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(54) **METHODS AND DEVICES FOR DETECTING UNSATURATED COMPOUNDS**

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(56) **References Cited**

U.S. PATENT DOCUMENTS

3,732,519 A \* 5/1973 Taguchi ..... 338/34  
4,000,089 A 12/1976 Senda

(Continued)

OTHER PUBLICATIONS

Reliability Test Methods for Media-Compatible Pressure Sensors  
Slobodan Petrovic, Adan Ramirez, Theresa Maudie, Dennis Stanerson, John Wertz, Gordon Bitko, Jeanene Matkin, and David J. Monk IEEE Transactions on Industrial Electronics vol. 45, No. 6, Dec. 1998.\*

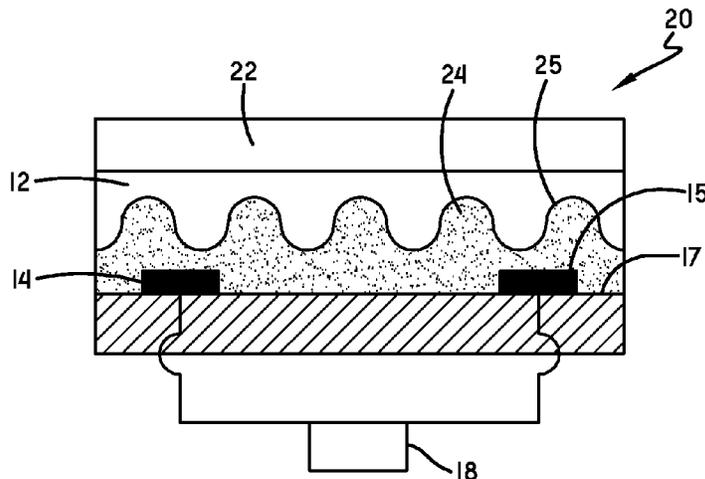
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(57) **ABSTRACT**

A method for detecting an unsaturated compound, the method comprising monitoring change in electrical properties of a substance that reacts or interacts with unsaturated compounds.

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(51)	<b>Int. Cl.</b>						
	<b>G01N 33/28</b>	(2006.01)		2003/0003589	A1	1/2003	Khalil et al.
	<b>G01N 33/543</b>	(2006.01)		2004/0129565	A1	7/2004	Prohaska et al.
	<b>G01N 27/403</b>	(2006.01)		2006/0034731	A1	2/2006	Lewis et al.
				2007/0062812	A1	3/2007	Weber et al.
				2007/0295203	A1*	12/2007	Shekarriz et al. .... 95/8
				2008/0149499	A1	6/2008	Ding et al.
				2008/0302672	A1*	12/2008	Sandvik et al. .... 205/775
				2009/0166197	A1	7/2009	Grincourt et al.
				2010/0120159	A1	5/2010	Lund et al.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,142,400	A	3/1979	Colla et al.	
4,226,798	A	10/1980	Cowfer et al.	
4,410,632	A	10/1983	Dilley et al.	
4,414,839	A	11/1983	Dilley et al.	
4,581,204	A	4/1986	Voit	
4,631,952	A	12/1986	Donaghey	
4,644,333	A	2/1987	Barendsz et al.	
4,674,320	A	6/1987	Hirschfeld	
4,822,465	A	4/1989	Jones et al.	
4,836,012	A	6/1989	Doty et al.	
5,047,214	A	9/1991	Fukui et al.	
5,215,643	A	6/1993	Kusanagi et al.	
5,322,602	A	6/1994	Razaq	
5,417,100	A	5/1995	Miller et al.	
5,417,821	A	5/1995	Pyke	
5,425,869	A	6/1995	Noding et al.	
5,536,473	A	7/1996	Monkman et al.	
5,591,321	A	1/1997	Pyke	
5,749,942	A	5/1998	Mattis et al.	
5,788,833	A	8/1998	Lewis et al.	
5,911,872	A	6/1999	Lewis et al.	
6,033,601	A	3/2000	Persaud et al.	
6,041,643	A	3/2000	Stokes et al.	
6,093,308	A	7/2000	Lewis et al.	
6,155,100	A	12/2000	Stokes et al.	
6,182,500	B1	2/2001	Stokes et al.	
6,202,473	B1	3/2001	Stokes et al.	
6,289,716	B1	9/2001	Lindgren	
6,331,244	B1	12/2001	Lewis et al.	
6,866,885	B1*	3/2005	Clough .....	427/212
6,890,715	B1	5/2005	Lewis et al.	
7,254,986	B2	8/2007	Stokes et al.	
7,367,217	B2	5/2008	Stokes et al.	
7,501,091	B2	3/2009	Munoz et al.	

OTHER PUBLICATIONS

Interaction of Acetylene with Films of the Transition Metals Iron, Nickel, and Palladium W. Alter, D. Borgmann, M. Stadelmann, M. Worn, and G. Wedler J. Am. Chem. Soc. 1994, 116, 10041-10049.\*

Jordan, Larry R. and Hauser, Peter C., "Electrochemical Sensor for Acetylene", Anal. Chem., 1997, 69, pp. 2669-2672.

Pickrell, G., Peng, W., and Wang, A., "Random-hole Optical Fiber Evanescent-Wave Gas Sensing", Optics Letters, vol. 29, No. 13, 2004, pp. 1476-1478.

Maitlis, Peter M., "The Palladium(II)-Induced Oligomerization of Acetylenes: An Organometallic Detective Story", Accounts of Chemical Research, vol. 9, 1976, pp. 93-99.

Yarai, Atsushi and Nakanishi, Takuji, "Optical Fiber Gas Sensor Based on Thermal Lens Spectroscopy", Review of Scientific Instruments, vol. 75, No. 10, 2004, pp. 3237-3241.

Alter, W. et al., "Interaction of Acetylene with Films of the Transition Metals Iron, Nickel, and Palladium", J. Am. Chem. Soc., 116, 1994, pp. 10041-10049.

Yang, Ralph T. and Foldes, Robert "New Adsorbents Based on Principles of Chemical Complexation: Monolayer-Dispersed Nickel(II) for Acetylene Separation by  $\pi$ -Complexation", Ind. Eng. Chem. Res. 1996, 35, pp. 1006-1011.

Lauque, Pascal, et al. "Highly Sensitive and Selective Room Temperature NH<sub>3</sub> Gas Microsensor using an Ionic Conductor (CuBr) Film", Analytica Chimica Acta 515 (2004) pp. 279-284.

Dutta, Prabir K., et al. "Sensing of Carbon Monoxide Gas in Reducing Environments" Sensors and Actuators B 84 (2002) pp. 189-193.

Azad, A.-M., et al. "A Highly SElective Acetylene Sensor" IMCS 12: Jul. 13-16, 2008, Columbus, OH, USA.

\* cited by examiner

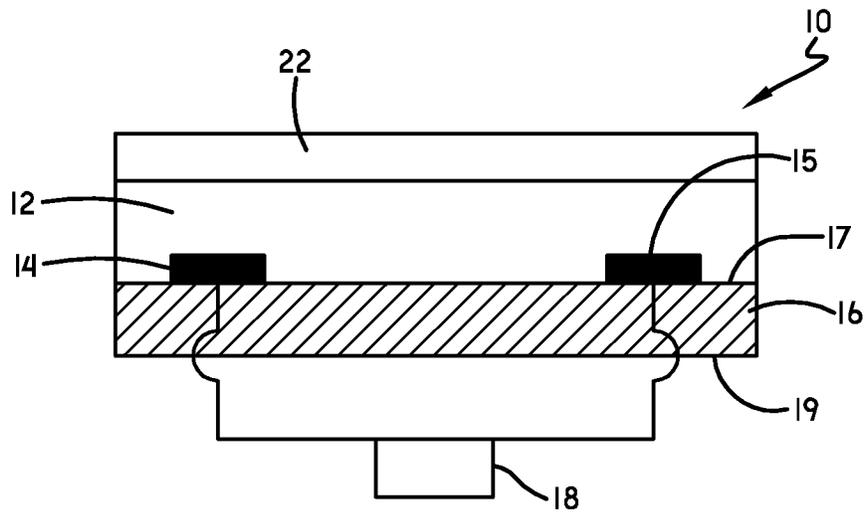


FIG.-1

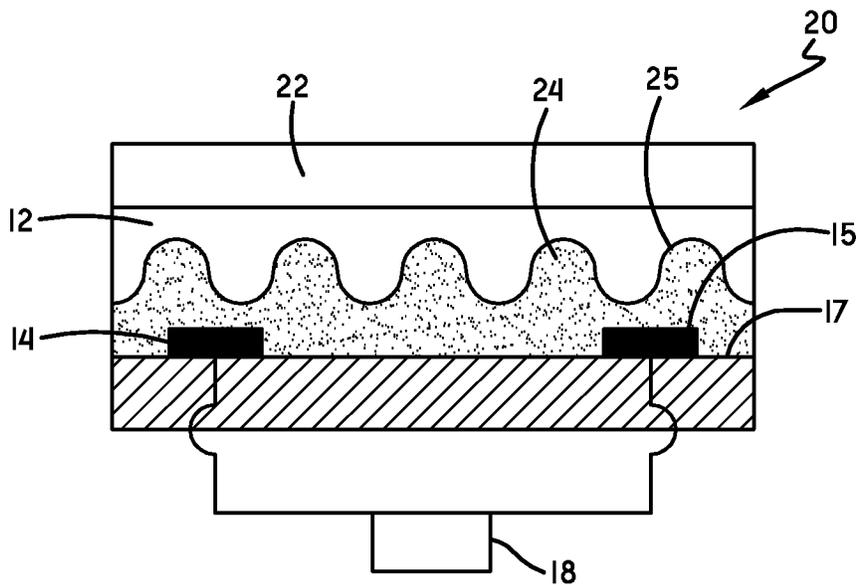


FIG.-2

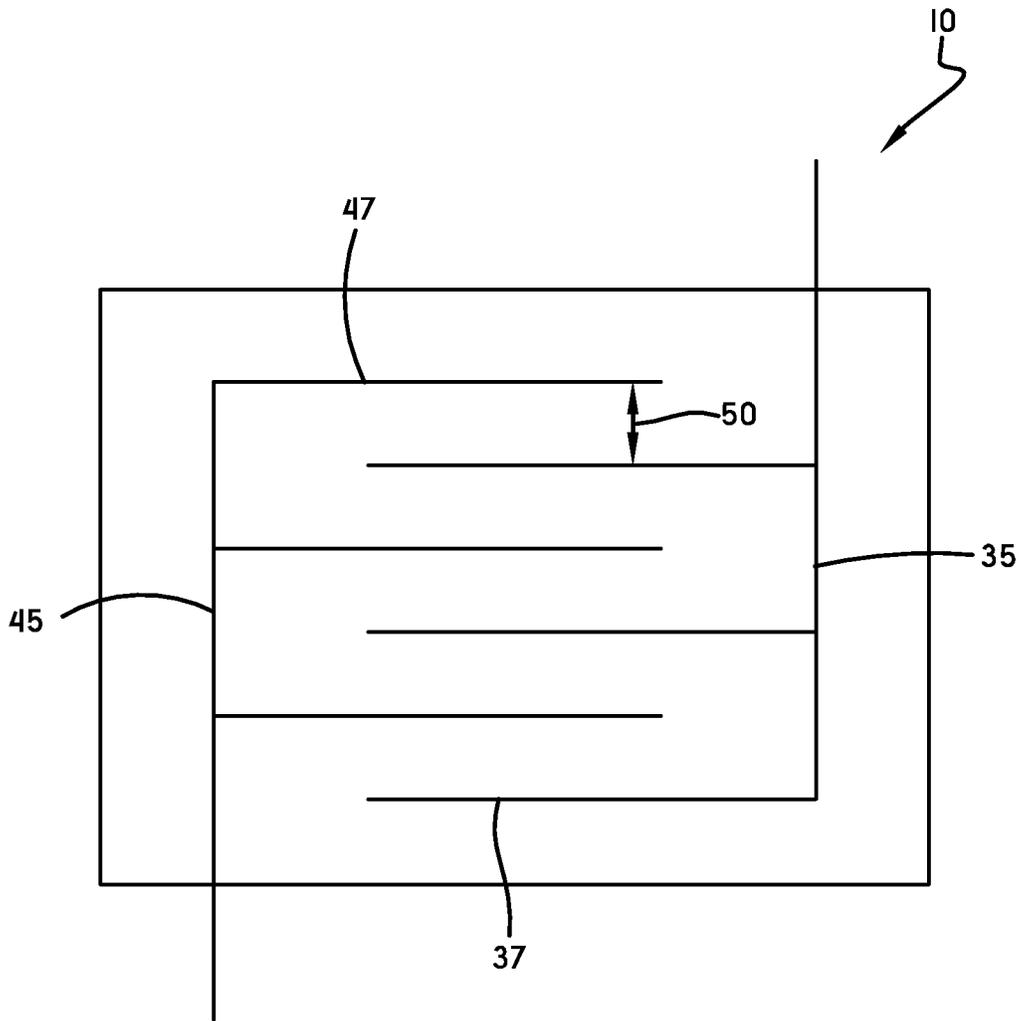


FIG.-3

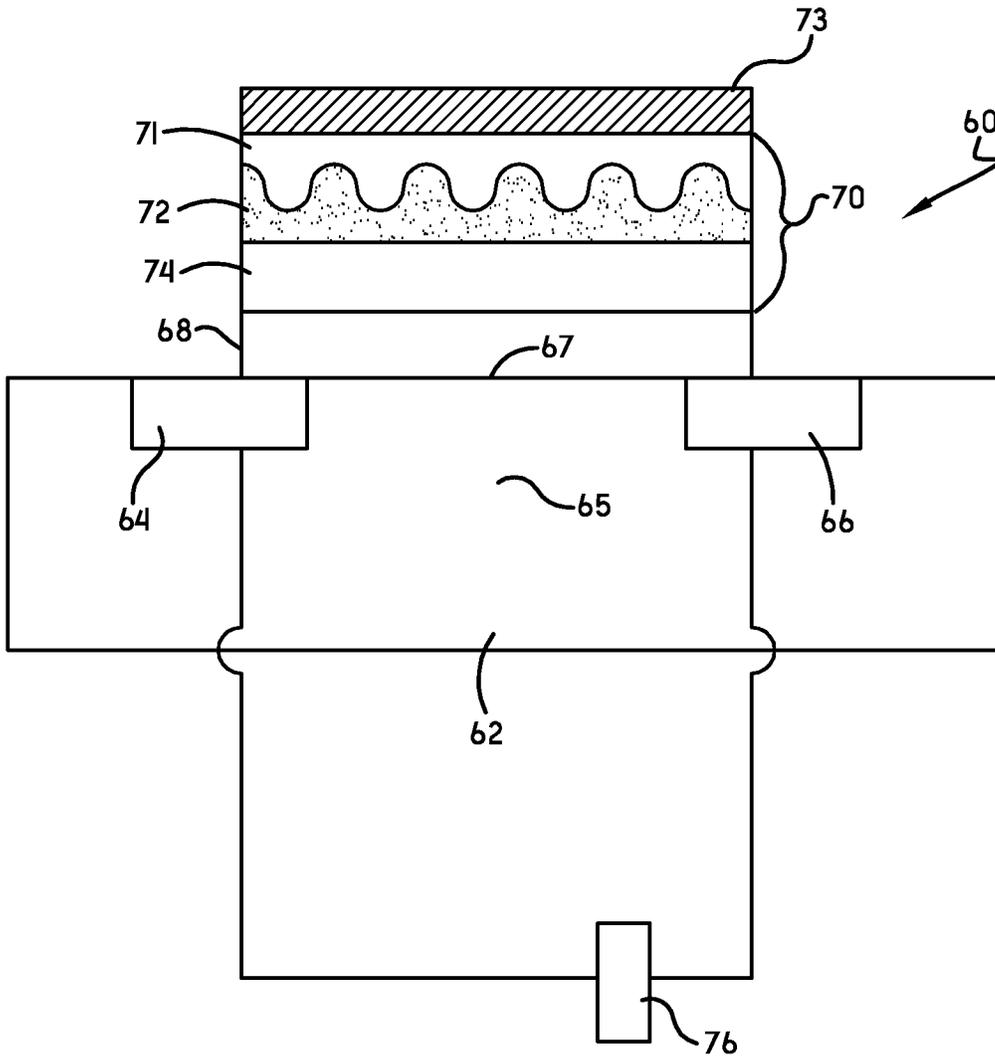


FIG.-4

## METHODS AND DEVICES FOR DETECTING UNSATURATED COMPOUNDS

This application is a U.S. National Stage Application of PCT/US10/057999 filed on Nov. 24, 2010, which is a continuation in part of U.S. Non-Provisional application Ser. No. 12/626,252, filed on Nov. 25, 2009, both of which are incorporated herein by reference.

### TECHNICAL FIELD

Embodiments of the invention are directed toward methods for detecting unsaturated compounds such as acetylene.

### BACKGROUND ART

In many situations there is a need to detect the presence of small unsaturated molecules such as those including alkenylic or alkynylic unsaturation. As those skilled in the art appreciate, these small molecules are often gases at standard conditions, which are the conditions under which detection is often needed. While elaborate systems for detecting these compounds exist, there is often a need to detect these molecules in situations or environments where known systems are too cumbersome, too expensive, and/or simply inoperable.

There is, therefore, a need for new techniques and/or devices to detect small unsaturated molecules.

### SUMMARY OF INVENTION

Embodiments of the present invention provide a method for detecting an unsaturated compound, the method comprising monitoring change in electrical properties of a substance that reacts or interacts with unsaturated compounds.

Further embodiments of the present invention provide a sensor for detecting acetylene gas comprising a substrate having a surface, electrodes in electrical communication with the surface, and a sensor layer formed of metal halide.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 cross-sectional view of a gas sensor device schematically connected to a detection circuit according to one or more embodiments of the invention;

FIG. 2 cross-sectional view of a gas sensor device schematically connected to a detection circuit according to one or more embodiments of the invention;

FIG. 3 is a schematic view of a gas sensor device according to one or more embodiments of the invention.

FIG. 4 is a schematic view of an IGFET-type device of the present invention.

### DETAILED DESCRIPTION OF THE ILLUSTRATIVE EMBODIMENTS

Embodiments of the invention are based, at least in part, on the discovery that unsaturated compounds react or interact with certain substances and thereby alter the electrical properties of the substance. As a result, useful techniques for detecting the presence of unsaturated compounds are provided. In one or more embodiments, detection devices (e.g., sensors) are provided that operate, at least in part, based on the change in electrical properties caused by the interaction or reaction of unsaturated compounds with the substance.

### Unsaturated Compounds

In one or more embodiments, unsaturated compounds include organic compounds including at least one double bond or at least one triple bond. In one or more embodiments, unsaturated compounds include hydrocarbons. In particular embodiments, the unsaturated compounds include alkenes (also known as olefins) such as, but not limited to, ethene, propene, 1-butene, 1-pentene, and 2-pentene. In other embodiments, the unsaturated compounds include alkynes such as, but not limited to, ethyne (also known as acetylene), propyne (also known as methylacetylene), butyne, and pentyne. In particular embodiments, the target unsaturated compound is acetylene. In one or more embodiments, unsaturated compounds include those compounds that include an alkenyl group. In these or other embodiments, unsaturated compounds include those compounds that include an alkynyl group. In one or more embodiments, the unsaturated compounds may be liquids at conditions of standard pressure and temperature. In other embodiments, the unsaturated compounds may be gases at conditions of standard pressure and temperature.

In particular embodiments, the unsaturated compounds may be characterized by having a relatively low molecular weight. For example, in one or more embodiments, the molecular weight of the unsaturated compounds may be less than 60 g/mole, in other embodiments less than 50 g/mole, in other embodiments less than 40 g/mole, and in other embodiments less than 30 g/mole.

### Substance that Interacts with Unsaturated Compounds

In one or more embodiments, the interaction between the unsaturated compound and the substance that interacts with the unsaturated compound results in changes in the electrical properties of the substance. In one or more embodiments, the change in electrical properties may be manifested, for example, in a change in the conductivity (or resistivity) or capacitance of the substance. Without wishing to be bound by any particular theory, it is believed that the change in electrical properties is caused by  $\pi$  bonding through electrons between the unsaturated compound and the substance. Nonetheless, for purposes of this specification, the term interact may be used to describe the phenomena that exhibits, demonstrates, undergoes or gives rise to the change in electrical properties and therefore encompasses any interaction or reaction that may occur.

In one or more embodiments, the substance that interacts with unsaturated compounds is a transition metal compound, such as a transition metal salt. Useful transition metals include, but are not limited to, copper (I), copper (II), nickel (II), cobalt (II), iron (II), zinc (II), and silver (I). Useful salts of these transition metals include halides, such as, but not limited to, chlorides, bromides, and iodides, as well as nitrates. Exemplary transition metal compounds include copper (I) chloride, nickel (II) chloride, cobalt (II) chloride, iron (II) chloride, zinc (II) chloride, and silver nitrate ( $\text{AgNO}_3$ ). In particular embodiments, the substance employed is copper (I) chloride. In other particular embodiments, the substance employed is nickel (II) chloride.

In particular embodiments, the purity of the substance (e.g. metal halide) impacts that ability of the substance to interact with the unsaturated compounds. Accordingly, in one or more embodiments, the purity of the metal halide (e.g. cuprous chloride) is at least 96%, in other embodiments at least 98%, and in other embodiments at least 99%. Stated another way, in one or more embodiments, the metal halide includes less than 5%, in other embodiments less than 3%, and in other embodiments 1% by weight impurity, which, for example, refers to

the weight of non-cuprous chloride atoms or molecules in the molecular arrangement or crystal lattice of the cuprous chloride.

Advantageously, the change in electrical properties can be monitored. For example, a voltage can be applied across the substance and changes in the current across the substance can be monitored. Advantageously, it has been discovered that the change in electrical properties (e.g. resistivity) in the presence of the unsaturated compounds is proportional to the concentration of the unsaturated compounds in the environment in which detection of the unsaturated compounds takes place. In one or more embodiments, the resistivity of the substance decreases proportionally with the increasing concentration of acetylene within the environment in which the substance exists. Moreover, the reaction or interaction between the substance and the unsaturated compounds is reversible. In other words, the change in electrical properties can be reversed as concentration of unsaturated compounds in the environment in which a sensor is placed is reduced. For example, as a sensor is moved from an environment having higher concentration of unsaturated compound to an environment having lower concentration of unsaturated compound, the conductivity of the sensor layer will decrease proportionally to the change in concentration of unsaturated compounds. Likewise, as the sensor is moved from an environment having lower concentration of unsaturated compound to an environment having higher concentration of unsaturated compound, the conductivity of the sensor layer will increase proportionally to the change in concentration of unsaturated compounds.

In one or more embodiments, the substance that interacts with the unsaturated compound exhibits an initial resistance of at least 0.1 kilohms, in other embodiments at least 1.0 kilohm, and in other embodiments at least 10 kilohms. In these or other embodiments, the initial resistance is less than 1,000 kilohms, in other embodiments less than 500 kilohms, and in other embodiments less than 100 kilohms. In one or more embodiments, the change in resistivity of the substance based upon interaction with the unsaturated compound is at least 1%, in other embodiments at least 5%, and in other embodiments at least 10% at a concentration of 1 ppm of the unsaturated compound. In one or more embodiments, the substance that interacts with the unsaturated compound shows a change in electrical properties in the presence of the unsaturated compound at a temperature in the range of 20 to 130° C., in other embodiments from 50 to 120° C., and in other embodiments from 60 to 110° C.

In particular embodiments, the use of nickel (II) chloride has proven to be unexpectedly useful in the detection of acetylene. Advantageously, acetylene interacts with nickel (II) chloride, and the interaction or reaction unexpectedly alters the electrical properties of the nickel (II) chloride such that the change in electrical properties can be detected. Advantageously, the initial resistivity of nickel (II) chloride is in the range of about 10 to about 100 kilohms (e.g., 20 to 80 kilohms), and the change in resistivity is proportional to the concentration of acetylene. And, the nickel (II) chloride demonstrates a change in resistivity of about 10% at a concentration of 1 ppm acetylene. This change in resistivity can be easily monitored in view of the initial resistivity. Further, the change in resistivity of the nickel (II) chloride in the presence of acetylene has been found to be reversible and reliable at temperatures up to 120° C. (e.g., 100-110° C.).

#### Device for Detecting Unsaturated Compounds

A device for detecting unsaturated compounds according to one or more embodiments of the present invention can be generally described with reference to FIG. 1. As those skilled

in the art will appreciate, FIG. 1, like other figures presented in this specification, is not drawn to scale and is primarily provided to illustrate the relationship of the various elements of the combinations presented.

The device 10 includes a substance 12 that reacts or interacts with unsaturated compounds and as a result exhibits a change in electrical properties as described above with respect to other embodiments or sub-embodiments of this invention. In particular embodiments, substance 12 is metal halide (e.g. cuprous chloride or nickel (II) chloride). In one or more embodiments, substance 12 is in the form of a continuous layer that allows electrons (i.e. a current) to travel across the layer; reference may simply be made to layer 12 or to sensor layer 12. The thickness of layer 12 can vary. For example, in particular embodiments, the thickness of layer 12 can be on the atomic level (e.g. the thickness may be one or more atoms thick) up to a thickness on the micron level (e.g. from 1 to 1000 microns).

In one or more embodiments, sensor layer 12 is disposed on at least a surface 17 of a substrate 16 and on at least a portion of first and second electrodes 14 and 15, which are thereby in electrical connection with sensor layer 12 and allow a voltage to be applied across sensor layer 12. As shown in FIG. 1, first and second electrodes may also be disposed on surface 17 of substrate 16. As those skilled in the art appreciate, these electrodes may be referred to as positive and negative electrodes (e.g. positive electrode 14 and negative electrode 15).

Substrate 16 may include or be formed from a non-conductive or semi-conductive material. In particular embodiments, substrate 16 is inert and non-conductive, where inert refers to the fact that the electrical properties of substrate 16 do not change as the result of any interaction with an unsaturated compound within the context of this specification. In these or other embodiments, substrate 16 does not interact with unsaturated compounds. Exemplary materials that may be used as substrate 16 include, without limitation, alumina (Al<sub>2</sub>O<sub>3</sub>) (e.g. high-density polycrystalline alumina), quartz (SiO<sub>2</sub>), magnesia (MgO), or zirconia (ZrO<sub>2</sub>).

In one or more embodiments, at least a second surface 19 of substrate 16 may be in contact with a heating device, such as a platinum resistance heater (not shown), as well as complementary detection and sensing devices, that can be used to heat and maintain the temperature of device 10 at a desired temperature.

As is generally known in the art, electrodes 14 and 15 may be fabricated from and therefore include any conductive material including those commonly employed in the art such as platinum, silver, and gold. Practice of the present invention is not limited by the number or type of electrodes employed. As those skilled in the art will appreciate, numerous electrode designs can be configured.

In one or more embodiments, electrodes 14 and 15 may include interdigitated electrodes (IDEs) 35 and 45 as generally shown in FIG. 3. IDEs are generally known in the art. Practice of the present invention is not necessarily limited by the selection of particular IDEs. As shown, the IDEs 35 and 45 may include interdigitated projections 37 and 47 respectively. Projections 37 and 47 may be spaced apart by gaps 50. As those skilled in the art will appreciate, practice of the present invention is not limited by the number of projections or the size of the gaps. These electrodes, in a manner consistent with that described above, include or are prepared from conductive material and are electrically connected with device or detection circuit 18, which may be accomplished through connection terminals (not shown) as know in the art.

In one or more embodiments, electrical detection device **18**, which may also be referred to as a detection circuit, is in electrical connection with electrodes **14**, **15**. For example, detection device **18** may include a current meter. In one or more embodiments, electrical detection device **18** applies a voltage across layer **12** and monitors the change in electrical resistivity (or conductivity) across layer **12**. Practice of the present invention is not limited by the selection of any particular electrical detection device **18** or devices (not shown). For example, electrical detection and monitoring may be provided by a single device or by two or more devices working in combination with each other (not shown). The voltage that can be applied across layer **12** may be in the form of alternating current (AC). As those skilled in the art appreciate, this AC can be rectified to DC, filtered, offset, and scaled to better detect changes in the electrical properties of layer **12**. As is known in the art, detection circuit **18** may include any hardware and/or software necessary for carrying out the various detecting functions. In one or more embodiments, detection circuit **18** may include a visual display, such as an LCD display, or other predetermined audible, mechanical, or visual alerts or prompts generated by detection circuit **18** when sensor layer **12** reacts or interacts with the target unsaturated compound.

In one or more embodiments, device **10** may include optional permeable-protective layer **22**, which may be simply referred to as protective layer **22** or protective coating **22**. Protective layer **22** may be disposed directly on sensor layer **12** as shown, or it may be disposed on other intermediary layers disposed between sensor layer **12** and protective layer **22**. In one or more embodiments, protective layer **22** includes or is formed from a material that is permeable to the unsaturated compound that is being detected and impermeable, or substantially impermeable, to other compounds or constituents in the environment that may deleteriously impact sensor layer **12** or the ability of sensor layer **12** to react or interact with the unsaturated compound that is being detected. For example, protective layer **22** may be impermeable to water or organic molecules that are larger than the unsaturated compound targeted for detection, while it is permeable to the unsaturated compound targeted for detection. In particular embodiments, protective layer **22** includes a hydrophobic coating.

Practice of the present invention is not necessarily limited by the thickness of protective layer **22**. In particular embodiments, the thickness of protective layer **22** may be on the micron level; for example, the thickness of layer **22** may be from about 2 or 4 microns to about 100 or 500 microns (e.g., up to 10 or 50 microns).

In one or more embodiments, protective layer **22** includes or is formed from a fluorinated material. Fluorinated coatings and coating compositions (i.e. the composition from which the coating derives) that are useful for this purpose are known in the art. For example, fluorinated alkyl silanes or siloxanes, which are often referred to as FAS coatings, are known in the art as exemplified in U.S. Publ. Nos. 2002/0081385 and 2006/0229424, which are incorporated herein by reference.

In one or more embodiments, FAS compounds may include compounds where a silicon atom is bonded to four chemical groups. One or more of these groups contains fluorine and carbon atoms, and the remaining group(s) that may be attached to the silicon atoms may include alkyl, alkoxy, or halide group(s). Exemplary types of FAS compounds for use in protective layer **22** include, without limitation,  $\text{CF}_3(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$  [i.e., 3,3,3 trifluoropropyl)trimethoxysilane];  $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$  [i.e., tridecafluoro-1,1,2,2-tetrahydrooctyl-1-triethoxysilane];  $\text{CF}_3(\text{CH}_2)_2\text{SiCl}_3$ ;  $\text{CF}_3$

$(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3$ ;  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ ;  $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ ;  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$ ;  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCH}_3\text{Cl}_2$ ; and/or  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_3)_2$ . These FAS material may be used either alone or in any suitable combination for protective layer **22**. At least partial hydrolyzed versions (hydrolysate) of any of these compounds may also be used.

As noted above, the detection devices of this invention, such as device **10**, may include multiple protective layers (not shown). Each protective layer should be permeable to the unsaturated compound or compounds being targeted for detection, and thereby allow the target unsaturated compounds to contact sensor layer **12**. Each of the one or more protective layers, however, may be selectively permeable or impermeable to other constituents that may come into contact with device **10** (i.e. are present in the environment where the target unsaturated compounds are sought to be detected).

Other embodiments of devices of the present invention may be described with reference to FIG. **2**. As shown, detection device **20** includes sensor layer **12**, first and second electrodes **14** and **15**, substrate **16**, electrical detection device **18**, and optional protective layer **22**, which may be consistent with the description provided above. In addition, detection device **20** may include optional support layer **24**, which may also be referred to as matrix **24**. Support layer **24** may be disposed on first surface **17** of substrate **16** and on at least a portion of electrodes **14** and **15**. Sensor layer **12** may then be disposed on first surface **25** of semi-conductor layer **24**. As a result of this arrangement, electrodes **14** and **15** are in electrical contact or communication with each other through sensor layer **12** and optionally through matrix **24**; in other words a voltage can be applied across sensor layer **12** between electrodes **14** and **15**, and optionally also across support **24** between electrodes **14** and **15**.

In one or more embodiments, support layer **24** is porous and/or has a degree of surface roughness. In one or more embodiments, support layer **24** is porous or partially porous with respect to the target unsaturated compound. As a result, the porosity, partial porosity, and/or surface roughness, at least first surface **25** of support layer **24** has increased surface area and may therefore provide increased surface area to sensor layer **12**, which is disposed on surface **25**.

In one or more embodiments, support or matrix layer **24** is a semi-conductor, and therefore layer **24** may also be referred to, in certain embodiments, as semi-conductor layer **24**. Semi-conductor layer may be formed from and therefore include a metal oxide such as, without limitation, titanium dioxide ( $\text{TiO}_2$  or Ti(IV) oxide or titania), tin dioxide ( $\text{SnO}_2$  or Sn(IV) oxide), zinc oxide ( $\text{ZnO}$  or Zn(II) oxide), molybdenum oxide ( $\text{MoO}_3$  or Mo(VI) oxide), tungsten oxide ( $\text{WO}_3$  or W(VI) oxide), and mixtures of two or more of these compounds. For example, a mixture of titanium dioxide and tin dioxide may be employed; in particular embodiments, the ratio of titanium dioxide to tin dioxide may continuously range from about 100:1 to about 1:100.

The thickness of support layer **24** can vary. For example, in particular embodiments, the thickness of layer **24** can be on the atomic level (e.g. the thickness may be one or more atoms thick) up to a thickness on the micron level (e.g. from 1 to 1000 microns).

In these or other embodiments, any relationship that may exist between the sensor layer **12** and the semi-conductor layer **24** may be expressed in terms of the weight of the sensor material as a ratio to the weight of the semi-conductor material present in any given unit of area. For example, the weight/weight ratio of sensor material to semi-conductive material is from about 0.02 to about 100.

In one or more embodiments, the sensor devices of this invention can be fabricated into an insulated-gate field-effect transistor (IGFET) as shown in FIG. 4. Transistor 60 includes a semiconductor substrate 62, a source region 64, and a drain region 66. Source region 64 is spaced apart from drain region 66, and both may be located at or near one surface 67 of substrate 62. The region of substrate 62 between source 64 and drain 66 is called the channel 65. A gate insulator 68, which may include a thin layer of insulating material, covers the surface 67 of channel 65. A gate electrode 70, which is a sensor layer within the context of this invention (e.g. metal halide layer), is disposed on and covers gate insulator 68. Gate electrode 70 includes a sensor substance 71 (e.g. metal halide) and optional support material (e.g. TiO<sub>2</sub>) 72. In one or more embodiments, gate electrode 70 may also include a conductive layer disposed between gate insulator 68 and gate electrode 70. In those embodiments where the device includes conductive layer 74, the device may be referred to as a metal insulator semiconductor (MIS). The IGFET devices of this invention may also include an optional protective layer 73.

When gate electrode 70 (e.g. metal halide sensor layer) is exposed to an unsaturated compound (e.g. acetylene), the electric field in gate insulator 68 is modified. The electric field attracts or repels charge carriers, electrons or holes, in adjacent semiconductor material 62 thereby changing the conductance of channel 65. The change in conductance of channel 65 is related to the concentration of unsaturated compound interacting with sensor substance 71 and can be measured by a current meter 76 connected in series with a potential source, source region 64, and drain region 66.

#### Method of Fabricating Device

While practice of the present invention is not necessarily limited by the method used to produce the device of one or more embodiments of the present invention, the following method has been found to be advantageous. An inert substrate, such as a thin plate or wafer of dense (~100%) crystalline  $\alpha$ -alumina, can be commercially obtained and may be optionally polished to provide at least one relatively smooth surface. A pair or multitude of electrodes, such as IDEs, can be placed on a surface (optionally a polished surface) of the alumina substrate by employing techniques known in the art of photolithography.

The substance that can interact with an unsaturated compound may then be deposited onto at least a portion of the substrate and onto at least a portion of each of the electrodes. In other embodiments, one or more semiconductor layers are first deposited onto at least a portion of the substrate and onto at least a portion of each of the electrodes, and then the substance that can react or interact with an unsaturated compound may then be deposited onto the at least a portion of the semiconductor layer.

In either event, the substance that can interact with an unsaturated compound may be deposited by using the following technique. In one embodiment, where cuprous chloride is employed, cuprous chloride may be commercially obtained at purity levels that are useful for practicing the present invention (e.g. 99%+). Where grades are obtained that include greater levels of impurities, or where further purification is desired, cuprous chloride may be further purified using techniques known in the art. For example, the cuprous chloride can be dissolved in concentrated hydrochloric acid, which will leave impurities, such as copper-II (cupric chloride) compounds undissolved, and allow for separation by using techniques such vacuum filtration; the cuprous chloride can then

be precipitated out using copious amounts of water and dried using glacial acetic acid and optional further drying in a vacuum oven.

The cuprous chloride can be dissolved in appropriate solvents, such as acetonitrile, to form a solution that can be deposited onto at least a portion of the substrate and onto at least a portion of each of the electrodes, or in other embodiments, onto at least a portion of the semiconductor layer and onto at least a portion of each of the electrodes. The substrate can be heated (e.g. up to about 60-65° C.) when the solution of cuprous chloride is applied, or it may be subsequently heated to drive off or evaporate the solvent.

In those embodiments where nickel (II) chloride is employed, the nickel chloride can be dissolved in appropriate solvents, such as water, acetonitrile or a mixture of the two, to form a solution that can be deposited onto at least a portion of the substrate and onto at least a portion of each of the electrodes, or in other embodiments, onto at least a portion of the semiconductor layer and onto at least a portion of the electrodes. The substrate can be heated when the solution of nickel chloride is applied to drive off the solvent, preferably above the vaporization temperature of the solution (e.g. from about 100° C.-150° C. for an acetonitrile, water mixture) for quick evaporation and dispersion of the nickel chloride.

Where the device includes a semi-conductor layer, such as titanium dioxide or tin oxide or other suitable oxides mentioned above, the semiconductor layer may be formed from a slurry containing the metal oxide that is deposited on the substrate, and at least a portion of the electrodes, and subsequently fired to obtain a porous or partially porous film with some surface roughness. For example, titanium oxide powder that is at least about 99.5% pure can be commercially obtained and sieved to obtain a desirable particle size. In one or more embodiments, the metal oxide is sieved or otherwise separated to provide particles having a particle size of less than 200  $\mu\text{m}$ , in other embodiments less than 40  $\mu\text{m}$ , or in other embodiments less than 1  $\mu\text{m}$ . The sieved powder can be formed into a slurry using an appropriate liquid vehicle such as 2-propanol. The slurry may then be applied to the target surface using known techniques (e.g. brushing or spraying), allowed to dry slowly in an air oven (e.g. overnight at 70° C.) and fired at appropriate temperatures for sufficient time (e.g. 700° C. for approximately 2 hours) to achieve a desired porous semiconductor layer.

The sensing layer can then be formed on the porous semiconductor layer by applying the solution (e.g. cuprous chloride in acetonitrile) described above to the surface of the semiconductor layer.

In one or more embodiments, the solution of the cuprous chloride is prepared and applied so as to deliver from about 1 microgram to about 200 micrograms, or in other embodiments from about 5 micrograms to about 50 micrograms, cuprous chloride per square mm of the substrate or semiconductor layer.

After the sensing material is applied to the substrate or semiconductor material and appropriately dried, it may be desirable to precondition the device. This may be accomplished by subjecting the device to an energy source. For example, the device can be heated in an oven under appropriate conditions. In other embodiments, an alternating current can be applied across the terminals (e.g. a 1-volt peak voltage at a frequency of between 10-100 Hz, although A.C. signals with other voltage magnitudes and frequencies may be used); this voltage may be applied for extended periods of time (e.g. 6 hours).

Protective layer(s) can be applied to the device by using known techniques for applying these coatings. For example,

solutions of FAS coatings can be applied by using known techniques (e.g. brushing or spraying), and the solvent within the solution can be driven off using known techniques (e.g. heat and/or vacuum). The protective layer can be applied before or after preconditioning the device.

#### Packaging

As those skilled in the art appreciate, the various other sensor configurations can incorporate the sensor layer or sensor substance contemplated by this invention. Moreover, these various devices can be packaged or assembled within various packages known in the art. For example, and without limitation, these devices can be assembled with dual in-line packages (DIPs), surface mount packages (SMPs), and metal can packages (TO-type).

#### INDUSTRIAL APPLICABILITY

In one or more embodiments, the techniques and devices of the present invention can advantageously be used to detect a number of unsaturated compounds in diverse environments. For example, where the unsaturated compound is in the gaseous state, the techniques and detectors of this invention can be used in liquid or gaseous environments. In other words, gaseous unsaturated compounds contained in a mixture of gases can be detected where the mixture of gases is in contact with the sensor. Or, unsaturated gaseous compounds dissolved in a liquid can be detected where the liquid is in contact with the sensor.

In particular embodiments, the sensors of the present invention are employed to detect the presence of acetylene in oil-filled electrical equipment such as power transformers. In these embodiments, the sensor can be placed in contact with the fluids contained in the electrical equipment (e.g. power transformer). A voltage (e.g. about 1 volt) can be applied across the sensor layer and/or semiconductor layer. In one or more embodiments, the sensing device can optionally be heated (e.g. to a temperature of about 100° C.). Using known techniques, a baseline voltage transmission can be determined for the device in the absence of acetylene within the transformer, which represents a degree of resistivity (or conductivity) across the device. This degree of conductivity can be continuously or intermittently monitored and compared to the base line. As acetylene is formed within the transformer and the concentration of the acetylene reaches concentrations that are detectable by the sensor, the conductivity of the sensor changes as the acetylene reacts or interacts with the sensor layer. The change in conductivity can be recorded on site at the transformer or communicated electronically to a location remote from the transformer.

In other particular embodiments, the sensors of the present invention are employed to detect the presence of acetylene or ethylene in food applications including, but not limited to, food ripening processes and food storage facilities.

Although the present invention has been described in considerable detail with reference to certain embodiments, other embodiments are possible. Therefore, the spirit and scope of the appended claims should not be limited to the description of the embodiments contained herein.

What is claimed is:

1. A method for detecting acetylene, the method comprising:

providing a sensor including an inert substrate, first and second electrodes deposited on said substrate, where the first and second electrodes have a space therebetween, and a sensor layer including nickel (II) chloride deposited on at least a portion of the substrate and in electrical communication with the first and second electrodes;

positioning the sensor device within an environment having a propensity for acetylene;  
applying a voltage across the sensor layer between the first and second electrodes; and

5 monitoring change in electrical properties of the sensor layer within the environment having a propensity for acetylene.

2. The method of claim 1, where the sensor material further includes a transition metal compound selected from the group consisting of cobalt (II) chloride, zinc (II) chloride, and silver nitrate.

3. The method of claim 1, where said step of monitoring takes place within a power transformer.

4. The method of claim 3, where said step of placing places the sensor device in contact with liquids that are contained within the power transformer.

5. The method of claim 1, where said step of monitoring includes monitoring a change in resistance of the sensor layer.

6. The method of claim 5, where the change in resistance is at least 10% at an acetylene concentration of 1 ppm.

7. The method of claim 5, where the change in resistance is at least 1% at an acetylene concentration of 1 ppm.

8. The method of claim 7, where said step of monitoring takes place at a temperature of from 20 to 130° C.

9. A sensor for detecting acetylene, the sensor comprising: a substrate having a surface, where the electrical properties of the substrate do not change based upon any reaction or interaction with acetylene;

first and second electrodes disposed on said surface, where said first and second electrodes are spaced from each other;

a sensor layer including nickel (II) chloride, where said sensor layer is disposed on at least a portion of said surface of said substrate, and where said sensor layer is in electrical communication with said first and second electrodes; and

a detection circuit coupled to said electrodes to identify a change in electrical properties of said sensor layer.

10. The sensor of claim 9, where said electrodes are sandwiched between said substrate and said sensor layer.

11. The sensor of claim 9, wherein said sensor layer forms at least one conductive path between said electrodes, and where the sensor layer changes electrical properties upon interacting or reacting with acetylene.

12. The sensor of claim 9, further comprising a detection circuit coupled to said electrodes to identify a change in electrical properties of said sensor layer.

13. The sensor of claim 3, where the sensor layer further includes a transition metal compound selected from the group consisting of cobalt (II) chloride, zinc (II) chloride, and silver nitrate.

14. The sensor of claim 9, further comprising a semiconductor layer disposed on said substrate and said electrodes, and where said sensor layer is disposed on or in said semiconductor layer.

15. The sensor of claim 14, where the semiconductor layer is selected from the group consisting of titanium dioxide (TiO<sub>2</sub> or Ti(IV) oxide or titania), tin dioxide (SnO<sub>2</sub> or Sn(IV) oxide), zinc oxide (ZnO or Zn (II) oxide), molybdenum oxide (MoO<sub>3</sub> or Mo (VI) oxide), tungsten oxide (WO<sub>3</sub> or W(VI) oxide), Mo (VI) oxide and/or W (VI) oxide, and/or their mixtures.

16. The sensor of claim 9, further comprising a protective layer disposed on said sensor layer.

17. The sensor of claim 16, where the protective layer is a fluorinated siloxane coating.

18. The sensor of claim 9, where said substrate includes a material selected from the group consisting of alumina, quartz, magnesia, and zirconia.

19. The sensor of claim 18, further comprising a heating device in thermal communication with said substrate. 5

20. In combination:

- i. a sensor for detecting acetylene, the sensor comprising a substrate having a surface, electrodes in electrical communication with said surface, and a sensor layer including nickel (II) chloride; and 10
- ii. a power transformer.

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