



Detection of random vapour concentrations using an integrating diamond gas sensor



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ABSTRACT

Hydrogenated diamond (HD) gas sensors feature an integrator-like response which occurs at room temperature and which is mediated by a thin layer of adsorbed water on the HD surface. In the present work a HD gas sensor had been exposed to randomly varying acid vapour concentrations to assess its potential in a practical gas monitoring situation. Our results demonstrate that the time-differentiated sensor output signal yields a detailed temporal image of the random vapour pulses with a time resolution in the order of 1 s. In contrast, the sensor signal itself provides a measure of the total vapour concentration that had been interacting with the HD sensor surface up to the point of sensor interrogation. Large accumulated vapour concentrations lead to sensor saturation. It is further demonstrated that saturated HD sensors can be repeatedly reset into a reproducible initial condition, simply by replacing the contaminated water adsorbate layer by a fresh one.

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1. Introduction

Water vapour is normally considered a nuisance when it comes to the detection of trace impurity gases using heated semiconductor gas sensors [1,2]. The reason is that water vapour can occur in high and highly variable quantities and that this vapour often produces sensor signals which are comparable in size or even larger than those produced by the trace impurity gases of main interest [3].

A fact that is not very well recognized is that water vapour, unlike most other gases of interest, has an abnormally high boiling point (100 °C), which means that on unheated or moderately heated sensor substrates water vapour will undergo multi-layer BET adsorption – even under conditions of low ambient humidity [4]. A second interesting point is that, once formed, such BET adsorbates are able to perform as sensing layers for reactive gases themselves. The sensor signal that is produced in this case are those changes in electrolytic conductivity which occur upon absorption of reactive gases such as NO₂ or NH₃, which may abound in the ambient air. The downside of such BET sensing layers is that they exhibit poor transport properties, i.e. a relatively low electrical conductivity and comparatively high noise levels [5]. Sensors with much more attractive chemical-to-electrical transducer properties can be obtained, in case the BET layers are adsorbed on

semiconductor substrates with high carrier mobility. In this latter case the semiconductor substrates may perform as high-quality electrical transducers which sense the pH value in the liquid adsorbate layer, which in turn depends on the reactive gas concentration in the ambient air [4,6,7].

A particularly well-documented example of this latter kind of sensor is gas sensors based on hydrogenated diamond (HD) specimens. Such sensors are known to feature a gas response which occurs at room temperature and which is mediated by a thin layer of adsorbed water which tends to accumulate on HD surfaces as these are exposed to normal atmospheric conditions [6–16]. This previous work has shown that HD sensors sensitively respond to all kinds of acid- or base-forming gases, rejecting at the same time many combustible gases that form huge sensor signals on conventional heated metal oxide (MOX) gas sensors [4,6,7]. Besides being sensitive and enabling room temperature operation, HD gas sensors therefore also feature a relatively high degree of selectivity with regard to an interesting group of analytes. Another attractive property of HD sensors is that these possess a water-saturated surface largely independent on the humidity level in the ambient air, which means that these do not respond to meteorological changes in the water vapour pressure [4,7].

More recent work has shown that diamond crystals with a pure H-termination feature a novel kind of accumulating gas response, which under favourable conditions can come close to an integrator-type behaviour [17]. In this integrator-limit of operation, the HD gas response becomes proportional to the total flow of reactive gases

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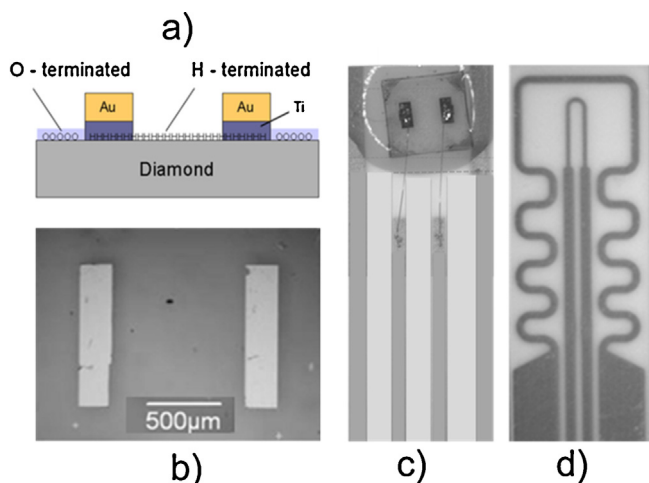


Fig. 1. (a) Cross section through the sensor chip distinguishing H- and O-terminated surface areas; (b) top view onto the diamond sensor chip; (c) sensor chip as mounted on a heatable ceramic substrate; (d) back surface of the ceramic heater substrate featuring a Pt heater meander and a Pt temperature sensor.

that had been interacting with the water adsorbate layer on top of the HD sensors. Under certain conditions, HD gas sensors therefore perform as gas dosimeters, which represent a novel class of gas sensors [18,19].

The present paper is concerned with an experimental assessment of such integrator-type gas sensors in a practical vapour monitoring application. Performing experiments in a laboratory environment, the integrator performance of HD gas sensors is demonstrated and a method of sensor reset is devised that allows saturated HD sensors to be reset into a reproducible initial condition to enable a new measurement run. Section 2 presents some background on diamond gas sensors which helps to acquaint the reader with this innovative kind of sensors. Section 3 firstly presents the results of gas exposure tests which demonstrate the dosimeter-type response of HD gas sensors and it secondly demonstrates a method of sensor reset which allows HD sensors to be reset into a reproducible initial state after a series of measurements had been performed and after sensor saturation has occurred. Section 4, finally, presents the results of field tests, in which freshly reset HD sensors have been exposed to random acid vapour pulses in an open-air environment. These latter measurements demonstrate the sensitivity and the rapid response of the HD gas sensors. Section 5 concludes the paper with a short summary and the main conclusions of our work.

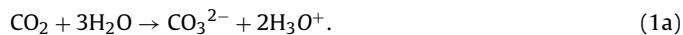
2. Diamond gas sensors and detection mechanisms

The kind of sensors investigated is displayed in Fig. 1. The left-hand side shows a schematic cross section and a top view onto the diamond sensor chip. The chip itself consists of a piece of monocrystalline diamond (Sumitomo) which has been processed to present an H-terminated surface in the area between the two Ti/Al contact pads and an O-terminated surface in all surrounding areas. For details of this processing the reader is referred to our previous papers [4,6,7]. As also described there, the H-termination – together with the ever-present water adsorbate layer – induces a hole conducting surface layer in between the two contact pads, while the O-termination in the surrounding areas suppresses such a surface conductivity. In order to allow for an easy handling of the sensor chip, the chip has been mounted onto a heatable ceramic carrier substrate which contained screen-printed Pt electrodes on its front side and a Pt heater meander and a Pt thermometer on its backside. While the front side contacts were used to connect the

diamond chip to the peripheral electronics, the backside heaters and the temperature sensors were not used during the acquisition of the sensor signals. Pictures of the front and back surfaces of these sensor chips are displayed in the right-hand part of Fig. 1.

Central to the understanding of the sensing mechanism are those processes that produce a p-type surface conductivity underneath an H-terminated diamond surface. These processes have been the subject of a series of papers [5–16]. Here, we concentrate on the main results which are relevant for the present investigations into the diamond sensor behaviour.

Central to the understanding is that undoped crystalline diamond with a band gap of 5.5 eV is a bona-fide insulator. Yet crystalline diamond has been demonstrated to exhibit an appreciable p-type surface conductivity when the surface dangling bonds are terminated by hydrogen. Explanations of this p-type surface conductivity [12,13] propose that a thin layer of water adsorbs on the H-terminated diamond surface whenever such diamond is exposed to normal ambient air. The water adsorbate layer, in turn, absorbs CO_2 from the ambient air, thus forming H_3O^+ ions inside the water adsorbate layer:



The H_3O^+ ions, in turn, get neutralized by a transfer of electrons (e) from the diamond valence band,



which results in a thin hole (h) conducting layer immediately beneath the diamond surface.

Upon diffusing to the water/air interface, the H_2 molecule can interact with an O_2 molecule from the air ambient, forming an H_2O molecule at the air/water interface:



The overall result of reactions (1a)–(1c) shows that, if the oxygen partial pressure in the air ambient is constant, the dissolution equilibrium in the water adsorbate layer and thus, the p-type surface conductivity of the diamond, is entirely determined by the CO_2 concentration in the ambient air [6,13]:



For clarity, the above-described processes are visualized in Fig. 2.

Other work in this area [4,7] has shown that the dissolution equilibrium in the water adsorbate layer is not simply determined by the CO_2 in the ambient air. In practice, the dissolution equilibrium can be determined by a whole variety of other acid- and base-forming gases, which may abound there. In particular, HD gas sensors exhibit a high sensitivity to NO_2 , which is a very strong acid forming molecule and which is omnipresent due to the combustion of hydrocarbons for supplying energy and mobility.

3. Measurement of acid vapours with an integrating HD sensor and sensor reset

The measurements presented below have been made with a freshly H-terminated diamond sensor. Such diamonds make gas sensors with a strongly accumulating sensing behaviour, which in the limit of low humidity ambients comes close to an integrator-like behaviour. In our previous publication [17] this integrator property has been demonstrated by performing detailed NH_3 and NO_2 gas sensing experiments with the help of a gas test rig.

In order to make a connection to our present field test with randomly fluctuating acid vapour sources, we first demonstrate this integrator property by placing a HD sensor inside a glass vessel

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