

Selective detection of phosgene by nanocrystalline diamond layer

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Nanocrystalline diamond (NCD) films were grown on gold/Al₂O₃ substrate using microwave plasma-enhanced chemical vapor deposition (PECVD) process. The NCD morphology was controlled by the deposition time and it was investigated by scanning electron microscopy (SEM). Gas sensing properties of NCD surface conductivity to humid air,

CO₂, NH₃, and COCl₂ gases were measured by impedance measurements at room and at high temperature (140 °C). The H-terminated NCD surface shows a significant response to oxidizing gas (humid air, COCl₂) in comparison to reducing gases (CO₂, NH₃).

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1 Introduction Diamond is a widely used material for many applications due to its unique advantages such as chemical inertness, large electrochemical potential window, possibility of operation in chemically harsh environment, and biocompatibility [1–3]. Furthermore, diamond is expected as a gas sensing material, which has high sensitivity at low temperatures with fast response and selectivity. Several types of gas sensor using diamond layer have been proposed. A gas sensor that uses H-terminated diamond nanocones as a gas adsorption material was reported in work [4]. Diamond gas sensors are based on a change of the surface conductivity of diamond with adsorbed gas molecules [3–5]. These sensors are expected to have sufficiently high sensitivity and fast response at different temperatures and compatibility with metal electrodes.

Most of the prototypes are based on H-terminated monocrystalline diamonds, which are still extremely expensive and limited in size. Therefore, polycrystalline diamond films have been used instead as their alternative. Selective detection of benzene and toluene by a polycrystalline

diamond was realized on Pd/i-diamond [5]. The top arrangement of Ti/Au pads was used for the detection of NH₃ and NO₂ gases [3]. However, the use of polycrystalline diamond films is limited because of high surface roughness where post-growth polishing is required. In recent years, nanocrystalline diamonds (NCDs) have attracted increased interest due to their flat surface and properties similar to the monocrystalline diamond. The NCD films have been intensively studied by several researchers and bio-sensors' uses were realized [6, 7].

Since diamond is used for detection gas molecules, different gases were tested. Some examined gases have various toxic levels. The gases like ammonia (NH₃) and phosgene (COCl₂) are toxic, but the smell of NH₃ is sensed in low concentration in the atmosphere, even if there is no health hazard yet. As regards the phosgene, which is also known as carbonyl chloride, it is a highly toxic gas that was used as a chemical weapon in World War I. Phosgene is a colorless gas that affects the lungs, eyes and skin. Though highly toxic, not everybody can smell it at low concentrations and the effects

of exposure can take hours to appear [8]. Various methods, including optical [9] and spectroscopic technique [10], have been used to detect phosgene. From our electronic point of view, the sensing element based on NCD film can open a new way for detection of such toxic gas.

In this study, we investigate gas sensing properties of O- and H-terminated NCD layer to different gases (humid air, CO₂, NH₃, and COCl₂). Impedance measurements show that H-terminated surface conductivity increases at oxidizing gases (humidity, COCl₂) and decreases at reducing gases (CO₂, NH₃). The effects of gas concentration and sensor temperature are studied.

2 Experimental The sensor arrangement is based on the sandwich structure of intrinsic H-terminated NCD layer/metal interdigitated electrodes/insulating ceramic. The NCD growth consisted of two steps: (i) seeding and (ii) microwave plasma enhanced chemical vapor deposition (PECVD). The seeding of ceramic substrates covered with Au interdigitated electrodes was realized by ultrasonic treatment in suspension of ultradispersed detonation diamond for 2 min. The growth of NCD film was provided on Au/Al₂O₃ substrate by microwave PECVD system (an ellipsoidal resonator, Aixtron P6, Germany) using a gas mixture of 1% methane diluted in hydrogen, gas pressure 30 mbar, and microwave power 1000 W. The substrate temperature was as low as 400 °C, as measured by the two-color pyrometer (Williamson type). The NCD films were grown for 5 or 17 h. After the CVD deposition, the methane flow was switched off and the diamond was exposed to hydrogen plasma for 10 min. Oxygen termination of NCD samples was realized by their exposure to oxygen plasma maintained at radiofrequency of 13.56 MHz, total power 300 W and duration 3 min. The final morphology and structure of grown films was characterized by scanning electron microscopy (SEM, Raith eLiNE).

Conventional micro-Raman measurements of the deposited materials were performed using a LabRAM HR (HORIBA Jobin Yvon, France) using a 458 nm excitation wavelength laser, which enabled us to determine the diamond character of the deposited films (*i.e.*, the sp³ hybridization). A 50× microscope objective was used to focus the laser onto a spot of approximately 1 μm in diameter, and to collect the backscattered light.

The impedance measurements were realized at two different temperatures, at room and high temperature of 140 °C, at voltage of 1 V, frequency of 3 kHz and measurement period of 5 s (LCR—HIOKI 3532-50). As testing gases humidity, carbon dioxide, ammonia, and phosgene were used in carrier gas which was either nitrogen or “synthetic air” (SA, 20% O₂ + 80 vol.% N₂). Before the impedance measurements, the holder with samples was put into a test chamber and flushed in nitrogen gas with and without SA for 15 min to stabilize the output characteristics. Subsequently the testing gas was injected into the chamber through the inlet port and surface conductivity was measured as a function of time.

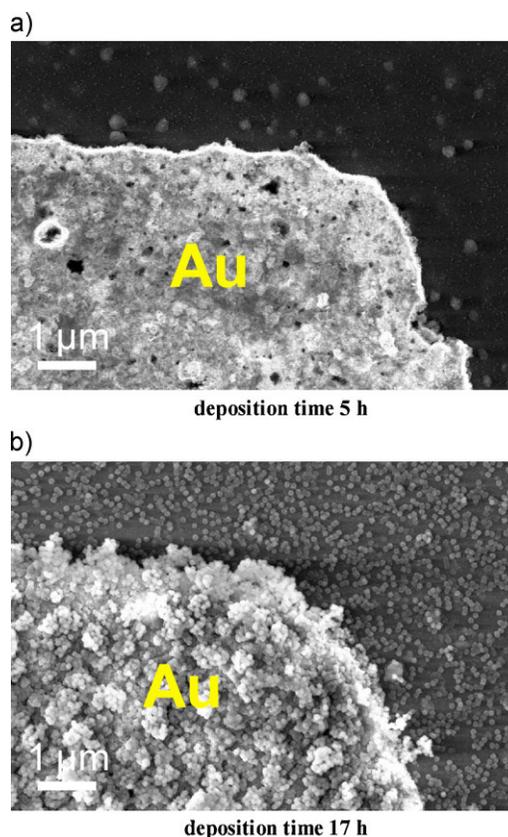


Figure 1 (online colour at: www.pss-a.com) Surface morphologies of NCD samples grown for (a) 5 and (b) 17 h.

3 Results and discussions Figure 1 shows SEM images of substrate surfaces of NCD samples deposited for 5 or 17 h. It is observed that NCD growth is mainly localized on Au electrodes. Figure 1a represents the NCD film grown for the time of 5 h. After this growth period, diamond nanograins with low density are observed. The size of these nanograins is less than 100 nm. The surface morphology significantly changes for the deposition time of 17 h. SEM measurements clearly indicate the morphology change to a complex 3D-like coverage containing of nanosized diamond grains (Fig. 1b). The density of these nanograins significantly increases.

The Raman spectrum of NCD samples exhibited one sharp peak centered at the wavenumber of 1330 cm⁻¹, which represents the optical phonon in diamond [11]. In addition, the Raman spectrum also showed two broad bands, one centered at 1350 cm⁻¹ and second centered at ~1590 cm⁻¹, which correspond to the E_{2g} and A_{1g} modes of graphite phase [12] (*i.e.*, they are assigned to sp² bonded carbon). Raman spectra for both sample types were nearly identical and they differed mainly in the intensity, *i.e.*, the measured intensity was higher for the deposition time of 17 h than for the deposition time of 5 h.

Figure 2 shows the time dependence of surfaces conductivity for O- and H-terminated NCD samples deposited for the period of 18 h. CO₂, NH₃, and COCl₂,

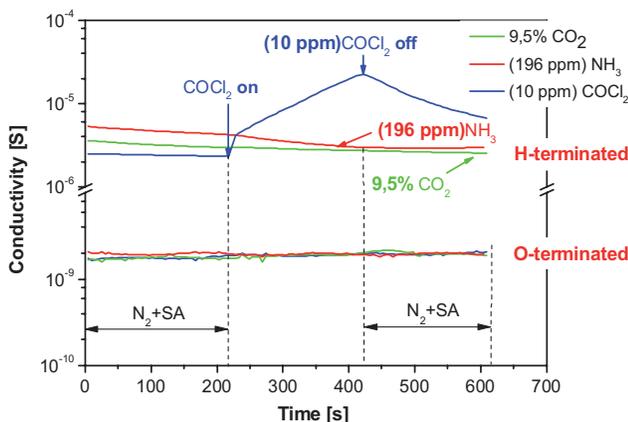


Figure 2 (online colour at: www.pss-a.com) Time dependence of surfaces conductivity of O- and H-terminated NCD films (deposited for the period of 18 h) to different gases. During the measurements the NCD samples were kept at 140 °C.

diluted in SA and N₂, were used as testing gases. The oxygen-terminated NCD surface exhibits non-conductive properties (1×10^{-8} S) and no change in conductivity was observed for different gas inlets. In the case of H-terminated NCD sample, the surface conductivity varies with respect to the used testing gas. It rises up to 1×10^{-4} S for 10 ppm of phosgene. The curves for ammonia (196 ppm) and carbon dioxide (9.5%) exhibit a slight decrease in surface conductivity. It should be noticed that we provided impedance measurement for virgin Au/Al₂O₃ substrates (without NCD layer). The measured curves indicated that the “virgin” sensor does not show any significant dependence on the used gases. Next, the surface conductivity of the virgin substrate was at least three orders lower in magnitude than the conductivity for the NCD samples.

Figure 3 shows the time dependence of surface conductivity of H-terminated NCD sample on the COCl₂ concentration, *i.e.*, 5 and 20 ppm, respectively. The time-conductivity curves were measured at 140 °C. In this case, the NCD samples were grown for 5 h. A steeper increase in the surface conductivity to higher values is observed for 20 ppm of COCl₂. These measurements indicate that the NCD samples are also sensitive to the phosgene concentration. Similar dependences were measured for both growth time periods, *i.e.*, 5 or 17 h, respectively.

Figure 4 shows the time dependence of surface conductivity of the NCD samples on the measured temperature (25 and 140 °C). The testing gas was 22% RH. These samples were grown for the period of 5 h.

Quite dynamic response is observed for room temperature 25 °C. Impedance measurement provided at 140 °C results in lowering the surface conductivity. These results suggest that the surface conductivity of NCD films in RH environment decreases on increasing the measurement temperature from 25 to 140 °C.

The basic model for the change of surface conductivity of H-terminated mono- or polycrystalline diamond surface on

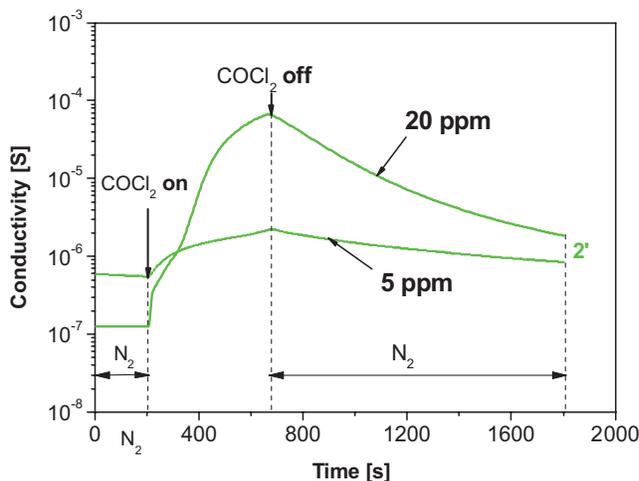


Figure 3 (online colour at: www.pss-a.com) Time dependence of H-terminated NCD surface conductivity on phosgene concentration after turning off the inflow of phosgene. During measurements samples were kept at 140 °C.

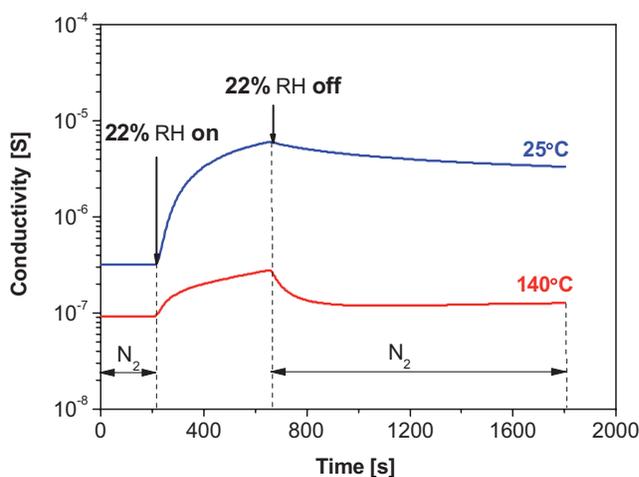


Figure 4 (online colour at: www.pss-a.com) Time dependence of H-terminated NCD surface conductivity to 22% of RH on the measured temperature (25 or 140 °C).

the used gas has been well explained by other works [4, 13, 14]. The surface conductivity changed due to the electron transfer between the diamond surface and oxidizing (O₂, NO₂, *etc.*) or reducing (CO, NH₃, H₂, *etc.*) gas molecules adsorbed on the diamond surfaces.

Only briefly—the common consensus is to the model in which the conductivity arises by transfer of electrons from the diamond to a redox couple in the “water film” adsorbed on the diamond surface [15–17].

For specific gas environments, the transfer of electrons will vary with the gas. For example, when the H-terminated diamond surface was in a contact with NH₃, a decrease in surface conductivity was observed. The decrease in the surface conductivity was explained by the reduced

concentration of holes [4]. Similar response was observed for carbon dioxide. Thus, in this meaning, ammonia or carbon dioxide behave as reducing gases. In our case, we have observed similar tendency; however, the decrease in surface conductivity was not so remarkable like in work of Wang et al. [4].

On the other hand, when the diamond surface is exposed to the “oxidizing” gases, its surface conductivity will increase. Such an increase has been observed for humidity or COCl_2 . In our case, the surface conductivity rose up on exposing the NCD sample to phosgene. Adopting the previously published model for oxidizing gases, we assume that the electrons are transformed from the diamond surface into the adsorbed “aqueous COCl_2 ” and the conductivity increases. Further experiments are required for a deeper insight for this explanation.

It should be noted that the gas sensitivity of NCD samples is only present, when they have sufficiently good electronic quality and exhibit p-type conductivity [18].

The presented NCD films still need some technological optimizations. One practical limitation is reproducible CVD deposition of NCD layer on Au metals. We observed that Au interdigitated electrodes deformed in the presence of hydrogen plasma. Next, the CVD deposition introduces a stress to the Au layer and in some cases, the Au interdigitated electrodes cracked and leaped away from the ceramic substrate. All these negative factors can significantly influence the starting “offset” value for the surface conductivity. Therefore, our “starting” surface conductivity varied by an order of magnitude in some cases. However, it should be further noted that this offset shifts in the starting surface conductivities did not influence the observed trends and/or dependences. Technological optimizations are in progress.

4 Conclusions NCD films were grown on Au interdigitated electrodes deposited on Al_2O_3 ceramic. The morphology of NCD films showed a dependence on the deposition time. We observed that oxygen-terminated NCD surface did not exhibit conductive properties. The H-terminated NCD samples exhibited a significant response to phosgene as the oxidizing gas. The conductivity of the NCD device increased with the increase in COCl_2 gas concentration. Less remarkable response was observed for reducing gases (CO_2 , NH_3). The surface conductivity of NCD

films increased for the relative humidity (RH) too. However, this increased doped down when the sensor was heated to 140°C . We can conclude that H-terminated NCD device is very promising for realizing the phosgene sensitive gas sensor element.

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