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Polymer-Amino Carbon Nanotube Nanocomposites for Surface Acoustic Wave CO_2 Detection

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Abstract. The synthesis of two new types of nanocomposite matrices, the first based on polyallylamine (PAA)and amino-carbon nanotubes (amino-CNTs), the second on polyethyleneimine (PEI) and amino-carbon nanotubes, are reported. The surface acoustic wave (SAW) sensors, coated with the two nanocomposites, showed good sensitivity when varying the CO_2 concentrations in the range (500–5000) ppm. The sensor sensitivity is larger when using polyethyleneimine amino-carbon nanotubes than in the case when only a pure polyethyleneimine layer is considered for coating. PAA-amino-CNTs films feature considerable frequency shifts under the influence of CO_2 molecules.

1. Introduction

Since CO_2 is an inert molecule, the design of a solid state room temperature sensor with sensor interface material is still a challenge for the scientific community. The researchers have been working to develop stable, reliable, and cost effective CO_2 sensors based on capacitive, electrochemical, and optical based technologies.

Recently, there has been some interest for developing gas sensors based on SAW devices. A lot of effort has been paid to develop new CO_2-sensitive coatings to be used on SAW devices. Examples of SAW devices coatings for CO_2 molecules-sensing are polymers with amino groups. Polyethyleneimine (PEI), a typical example, can sense CO_2 at room temperature. The sensitivity is high, but this material has some drawbacks: cross sensitivity (acidic gases like NO_x, SO_x also react with PEI), and hygroscopicity [1–4].

Other amino groups containing polymers which were tested for sensitive coating are: poly (3-aminopropyltrimethoxysilane-octadecyltriethoxysilane copolymer (PAPOS), polypropyleneimine (PPI), polypropyleneimine polystyrene-bound ethylenediamine (PS-EDA), aminoalkylpoly (dimethylsiloxane) (APDMS), Poly (3-aminopropyltrimethoxysilane propyltrimethoxysilane copolymer) (PAPPS). The detection limit varies between 50 and 200 ppm [5-7].

Several simple or functionalized amines were investigated as sensitive layers for CO_2 detection when using surface acoustic wave devices: 1,8 diamino-p-menthane,tetraethylenepentamine, tri-n-octylamine, 1-naphtylamine, benzylamine, dipropylamine, triethanolamine, 7,10, dioxa-3,4 diaza-1,5,12, 16, hexadecatetrol. The fundamental mechanism at work in these materials for CO_2 sensing is the interaction of amino groups with CO_2 at room temperature to form carbamates by a reversible reaction. The response of the SAW sensors coated with such materials is reproducible and fast; however, the sensitivity is small. Additionally, the cross interference with water still remains a major drawback.

In this paper, we report the synthesis of new sensing layers for CO_2 gas detection, at room temperature using SAW devices. The new sensing interface materials are prepared by forming composites of selected polymer materials with carbon nanotubes (CNTs) of improved sensitivity, repeatability, and long term stability compared to materials used so far [8–9].

2. Experimental

Nanocomposites of PEI-amino-CNTs and polyallylamine-amino-CNTs were prepared from PEI (Mw = 25 000), polyallylamine hydrochloride (Mw = 15 000), dimethylformamide, deionizated water (Aldrich) and amino-CNTs functionalized with amino groups (Nanocyl, Belgium).

The nanocomposite matrix based on PEI and amino-CNTs was synthesized according to the following procedure (see Fig. 1):

- **Step 1** – A solution of 1% PEI in dimethylformamide (DMF) was prepared;
- **Step 2** – A solution of 0.1% double wall amino-CNTs in dimethylformamide was prepared and then sonicated for six hours in an ultrasonic bath in order to disperse the bundled carbon nanotubes;
- **Step 3** – Equal volumes of each of the solutions prepared at the previous two steps were mixed and sonicated in ultrasonic bath for twelve hours.

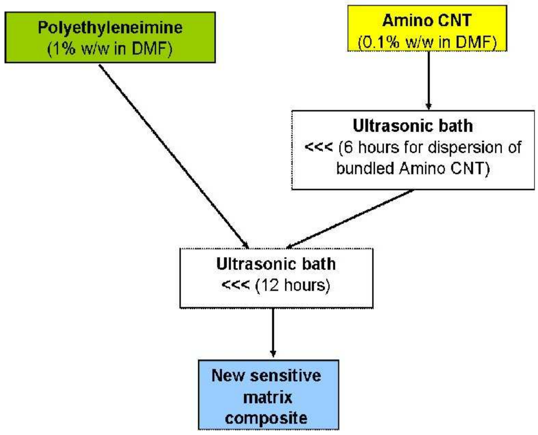

Fig. 1. Synthesis of polyethyleneimine-aminocarbon nanotubes (PEI+amino-CNTs) nanocomposite matrix.

The nanocomposite matrix based on PAA and amino-CNTs was synthesized following the next steps (see Fig. 2):

- **Step 1** – A solution of 1% PAA in water was prepared;
- **Step 2** – A solution of 0.1% double wall amino-CNTs in water was prepared and then sonicated for six hours in an ultrasonic bath in order to disperse the bundled carbon nanotubes;
- **Step 3** – Equal volumes of each of solutions prepared at the previous two steps were mixed and sonicated in ultrasonic bath for twelve hours [10].

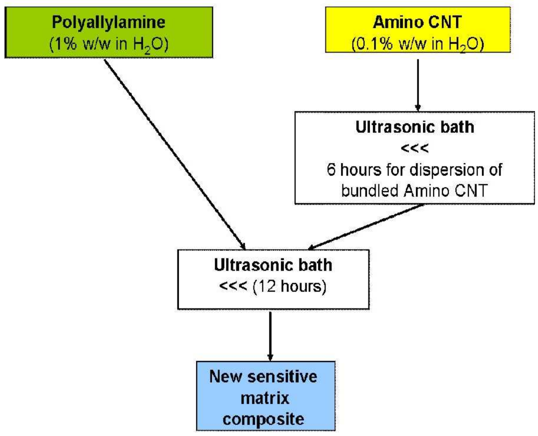

Fig. 2. Synthesis of polyallylamine aminocarbon nanotubes (PAA+amino-CNTs) nanocomposite matrix.

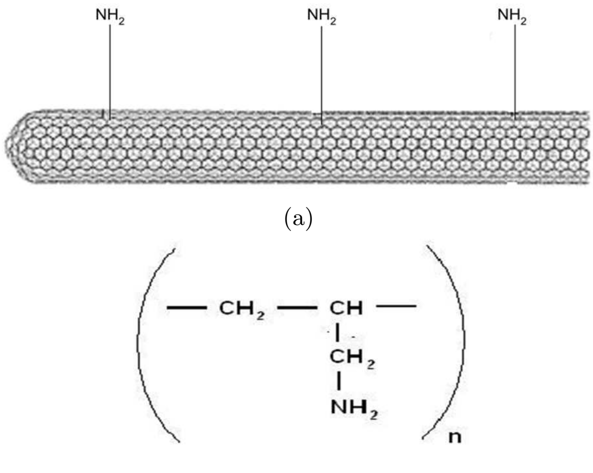

Fig. 3. Structure of amino-carbon nanotube (a) and polyallylamine (b).

Film deposition

The composites prepared (PEI+amino-CNTs and PAA+amino-CNTs) in the previous section were coated on SAW devices (see Fig. 4) using the following spin coating procedure: step 1 – 1500 rpm for 15 sec; step 2 – 3000 rpm for 60 sec; step 3 – 2000 rpm for 30 sec; step 4 – 100 rpm for 15 sec.

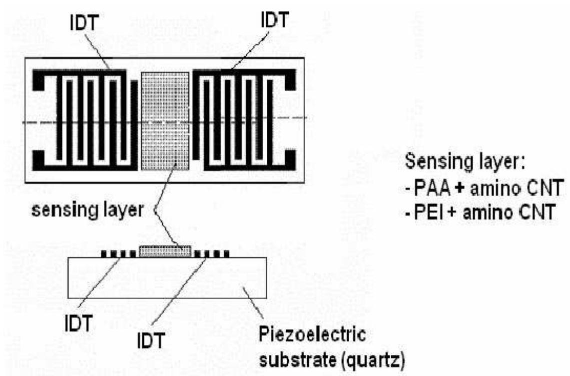

Fig. 4. SAW delay line device for CO_2 sensing.

SAW sensor test facility

The experimental set-up for carbon dioxide measurements is showed in Fig. 5. The gas sensor test facility includes a mass flow controller and an 8-channel multi-gas controller, both from MKS. When using this installation, gas flow at part per million levels can be achieved. One can carry out experiments using N_2, O_2, CO, CO_2, NH_3, SO_2, NO, NO_2 and Hydro Carbons. After mixing the required gases, a solenoid valve controls the flow of these gas mixtures to the test chamber.

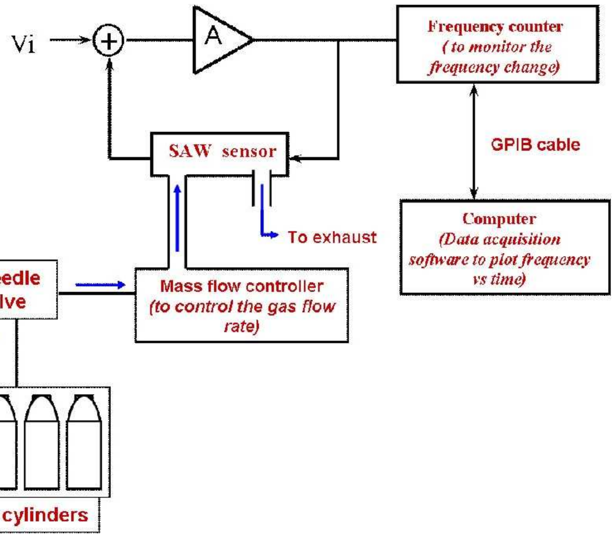

Fig. 5. The experimental set-up for CO_2 sensing measurements.

The test chamber consists of a small air tight metallic box, which can accommodate two SAW sensors, and has the option to insert the humidity sensor to monitor the relative humidity in the test chamber during experiments. The controlled flow of the gases was made through the test chamber and the data were gathered using an automatic data acquisition system.

The automatic data acquisition system comprises an oscillator circuit, a frequency counter to monitor the fundamental oscillation frequency, and a computer to acquire the frequency data from the counter using GPIB card and cable.

In order to remove the effects of humidity, the testing of the CO_2 sensitivity was carried out using dry air (80% N_2 and 20% O_2) as baseline.

3. Results and discussions

The selection of PEI and PAA for making composites with amino-CNTs was based on the Hard Soft Acid Base (HSAB) rule. According to this theory, a hard Lewis base prefers to bond to a hard Lewis acid, and a soft Lewis base prefers to bond to a soft Lewis acid [11].

Both PAA and PEI are hard bases and CO_2 is a hard acid. Thus, according to the HSAB rule, they can interact with CO_2 molecules at room temperature by means of the amino groups which exist in the backbone of each polymer (see Fig. 3). This interaction is an acid-base equilibrium, which is reversible and leads to the formation of carbamates (see Fig. 6).

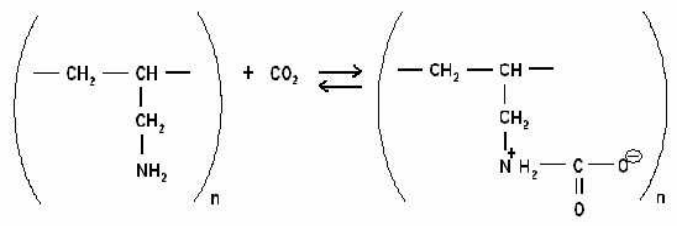

Fig. 6. Reaction of PAA with CO_2 at room temperature.

The two nanocomposites , PEI+amino-CNTs and PAA+amino-CNTs, have several advantages over simple functionalized amino groups. Though, as per the HSAB theory, the amino-CNTs are borderline bases, similar to aromatic amines, they are still able to interact with the CO_2 molecules, because the amino groups are situated at the layer surface (due to the nanometer size of carbon nanotubes). The CNTs also posses good hydrophobicity and thus can limit the cross-sensitivity due to humidity (PEI also shows good response to water molecules). Finally, the CNTs improve the mechanical properties and may increase the lifetime of the polymer due to their antioxidant character [12].

Sensitivity measurements

The CO_2 sensitivity tests have been carried out on the sensors coated with PEI-amino CNTs and PAA-amino-CNTs. Figure 7 shows the CO_2 sensitivity test for PAA-amino CNT coated sensor by varying the CO_2 gas concentration between 500 ppm and 5 000 ppm. One can see that the sensor shows sensitivities to the whole range of concentrations studied. At the same time, the frequency shift versus CO_2 concentration curve exhibits a linear trend for the PAA+amino-CNTs coated sensor, as shown in Fig. 8.

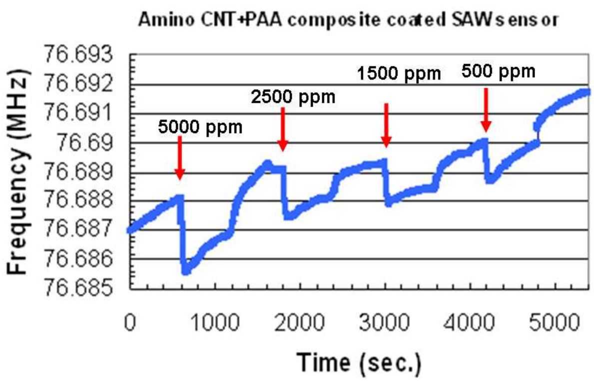

Fig. 7. The resonance frequency of the SAW device for various CO_2 concentrations (5 000, 2 500, 1 500, and 500 ppm from left to right) for the PAA composite sensor.

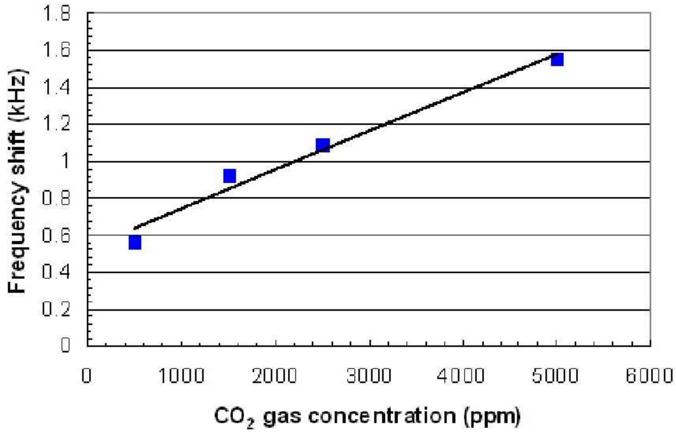

Fig. 8. The dependence of the frequency shift on the CO_2 concentration for the PAA composite sensor.

The CO_2 sensitivity test result for the PEI-amino CNTs is shown in Fig. 9. A frequency shift of 700 Hz is obtained when the PEI-amino-CNTs composite coated SAW sensor is exposed to 2 500 ppm CO_2 gas concentration, whereas, for a single layer PEI coated sensor, the equivalent values reported in literature [2, 3], are between 200 and 300 Hz. This shows that improved sensitivity can be achieved with PEI-amino-CNTs composites. The presence of amino-CNTs in the composite could be the possible reason for this higher sensitivity.

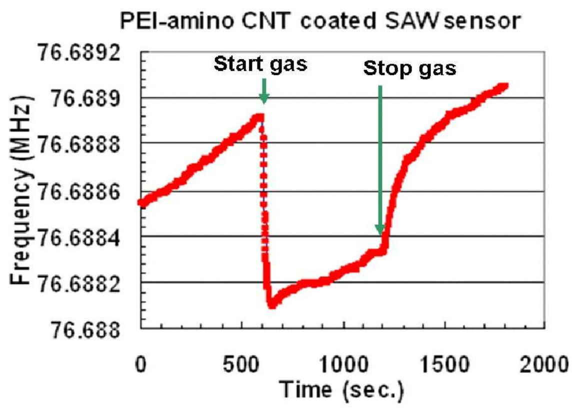

Fig. 9. Frequency variation when the PEI composite sensor is exposed to 2 500 ppm CO_2.

The amino-CNTs composite layers exhibited good uniformity, as observed from AFM topography measurements shown in Figs. 10 and 11.

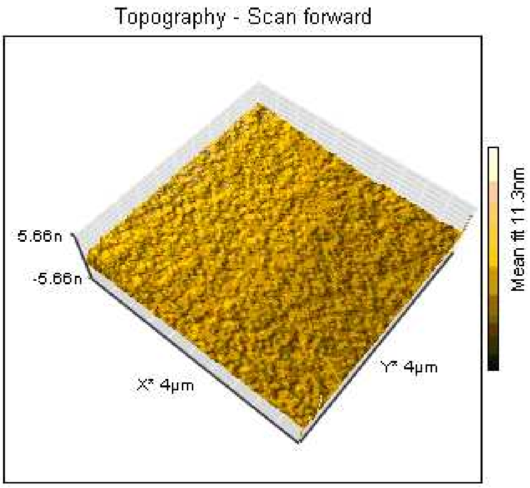

Fig. 10. AFM image of the PAA-amino-CNTs layer (40 nm thickness).

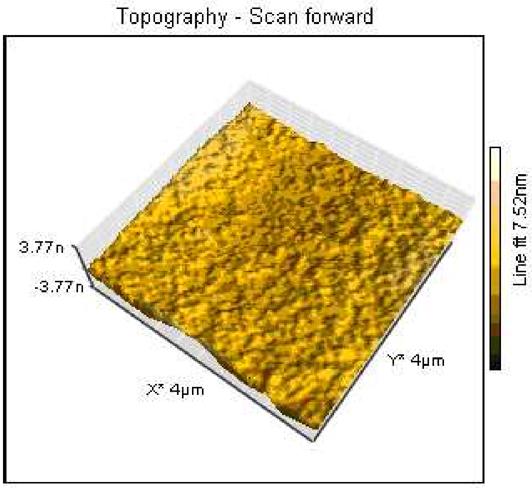

Fig. 11. AFM image of the PEI-amino-CNTs layer (35 nm thickness).

4. Conclusions

Two new nanocomposite matrices, PEI+amino-CNTs and PAA+amino-CNTs, were synthesized. PAA-amino-CNTs films featured considerable frequency shifts under the influence of CO_2 molecules. The sensitivity of PEI+amino-CNTs composite coated sensors has been found to be larger than that of single PEI layer coated sensors reported in literature. The results indicate that sensing interface materials made out of nanocomposites are potential candidates for next generation of gas sensing technologies.

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