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NEW SENSING LAYER FOR GRAVIMETRIC CARBON DIOXIDE SENSOR

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Introduction

Detection and measurement of CO₂ are crucial in many fields, such as demand control ventilation, the food industry, geological research, green chemistry, agriculture, the chemical industry, and environmental monitoring. This paper reports the design and manufacturing processes for a surface acoustic wave (SAW) CO₂ sensor, employing carbon nanohorns functionalized with amino groups (CNHs-NH₂-Fig.1a) and onion-type nanocarbon materials functionalized with amino groups (CNOs-NH₂-Fig.1b) as sensing layer, a quartz piezoelectric substrate, and interdigital transducers. The grafting of amino groups is carried out by treating nanocarbon materials in Ar-N₂-H₂ plasma. Nitriogen (N•) radical species, which functionalize carbon nanohorns and onion-like carbon nanomaterials, react with hydrogen atoms (also produced in plasma) to generate primary amino groups.



Figure 1. a) structure of CNHs-NH₂ b) structure of CNOs-NH₂

Sensor architecture

1. Nanohorn-type nanocarbon materials (40 mg), purchased from Sigma Aldrich, undergo treatment in Ar-N₂-H₂ plasma, in order to graft amino groups.

2. $CNH_{s}-NH_{2}$ or $CNO_{s}-NH_{2}$ obtained is washed with ethanol, acetone and deionized water.

3. A solution of CNHs-NH₂ (3 mg) in 30 mL dimethylformamide is prepared and subjected to ultrasound at room temperature for 12 hours.

4. The obtained solution is deposited by the spin coating method on the quartz substrate (2000 rpm, for 60 s).

5. The obtained film is subjected to heating at 100 °C for 90 minutes.

6. The obtained film is subjected to a final thermal treatment, at 200 °C, for 10 minutes

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This type of functionalization gives selectivity to nanocarbon materials for carbon dioxide detection. Optimization of the percentage of nitrogen in the functionalized nanocarbon material (in fact, the population of primary amino groups) can be achieved by varying the plasma exposure time of the nanocarbon material and changing the plasma's power and composition. The sensing structure is of the "delay line" type, with a double delay line to compensate for the thermal drift. Sensitive layers such as nanohorns functionalized with amino groups (generically denoted CNHs-NH₂, Fig.1a) and onion-type nanocarbon materials functionalized with amino groups (generically denoted CNOs-NH₂) interact with carbon dioxide molecules. The adsorption and absorption of CO₂ molecules changes the mechanical and electrical properties of the sensing layer of CNHs-NH2 or CNOs-NH2, which leads to the change of the propagation velocity and frequency of the surface acoustic wave. The degree of change in the velocity and frequency of the acoustic wave is proportional to the amount of CO₂ ad/absorbed in the functionalized nanocarbon film.

Advantages of the proposed sensing layer

The use of CNH-NH₂ as well as CNOs-NH₂ gives the sensor significant advantages:

- superior mechanical properties;
- the presence of CNHs-NH₂ and CNOs-NH₂ confers a high specific surface/volume ratio, affinity for CO₂ molecules through interactions with amino groups as well as a variation of the resistance of the sensitive layer upon contact with them ("electric loading");
- fast response of the sensor to variations in the CO₂ concentration value;
- reversibility;
- •detection at room temperature.

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