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New sensitive coating based on modified diamond nanoparticles for chemical SAW sensors

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ABSTRACT

A growing interest in diamond materials has been shown in the recent year for the design of smart chemical and biochemical sensors due to the remarkable physical and chemical properties of diamond. In this paper, modified diamond nanoparticles (DNPs) coatings are investigated as sensitive layers on surface acoustic wave sensor (SAW sensor) for the detection of volatile chemicals. DNPs are deposited onto SAW transducers by a layer-by-layer deposition method and then surface treated to fix them on the substrate and to enhance their affinity to specific compounds such as nitro-aromatic compounds, nerve-agent stimulants, or toxic gases. Homogeneous and reproducible coatings were achieved. The diamond coatings' surface was either oxidised or reduced to see the effect on the response to ammonia gas, ethanol, DNT or DMMP vapours exposures. The sensors were generally very sensitive to the target chemicals and the response fully reversible. Oxidation of the surface promoted hydrogen-bond formation and therefore enhanced the response to most vapours under test. Even though the sensors were not very selective, we demonstrated the suitability of DNP coatings as stable and reliable sensing interface. This opens up wide opportunities for immobilizing more selective and highly sensitive chemical/biochemical receptors onto SAW transducer surfaces via strong covalent binding of those receptors on diamond nanoparticles deposited homogeneously on the SAW sensors surfaces.

1. Introduction

SAW sensors are promising for the detection of toxic volatile chemicals due to their extremely high sensitivity. Indeed, the success of this technology has been recently demonstrated by the arrival of handheld portable warfare agents detectors based on the SAW sensors on the market [1]. Nevertheless the sensitive coating deposited on such transducers is generally a limiting element in terms of selectivity, but also strongly in terms of sensor to sensor repeatability, reliability and long term stability. Indeed in most cases the sensitive coatings are based on polymers that are generally difficult to deposit homogeneously onto the transducer surface [2]. A strict control of the thickness, uniformity, viscosity and film adherence of the coating is necessary in order to obtain reliable performances. However, the deposition methods that may potentially satisfy these conditions are limited to some polymer/surface systems with specific properties [3,4]. Moreover, the common techniques employed with a majority of polymers, such as spin coating, dip coating or spray coating, do not enable sufficient uniformity of the sensitive layers especially on such small substrates. Indeed, the defects generated from such deposition methods are known to degrade the performances of the sensors [5]. Finally, the response signal of SAW sensors coated with polymers may also include a large contribution from swelling induced modulus changes in the film due to vapour sorption [4]. Other types of coatings have been considered, such as carbon nanotubes [6] or more recently graphene sheets [7] but they also suffer from the lack of reproducibility and the difficulty to deposit uniform coatings of such materials onto the transducer surfaces.

In this context, we consider here modified diamond nanoparticles (DNPs) as an alternative sensitive coating that could solve some of the issues encountered with other known sensitive coatings. Indeed, DNPs may be found in nanometer sizes and can be deposited as single or multiple layers on a variety of sensor surfaces with uniform thicknesses and high surface area, which is in favour of high sensitivity. DNPs feature also other attractive properties for chemical detection: on the one hand they are mostly made of sp3 carbon which is very stable in time; it is intrinsically inert hence it can be considered as a stable sensor platform onto which specific receptors are immobilized. On the other hand the carbon terminated surface of diamond offers wide perspectives from organic chemistry and biochemistry for strong attachment of specific receptors on the diamond surface via covalent bonding [8–12]. Those receptors will be chosen for their high affinity with the target species that need to be detected. The sensor response will then be either reversible or non-reversible depending on the

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type of interactions between the receptor molecule and the target analyte.

In this paper, we show that DNPs coatings can be deposited uniformly and reproducibly over acoustic wave sensor surfaces and that they are suitable for gas or VOC detection. We also demonstrate that DNPs exhibit very interesting surface properties that can largely be exploited to tune the sensitivity and or selectivity of the sensors to target chemical vapours.

2. Experimental

2.1. Materials and apparatus

The DNP used is the Syndia® SYP 0-0.02 supplied by Van Moppes, Switzerland. It is made from high pressure high temperature (HPHT) synthetic diamond and has a mean particle size of 30 nm. Poly(diallyldimethyl-ammonium chloride) (PDDAC) solution, dimethylmethylphosphonate (DMMP, 97%), 2.4-dinitrotoluene (DNT, 97%) and ethanol were purchased from Aldrich, France and used without further purification. Ammonia vapour was obtained from a gas cylinder calibrated at 30.0 ± 0.6 ppmv.

The Microwave Plasma Chemical Vapour Deposition (MPCVD) reactor used is a home-made reactor dedicated to synthetic diamond growth and equipped with a 2.45 GHz–2 kW Sairem microwave generator. It is a full metal double wall reactor, similar to the Astex PDS system. The temperature of SAW transducers placed in the MPCVD reactor was controlled using a Modline 3 Ircon optical pyrometer.

The SAW transducers were purchased from Forschungszentrum Karlsruhe and consist of 433 MHz quartz resonators with gold IDT electrodes (IterDigital Transducers). Gas sensing measurements were performed using the SAGAS instrument developed by Forschungszentrum Karlsruhe [13,14]. This instrument allows data acquisition from eight sensors simultaneously.

Images of the coated surfaces were obtained using an optical microscope and a Field Emission Gun Scanning Electron Microscope (Hitachi S-4500 FEG-SEM).

2.2. Diamond nanoparticles coatings

The DNP were initially dispersed in pure water using intense ultrasonic treatment for 2 h to make a colloidal solution of concentration 0.1% wt/wt. The HPHT nanoparticles have a zeta potential of typically −40 mV when dispersed in water [15]. This negative charge is attributed to carboxylic acid groups present at the diamond surface. Indeed FTIR analysis indicates the presence of carboxylic acid and acid anhydride groups with a broad band centred at 1775 cm^{-1} (C=O stretching bond). This is confirmed by Refs. [16,17]. Thus, using this property of the nanoparticles, it was possible to deposit the DNP onto the SAW sensors surfaces using a layer-by-layer deposition method as reported in the literature [15,18].

In brief, the principle consists of attracting electrostatically the negatively charged HPHT nanoparticles onto a substrate coated with the cationic polymer PDDAC [15,18]. Prior to DNP coating, the SAW transducers were individually washed thoroughly in acetone, iso-propanol, and deionised water for several times. Finally the SAW sensors were rinsed with deionised water and dried under nitrogen flow. Then each SAW sensor was dipped into the PDDAC polymer aqueous solution (stock solution diluted by 10 in deionised water) for 5 min. The SAW sensors were subsequently rinsed with deionised water and dried under nitrogen flow. It has been demonstrated in Ref. [15] by ATR-FTIR analysis that this process leaves a thin polymer film on the substrate despite its solubility in water. Then the SAW sensors were immersed into the DNP colloidal solution for another 5 min and finally rinsed with deionised water and dried under nitrogen flow. Unless specified, this procedure was repeated three times in order to obtain three quasi monolayers of nanoparticles onto the surface. Finally, the SAW sensors were washed with deionised water and dried under gentle nitrogen flow.

After the DNP coating step, the substrates were exposed to CH_4/H_2 plasma in the Microwave Plasma Chemical Vapour Deposition (MPCVD) reactor. The CVD diamond growth reactor parameters were set to a pressure of 20 mbar, a CH_4/H_2 ratio of 1/99, and a microwave power adjusted to 500 W in order to reach a maximum temperature of 490 °C as measured in situ using the optical pyrometer. A short plasma exposure (typically 3 min) was sufficient to burn off the polymer and clean up the DNP surface, while longer plasma exposures of typically 45 min resulted in a slight growth of the DNP into a quasi-coalescent diamond film. During plasma exposure the experimental conditions were kept so that the Curie temperature of the piezoelectric quartz making the transducer is not reached, to avoid losing the piezoelectric characteristics of the substrate. Also, adding too much mass load on the transducer as well as reducing the porosity and hence the specific surface area of the diamond layer would lead to a decrease in the resulting sensor sensitivity.

2.3. DNP coatings post-treatments

For experimental purpose, two sets of DNP coatings were surface treated differently in order to study their sensing behaviour while being exposed to different chemical vapours of interest. The first set of coatings was exposed to a hydrogen plasma for 30 min in the CVD reactor (experimental conditions: 100% H_2, 20 mbar, microwave power adjusted to 500 W and maximum temperature at 490 °C). This was expected to reduce the DNP surface to a fully hydrogenated surface (mainly C–H bonds in surface) [19]. The second set of sensors underwent the same treatment but then the sensors were dipped into a solution of 30% hydrogen peroxide in water while being at the same time insolated by UV lamp (Mercury Lamp HBO 200 W, 4 A, at 258 nm: 0.3 mW cm^{-2}) for 3 h in order to initiate photo-oxidation of the surface. This is expected to oxidise the diamond surface with for instance hydroxyl groups.

2.4. Gas sensors characterization

The experimental gas rig used for the characterisation of the modified DNP coated SAW sensors is depicted in Fig. 1. The sensors were tested against different vapours generated either from diffusion (DNT), or permeation tubes (DMMP, ethanol) placed in a permeation oven (Calibrage, France) under flow and temperature control. The home-made permeation tubes consisted of Teflon-PFA tubes sealed at both ends using stainless steel beads. The diffusion tubes were purchased from Calibrage, France. The vapour sources were calibrated gravimetrically after a five days stabilisation period in the permeation ovens by weighting the mass loss of the permeation or diffusion tube every four days, using a micro-scale with 0.001 mg readability (Mettler Toledo MX5) over a period of 20 days. Table 1 summarises the mean diffusion or permeation rates obtained for DNT, DMMP and ethanol during the calibration. The temperature within the gas cell containing the sensors was measured by using a thermocouple when cycling between clean nitrogen and contaminated nitrogen passing through the permeation ovens. No significant temperature variation was measured. Nevertheless, to avoid eventual significant temperature variation of the sensors within the gas cell, the temperature of the sensors was kept constant at 23.4 °C using a Peltier element located underneath the sensors. Ammonia vapour at 30 ppmv was obtained from a gas cylinder. The use of computer-controlled mass flow valves