

CARBON DIOXIDE SENSITIVE DIELECTRIC MATERIALS AND METHODS OF MAKING

TECHNICAL FIELD

[0001] The present invention generally relates to materials, methods and apparatuses for carbon dioxide detection, and more particularly relates to carbon dioxide sensitive dielectric materials and methods of making such materials.

BACKGROUND OF THE DISCLOSURE

[0002] Carbon dioxide detection is important for environmental monitoring, household security, medicine and food packaging. In recent years, a wide variety of sensor technologies have been developed for detecting carbon dioxide. Among these technologies, capacitive solid-state sensors are preferred due to their low cost, low power and durability. Capacitive sensors are sensors in which the capacitance of the device changes when a particular gas is absorbed into the sensitive elements.

[0003] Small size capacitive sensors which have low part per million (PPM) carbon dioxide at room temperature are commercially attractive and, thus, there is an increasing demand for new sensitive materials with high sensitivity, selectivity and reversibility at room temperature for small size low power capacitive sensors for inclusion in semiconductor integrated circuits.

[0004] Organic polymers are widely used as gas sensitive materials. Their attractiveness originates from their ability to operate at room temperature. Many efforts have been made to improve the sensitivity and selectivity of such organic polymers. For example, nanocomposites comprising polymer matrices and nanoparticles with high surface-area-to-volume ratios have been used for gas detection. Carbon nanotubes and amino functionalized carbon nanotubes have been

utilized to increase surface area and the concentration of amine groups at the surface of nanocomposites. To improve the permeability of the matrix in such nanocomposites, carbon nanotube concentrations greater than five wt% are used. However such materials become conductive with high power consumption and have poor stability, limited sensitivity and slow response time. Therefore, they are not suitable for low power consumption capacitive sensors.

[0005] Thus, what is needed is carbon dioxide sensitive materials which at least partially overcome the drawbacks of present approaches and provide suitable material for producing low power capacitive sensors. Furthermore, other desirable features and characteristics will become apparent from the subsequent detailed description and the appended claims, taken in conjunction with the accompanying drawings and this background of the disclosure.

SUMMARY

[0006] According to at least one embodiment of the present invention a carbon dioxide (CO₂) sensitive dielectric nanocomposite is provided. The CO₂ sensitive dielectric nanocomposite includes a low molecular weight organic containing a CO₂ sensitive functional group, a resin, and P-type carbon nanotubes (CNTs).

[0007] According to another embodiment of the present invention a capacitive carbon dioxide (CO₂) sensor is provided. The capacitive CO₂ sensor includes a substrate, a plurality of capacitive electrodes patterned onto the substrate, and a CO₂ sensitive dielectric nanocomposite film on the plurality of capacitive electrodes for altering a capacitance between a pair of the capacitive electrodes in response to CO₂. The CO₂ sensitive dielectric nanocomposite film includes a low molecular weight

organic containing a CO₂ sensitive functional group, a resin, and P-type carbon nanotubes (CNTs).

[0008] According to a further embodiment of the present invention a method for fabrication of a capacitive carbon dioxide (CO₂) sensor is provided. The method includes forming a carbon dioxide (CO₂) sensitive dielectric nanocomposite including dissolving a CO₂ sensitive functional group in an organic solvent to form a first solution, dispersing P-type carbon nanotubes in an organic solvent to form a second solution, mixing the first solution and the second solution to form a nanocomposite solution, and adding a resin to the nanocomposite solution. The method further includes depositing the nanocomposite solution with the resin as a nanocomposite film on a surface of the substrate with capacitive electrodes, and curing the nanocomposite film on the capacitive electrodes to form the capacitive CO₂ sensor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The accompanying figures, where like reference numerals refer to identical or functionally similar elements throughout the separate views and which together with the detailed description below are incorporated in and form part of the specification, serve to illustrate various embodiments and to explain various principles and advantages in accordance with a present embodiment.

[0010] FIG. 1, comprising FIGs. 1A and 1B, depicts illustrations of the microstructure of a nanocomposite of P-type carbon nanotubes in accordance with the present embodiment, wherein FIG. 1A depicts a top planar view of the microstructure of the nanocomposite with a low molecular weight organic containing diamine or amidine and a resin, and FIG. 1B depicts a front top left perspective enlarged view of

an area of the microstructure of the nanocomposite of FIG. 1A showing injected electrons in a carbon dioxide atmosphere.

[0011] FIG. 2 depicts a flow diagram of a fabrication process for preparing a nanocomposite of a P-type carbon nanotube and the low molecular weight organic containing diamine or amidine for forming capacitive carbon dioxide sensor in accordance with the present embodiment.

[0012] FIG. 3, comprising FIGs. 3A and 3B, depicts top planar views of capacitive sensors containing a patterned nanocomposite film on the sensor electrodes in accordance with the present embodiment, wherein FIG. 3A depicts a capacitive sensor with meandering electrodes and FIG. 3B depicts a capacitive sensor with interdigitated electrodes.

[0013] FIG. 4 depicts a graph of change of capacitance (C_p) in response to carbon dioxide in dry nitrogen gas (N_2) for (1R,2R)-(+)-1,2-diphenylethylenediamine/resin (40%/60%) at room temperature in accordance with an Example 1.

[0014] FIG. 5 depicts the chemical reaction of (1R,2R)-(+)-1,2-diphenylethylenediamine with carbon dioxide (CO_2) in accordance with the present embodiment.

[0015] FIG. 6, comprising FIGs. 6A, 6B and 6C, depicts graphs of capacitance change (C_p) in response to carbon dioxide (CO_2) in dry atmosphere for a nanocomposite of (1R,2R)-(+)-1,2-diphenylethylenediamine with 0.5 wt% P-type multi-walled carbon nanotubes (MWCNT) at room temperature in accordance with the present embodiment, wherein FIG. 6A depicts a graph of the C_p in response to the CO_2 during the first 33,000 seconds, FIG. 6B depicts a graph of the C_p in response to the CO_2 during the first 11,500 seconds and FIG. 6C depicts a graph of the C_p in response to the CO_2 between 23,500 seconds and 32,500 seconds.

[0016] FIG. 7 depicts a graph of change of capacitance (C_p) in response to carbon dioxide (CO_2) in nitrogen gas (N_2) with 25% relative humidity (RH) for the nanocomposite of (1R,2R)-(+)-1,2-diphenylethylenediamine/resin (40%/60%) with 0.5 wt% P-type MWCNT at room temperature in accordance with an Example 4.

[0017] FIG. 8 depicts a graph of change of capacitance (C_p) in response to carbon dioxide (CO_2) in dry nitrogen gas (N_2) for a nanocomposite of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene/resin (40%/60%) at room temperature in accordance with an Example 5.

[0018] FIG. 9 depicts the chemical reaction of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene with carbon dioxide (CO_2) in accordance with the present embodiment.

[0019] And FIG. 10 depicts a graph of change of capacitance (C_p) in response to carbon dioxide (CO_2) in dry nitrogen gas (N_2) for the nanocomposite of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene/resin (40%/60%) with 0.5 wt% P-type MWCNT in accordance with the present embodiment (Example 6).

[0020] Skilled artisans will appreciate that elements in the figures are illustrated for simplicity and clarity and have not necessarily been depicted to scale.

DETAILED DESCRIPTION

[0021] The following detailed description is merely exemplary in nature and is not intended to limit the invention or the application and uses of the invention. Furthermore, there is no intention to be bound by any theory presented in the preceding background of the invention or the following detailed description. It is the intent of the present embodiment to present a dielectric nanocomposite as a carbon dioxide (CO_2) sensitive material comprising P-type carbon nanotubes as filler and a mixture of a low molecular weight organic containing amidine or diamine with a resin

as a matrix, and a method for preparing the nanocomposite. In this nanocomposite, a small amount (<1 wt% of solid film) of P-type carbon nanotubes (single-walled carbon nanotubes (SWCNT) or multi-walled carbon nanotubes (MWCNT)) is homogeneously dispersed in the nanocomposite matrix.

[0022] The nanocomposite matrix is a mixture of a low molecular weight (<500 g/mol) organic containing diamine or amidine groups and an ultraviolet (UV) curable urethane acrylate resin. The sensitivity of the nanocomposite comprising the P-type carbon nanotubes and the matrix is realized with the amino and amidine groups that can react at room temperature with carbon dioxide (CO₂) in a reversible acid-base reaction and is significantly improved with the presence of the P-type carbon nanotubes.

[0023] In accordance with the present embodiment, (1R,2R)-(+)-1,2-diphenylethylenediamine and 1,5,7-Triazabicyclo[4.4.0]dec-5-ene are used as examples of the low molecular weight (<500 g/mol) organics containing diamine and amidine, respectively. The capacitive sensor with the nanocomposite in accordance with the present embodiment can detect CO₂ at room temperature with concentrations in the parts per million (ppm) range.

[0024] The CO₂ sensitive material in accordance with the present embodiment is a dielectric nanocomposite containing at least three parts (a low molecular weight organic, a resin, and P-type carbon nanotubes (CNTs)) that can be used as a sensing layer in a small size capacitive sensor for detecting CO₂. In contrast to conventional CO₂ sensitive composites wherein polymers are utilized as a matrix, in the dielectric nanocomposite in accordance with the present embodiment, a low molecular weight organic containing a CO₂ sensitive functional group (either amidine or diamine) with a molecular weight less than 500 g/mol is used. This low molecular weight organic is

stabilized with a UV curable resin. Using the low molecular weight organics instead of polymers improves sensitivity due to higher and tuneable concentrations of the functional groups. Moreover, the response of the low molecular weight organics is significantly faster than the conventional high molecular weight polymers.

[0025] Conventional nanocomposites utilize conductive CNTs or amino functionalized CNTs with concentrations higher than 5 wt% to improve the gas permeability of the polymers or increase the concentration of the amine groups. In the nanocomposite in accordance with the present embodiment, the P-type carbon nanotubes with a concentration less than 1 wt% are used to improve the sensitivity of the low molecular weight organic containing diamine or amidine groups by charge transfer and improve the basicity of the matrix. In addition, P-type CNTs may also improve the gas diffusion. Conventionally, a carbon nanotube is either used as a conductive tube or used for physically enhancing gas permeability, without the motivation to specify P-type due to the different purpose.

[0026] By introducing the P-type carbon nanotubes with a low concentration of only 0.5 wt% in the dielectric nanocomposite in accordance with the present embodiment, the CO₂ sensitivity of the resulting dielectric nanocomposite is improved by more than one hundred times (with diamine as the sensitive organic in the nanocomposite) with further improved response speed and improved stability.

[0027] Referring to FIG. 1 illustrations of the microstructure of a nanocomposite of P-type carbon nanotubes in accordance with the present embodiment are depicted. FIG. 1A depicts a top planar view 100 of the microstructure of the nanocomposite with a low molecular weight organic containing diamine or amidine and a resin and FIG. 1B depicts a front top left perspective enlarged view 150 of an area of the microstructure of the nanocomposite of FIG. 1A showing injected electrons 152 in a

carbon dioxide atmosphere. The low molecular weight organic 102 shown in FIG. 1A is diphenylethylenediamine (DPED) shown as an example. The present embodiment is related to a dielectric nanocomposite comprising P-type carbon nanotubes 104 (multi-walled or single-walled) and a mixture of a low molecular weight organic 102 containing diamine or amidine and a UV curable resin 106. The mixture is hereinafter referred to as a polymer matrix and is depicted in FIG. 1A. The polymer matrix is used as a dielectric sensitive layer for CO₂ 154 detection by means of a capacitive sensor device. A dielectric spectroscopy technique is used to determine changes in the dielectric constant of the sensitive layer due to any chemical or physical reaction with CO₂. The CO₂ sensitivity of the nanocomposite comprising P-type nanotubes and the polymer matrix in accordance with the present embodiment is realized with the diamine and amidine groups that can react with CO₂ at room temperature through a reversible acid-base reaction and is significantly improved with the presence of the P-type carbon nanotubes.

[0028] Incorporation of the P-type carbon nanotubes 104 in the matrix containing diamine or amidine significantly improves the CO₂ sensitivity. The present embodiment can utilize either single-walled or multi-walled P-type carbon nanotubes 104. Interaction of diamine and amidine with CO₂ and formation of carbamate decreases the capacitance of the nanocomposite. The absorption of the CO₂ molecules 154 into the P-type carbon nanotubes 104 injects electrons 152 into the carbon nanotubes 104 and can further decrease the capacitance of the nanocomposite. The injected electrons 152 also increase the basicity of the amidine and diamine groups which improves formation of carbamate. In addition, the carbon nanotubes 104 are not compatible with many types of polymers and polymer chains could not

bind carbon nanotube walls tightly, forming narrow gaps 156 surrounding the carbon nanotubes 104 that can facilitate gas diffusion and formation of the carbamate.

[0029] Referring to FIG. 2, a flow diagram 200 depicts a fabrication process for preparing a nanocomposite of a P-type carbon nanotube and the low molecular weight organic containing diamine or amidine for forming a capacitive carbon dioxide sensor in accordance with the present embodiment. To fabricate the nanocomposite, a solution of diamine or amidine organics (e.g., (1R,2R)-(+)-1,2-diphenylethylenediamine or 1,5,7-Triazabucyclo[4.4.0]dec-5-ene) in an organic solvent like tetrahydrofuran (THF) (0.66 g in 5 ml THF) is prepared at step 202. At step 204, 0.01g of a UV cross-linker (e.g., Irgacure 819) was added to the diamine or amidine solution. At step 206, P-type carbon nanotubes (0.5 wt% in the final solid film) were dispersed in five milliliters of THF and sonicated for six hours in an ultrasonic bath. Then, at step 208, both solutions were mixed together and, at step 210, one gram of a resin of a urethane acrylate monomer was added to the mixture. The resultant nanocomposite solution was sonicated for a further three hours. The nanocomposite solution is then deposited on metal electrodes at step 212 by aerosol spray as a film with a thickness of 2 to 25 micrometers and patterned through a shadow mask on a top surface of the prior-patterned metal electrodes. At step 212, the nanocomposite film is heated for two hours at 55°C to remove the solvent. And, finally, at step 214 the nanocomposite film on the metal electrodes is cured by exposure to UV radiation for ninety to two hundred seventy seconds to cure the nanocomposite matrix and form the capacitive CO₂ sensor.

[0030] FIG. 3, comprising FIGs. 3A and 3B, depicts top planar views 300, 350 of capacitive sensors containing a patterned nanocomposite film on the sensor electrodes in accordance with the present embodiment. The view 300 depicts a capacitive sensor

with meandering electrodes and the view 350 depicts a capacitive sensor with interdigitated electrodes. The metal electrodes 302, 304 each have a width of approximately one μm and are laterally separated by approximately one μm . In the view 300, the metal electrodes 302a, 304a are a pair of meandering electrodes, and in the view 350, the metal electrodes 302b, 304b are a pair of interdigitated electrodes.

[0031] Electrical characterization was performed on CO_2 sensitive sensors including the capacitive structure with the pair of laterally separated meandering or interdigitated electrodes 302, 304. During electrical characterization, the capacitance of the sensitive layer (C_p) was measured at different CO_2 concentrations on N_2 at various frequencies in an atmosphere controlled sensor testing chamber. The CO_2 sensitivity in ppm CO_2 concentration is defined in Equation (1).

$$\text{CO}_2 \text{ sensitivity (ppm } C_p/\text{ppm CO}_2) = \frac{\Delta C_p}{C_p(\text{at } 0\% \text{ CO}_2)} / \text{ppm CO}_2 \quad (1)$$

Cross-sensitivities to relative humidity (RH) and temperature (T) were determined by gradually changing RH and T. The RH and T cross-sensitivities were calculated based on Equations (2) and (3) below.

$$\text{RH cross-sensitivity (ppm } C_p/\% \text{RH)} = \frac{\Delta C_p}{C_p(\text{at } \% \text{RH})} / \% \text{RH} \quad (2)$$

$$\text{T cross-sensitivity (ppm } C_p/0.1^\circ \text{C)} = \frac{\Delta C_p}{C_p(\text{at } 25^\circ \text{C})} / 0.1^\circ \text{C} \quad (3)$$

Example 1

[0032] A mixture of (1R,2R)-(+)-1,2-diphenylethylenediamine and urethane acrylate monomer in a 40%/60% weight ratio (THF as the solvent and Irgacure 819 as the cross-linker) was prepared and sprayed on a substrate with the capacitive electrodes. Referring to FIG. 4, a graph 400 presents the change of capacitance (C_p)

408 plotted on a left y-axis 402 as a function of CO₂ concentration 410 plotted on a right y-axis 404 in dry N₂ for (1R,2R)-(+)-1,2-diphenylethylenediamine at 5 kHz over a time plotted on a x-axis 406. The sensing layer of this Example 1 cannot detect CO₂ in the ppm range and only responds at percentage levels of CO₂. The CO₂ sensitivity of this sample was 635 ppm Cp/% CO₂. The recovery time also was long, in the range of two to three hours.

[0033] Referring to FIG. 5, a chemical reaction of (1R,2R)-(+)-1,2-diphenylethylenediamine with CO₂ forms carbamate in accordance with the present embodiment. A change of capacitance in CO₂ sensors in accordance with the present embodiment is largely due to a configuration flip of the molecule upon reaction with CO₂ in the (1R,2R)-(+)-1,2-diphenylethylenediamine.

Example 2

[0034] A nanocomposite of (1R,2R)-(+)-1,2-diphenylethylenediamine/urethane acrylate resin (40%/60% by weight) with 0.5 wt% P-type MWCNT in accordance with the present embodiment (with THF as the solvent and Irgacure 819 as the UV cross-linker) was prepared and deposited by spray on the structure with capacitive electrodes. The thickness of the sensing layer after curing was 6 μm. FIG. 6 shows the capacitance change (Cp) as a function of CO₂ concentration in dry N₂ for the nanocomposite at 5 kHz. Clear steps are visible when the CO₂ concentration is changed in the ppm range. Referring to FIG. 6, comprising FIGs. 6A, 6B and 6C, graphs 600, 630, 660 depict change of capacitance (Cp) in response to CO₂ in dry atmosphere for the nanocomposite of (1R,2R)-(+)-1,2-diphenylethylenediamine with 0.5 wt% P-type MWCNT at room temperature in accordance with the present embodiment. The graph 600 plots time in seconds on an x-axis 602, the Cp in farads

on a left hand y-axis 604 and the CO₂ concentration in parts per million (ppm) on a right hand y-axis 606 during the first 33,000 seconds. The change of capacitance (Cp) 608 is graphed as a function of the CO₂ concentration 610 in dry N₂ for the nanocomposite at 5 kHz.

[0035] The graph 630 plots time in seconds on an x-axis 632, the Cp in farads on a left hand y-axis 634 and the CO₂ concentration in parts per million (ppm) on a right hand y-axis 636 during the first 11,500 seconds. The change of capacitance (Cp) 638 is graphed as a function of the CO₂ concentration 640 in dry N₂ for the nanocomposite at 5 kHz. And the graph 660 plots time in seconds on an x-axis 662, the Cp in farads on a left hand y-axis 664 and the CO₂ concentration in parts per million (ppm) on a right hand y-axis 666 between 23,500 seconds and 32,500 seconds. The change of capacitance (Cp) 668 is graphed as a function of the CO₂ concentration 670 in dry N₂ for the nanocomposite at 5 kHz.

[0036] Cross-sensitivity to RH and T has also been investigated in the chamber with tunable humidity and temperature. After equivalent conversion in comparison with the CO₂ sensitivity, the RH cross-sensitivity of the nanocomposite of (1R,2R)-(+)-1,2-diphenylethylenediamine/resin (40%/60% by weight) with 0.5 wt% P-type MWCNT was 445 ppm CO₂/ %RH, and T cross-sensitivity was 167 ppm CO₂/0.1°C. Both of the cross sensitivities to RH and T were greatly suppressed as compared with the counterpart composite materials without P-type nanotubes of Example 1, and were in the order of that which can be compensated for using RH and T sensors.

Example 3

[0037] A nanocomposite of (1R,2R)-(+)-1,2-diphenylethylenediamine/urethane acrylate resin (40%/60% by weight) with 1 wt% P-type MWCNT (with THF as the

solvent and Irgacure 819 as the UV cross-linker) was prepared and sprayed on the substrate with the electrodes. The thickness of the sensing layer after curing was 6 μm . A CO_2 sensitivity of 900 ppm Cp/% CO_2 was obtained for this nanocomposite.

Example 4

[0038] A nanocomposite of (1R,2R)-(+)-1,2-diphenylethylenediamine/urethane acrylate resin (40%/60% by weight) with 2 wt% P-type MWCNT (with THF as the solvent and Irgacure 819 as the UV cross-linker) was prepared and sprayed on the substrate with the electrodes. The thickness of the sensing layer after curing was 6 μm . A CO_2 sensitivity of 200 ppm Cp/% CO_2 was obtained for this nanocomposite.

[0039] Comparing Examples 4 and 3 with Example 2 shows that increasing the concentration of P-type MWCNT from 0.5 wt% to concentrations higher than 1 wt% significantly decreases the CO_2 sensitivity of the nanocomposite. A CO_2 sensitivity of 6.5 ppm Cp/ppm CO_2 was obtained for the nanocomposite of (1R,2R)-(+)-1,2-diphenylethylenediamine with 0.5 wt% P-type MWCNT. Comparing Example 2 and Example 1 shows that adding a small amount of P-type carbon nanotubes (0.5 wt%) into the (1R,2R)-(+)-1,2-diphenylethylenediamine/resin drastically improves the CO_2 sensitivity by approximately one hundred times. The recovery time is also decreased from more than two hours to just twelve minutes for this nanocomposite.

[0040] FIG. 7 depicts a graph 700 of change of capacitance (Cp) in response to carbon dioxide (CO_2) in nitrogen gas (N_2) with 25% RH for the nanocomposite of (1R,2R)-(+)-1,2-diphenylethylenediamine/resin (40%/60%) with 0.5 wt% P-type MWCNT at room temperature. The graph 700 plots time in seconds on an x-axis 702, the Cp in farads on a left hand y-axis 704, the CO_2 concentration in parts per million (ppm) on a first right hand y-axis 706 and the relative humidity (RH) in percentage

(%) on a second right hand y-axis 708 during the first 47,000 seconds. The change of capacitance (Cp) 710 is graphed as a function of the CO₂ concentration 712 in N₂ with a 25% RH 714 for the nanocomposite at 5 kHz. The CO₂ sensitivity of the nanocomposite of (1R,2R)-(+)-1,2-diphenylethylenediamine/resin (40%/60%) with 0.5 wt% P-type MWCNT was 5.4 ppm Cp/ppm CO₂ in N₂ with the 25% RH at room temperature.

Example 5

[0041] A mixture of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene and a urethane acrylate monomer in a (40%/60% by weight) (with THF as the solvent and Irgacure 819 as the UV cross-linker) was prepared. The solution was sprayed on the substrate with the electrodes and cured under ultraviolet radiation. FIG. 8 depicts a graph 800 of capacitance change (Cp) in response to carbon dioxide (CO₂) in dry nitrogen gas (N₂) for a nanocomposite of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene/resin (40%/60%) at room temperature. The graph 800 plots time in seconds on an x-axis 802, the Cp in farads on a left hand y-axis 804 and the CO₂ concentration in parts per million (ppm) on a right hand y-axis 806 between 1,900 and 10,500 seconds. The change of capacitance (Cp) 808 is graphed as a function of the CO₂ concentration 810 in dry N₂ for the nanocomposite at 5 kHz. A CO₂ sensitivity of 10.2 (ppm Cp/ppm CO₂) was obtained for the 1,5,7-Triazabicyclo[4.4.0]dec-5-ene/resin (40%/60%).

[0042] FIG. 9 depicts the chemical reaction of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene with carbon dioxide (CO₂) and the formation of carbamate in accordance with the present embodiment. The experimental testing showed the RH cross-sensitivity and T cross-sensitivity of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (40%/60%) was 3800 ppm CO₂/°RH and 892 ppm CO₂/0.1°C, respectively.

Example 6

[0043] A nanocomposite of 1,5,7-Triazabicyclo[4,4,0]dec-5-ene/urethane acrylate resin (40%/60% by weight) with 0.5 wt% P-type MWCNT in accordance with the present embodiment (with THF as the solvent and Irgacure 819 as the cross-linker) was prepared and sprayed on the substrate with the electrodes. The thickness of the sensing layer after curing was 6 μm . FIG. 10 depicts a graph 1000 of change of capacitance (C_p) in response to carbon dioxide (CO_2) in dry nitrogen gas (N_2) for the nanocomposite of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene/resin (40%/60%) with 0.5 wt% P-type MWCNT in accordance with the present embodiment. The graph 1000 plots time in seconds on an x-axis 1002, the C_p in farads on a left hand y-axis 1004 and the CO_2 concentration in parts per million (ppm) on a right hand y-axis 1006 between 1,000 and 11,000 seconds. The change of capacitance (C_p) 1008 is graphed as a function of the CO_2 concentration 1010 in dry N_2 for the nanocomposite at 5 kHz.

[0044] The nanocomposite of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene/urethane acrylate resin (40%/60% by weight) with 0.5 wt% P-type MWCNT showed CO_2 sensitivity of 25.5 ppm C_p /ppm CO_2 . Comparing Examples 5 and 6 shows that adding 0.5 wt% P-type carbon nanotubes to the 1,5,7-Triazabicyclo[4.4.,0]dec-5-ene can enhance the CO_2 sensitivity by ~ 2.5 times. RH cross-sensitivity of the nanocomposite of 1,5,7-Triazabicyclo[4.4.0]dec-5-ene with 0.5 wt% P-type MWCNT was 1200 ppm CO_2 / %RH and T cross-sensitivity of this nanocomposite was 742 ppm CO_2 /0.1°C. Comparing the cross-sensitivities in Examples 5 and 6 shows that adding the P-type MWCNT also decreases cross-sensitivity to both RH and T.

[0045] There are some other factors that affect the CO_2 sensitivity, such as the thickness of the nanocomposite film and the concentration of the low molecular

weight organic containing amidine or diamine. Table 1 summarizes the properties and sensitivities of the compositions investigated. A comparison between Example 7 and Example 1 in Table 1 shows that increasing the concentration of the low molecular weight organic increases the CO₂ sensitivity of the nanocomposite. Comparing Example 8 and Example 1 shows that increasing the thickness of the nanocomposite layer decreases the CO₂ sensitivity of the nanocomposite.

TABLE 1

Example	Organic/Resin	MWCNT (wt %)	Thickness (μ m)	ppm CO ₂ sensitivity (ppm per ppm CO ₂)
1	DPED/resin (40%/60%)	0	6	0.06
2	DPED/resin (40%/60%)	0.5	6	6.4
3	DPED/resin (40%/60%)	1	6	0.09
4	DPED/resin (40%/60%)	2	6	0.02
5	DPED/resin (40%/60%)	0.5	6	10.2
6	TBD/resin (40%/60%)	0.5	6	25.5
7	DPED/resin (20%/80%)	0.5	6	1.2
8	DPED/resin (40%/60%)	0.5	10	4.2

[0046] Thus, it can be seen that the present embodiments can provide improved carbon dioxide (CO₂) sensitive materials which at least partially overcome the drawbacks of conventional CO₂ sensitive materials and provides suitable material for low power capacitive sensors. The present embodiments provide a novel capacitive CO₂ sensor that is capable of realizing CO₂ sensing with sensitivity in the ppm range

at room temperatures. The capacitive CO₂ sensor in accordance with the present embodiments consumes low power and small size due to its capacitive operation and is compatible and scalable with low cost CMOS processes. The present embodiments also provide selectivity and stability with high sensitivity for CO₂ detection and low sensitivity to relative humidity and temperature.

[0047] Potential applications for the capacitive CO₂ sensor in accordance with the present embodiments include environmental monitoring (including air quality), determining CO₂ content of ambient air (including household, industrial and vehicle applications), applications in medicine and food industry quality control, and breathing apparatuses. While exemplary embodiments have been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should further be appreciated that the exemplary embodiments are only examples, and are not intended to limit the scope, applicability, operation, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention, it being understood that various changes may be made in the function and arrangement of steps and method of operation described in the exemplary embodiment without departing from the scope of the invention as set forth in the appended claims.

CLAIMS

What is claimed is:

1. A carbon dioxide (CO₂) sensitive dielectric nanocomposite comprising:
a low molecular weight organic containing a CO₂ sensitive functional group,
wherein the low molecular weight organic has a molecular weight less than five hundred grams per mole (<500 g/mol);
a resin; and
P-type carbon nanotubes (CNTs), wherein a concentration of the P-type carbon nanotubes in the CO₂ sensitive dielectric nanocomposite is less than 1 wt%.
2. The CO₂ sensitive dielectric nanocomposite in accordance with Claim 1 wherein the low molecular weight organic comprises amidine as the CO₂ sensitive functional group.
3. The CO₂ sensitive dielectric nanocomposite in accordance with Claim 2 wherein the CO₂ sensitive functional group comprises 1,5,7-Triazabicyclo[4.4.0]dec-5-ene.
4. The CO₂ sensitive dielectric nanocomposite in accordance with Claim 1 wherein the low molecular weight organic comprises diamine as the CO₂ sensitive functional group.

5. The CO₂ sensitive dielectric nanocomposite in accordance with Claim 4 wherein the CO₂ sensitive functional group comprises (1R,2R)-(+)-1,2-diphenylethylenediamine.

6. The CO₂ sensitive dielectric nanocomposite in accordance with Claim 1 wherein the resin comprises an ultraviolet (UV) curable urethane acrylate resin.

7. The CO₂ sensitive dielectric nanocomposite in accordance with Claim 8-1 wherein a concentration of the P-type carbon nanotubes in the CO₂ sensitive dielectric nanocomposite is 0.5 wt%.

8. The CO₂ sensitive dielectric nanocomposite in accordance with Claim 1 wherein the CO₂ sensitive dielectric nanocomposite is formed as a solid film CO₂ sensitive dielectric material.

9. A capacitive carbon dioxide (CO₂) sensor comprising:
a substrate;
a plurality of capacitive electrodes patterned onto the substrate; and
a CO₂ sensitive dielectric nanocomposite film on the plurality of capacitive electrodes for altering a capacitance between a pair of the capacitive electrodes in response to CO₂, wherein the CO₂ sensitive dielectric nanocomposite film comprises:

a low molecular weight organic containing a CO₂ sensitive functional group, wherein the low molecular weight organic has a molecular weight less than five hundred grams per mole (500 g/mol);

a resin; and

P-type carbon nanotubes (CNTs), wherein a concentration of the P-type carbon nanotubes in the CO₂ sensitive dielectric nanocomposite is less than 1 wt%.

10. The CO₂ sensor in accordance with Claim 9 wherein the pair of the plurality of capacitive electrodes comprises a pair of laterally separated capacitive electrodes.

11. The CO₂ sensor in accordance with Claim 10 wherein the pair of laterally separated capacitive electrodes comprises a pair of laterally separated meandering electrodes.

12. The CO₂ sensor in accordance with Claim 10 wherein the pair of laterally separated capacitive electrodes comprises a pair of laterally separated interdigitated electrodes.

13. The CO₂ sensor in accordance with Claim 9 wherein the CO₂ sensitive dielectric nanocomposite film comprises a CO₂ sensitive dielectric nanocomposite film with a thickness of two to twenty-five micrometers.

14. A method for fabrication of a capacitive carbon dioxide (CO₂) sensor comprising:

forming a CO₂ sensitive dielectric nanocomposite comprising:

dissolving a low molecular weight organic containing a CO₂ sensitive functional group in an organic solvent to form a first solution, wherein the low molecular weight organic has a molecular weight less than five hundred grams per mole (500 g/mol);

dispersing P-type carbon nanotubes in an organic solvent to form a second solution;

mixing the first solution and the second solution to form a nanocomposite solution; and

adding a resin to the nanocomposite solution;

depositing the nanocomposite solution with the resin as a nanocomposite film on a surface of a substrate with capacitive electrodes, wherein a concentration of the P-type carbon nanotubes in the nanocomposite film is less than 1 wt%; and

curing the nanocomposite film on the capacitive electrodes to form the capacitive CO₂ sensor.

15. The method in accordance with Claim 14 wherein the organic solvent is tetrahydrofuran (THF).

16. The method in accordance with Claim 14 wherein the step of dissolving the CO₂ sensitive functional group in the organic solvent comprises dissolving a diamine in the organic solvent

17. The method in accordance with Claim 16 wherein the step of dissolving diamine in the organic solvent comprises dissolving (1R,2R)-(+)-1.2-diphenylethylenediamine in the organic solvent.

18. The method in accordance with Claim 14 wherein the step of dissolving the low molecular weight organic containing the CO₂ sensitive functional group in the organic solvent comprises dissolving an amidine in the organic solvent.

19. The method in accordance with Claim 18 wherein the step of dissolving the amidine in the organic solvent comprises dissolving 1,5,7-Triazabucyclo[4.4.0]dec-5-ene in the organic solvent.

20. The method in accordance with Claim 14 wherein forming the CO₂ sensitive dielectric nanocomposite further comprises adding an ultraviolet (UV) cross-linker to the first solution before mixing the first solution and the second solution to form the nanocomposite solution, and wherein the step of curing the nanocomposite film comprises curing the nanocomposite film on the capacitive electrodes by UV radiation to form the capacitive CO₂ sensor.

21. The method in accordance with Claim 14 wherein the step of depositing the nanocomposite film on the surface of the capacitive electrodes comprises depositing the nanocomposite solution with the resin as a nanocomposite film with a thickness of two to twenty-five micrometers on the surface of the capacitive electrodes by an aerosol spray method.