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Sensing of phosgene by a porous-like nanocrystalline diamond layer with buried metallic electrodes

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ABSTRACT

Nanocrystalline diamond with a porous-like morphology was used as the functional part of a semiconductor gas sensor. The device function is based on the two-dimensional p-type surface conductivity of intrinsic diamond with a H-terminated surface. Metallic electrodes are buried beneath the diamond film. Therefore, these electrodes are protected from harmful substances, and the electronic connection is facilitated by grain boundaries. The gas sensing properties of the sensor structure were examined using oxidising gases (i.e., phosgene, humid air) at various operating temperatures. A pronounced and selective increase by two orders of magnitude was found in the surface conductivity after sensor exposure to phosgene gas (20 ppm) at 140 °C. Density functional theory calculations indicated no direct charge transfer between the phosgene molecule and diamond. We present a model in which phosgene indirectly yet efficiently increases the H_3O^+ concentration, which consequently leads to multiplied electron transfer and a pronounced sensor response.

1. Introduction

Air quality is one of the major environmental concerns in our industrialised world. Increasing amounts of noxious pollutants are emitted into the atmosphere, resulting in negative effects on human health and the environment. More than 80% of fire-related deaths are due to smoke inhalation [1]. Smoke itself is a complex mixture of vapours, gases, fumes, and heated air as well as liquid and solid aerosols produced by thermal decomposition. In recent years, the use of new synthetic building materials and furnishings has led to a rise in inhalation injuries caused by fires [2]. Toxic combustion products generated by fires are classified into three categories including simple asphyxiants, chemical asphyxiants, and irritant toxins [3]. Phosgene ($COCl_2$) is a very common irritant gas that is a highly reactive non-flammable colourless gas at room temperature and ambient pressure and has a suffocating odour similar to mouldy hay. It is a lung irritant and a very insidious poison, which is not immediately irritating, even when fatal concentrations are inhaled. The odour is detectable at levels between 1.6 and 6 mg/m^3. Environmental phosgene levels arise from industrial emissions and thermal decomposition of some chlorinated solvents and chlorinated polymers (especially polyvinyl chloride (PVC)) [4,5]. The main risk posed by phosgene is inhalation of the gas, leading to pulmonary oedema, which can develop 8–24 h after exposure, and death due to anoxia. The lethal concentration of phosgene for humans is estimated to be 500–800 ppm per minute. Levels of 2–5 ppm induce mild respiratory symptoms, and prolonged exposure to such levels is considered dangerous [4].

There are several commercially available phosgene sensors on the market. According to the accessible information, most of these sensors are based on electrochemical principles (amperometric three-electrode sensor cells with fixed organic electrolyte [6], electrochemical fuel cells [7]), which lead to a high cost (over 450 USD) and a relatively slow response (response time at $T = 50\,^\circ C$ is 20–120 s).

Diamond represents a promising new material in this area and can be deposited on the existing sensor elements. Undoped, high-quality diamond is one of the best electrical insulators.

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However, diamond with chemically bound hydrogen on the surface exhibits pronounced conductivity (i.e., p-type surface semiconducting properties) when exposed to air [8]. This conductivity arises from free positive charge carriers (holes) in the sub-surface region and is highly sensitive to surrounding gases and/or liquids. The surface conductivity of H-terminated nanocrystalline diamond (NCD) thin films can be modified by exposure to different gases [8]. An especially high response was observed for an oxidising gas (i.e., phosgene) [10,11]. In addition, our previous work revealed that O-terminated nanocrystalline diamond exhibits highly resistive properties (conductivity 1×10^{-8} s) and that no change in resistance was observed after its exposure to various gases [10]. In addition, we observed that the sensor sensitivity is strongly dependent on the total surface area. Our previous study showed that the porosity of the diamond film could be controlled by the nucleation and/or deposition time [10]. It has been previously shown that the surface ratio, which is defined as the ratio of the unit area to the area calculated by AFM measurements, increased to 13% under optimal process conditions. For comparison, we also employed vertically aligned diamond nanorods, which were fabricated by RF-plasma etching in a CF_4/O_2 gas mixture [11]. In this case, the surface area was directly calculated, and its increase, which was controlled by the etching time, was correlated with the sensor sensitivity. However, the details of the phosgene sensing mechanism and operation have not yet been elucidated.

In this paper, we report on the change in the H-terminated diamond surface conductivity after its exposure to different gas environments (i.e., humid air and phosgene). We discuss the gas selectivity dependence on the operating temperature of the sensor element coated by the H-terminated porous-like nanocrystalline diamond layer. We propose a sensing mechanism based on dissolution of phosgene gas molecules followed by chemical reactions in the adsorbed water layer and related electron charge transfer. The proposed mechanism is discussed in correlation with theoretical DFT calculations.

2. Experimental details

The first step in the gas sensor fabrication involved the deposition of metal interdigitated electrodes (IDEs). The Ti/Au (30/50 nm) IDEs were fabricated on Al_2O_3 substrates by standard UV lithography followed by the thermal evaporation method and the lift-off technique. The fabrication procedure is described briefly below. The Al_2O_3 substrates were spin-coated (3000 rpm for 1 min) with ma-P 1215 positive photoresist and backed on a hotplate at 100 °C for 40 min. A mask containing the electrode design was employed to selectively expose the ceramic substrates to UV light. Following UV exposure, the photoresist was developed in a positive developer (ma-D331). Then, the Al_2O_3 substrates were loaded in an evaporation chamber, and the Ti/Au metal films deposited over the photoresist and the Al_2O_3 substrates. Next, portions of the metal film on the photoresist were removed by selective dissolution of the resist layer in an appropriate etching liquid. By employing this procedure, the overlaying metal film was lifted off and removed, resulting in fabrication of Ti/Au IDEs (Ti/Au = 30/50 nm). The IDEs were prepared as six electrodes that were patterned with a separation of 50 μm (Fig. 1b).

Fig. 1a illustrates the growth mechanism of the nanocrystalline diamond film. Initially, the seeding of the ceramic substrate covered with metal IDEs was achieved by their immersion for 2 min in an ultrasonic bath containing ultradispersed detonation diamond. Next, the growth of the NCD film was performed by a microwave plasma-enhanced chemical vapour deposition process (PECVD, Aixtron reactor P6). Deposition of the NCD layer was achieved using a constant methane concentration (1% CH_4 in H_2) with a gas pressure of 30 mbar, a microwave power of 1000 W, and a deposition time of 17 h. The deposition temperature for the growth of the diamond structure was chosen to be a low as possible (400 °C) to avoid degradation of the electronic parts (metal electrodes). Finally, the samples were treated in hydrogen plasma for 10 min and exposed to ambient air for 60 min to generate p-type surface conductivity [8]. The resulting morphology of the NCD film was characterised by SEM measurements (Fig. 1c). The film thickness was estimated to be ∼150 nm, based on our previous study in which the same deposition conditions were employed to grow a diamond layer on glass substrates [12].

Gas sensing properties, which were determined by electrical conductivity measurements, were characterised at room temperature and at an elevated temperature of 140 °C. The conductivity measurements were performed at a voltage of 1 V and a frequency of 3 kHz with measurement duration of 5 s using an LCR metre (HIOKI 3532-50). The following testing gases were used: (i) humid air (relative humidity RH = 23% or 43%) and (ii) $COCl_2$ (20 ppm). A detailed description of the gas sensing setup can be found in Ref. [13].

Prior to the conductivity measurement, the sample was mounted in a testing chamber, and the chamber was flushed with dry nitrogen gas (N_2) for 15 min to stabilise the output characteristics. Subsequently, the specific testing gas was injected into the chamber through the inlet port, and the surface conductivity was measured as a function of time.

3. Results

Fig. 1c shows the SEM images of the surface morphology of the sensor substrate (Al_2O_3 + electrodes) coated with the NCD layer. The coating exhibits a porous-like structure that contains nano-sized diamond grains up to 80 nm in size.

Fig. 2 displays the conductivity response of the H-terminated NCD surface to phosgene (20 ppm) and humid air (RH = 23%) measured at 25 °C and 140 °C as a function of time. As illustrated in Fig. 2a, a pronounced increase in the surface conductivity by one order of magnitude is observed for both gases at room temperature. The gas sensing properties were also characterised at an elevated temperature (140 °C), and we expected faster response and recovery compared to the room temperature properties [9]. A steep increase in the surface conductivity by two orders of magnitude was observed when the sensor was exposed at 140 °C to 20 ppm of $COCl_2$ (Fig. 2b). However, only a small increase in the surface conductivity was observed (from 1.2×10^{-7} s to 3.5×10^{-7} s) after exposing the sensor to humid air.

To understand the difference between humid air and $COCl_2$, Fig. 3a compares the temperature dependence of the surface conductivity of the H-terminated sensor devices for phosgene (20 ppm) and humid air (RH = 43%). Both curves display hysteresis behaviour and exhibit a conductivity maximum at a specific temperature. These temperature values are 70 °C (T_1) and 91 °C (T_2) for humid air and $COCl_2$, respectively.

The surface conductivity for higher humidity conditions (RH = 43%) measured at 140 °C (4.5×10^{-7} s) is even lower than the value measured at room temperature (1.5×10^{-6} s). The percentage difference in the initial surface conductivity value and the value measured at 140 °C is −70%. The maximum value of the surface conductivity is 2.4×10^{-6} s at a temperature of 70 °C (i.e., the percentage difference is 60%). During the cooling period, the conductivity monotonically increases until the end of the measurement at 60 °C.

For phosgene, a steep increase in the surface conductivity is observed during the heating period. The maximum conductivity value is 1×10^{-5} s, which is observed at 91 °C (T_2). During the cooling period, the surface conductivity dramatically increases until the end of the measurement (point B).