacrylates.

15. The calorimetric sensor of claim 1 wherein at least one polymer in the detection layer is a copolymer.

16. The colorimetric sensor of claim 1 wherein one or both of the reflective and semi-reflective layer comprises a metal.

17. The colorimetric sensor of claim 1 wherein the semi-reflective layer has a visible light transmittance of about 30 to about 70%.

18. An array comprising two or more of the calorimetric sensors of claim 1.

19. The array of claim 18 wherein at least two sensors are on opposite sides of a substrate.

20. The calorimetric sensor of claim 1 further comprising molecular receptors in the detection layer.

21. The colorimetric sensor of claim 20 wherein the molecular receptors are selected from the group consisting of calixarenes, cyclodextrins, azacrowns, crown ethers, porphyrins, metalloporphrins, peptides, proteins, nucleic acids, and oligonucleotides.

22. A device comprising the calorimetric sensor of claim 1 and a light source.

23. The device of claim 22 further comprising a photo-detector.

24. A method of detecting the presence or absence of an analyte comprising

providing the calorimetric sensor of claim 1,

providing a light source,

contacting the sensor with a medium that may contain an analyte, and

monitoring the sensor for a change in optical properties.

25. The method of claim 24 wherein a photo-detector is used to monitor the sensor for a change in optical properties.

26. The method of claim 25 wherein the change in optical properties produces a visible change.

27. The method of claim 24 wherein the medium is a gas.

28. The method of claim 24 wherein the medium is a liquid.

29. The method of claim 24 wherein the analyte is a gas.

30. The method of claim 24 wherein the analyte is a liquid.

31. A calorimetric sensor for measuring one or both of the presence and concentration of an analyte comprising:

a substantially continuous reflective layer;

a detection layer over the reflective layer, the detection layer comprising at least one polymer component; and

a substantially continuous semi-reflective layer over the detection layer, the semi-reflective layer having an index of refraction different from the index of refrac-

tion of the detection layer, said sensor being capable of a change in color upon exposure to said analyte.

32. The colorimetric sensor of claim 31 wherein the change in color is from a visible color to a lack of visible color.

33. The calorimetric sensor of claim 31 wherein the change in color is due to delamination of the detection layer from an adjacent layer.

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