

HYDROGEN-TERMINATED DIAMOND SURFACE AS GAS SENSING LAYER WORKING AT ROOM TEMPERATURE

DAVYDOVA Marina^{1*}, KULHA Pavel², BABCHENKO Oleg¹, KROMKA Alexander¹

¹*Institute of Physics, Academy of Science of the Czech Republic, v.v.i., Prague, Czech Republic, EU*

²*Czech Technical University in Prague, Department of Microelectronics, Faculty of Electrical Engineering, Prague, Czech Republic, EU*

* davydova@fzu.cz

Abstract

Since the world has become industrialized, as a consequence, there is an increasing demand for gas sensors. Nanocrystalline diamond (NCD) films were grown on the commercially available sensor product consisted of a built-in microheater, a platinum temperature sensor, and a pair of Pt interdigitated electrodes using microwave plasma enhanced chemical vapor deposition process. We investigated the effect of fluorine- and hydrogen-terminated diamond surface on the gas sensing properties at room temperature. The gas sensing properties diamond-based sensor were measured by the changes of electrical resistance to various volatile organic compounds (C₆H₆, C₃H₆O, isopropylalcohol) and relative humidity. The comparative sensing performance of hydrogenated diamond surface shows improvement in sensitivity toward benzene, acetone, isopropylalcohol and humid air in contrast to fluorinated diamond surface, where the surface conductivity was suppressed. The sensor functionality was explained by the surface transfer doping effect.

Keywords: Diamond, gas sensor, response, sensitivity

1. INTRODUCTION

The demand of gas sensors has been increased extensively due to increasing industrialization which leads to increase the level of air pollution. Diamond has found wide practical applications in many industrial sectors thereby it has attracted considerable interest. Apart from variety of diamond application, due to the possibility of tailoring diamond surface by various atomic terminations, many recent efforts have been made to utilize diamond as a gas sensor [1-5]. It is known that the hydrogen-terminated diamond shows *p*-type surface conductivity even in undoped diamond [6, 7]. This surface also shows hydrophobic properties, positive charge and negative electron affinity (NEA). On the other hand, hydrophilic properties, positive charge and positive electron affinity (PEA) are obtained by oxygen-terminated diamond surface. Fluorine (F) termination of diamond surfaces has been investigated also [8-12] and has recently been employed as an alternative to oxygen and hydrogen termination in drug delivery and other biomedical applications [10]. These surfaces are negatively charged and super hydrophobic [8]. However, despite its potential application to a number of fields, the gas sensing properties of the F-terminated diamond surface remarkably are not known.

In this work we performed nanocrystalline diamond (NCD) films grown on the fully-integrated sensor substrate of the intrinsic NCD layer/metal IDEs/insulating substrate. We investigate room-temperature gas sensing behavior of H- and F-terminated NCD layer to various volatile organic compounds (C₆H₆, C₃H₆O, isopropylalcohol) and relative humidity. The influence of the NCD sensor operation temperature on the sensitivity and gas sensing mechanism is discussed.

2. EXPERIMENTAL

The deposition of nanocrystalline diamond layer was carried out on the commercially available sensor product consisted of a built-in microheater, a platinum temperature sensor, and a pair of platinum (Pt) interdigitated electrodes with a 15 μm width. The NCD growth proceeded in two steps: i) seeding 20 min and ii) microwave plasma-enhanced chemical vapor deposition (PECVD). Diamond layers were grown by pulsed-linear antenna

microwave plasma-enhanced CVD (Roth&Rau AK 400) [13]. The process conditions were the following: gas pressure 0.1 mbar, microwave power 1700 W, methane (CH₄) gas flow 5 sccm, and different ratios of carbon dioxide (CO₂) and hydrogen (H₂) gas flow. The flow of H₂ gas was changed from 25 sccm to 100 sccm and the CO₂ flow rate varied between 20 sccm and 30 sccm. During the deposition process the substrate temperatures was maintained at 470°C. After the PECVD deposition, the samples were exposed to pure hydrogen plasma for 5 min to induce a *p*-type surface conductivity [1, 7] and thereafter, cooled down to the room temperature. The replacement of hydrogen termination with fluorine (F₂) was provided by 100 W radio frequency (RF) plasma maintained reactive ions in CF₄ (Phantom LT Reactive Ion Etch (RIE) System, Trion Technology). The total gas pressure was 150 mTorr and the duration 30 s.

The resulting morphology of each structured NCD film was characterized by scanning electron microscopy (SEM, Raith e_LiNE). The diamond character of the sensor element was confirmed by UV-Raman spectroscopy (Renishaw In Via Reflex Raman spectrometer, 442 nm excitation wavelength).

The sensing characteristics were measured as DC voltage drop on the sensor, using precise sourcemeter Kethely 2401, with constant current of 1μA flowing through the sensitive layer. A custom LabView program was used which allowed the temperatures and gas-flow rates to be automatically controlled by a computer [14]. Prior to the measurements, the sample was mounted in a gas-flow apparatus, and the chamber was flushed with dry nitrogen gas (N₂) for 15 min to stabilize the output characteristics. Then, the specific testing volatile organic compound (acetone, benzene, isopropylalcohol) was injected into the chamber through the inlet port, and the change in the resistance of the sensors was investigated as a function of exposure time.

3. RESULTS AND DISCUSSION

Fig. 1a shows surface morphology of fully-integrated sensor substrate coated with hydrogenated NCD films. The top view depicts the presence of relatively smooth and continuous diamond film with amorphous carbon shell at the diamond. Moreover, the NCD primarily grew on the IDEs as was proved in our previous study [3]. The Raman spectrum (**Fig. 1b**) is characterized by three strong contributions: the peak characteristic for diamond centered at 1330 cm⁻¹ (D- peak), disorder peak at 1365 cm⁻¹ (D- band) disorder peak and the broad band at approximately 1590 cm⁻¹ attributed to the non-diamond phase (G- band), i.e., sp²-bonded carbon atoms [13].

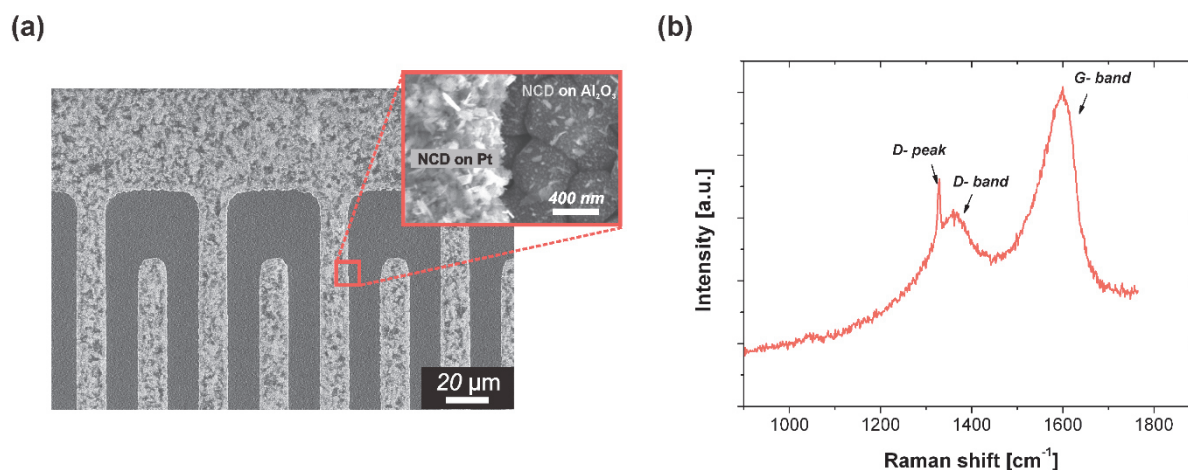


Fig. 1 SEM image of NCD coated fully integrated sensor substrate on micro-hot-plate with Pt IDEs with separation of 15 μm (a) and Raman spectrum of NCD film (b). The sharp peak at 1330 cm⁻¹ proves the diamond character of the deposited films

Fig. 2 displays the resistance response of the hydrogen- and fluorine- terminated NCD surface to relative humidity (RH) and to various volatile organic compounds (VOCs) measured at 25°C. As illustrated in **Fig. 2a**, the response (the change in the resistance) of the F-terminated diamond based gas sensor was negligible.

The curves for relative humidity (50%), isopropylalcohol (0.6%), benzene (1.5%), and acetone (4%) exhibit a slight increase in resistance (**Fig. 2**). However, quite dynamic response (decrease in the resistance) is observed for the H-terminated diamond surface for all tested VOCs. Moreover, as illustrated in **Figs. 2c** and **2d**, the sensor response of H-terminated diamond surface is the highest for benzene and acetone in comparison to the rest VOCs (**Figs. 2a, 2b**). These results suggest that the surface termination of NCD film has a great influence on the gas sensing performance.

It should be also noted, that a variation or shifting of the “starting” resistance value was observed. The origin for this difference can be attributed to several factors, e.g., low quality ohmic contacts, memory effects of the surface state of NCD, etc. A technological optimization is still required for achieving better reproducibility and device reliability.

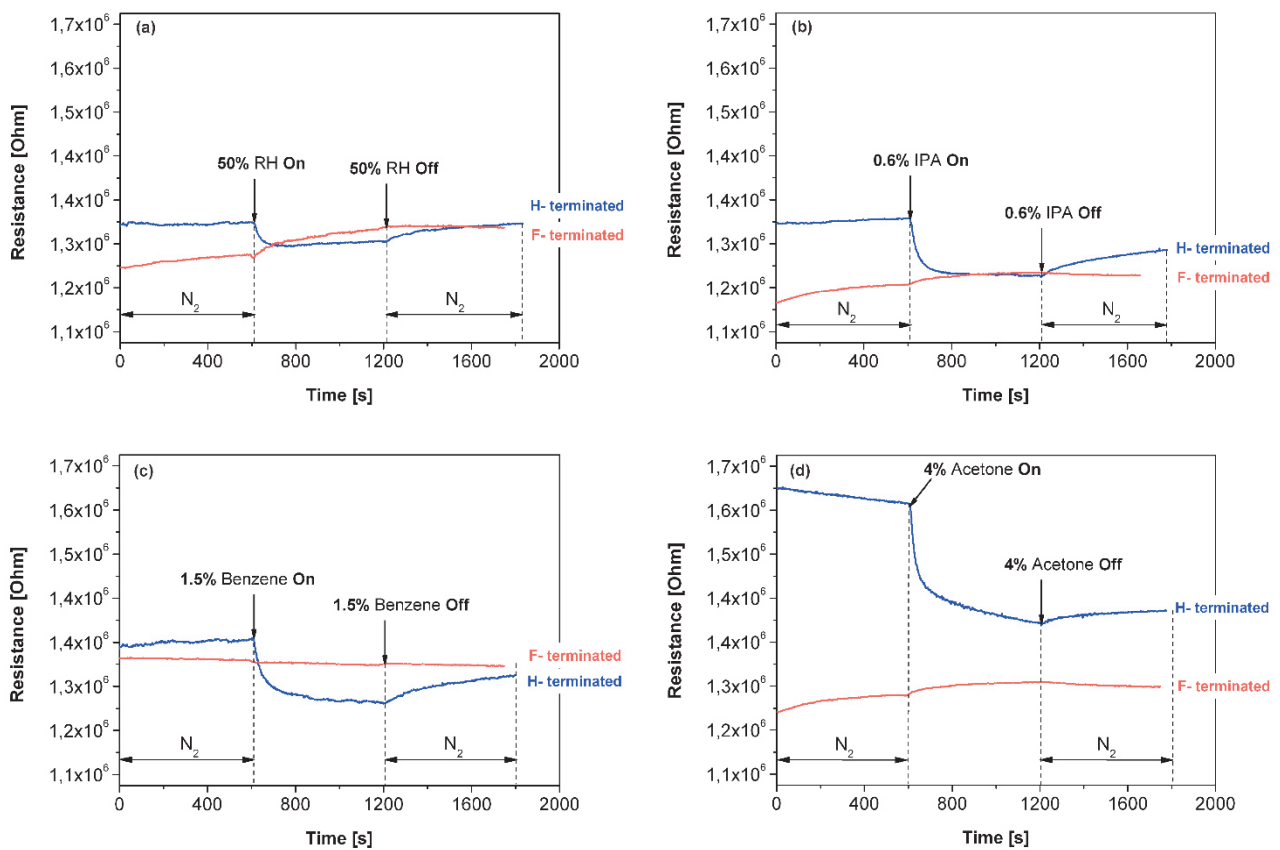


Fig. 2 Time dependence of resistance of fully-integrated sensor substrates coated with H-terminated and/or F-terminated NCD: with 50% of relative humidity (a), 0.6% of isopropylalcohol (b), 1.5% of benzene (c), and 4% of acetone (d) measured at room temperature

The electrical sensitivity of H-terminated NCD surface to various concentrations of VOCs proves that the H-NCD surface is electrically active and an electronic interaction between surface and its vicinity occurs (**Fig. 2**). It can be seen that our H-terminated NCD sensor shows response to all tested VOCs in contrast to F-terminated diamond surface. However, this response is too low for industrial uses. Decrease in the response value can be explained due to the low operating temperature (25°C) dissociation of a large molecule, such as e.g. benzene [15]. The improvement in the sensor design such as increasing surface-to-volume ratio may increase the sensor response.

The basic model for the change of surface conductivity (resistance) of H-terminated diamond surface on the gas type has been well discussed by other works [1, 2, 16]. In general, when oxidizing or reducing agents

(gases) appear in the atmosphere, the charge exchange between the diamond and adsorbed molecules causes an increase or a decrease in the resistance. This mechanism could be interpreted by widely established the surface transfer doping mechanism of the H-terminated diamond [17, 18]. Because the surface conductivity of diamond relies on the presence of an adsorbed water film on the H-terminated diamond surface, the surface resistance decrease at first (**Fig. 2**). Based on the surface transfer doping model, the sensitivity of the H-terminated NCD to NO₂ and NH₃ gases was confirmed and explained by other group [2]. In the same manner we explained the increase of the surface conductivity of H-terminated NCD upon exposure to phosgene and humid air [19].

According to the above mentioned mechanism, since the benzene is reducing agent, the surface resistance should be increased; however in our case the decrease of surface resistance was observed (**Fig. 2c**). This behaviour can be explained by the presence of carbon composites on diamond film which can also lead to an increase of the resistance. Another possible mechanism may be similar as reported by Gurbuz et al. for detection of benzene and toluene [15]. The concept of this mechanism was the dissociation of H₂ into hydrogen atoms and subsequent diffusion through the Pt catalyst (Pt IDEs) causing a change in the work function and a subsequent change in the resistance.

For a deeper insight into theories mentioned above further experiments are required for elucidation of the mechanism.

4. CONCLUSION

The nanocrystalline diamond film was used as the functional layer of a semiconductor gas sensor where Pt electrodes were buried beneath the diamond film. We observed that the fluorinated NCD functional layer did not show almost any response toward testing gases, whereas the H-terminated NCD exhibited the sensitivity towards VOCs such as benzene, acetone, and IPA. Moreover, the highest room temperature sensor response was found for benzene and acetone. The gas sensing mechanism was explained and attributed to: i) dissolution of gas molecules and their subsequent chemical reactions in the adsorbed water layer on the H-terminated NCD, and ii) dissociation of H₂ into hydrogen atoms and subsequent diffusion through the Pt catalyst. We can conclude that these results are promising for practical industrial applications in which small and simple H-NCD sensors can be used as gas sensors at room temperature.

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REFERENCES

- [1] WANG Q, QU S. L. Chemical gases sensing properties of diamond nanocone arrays formed by plasma etching. *Journal of Applied Physics*, Vol. 102, 2007, pp. 103714-103718.
- [2] HELWIG A, MULLER G. Gas sensing properties of hydrogen-terminated diamond. *Sensors and Actuators A*, Vol. 133, 2008, pp. 156-165.
- [3] KROMKA A., DAVYDOVA M. Gas sensing properties of nanocrystalline diamond films. *Diamond and Related Materials*, Vol. 19, 2010, pp. 196-200.
- [4] DAVYDOVA M., KULHA P. Gas sensing properties of nanocrystalline diamond at room temperature *Beilstein Journal of Nanotechnology*, Vol. 5, 2014, pp. 2339-2345.
- [5] STEHLIK S., IZAK T. Sensitivity of diamond-capped impedance transducer to Tröger's base derivatives, *ACS Applied Materials and Interfaces*, Vol. 4, 2012, pp. 3860-3865.
- [6] LANDRASS M. I., RAVI K. V. Resistivity of chemical vapour deposited diamond films. *Applied Physics Letter*, Vol. 55, 1989, pp. 975-977.

- [7] HAYASHI K., YAMANAKA S., Investigation of the effect of hydrogen on electrical and optical properties in chemical vapor deposited on homoepitaxial diamond films. *Journal of Applied Physics*, Vol. 81, 1997, pp. 744-754.
- [8] KUGA S., YANG J. H. Detection of mismatched DNA on partially negatively charged diamond surface by optical and potentiometric methods. *Journal of the American Chemical Society*, Vol. 130, 2008, pp. 13251-13263.
- [9] RAY M. A., TYLER T. Cool plasma functionalization of nano-crystalline diamond films. *Diamond and Related Materials*, Vol. 16, 2007, pp. 2087-2089.
- [10] POPOV C., KULISCH W. Surface modification of nanocrystalline diamond/ amorphous carbon composite films. *Diamond and Related Materials*, Vol. 17, 2008, pp. 1229-1234.
- [11] STROTHER T., KNICKERBOCKER T. Photochemical functionalization of diamond films. *Langmuir*, Vol. 18, 2002, pp. 968-971.
- [12] YAMADA T., CHUANG T. J. Chemisorption of fluorine, hydrogen and hydrocarbon species on the diamond C(111) surface. *Molecular Physics*, Vol. 76, 1992, pp. 887-908.
- [13] KROMKA A., BABCHENKO O. Linear antenna microwave plasma CVD deposition of diamond films over large areas. *Vacuum*, Vol. 86, 2012, pp. 776-779.
- [14] VARGA M., LAPOSA A. Quartz Crystal Microbalance Gas Sensor with Nanocrystalline Diamond Sensitive Layer. *Physica Status Solidi B*, 2015, DOI: 10.1002/pssb.201552229.
- [15] GURBUZ Y., WENG P.K. Diamond microelectronic gas sensor for detection of benzene and toluene. *Sensors and Actuators B*, Vol. 99, 2004, pp. 207-215.
- [16] GI R. S., TASHIRO K. Hall effect measurements of surface conductive layer on undoped diamond films in NO₂ and NH₃ atmospheres, *Japanese Journal of Applied Physics*, Vol. 38, 1999, pp. 3492-3496.
- [17] MAIER F., RIEDEL M. Origin of surface conductivity in diamond. *Physical Review Letters*, Vol. 85, 2000, pp. 3472-3475.
- [18] CHAKRAPANI V., ANGUS J. C. Charge transfer equilibria between diamond and an aqueous oxygen electrochemical redox couple. *Science*, Vol.318, 2007, pp. 1424-1430.
- [19] DAVYDOVA M., STUHLIK M. Sensing of phosgene by a porous-like nanocrystalline diamond layer with buried metallic electrodes. *Sensors and Actuators B*, Vol. 188, 2013, pp. 675-680.