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Resettable, low-temperature accumulation gas sensors based on hydrogenated diamond transducers

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Abstract

Diamonds with hydrogenated surfaces feature a gas sensitivity which is mediated by a thin layer of BET-adsorbed water (BET: Brunauer, Emmet, Teller). Gases capable of undergoing acid-base reactions in liquid water are absorbed in the BET adsorbate, producing pH changes there and easily observable changes in the sub-surface hole conductivity of the diamond substrates. In this contribution we report on vapor sensing tests with diamond sensors which have been performed at normal ambient temperatures in a free-space environment. We show that such sensors exhibit an integrating dosimeter type response, which follows the temporal vapor concentrations with a time resolution of the order of one second or less. Upon saturation the sensors can be repeatedly reset to baseline by replacing contaminated BET adsorbates by fresh-water ones.

1. Introduction

Water vapor is normally considered a nuisance in gas detection. Unlike most other gases of analytical interest, water vapor has an abnormally high boiling point and occurs at comparably large and largely variable concentrations. Considering the hydrophilic properties of metal oxide surfaces, BET water adsorbates will form on
metal oxide (MOX) gas sensor surfaces at normal ambient temperatures [1]. In the current state of the art, MOX gas detectors are heated beyond the water evaporation point to allow the analytes of interest to interact directly with the sensor surface.

Once heating is avoided, the BET multi-layer adsorbates make the underlying semiconductor surfaces inaccessible to all kinds of analytes which do not readily dissolve in water. Analytes, however, which can dissolve in water and which are able to undergo electrolytic dissociation there, do produce an indirect gas response. Although this indirect kind of gas response can be observed on conventional MOX surfaces, the prototype material on which this form of gas sensitivity has been investigated in most comprehensive form is hydrogenated diamond (HD) [2, 3]. A main advantage of this unconventional sensing material is that it exhibits both a high hole density and a high hole mobility which facilitates electronic readout at normal ambient temperatures.

In the present paper we briefly demonstrate the capability of HD sensors of detecting water-soluble gases and of supporting a dosimeter-type gas response. We then demonstrate their performance in a practical vapor sensing application. Finally, a reset procedure is demonstrated which allows saturated HD-dosimeters to be reset to baseline.

2. Lab test demonstration of sensor performance

Before turning to our open-air vapor sensing experiment, we briefly demonstrate some key results on the HD sensor performance as revealed from gas sensing tests performed using conventional gas test equipment. Fig. 1a compares the response of a room-temperature-operated HD sensor to the response of a normal, heated MOX gas sensor. Exposing both sensors to a series of NO2 pulses, the heated MOX gas sensor simply mirrors the timing of the NO2 pulses. The HD sensor, in comparison, produces an integrator-like response and thus performs as a gas dosimeter. This dosimeter performance is a direct consequence of the rapid absorption of the NO2 in the BET adsorbed water layer on the HD specimen and the very slow desorption of the electrolytically dissociated acid (HNO3) back into the gas ambient. Fig. 1b summarizes gas response data obtained on a similar, room-temperature-operated HD sensor. It demonstrates good sensitivity to water soluble gases (NO2, NO, NH3) and a much poorer response towards the less water-soluble gas N2O.

![Fig. 1. (a) Response of a room-temperature-operated HD sensor and a heated MOX gas sensor to a series of NO2 exposure pulses; (b) response of a similar HD sensor to gases with good and poor water solubility.](image)

3. Vapor sensing performance in open air environments

After these preparations we have performed vapor sensing tests in an open-air environment using boiling HNO3 as a liquid source of NO2 (Fig. 2a). HD sensors were positioned in locations directly over a pot of boiling HNO3 or laterally displaced from this vapor source. In both cases we have observed a dosimeter-type gas response as shown in the top panel of Fig. 2b (I, III). As boiling NO2 in slightly windy conditions presents a fairly noisy vapor source, the rate of increase in the sensor response exhibits random variations, with a sharp increase whenever a slight breeze of wind interacts with one of those sensors. In the differentiated sensor response (Figs. 2b II, IV) sharp wiggles are
detected, which reproduce the variation of the sensor response as the HD sensors interact with this fast varying and noisy vapor source. A closer look into these differentiated response curves reveals that the HD sensors are able to respond to gas concentration changes with a speed in the order of one second or less. This response is extremely fast considering the fact that the diamond sensors have been operated at normal ambient temperatures without supplying any electrical heating power. We believe that this rapid response is a consequence of the rapid absorption and dissociation of the NO$_2$ molecules in the water adsorbate layers, the forced convective flow of the NO$_2$ away from the evaporation source and the absence of a hot air plume, which normally forms around heated MOX gas sensors. We have shown in previous work [4] that such hot air plumes acts as diffusion barriers, separating the sensor surface from the reactive gases in the air ambient.

Fig. 2. (a) Vapor sensing experiment exposing two HD sensors to NO$_2$ vapors emerging from a pot of boiling HNO$_3$. (b) Direct, dosimeter-type (top panels) and differentiated (bottom panels) HD sensor responses as observed in positions 1 and 2 relative to the NO$_2$ vapor source. Steep increases in the dosimeter-type response and sharp wiggles in the differentiated response occur whenever a slight breeze of wind carries a large concentration of vapor to the HD sensors.

Fig. 3. Differentiated response of sensor 1 (vertical). The close-up into a smaller time interval reveals a time resolution in the order of 1s.
4. Reset to baseline after sensor saturation

A seeming disadvantage of accumulating gas sensors is that these get saturated after some time of operation. The sketch in Fig. 4 shows that such sensors can be re-set to baseline by replacing contaminated BET adsorbates by fresh-water ones. Fig. 5 demonstrates the success of this procedure. Because of the absence of atmospheric CO₂ in DI water and the slow dissociation of CO₂ in liquid water, the return to the clean-air baseline (~1.7x10⁻⁵ Ω⁻¹) is slow (~1 hour). A much faster method of operating BET dosimeter-type sensors has been demonstrated in ref. [5]. In this breathing mode of operation a sensor is cycled through long sequences of aspiration and reset steps, thus providing a fast (seconds), sensitive and drift-free room-temperature sensor response [5].

Fig. 4. Re-setting a saturated HD sensor to baseline by contact with a drop of de-ionized (DI) water. (b) Variation of the HD sensor response upon successive exposures of NO₂ (a), retaining the saturated sensor in clean air (b), making contact with a drop of de-ionized water (c), upon forced evaporation of excess water, and exposure to ambient air containing ~400ppm of CO₂.

Fig. 5. Variation of the HD sensor response upon successive exposures of NO₂ (a), retaining the saturated sensor in clean air (b), making contact with a drop of de-ionized water (c), upon forced evaporation of excess water, and exposure to ambient air containing ~400ppm of CO₂.

References