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Research Article

SnO_2 Nanoparticle-Based Passive Capacitive Sensor for Ethylene Detection

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A passive capacitor-based ethylene sensor using SnO_2 nanoparticles is presented for the detection of ethylene gas. The nanoscale particle size (10 nm to 15 nm) and film thickness (1300 nm) of the sensing dielectric layer in the capacitor model aid in sensing ethylene at room temperature and eliminate the need for microhotplates used in existing bulk SnO_2-resistive sensors. The SnO_2-sensing layer is deposited using room temperature dip coating process on flexible polyimide substrates with copper as the top and bottom plates of the capacitor. The capacitive sensor fabricated with SnO_2 nanoparticles as the dielectric showed a total decrease in capacitance of 5 pF when ethylene gas concentration was increased from 0 to 100 ppm. A 7 pF decrease in capacitance was achieved by introducing a 10 nm layer of platinum (Pt) and palladium (Pd) alloy deposited on the SnO_2 layer. This also improved the response time by 40%, recovery time by 28%, and selectivity of the sensor to ethylene mixed in a CO_2 gas environment by 66%.

1. Introduction

In the United States, almost 23 percent wastage of fruit occurs every year in the postharvest handling [1]. Ethylene gas is the key factor for initiating the ripening process in climacteric fruits and for accelerating the aging process, thereby reducing the quality and shelf life of production during postharvest transits. Climacteric fruits, such as, apples, peaches tend to emit different concentrations of ethylene at various stages of ripening [2, 3]. Thus, by using ethylene gas sensors, the condition of the fruit can be monitored based on the concentrations of ethylene emitted.

The most common material used for sensing ethylene in the ethylene sensor is tin dioxide [4–6]. Other materials used are tungsten trioxide [7], palladium [8], platinum [9], titanium dioxide [10], and zinc oxide [11]. Most of these materials are used to model resistor-based devices, where the conductivity of these materials either increases or decreases based on the exposure to different concentrations of ethylene gas. The usual techniques followed to fabricate the sensing layer are ceramic paste [12], thick film printing [13], sol gel [6], and chemical vapor deposition [14] which requires high-temperature heating and complex material mixing techniques. Further, the ethylene detection also requires expensive and complex methods like Quantum-cascade laser [15], gas chromatography [16], photoluminescence [17], and chemiluminescence [18].

The ethylene sensor presented in this paper is a simple capacitor-based sensor fabricated and tested at room temperature. The active sensing layer is tin dioxide used as the dielectric material, fabricated at room temperature using low-cost dip coating technique or layer-by-layer (LbL) self-assembly technique [19]. These fabrication techniques that are used for coating nanolayer thickness of active layers also allow the ease of coating the sensing layer on any surface, even on surface-like plastic, flexible polyimide sheets, or paper. The coated nanoorganized-sensitive layers have thickness of ca. 1300 nm and can be further reduced down to 600 nm which is less than the traditionally used coating technologies. The SnO_2 nanoparticle used for fabrication in this work has a particle diameter of 10 to 15 nm. This nm particle size aids in enhancing the sensitivity of SnO_2 as studied by Korotcenkov [20]. The increase in grain boundary area to grain volume ratio of the SnO_2 nanoparticles,

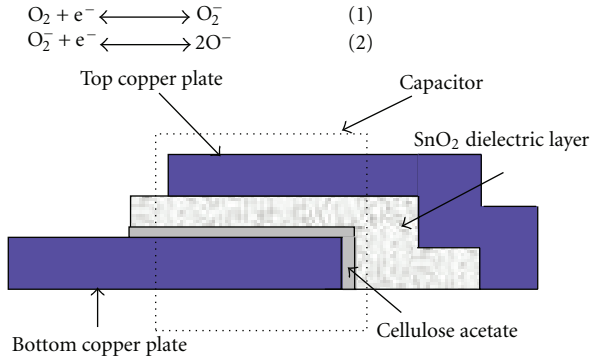

Figure 1: Model of ethylene gas sensor.

exceeding a certain threshold value, increases the sensitivity [21, 22]. In addition the adsorption of Pd and Pt ions to the SnO_2 nanoparticles reduces the threshold value thereby increasing the sensitivity as described by Straumal et al. in [22]. Moreover, the passive nature of the SnO_2 capacitive ethylene sensor aids in the integrated with a triangular microstrip patch antenna which represents a one of a kind passive wireless sensor tag used for detecting freshness of climacteric fruit [23].

2. Theory

The capacitive ethylene sensor developed has a top and bottom copper plate. Cellulose acetate is used as an insulating layer to prevent shorting of plates (see Figure 1). The sensing material is SnO_2 nanoparticles coated as the dielectric layer. In this work, the SnO_2 nanoparticles are n-type material with electrons (e^-) as the majority carriers. In air, for the nanoparticles where oxygen is absorbed, a depletion layer (depleted of e^-) consisting of O^- ionic species is formed [24]. This reaction mechanism is given by (1) and (2):

$$O_2 + e^- \longleftrightarrow O_2^-, \quad (1)$$

$$O_2^- + e^- \longleftrightarrow 2O^-. \quad (2)$$

As more oxygen is absorbed, the depletion region increases and the conduction region decreases in thickness. When ethylene is encountered, the depleted electrons are replenished back to the SnO_2 surface, thereby increasing the conduction region and reducing the depletion region (3) [6]:

$$C_2H_4 + O^- \longleftrightarrow C_2H_4O + e^-. \quad (3)$$

Figure 2 shows a schematic representation of the top view of a portion of the dielectric region containing the SnO_2 nanoparticles with depletion region and conduction region as seen through the top copper plate before and after exposure to ethylene gas. In this model, the diffusion of ethylene and air is only through the sides of the device. Moreover, complete diffusion of ethylene and air over the entire sensing dielectric region occurs in this case because of the selected size of SnO_2 nanoparticles. The change in the depletion region of the SnO_2 nanoparticles in the presence of ethylene changes the capacitance of the sensor.

Let us assume that the particles are closely packed next to each other with the nanoparticles of the bottom layer

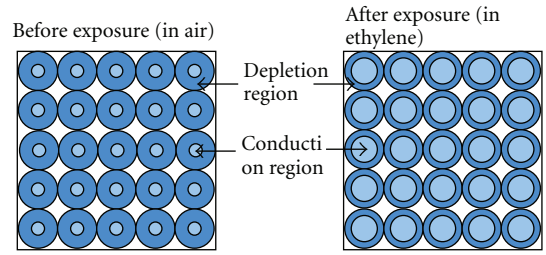

Figure 2: Top view of dielectric region with SnO_2 nanoparticles seen through the top copper plate before and after exposure to ethylene gas.

aligning vertically below the top layer of nanoparticles. Let C_B be the initial capacitance of the capacitive sensor before exposure to ethylene gas:

$$C_B = \frac{\varepsilon_0 \varepsilon_r A_1}{d}, \quad (4)$$

where, ε_0 is the permittivity of free space, ε_r is the dielectric constant of SnO_2 nanoparticles, A_1 is the area of the dielectric, that is, sum of the total depletion region of the nanoparticles and the dielectric regions between nanoparticles before exposure to ethylene gas (in air), and d is the thickness of the dielectric region. Let C_A be the capacitance of the capacitive sensor after exposure to ethylene, thus,

$$C_A = \frac{\varepsilon_0 \varepsilon_r A_2}{d}, \quad (5)$$

where, A_2 is the area of the dielectric, that is, sum of the total depletion region of the nanoparticles and the dielectric regions between nanoparticles after exposure to ethylene gas. The dielectric thickness d remains the same after exposure to ethylene gas as the changes in the depletion thickness after exposure to ethylene happen inside the nanoparticles and the overall thickness of the nanoparticles still remains the same.

As shown in Figure 2, the depletion region reduces in the presence of ethylene, which causes the plate area A_2 to decrease in value. If we assume that the depletion region reduces in thickness by about 1.5 nm, the capacitance is reduced by 5 pF, which is similar to the reduction in capacitance obtained experimentally. The use of nanoparticles increases the grain surface area to grain volume ratio. The addition of Pd/Pt layer creates a contact between the nanoparticle and the metals which induces adsorption of Pd and Pt ions to the SnO_2 nanoparticles reducing the threshold value thus increases the sensitivity of the sensor [22].

3. Fabrication

The deposition of the insulator and sensing layers of the capacitor has been done using dip coating, spin coating, and LbL nanoassembly technique. The ethylene sensor given in this paper is fabricated by dip coating technique on a flexible polyimide substrate (Pyralux FR copper-clad laminate, DuPont). The bottom plate is the copper layer of the substrate, and the top plate of the capacitor is copper of thickness 300 nm deposited by E-beam evaporation technique. The thickness of the insulator (cellulose acetate) is about 1200 nm

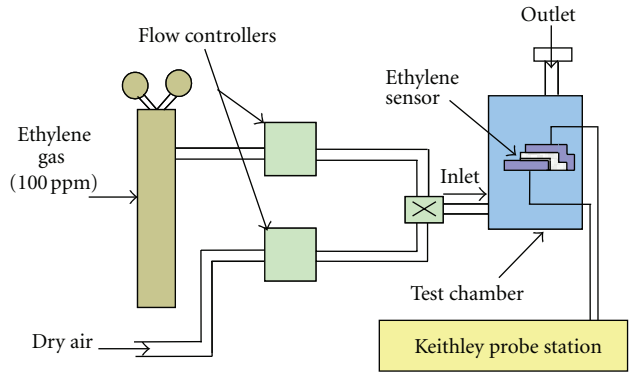

FIGURE 3: Experimental set-up for measuring ethylene sensors characteristics.

and SnO_2 coated is about 1300 nm. Initially the cellulose acetate is dip coated and dried at room temperature (in acetone solvent). The sensing layer of SnO_2 colloids (Nyacol Colloidal Tin 10 to 15 nm particle size and counter ion concentration of 0.23% NH_3) was mixed with 50%, and DI water was coated using simple dip coating technique and dried at room temperature. For uniform coating of SnO_2 and for better adherence of the sensing layer to the substrate, a very thin layer of poly(diallyldimethylammonium chloride) (PDDA) of thickness 100 nm with polycationic property was used as in LbL fabrication technique [19]. A 10 nm layer of Pd/Pt nanoparticles deposited using sputtering technique was coated on the SnO_2 sensing layer to increase sensitivity and selectivity of the ethylene sensor.

4. Results and Discussions

The SnO_2 capacitors were tested for capacitance using Keithley electrical probe station using the set-up shown in Figure 3. The ethylene gas concentration from 0 ppm to 100 ppm was used for testing purpose. Dry air was used to flush the experimental chamber to bring the sensor back to the original value. As Pt and Pd particles are known for their catalytic effect to enhance the sensitivity of SnO_2 nanoparticles to ethylene gas stimulant [4], a layer of 10 nm thickness of Pt/Pd alloy (80 : 20) was deposited by sputtering technique. Thus, two sets of sensors were developed, with and without the Pt/Pd layer. The sensor characteristics were measured and compared for both pure SnO_2 and SnO_2 with Pt/Pd layer devices (see Figure 4)

From the results obtained, it is observed that the capacitance of the sensor device decreases linearly with different concentration of ethylene. ΔC represents the amount of change in capacitance when ethylene is sensed compared to the original value of sensor capacitance in air, as given below:

$$\Delta C = C - C_0, \tag{6}$$

where, C_0 is the capacitance of the sensor in air (0 ppm) and C is the capacitance at varying ethylene gas concentrations. The negative value indicates that the capacitance decreases for an increase in ethylene concentration. From Figure 4, we can see that the overall change in capacitance of pure SnO_2 device to ethylene gas concentration from 0 to 100 ppm is

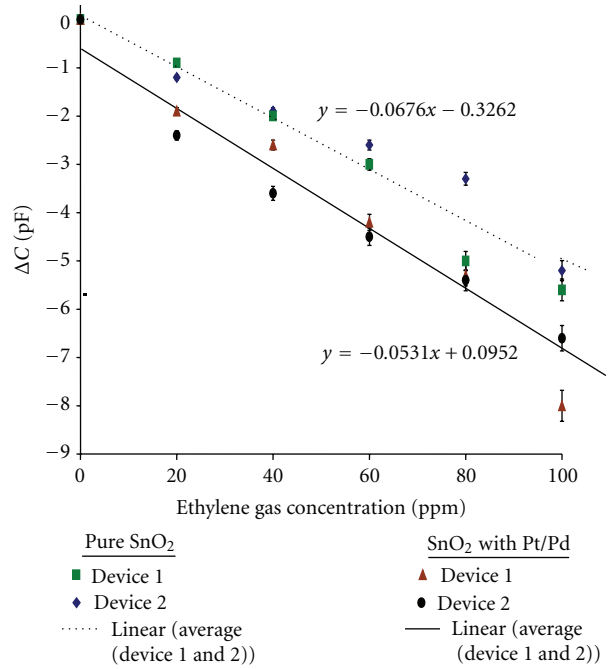

FIGURE 4: Sensitivity and reproducibility of capacitive ethylene sensor to ethylene gas.

5 pF and for SnO_2 with Pt/Pd device is 7 pF, thus showing that the Pt/Pd layer on the SnO_2 has enhanced the sensitivity of SnO_2 nanoparticles to ethylene gas by 39%. This is attributed to the absorption of Pt and Pd ions into the SnO_2 nanoparticles which reduces the threshold value as described by Straumal et al. in [22]. During measurements, it was observed that SnO_2 with Pt/Pd layer showed hysteresis similar to the hysteresis effect observed by Dennis et al. [25], the cause of which is attributed to the imbalances in the catalytic nature of Pd nanoparticles dissociating oxygen and producing O^- ions.

Figure 5 shows the degradation of the sensor over time. The same device was tested for 5 days under the same testing condition. The dotted line indicates the pure SnO_2 device and the solid line indicates the SnO_2 with Pt/Pd device, showing an overall change of 5 pF and 7.5 pF for pure SnO_2 and SnO_2 with Pt/Pd devices, respectively.

From Figure 5, it can be observed that the device with pure SnO_2 has slightly less degradation than the SnO_2 device with the Pt/Pd layer. The variations in the data points for 20 ppm and 40 ppm for the SnO_2 device with the Pt/Pd layer can be attributed to the variations in the oxygen dissociation on Pd particle surface at room temperature [26]. Oxygen dissociates into O^- ions when it encounters Pd which acts as a catalyst. This atomic oxygen spills over from the Pd to the SnO_2 surface enhancing the reaction of ethylene gas with the SnO_2 nanoparticles. The effect can be clearly observed from Figure 5, as only the first two ethylene concentrations show more variations in data values which later stabilize to more repeatable data values.

The sensor response time and recovery time are given in Figure 6. From the figure we can see that SnO_2 with the Pt/Pd layer has the faster response time of about 3 min

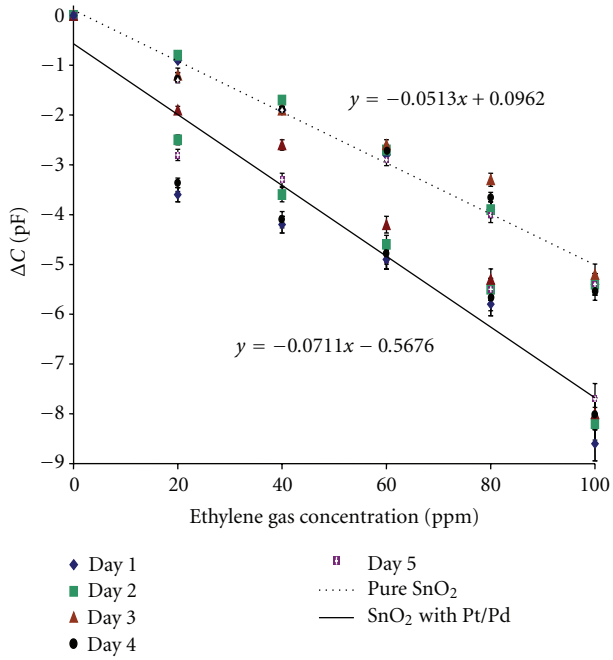

Figure 5: Degradation of ethylene sensor for varying ethylene concentrations.

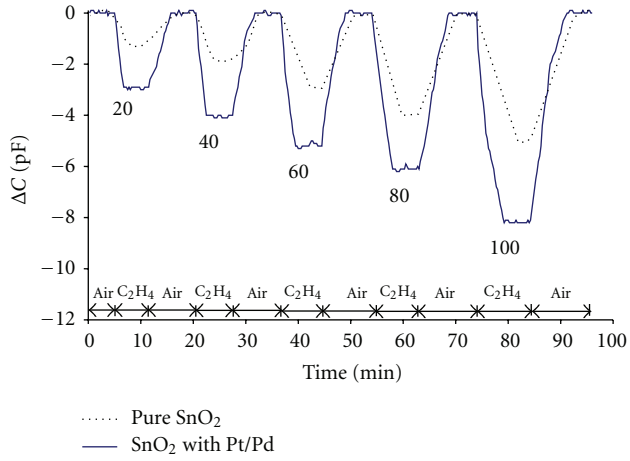

Figure 6: Response time and recovery time of pure SnO_2 and SnO_2 with Pt/Pd to ethylene concentration.

as compared to the pure SnO_2 device with 5 min response time. The recovery time for pure SnO_2 is higher at 7 min as compared to SnO_2 with the Pt/Pd layer which has a faster recovery time of 5 min. Therefore, the overall response time and recovery time are improved by 40% and 28%, respectively. The faster response time and recovery time are also attributed to the catalytic effect of platinum and palladium in SnO_2 to ethylene gas.

In this work, the developed sensor is proposed to sense ethylene emanated from fruits, which also means that it should be able to detect ethylene from among other gases present in the environment. As given in [27], carbon dioxide (CO_2) is another gas most commonly present in environments as in warehouses. CO_2 emanates from both

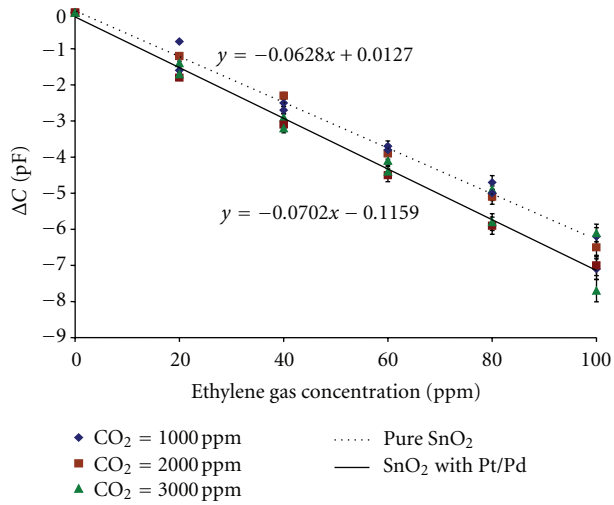

Figure 7: Sensitivity of pure SnO_2 and SnO_2 with Pt/Pd layer to ethylene gas concentration mixed with CO_2 gas.

climacteric and nonclimacteric fruits. Therefore, we have checked the sensor's sensitivity to ethylene in a carrier CO_2 gas concentration of 1000, 2000, and 3000 ppm (see Figure 7).

The capacitive sensor with pure SnO_2 dielectric layer shows an overall decrease of 6 pF in capacitance and SnO_2 with Pt/Pd shows an overall decrease of 7.2 pF for an increase in concentration of ethylene from 0 to 100 ppm. When comparing Figures 4 and 7, the overall change of pure SnO_2 has increased from 5 pF to 6 pF, whereas for SnO_2 with a Pt/Pd layer the capacitance has almost remained the same. This clearly indicates that pure SnO_2 has cross sensitivities to CO_2 gas and that the addition of Pt/Pd layer to SnO_2 has increased the sensor selectivity by 66%.

5. Conclusion

A capacitor-based ethylene sensor fabricated at room temperature with SnO_2 nanoparticles as the active dielectric layer is presented. Devices with dielectric layer as SnO_2 and SnO_2 with Pd/Pt were tested. The use of Pd/Pt nanoparticles with SnO_2 improved the sensor's sensitivity (39%), selectivity (66%), response time (40%), and recovery time (28%) when compared to pure SnO_2 devices. The proposed sensor is a low cost, passive and planar, and capacitor-based device, which make it possible to be easily integrated with passive RFID tags for wireless detection.

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