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Modified diamond nanoparticles as sensitive coatings for chemical SAW sensors

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Abstract

Modified diamond nanoparticles (DNP) are investigated as sensitive coatings for use with Surface Acoustic Wave (SAW) transducers. DNP were surface treated (e.g. hydroxylation, hydrogenation) to enhance their affinity to specific compounds such as nitro-aromatic compounds, nerve-agent stimulant, or toxic gases. They were deposited onto SAW transducers by a layer-by-layer deposition method to assess their performances for chemical vapor sensing. The DNP coated sensors were tested towards dinitrotoluene (DNT), dimethylmethylphosphonate (DMMP), ammonia (NH_3) and relative humidity (RH). The sensors showed high sensitivity to the target compounds, good repeatability and low detection limit at sub-ppm levels, at room temperature.

Keyword : Functionalised diamond nano-particles, SAW chemical sensors, gas detection

1. Introduction

SAW sensors are promising for the detection of toxic chemicals due to their extremely high sensitivity. Nevertheless the sensitive coating deposited on such transducers is a limiting element. Indeed in most cases the sensitive coatings are based on polymers that are generally difficult to deposit homogeneously onto the transducer's surface [1]. The use of these transducers requires a strict control of the coatings' properties in terms of thickness, uniformity, viscosity and film adherence 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 [2, 3]. Moreover, the common techniques employed with a majority of polymers, such as spin coating, do not enable sufficient uniformity of the sensitive layers especially on such small substrates. Indeed, the defects observed on films deposited in such a way are well-known to degrade the performances of the sensors [4]. Finally, the response signal of SAW sensors coated with polymers may also include a large contribution from modulus decreases in the film due to vapour sorption (swelling induced modulus change) [3].

In this context, it is though that modified DNP could solve some of the issues encountered with other common sensitive coatings such as polymers. Indeed, DNP can be deposited homogeneously as thin films. Also diamond features attractive properties for chemical detection: on the one hand it is chemically inert so it is considered as a stable sensor platform, and on the other hand it's carbon terminated surface offers wide perspectives from organic chemistry and biochemistry for covalent attachment of specific receptors. Finally it is expected to be less subject to swelling than polymer films.

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2. Experimental

2.1. Diamond nanoparticles coatings

DNP were produced by High Pressure High Temperature HPHT synthesis and have a particle size ranging from 10 to 20 nm. They were dispersed in pure water by intense ultrasonic treatment to make a colloidal solution of concentration 0.1% wt/wt. The DNP coating was carried out by a layer-by-layer deposition method [6]. The method proved itself to be very reproducible and homogeneous and controllable DNP coatings are formed in this way independently of the substrate's nature and shape. After the DNP coating, the substrates were exposed shortly to H_2/CH_4 plasma in a Microwave Plasma Chemical Vapor Deposition (MPCVD) reactor to burn off the polymer, clean up the DNP surface. When plasma exposure was carried out for longer time, this had for effect to slightly grow the DNP into a quasi-coalescent diamond film. The qualities of the coatings were assessed by SEM imaging. Surface treatment of the DNP was carried out either by H_2 plasma exposure (hydrogenation or "treated-H_2") in the CVD reactor or by insolating them by UV (Mercury Lamp HBO 200 watts, 4A, at 258nm: 0.3mw/cm^2)in a solution of H_2O_2 (hydroxylation or "treated-OH").

2.2. Measuring setup and characterization

The SAW transducers were purchased from Forchungszentrum Karlsruhe and consist of 433MHz quartz resonators with gold IDE electrodes. Gas sensing measurements were performed using the SAGA instrument developed by Forchungszentrum Karlsruhe [5]. This instrument allows data to be acquired from eight sensors simultaneously. The modified DNP coated SAW sensors were tested against different vapours generated from diffusion or permeation tubes placed in a permeation oven under flow and temperature control. Dry nitrogen was used as reference gas and carrier gas to transport the single chemical substances (either DNT, DMMP, NH_3 or relative humidity) through the gas cell containing the sensors. The total flow rate above the sensors was kept constant at 100 sccm using mass flow controllers and the experiments were carried out at room temperature. The test gas or organic vapours concentrations were 25–100ppbv, 1ppmv and 30 ppmv for DNT, DMMP and NH_3 respectively. For all tests a raw SAW transducer was used for reference measurements. Exposures to 50% relative humidity were performed in order to assess the sensitivity of moisture at a typical environmental concentration. Additionally the resonators operating frequencies before or after DNP deposition were verified using a networks analyzer (Rohde and Schwarz® ZVB20).

3. Results and discussion

Figure 1 shows images of a SAW sensor taken before and after DNP coating. Homogeneity and reproducibility were confirmed both by optical microscopy and SEM imaging. Also the frequency shift due to DNP deposition was measured by the network analyzer and revealed less than 1% difference in Δf from sensor to sensor.

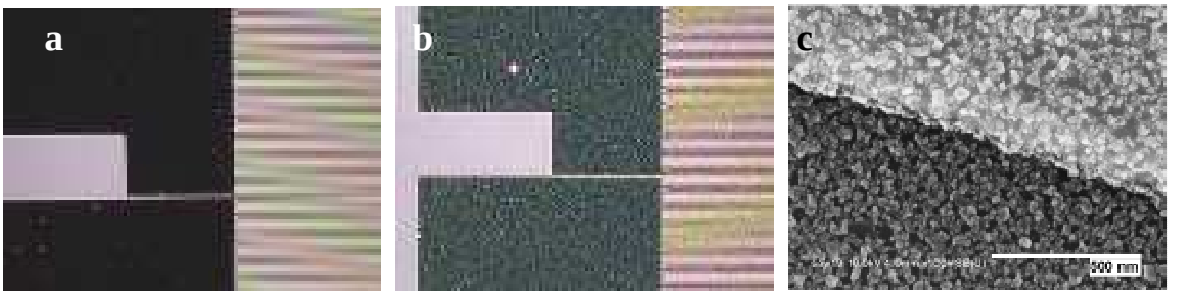

Fig. 1. (a) optical image X10 of raw SAW; (b) optical image X10 of SAW with DNP coating; (c) SEM image of SAWwith DNP coating

After deposition of the nano-particles on the SAW, a shift towards lower frequencies is observed that corresponds to mass loading. Then, after significant diamond growth, a larger shift towards higher frequencies is observed (Fig. 2) that is probably due to the acoustic wave being coupled to the diamond layer where it travels faster. When the sensors are exposed to gases or organic vapours, a negative frequency shift is measured that corresponds mainly to mass loading. Since diamond is very dense, we believe that absorption does not occur and viscoelastic effects are negligible. Note that during NH_3 exposures a positive frequency shift is observed which suggests that mass loading is not predominant in the sensing mechanism in contrary to eg. ethanol (Fig.3). The reason for the positive shift in this particular case remains unclear. For clarity reasons, the transient responses below are all plotted in absolute value.

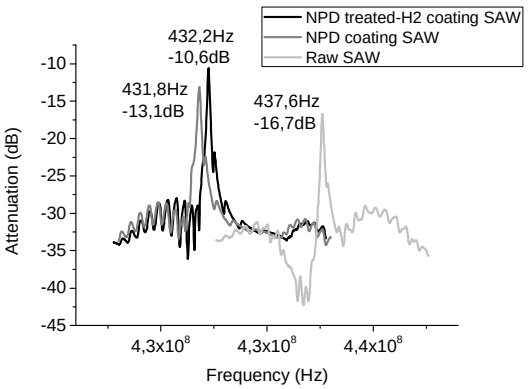

Fig. 2 Frequency response of raw SAW transducer (black curve), after DNP coating (dark gray curve) and after DNP coalescence (light gray curve)

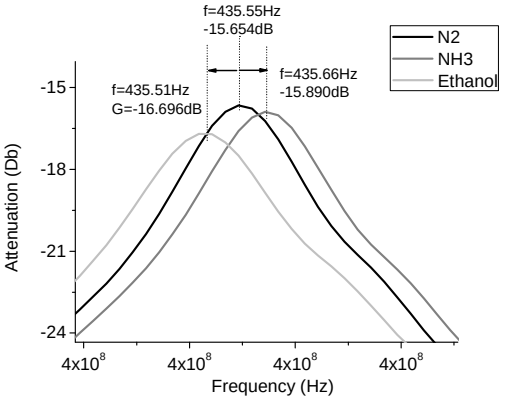

Fig. 3 Frequency response of hydroxylated DNP coated SAW sensors to N_2, NH_3 and ethanol exposures

Figure 4 shows the typical response of two hydrogenated DNP coated sensors as well as of a raw transducer to four successive exposures to 100ppbv DNT. The DNP modified transducer is very sensitive to DNT (80Hz/ppbv) with sensitivity approximately 20 times higher than the raw transducer. The sensing mechanism is certainly driven by hydrogen bond formation between the diamond surface and the DNT nitro groups. Note that the significant sensitivity of the raw transducer is due to non-specific adsorption of the target compounds directly onto the transducer's surface.

Figure 5 shows the response of two hydrogenated DNP coated transducers and of a raw transducer to four successive exposures to 0.2 ppmv and 0.5 ppmv DMMP, respectively. A good sensitivity of the DNP coated sensors towards DMMP is observed with a typical value of 4Hz/ppbv. Nevertheless the sensitivity of the raw sensor is also fairly high (1Hz/ppbv) which may be due to the high affinity of DMMP with the gold layer constituting the transducers IDEs.

The sensitivity of a hydrogenated DNT coated SAW to 30ppmv NH_3 gas was found to be in the order of 70Hz/ppmv. Figure 6 shows that after hydroxylation of the DNP surfaces the sensitivity is increased by typically a 6 fold (430Hz/ppmv).

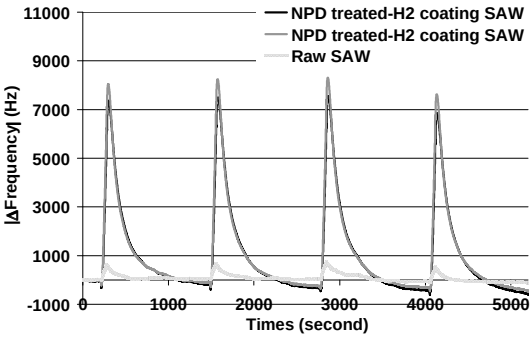

Fig. 4 Transient responses of DNP coated SAW sensors and raw transducer tocyclic exposures to 100ppbv of DNT.

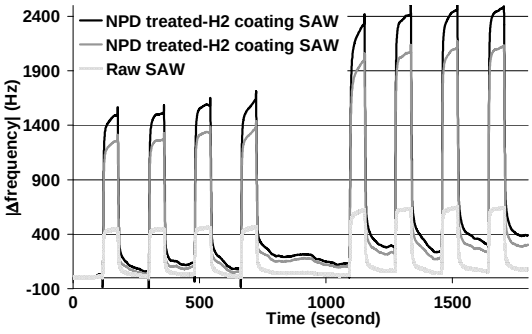

Fig. 5 Transient responses of DNP coated SAW sensors and raw transducer of cyclic exposures to 0.2ppmv then 0.5ppmv DMMP.

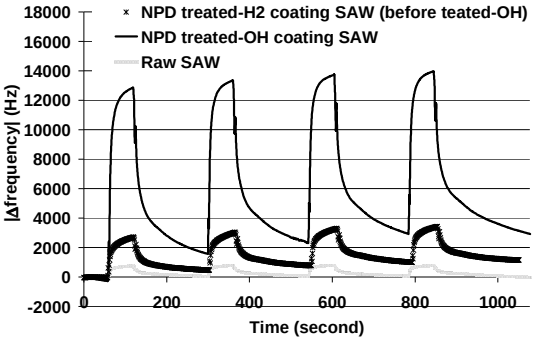

Fig. 6 Transient responses of SAW sensors coated by DNP treated-OH and raw SAW of cyclic exposures of NH_3 at 30ppmv.

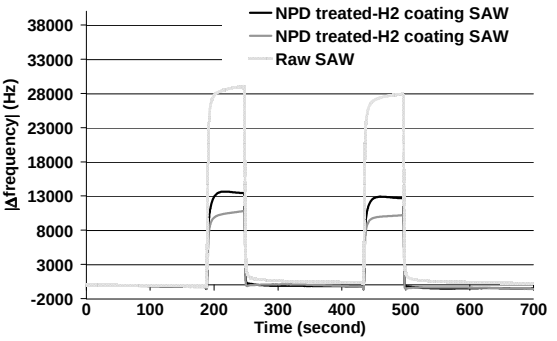

Fig. 7 Transient responses of SAW sensors coated by DNP treated-OH (black and gray curves) and raw SAW (clear gray curve) to cyclic exposures of 0 and 50%RH

Interestingly, the hydrogenated DNP coated sensors are typically three times less sensitive to the moisture variations from 0 to 50%RH than a raw sensor (Fig.7). Further measurements are in progress in order to study the effect of humidity fluctuation in environmental conditions on the sensors' response to target gases.

4. Conclusion

A new sensitive coating for use with Surface Acoustic Wave transducers (SAW) sensors based on treated diamond nano particles was studied. A process was developed that enables deposition of very uniform such sensing layers onto the SAW transducers. This uniformity is crucial for the reliability and reproducibility of SAW chemical sensors. The resulting sensors were investigated for the detection of DNT, DMMP, NH_3 gases and relative humidity at room temperature. The sensitivity of the sensors with hydrogenated diamond layers was found to be 80Hz/ppbv for DNT, 4Hz/ppbv for DMMP and 70Hz/ppmv for NH_3. The sensitivity to NH_3 was improved considerably when the diamond layer was hydroxylated. The response to all target gases was fully reversible. Future work will focus on the specificity of the responses to target gases by grafting chemical or biological receptors onto the diamond surface. Indeed, the carbon terminated surface of diamond is particularly suitable for stable covalent bonding of a wide variety of organic receptors.

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