Biosensors and Bioelectronics 24 (2009) 1298–1304

Contents lists available at ScienceDirect

Biosensors and Bioelectronics

journal homepage: www.elsevier.com/locate/bios

Characterisation of capacitive field-effect sensors with a nanocrystalline-diamond film as transducer material for multi-parameter sensing

M.H. Abouzar[a,b], A. Poghossian[a,b,*], A. Razavi[a,b], O.A. Williams[c], N. Bijnens[c], P. Wagner[c,1], M.J. Schöning[a,b,2]

[a] Institute of Nano- and Biotechnologies, Aachen University of Applied Sciences, Campus Jülich, Germany
[b] Institute of Bio- and Nanosystems-2, Research Centre Jülich, Germany
[c] Institute for Materials Research, Hasselt University, Diepenbeek, Belgium

ARTICLE INFO

Article history:
Received 14 April 2008
Received in revised form 7 July 2008
Accepted 22 July 2008
Available online 5 August 2008

Keywords:
Nanocrystalline diamond
Capacitive field-effect sensor
pH sensor
Penicillin sensor
Charged macromolecules
Polyelectrolyte

ABSTRACT

The feasibility of a capacitive field-effect EDIS (electrolyte-diamond-insulator-semiconductor) platform for multi-parameter sensing is demonstrated by realising EDIS sensors with an O-terminated nanocrystalline-diamond (NCD) film as transducer material for the detection of pH and penicillin concentration as well as for the label-free electrical monitoring of adsorption and binding of charged macromolecules, like polyelectrolytes. The NCD films were grown on *p*-Si-SiO_2 substrates by microwave plasma-enhanced chemical vapour deposition. To obtain O-terminated surfaces, the NCD films were treated in an oxidising medium. The NCD-based field-effect sensors have been characterised by means of constant-capacitance method. The average pH sensitivity of the O-terminated NCD film was 40 mV/pH. A low detection limit of 5 μM and a high penicillin G sensitivity of 65–70 mV/decade has been obtained for an EDIS penicillin biosensor with the adsorptively immobilised enzyme penicillinase. Alternating potential changes, having tendency to decrease with increasing the number of adsorbed polyelectrolyte layers, have been observed after the layer-by-layer deposition of polyelectrolyte multilayers, using positively charged PAH (poly (allylamine hydrochloride)) and a negatively charged PSS (poly (sodium 4-styrene sulfonate)) as a model system. The response mechanism of the developed EDIS sensors is discussed.

1. Introduction

Due to the outstanding electrochemical properties, superior chemical inertness and biocompatibility, artificially grown diamond has been recognised as an extremely attractive material for both (bio-)chemical sensing and as an interface to biological systems (e.g., Hamers et al., 2005; Vermeeren et al., 2007; Bajaj et al., 2007; Rubio-Retama et al., 2006). Most of diamond-based field-effect (bio-)chemical sensors reported so far have been on the basis of polycrystalline or monocrystalline diamond films using a transistor structure. For instance, the potential use of diamond for direct electrical sensing of biological binding events such as DNA hybridisation and antibody-antigen binding was demonstrated in (Yang and Hamers, 2004; Song et al., 2006a; Yang et al., 2006; Nebel et al., 2007). An enzyme-modified diamond-based field-effect transistor (FET) has been realised for the detection of urea and glucose (Song et al., 2004). The pH- and ion-sensitive properties of an electrolyte-gate FET with monocrystalline and polycrystalline diamond surfaces have been investigated in (Song et al., 2003, 2006b; Kanazawa et al., 2003; Kawarada et al., 2001; Denisenko et al., 2007; Garrido et al., 2005; Rezek et al., 2006, 2007; Nebel et al., 2006a, 2006b; Dankerl et al., 2008). It has been observed that the electrical and electrochemical properties as well as the pH and ion (or salt) sensitivity of diamond are strongly affected by the surface termination. However, the origin of pH and ion sensitivity of diamond surfaces is still under discussion (see e.g., Nebel et al., 2006b; Rezek et al., 2006; Garrido et al., 2005; Kanazawa et al., 2003; Dankerl et al., 2008).

Recently, we have introduced a field-effect capacitive EDIS (electrolyte-diamond-insulator-semiconductor) structure as a platform for (bio-)chemical sensing (Christiaens et al., 2007). In contrast to transistor structures, EDIS sensors are simple in layout

* Corresponding author. Tel.: +49 2461 612605.
E-mail addresses: a.poghossian@fz-juelich.de (A. Poghossian), patrick.wagner@uhasselt.be (P. Wagner), m.j.schoening@fz-juelich.de (M.J. Schöning).
[1] Tel.: +32 11268882.
[2] Tel.: +49 241 6009 53215.

0956-5663/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.bios.2008.07.056

and cost-effective in fabrication. Usually, no photolithographic process steps or complicated encapsulation procedures are required in case of the capacitive field-effect EDIS structure. In addition, alternating current (AC) measurements with the EDIS structure are often more informative than static direct current (DC) measurements with the transistor structure. A feasibility of this platform has been exemplarily demonstrated by realising a pH-sensitive EDIS sensor with nanocrystalline-diamond (NCD) films (Christiaens et al., 2007).

In this work, capacitive field-effect EDIS structures with O-terminated NCD films as transducer material have been applied for the multi-parameter detection of pH and penicillin concentration as well as for the label-free electrical monitoring of adsorption and binding of charged macromolecules. Polyelectrolyte (PE) multilayers of positively charged PAH (poly (allylamine hydrochloride)) and negatively charged PSS (poly (sodium 4-styrene sulfonate)) deposited by layer-by-layer adsorption technique were chosen as a model system.

2. Experimental

2.1. Growth and physical characterisation of NCD films

Undoped NCD thin films of ~100 nm thickness were grown on *p*-Si-SiO_2 (ρ = 1–10 Ω cm, 50 nm thermally grown SiO_2) substrate by a microwave (2.45 GHz) plasma-enhanced chemical vapour deposition from a mixture of methane (CH_4) and hydrogen (H_2) in an ASTeX reactor. A schematic of the growth process is presented in Fig. 1(a). Prior to growth, the SiO_2 surface was seeded with a monodisperse colloid of nanocrystalline-diamond particles in water with an ultrasonic bath. In this work, the NCD grow process has been optimised to provide non-porous NCD thin films onto the Si-SiO_2 substrate. The gas flow rate, gas pressure, microwave power, substrate temperature and growth time were 485 sccm H_2, 15 sccm CH_4, 22 Torr, 3000 W, 490 °C and 240 min, respectively. For the details of NCD film's preparation, see (Daenen et al., 2006; Williams et al., 2007). An Al-film was deposited on the rear side of the sensor chip as a contact layer. The chip size of the EDIS sensor was 9.5 mm × 9.5 mm.

The NCD films have been characterised by scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) methods. The SEM micrograph in Fig. 1(b) demonstrates an example of the surface morphology of a 100 nm thick NCD film. As it can be seen, the films comprise randomly oriented fine grains and are totally closed. In addition, no pinholes have been observed in the film. AFM (Veeco, Multi-Mode) surface topography analysis of the samples (see Fig. 1(c)) has shown a surface roughness of 11 nm for a 100 nm thick NCD film. AFM images were recorded in the tapping mode with standard silicon tips.

Typically, as-prepared NCD surfaces are hydrogen (H)-terminated. To obtain oxygen (O)-terminated surfaces, the NCD films were treated in an oxidising boiling mixture of H_2SO_4 and KNO_3 at 338 °C for about 45 min. In order to establish the types and relative coverage of the surface functional groups generated by the oxidation of NCD surfaces, XPS analysis was carried out. XPS measurements were done using a PHI 5600 equipped with a monochromatic Al Kα radiation source. The O1s/C1s atomic concentration ratio for the O-terminated NCD films is about 10 at.%, as calculated by dividing the relevant peak areas in the recorded spectra by appropriate bulk atomic sensitivity factors. These values are comparable to those that have been reported in Liu et al. (2007) and Christiaens et al. (2007).

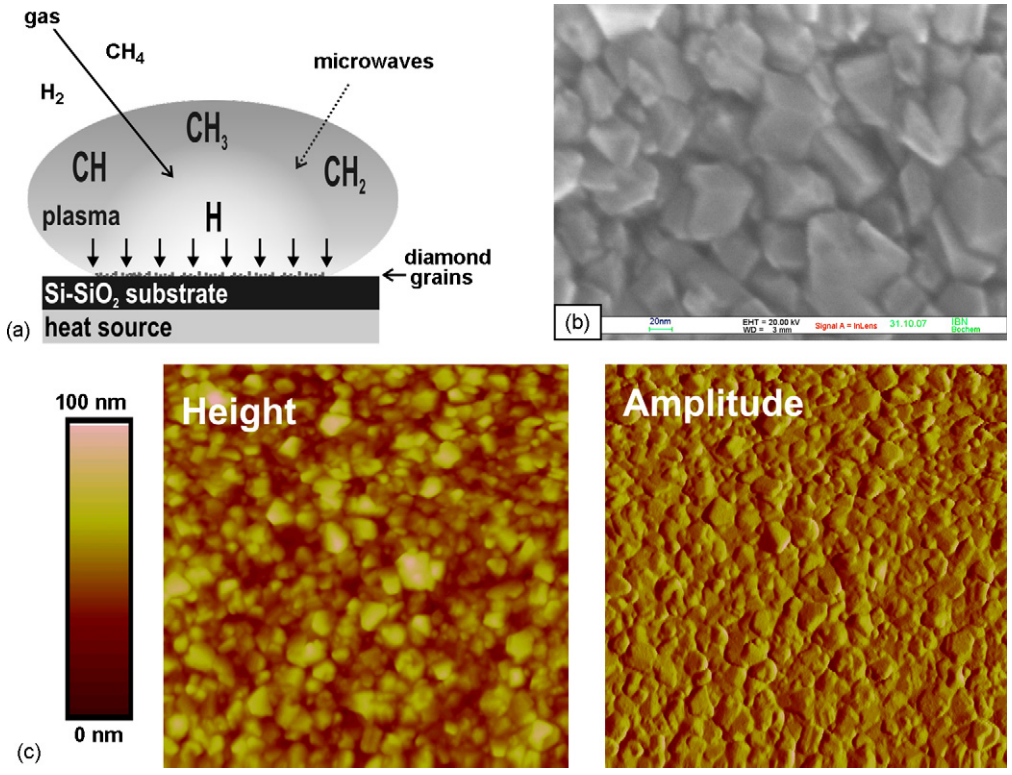


Fig. 1. (a) Schematic of the NCD growth process by a microwave plasma-enhanced chemical vapour deposition from a mixture of methane (CH_4) and hydrogen (H_2). (b) SEM picture of the surface morphology of a 100 nm thick NCD film deposited on a *p*-Si-SiO_2 substrate. (c) AFM image of a 100 nm NCD film grown on a *p*-Si-SiO_2 structure. The scan size was 2 μm × 2 μm. RMS roughness: 11 nm.

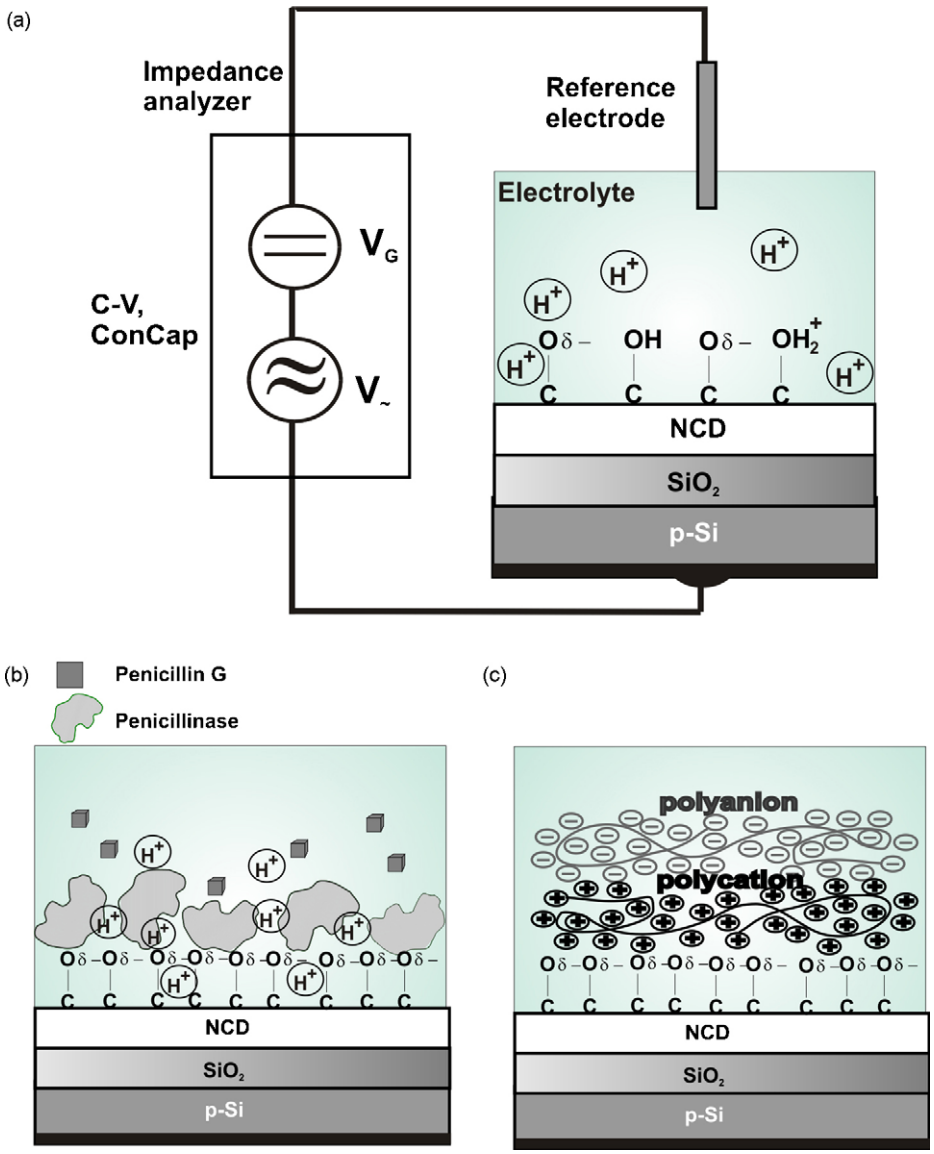


Fig. 2. Schematic cross-section of the pH (a), penicillin (b) and polyelectrolyte (c) sensor based on an O-terminated EDIS structure.

2.2. Measurement set-up

The bare O-terminated as well as functionalised (with enzyme penicillinase or polyelectrolyte mono- and multilayers) EDIS sensors (see Fig. 2) have been characterised by means of constant-capacitance (ConCap) method using an impedance analyzer (Zahner Elektrik) and a measuring set-up as presented in Fig. 2(a). The ConCap mode allows to measure the dynamic characteristics of the EDIS sensors. In the ConCap mode, the capacitance of the EDIS sensor is kept constant (usually within the depletion region of the capacitance–voltage curves at ~60% of the maximum capacitance) using a feedback-control circuit, and potential changes at the diamond/electrolyte interface have been directly monitored. For operation, a DC polarisation voltage is applied via the reference electrode (conventional liquid-junction Ag/AgCl electrode, Metrohm) to set the working point of the EDIS sensor, and a small AC voltage (20 mV) is applied to the system in order to measure the capacitance of the sensor. The measurements were carried out at a frequency of 100 Hz. All potential values are referred to a Ag/AgCl electrode.

For the experiments, the EDIS sensor was mounted into a home-made measuring cell, sealed by an O-ring and contacted on its front side by the electrolyte and a reference electrode, and on its rear side by a gold-plated pin. The sidewalls and backside contact of the EDIS sensor chip were protected from the electrolyte solution by means of an O-ring, thus, avoiding the complicated encapsulation process. The contact area of the EDIS sensor with the solution was about 0.5 cm^2. The measurements have been performed in a dark Faraday cage at room temperature.

3. Results and discussion

3.1. O-terminated EDIS structure as pH sensor

Fig. 3 demonstrates a typical ConCap response and calibration curve of an EDIS sensor with a 100 nm thick undoped O-terminated NCD film measured in Titrisol buffer with different pH values from pH 4 to 12. The O-terminated EDIS sensors show an average pH sensitivity of 40 mV/pH (evaluated from the ConCap response) in the range of pH 4–12 that is slightly higher than that has been reported

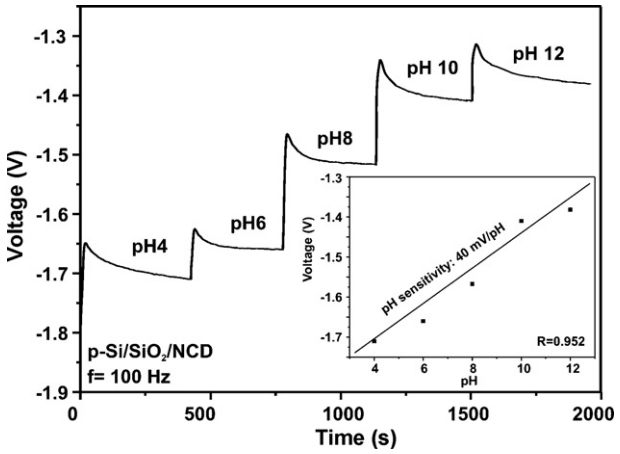


Fig. 3. Typical ConCap response of an EDIS structure with O-terminated NCD layer recorded in Titrisol buffer of different pH values from pH 4–12 and calibration curve (inset) of the pH sensor evaluated from ConCap response.

(38 mV/pH) previously (Christiaens et al., 2007). The response time ($t_{90\%}$) was about 60 s.

The mechanism of pH sensitivity of O-terminated NCD surfaces can be explained by using the site-binding model, similar to ion-sensitive field-effect transistors with oxide gate-insulators (see, e.g. Poghossian and Schöning, 2006a; Hal et al., 1996, and references there). Similar to the oxide/electrolyte interface, the presence of hydroxyl groups at the oxidised diamond surface could result in neutral (C–OH), negatively charged ($C–O^-$), or positively charged ($C–OH^{2+}$) surface groups (Song et al., 2006b; Garrido et al., 2005; Christiaens et al., 2007), depending on the pH value of the solution. As a result, at $pH > pH_{pzc}$ (where pH_{pzc} is the pH value at the point of zero charge), the diamond surface will be charged negatively, and at $pH < pH_{pzc}$ it will be positively charged. The resulting pH-dependent electrical surface charge of NCD leads to a modulation of the space-charge capacitance in the Si, thus, generating a pH-dependent sensor signal that, in fact, was observed during the ConCap measurements. According to this model, a distinct pH sensitivity is expected if surface hydroxyl groups are present on the NCD surface. An existence of hydroxyl groups on the oxidised diamond surfaces has been observed in (Kondo et al., 2005; Theije et al., 2001).

The obtained pH sensitivity of NCD films is higher as reported for SiO_2 layers (25–35 mV/pH) in (Cane et al., 1996), and smaller than that of Si_3N_4 (46–56 mV/pH), Al_2O_3 (49–57 mV/pH) and Ta_2O_5 films (55–59 mV/pH), which have often been utilised as pH-sensitive transducer material (see, e.g. recent review Poghossian and Schöning, 2006a). An improvement of the pH sensitivity of NCD surfaces is possible by increasing the density of O-terminated groups. The main advantages of NCD films are a superior chemical inertness, the possibility of operation in a chemically harsh environment without passivation of the surface, the possibility of creation of interfaces to biological systems by direct coupling of biomolecules onto the diamond surface via carbon groups, and biocompatibility.

3.2. NCD-based field-effect penicillin biosensor

The pH-sensitive properties of NCD films have been used to develop an EDIS-based penicillin biosensor. The determination of different kinds of penicillin is very important in medicine, pharmaceutical production, process control in fermentation broths, food industry and environmental monitoring. Most of Si-based penicillin biosensors have been developed for the determination of relatively high concentrations of penicillin in fermentation broths (see e.g., Poghossian and Schöning, 2006a; Schöning and Poghossian, 2006, and literature there). However, for several fields of application (e.g., drug control analysis of antibiotic tablets, capsules and injectables, food control) (bio-)chemical microsensors for the detection of small amounts of penicillin are also needed (Poghossian et al., 2001a, 2001b). For instance, antibiotic penicillin G is frequently used in veterinary practice for prevention and treatment of bacteria infection (Thavarungkul et al., 2007). This may lead to the presence of penicillin residues in foods (milk, meat, etc.) obtained from medicated animal and a small quantity of this compound might be responsible for allergic reactions in humans.

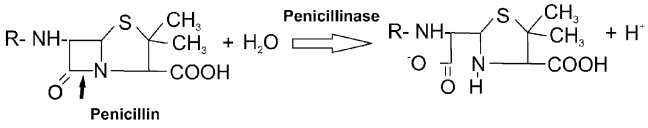
3.2.1. Enzyme immobilisation

The structure of the EDIS penicillin biosensor is schematically depicted in Fig. 2b. The developed penicillin biosensor consists of a pH-sensitive field-effect EDIS structure with immobilised β-lactamase (enzyme penicillinase). In this study, we have examined the performance of the EDIS penicillin biosensor with adsorptively immobilised penicillinase (EC 3.5.2.6, *Bacillus cereus* from Sigma, specific activity: 1650 units/mg protein) directly onto the O-terminated NCD film. The main advantages of the adsorptive immobilisation technique are its simplicity and cheapness without any loss of the enzyme activity and the possibility of a subsequent enzyme (sensor) regeneration, i.e. the possibility of a repeated enzyme immobilisation in the case of loss of enzyme activity (Poghossian et al., 2001a, 2001b; Poghossian and Schöning, 2006a).

The enzyme solution was prepared by dissolving the enzyme penicillinase in a 200 mM TEA buffer, pH 8. 10 μl enzyme solution per sensor was pipetted onto the samples, incubated at room temperature for about 1 h and dried in N_2 atmosphere. Finally, the sensors were rinsed in Titrisol buffer, pH 7. Before their first use, the penicillin sensors were incubated in working buffer for a least 1 h to let the enzyme membrane equilibrate. When not in use, the sensors were stored in Titrisol buffer, pH 7, at 4 °C.

3.2.2. Penicillin detection with EDIS sensor

The functioning of the EDIS penicillin biosensor is based on the detection of the local pH decrease near the surface of the pH-sensitive O-terminated NCD layer (see Fig. 2b) resulting from the catalysed hydrolysis of penicillin by the enzyme penicillinase according to the following reaction:



(1)

For the measuring procedure, about 1 ml of the working buffer or particular penicillin solution was applied to the EDIS gate surface, and the sensor output signal was recorded for about 3–5 min. After each measurement, the EDIS gate region was rinsed with distilled water or buffer solution. The penicillin solutions were prepared by dissolving penicillin G (benzyl penicillin, 1695 units/mg, Sigma) in the working buffer. As a working buffer, a 0.5 mM polymix multi-component buffer solution (pH 8) containing 100 mM KCl as an ionic-strength adjuster (Poghossian et al., 2001a, 2001b) or 0.5 mM phosphate buffer (100 mM KCl, pH 8) was used. The pH of the polymix buffer was adjusted to pH 8 by titration with NaOH solution.

The characteristics of the NCD-based penicillin biosensor were tested over a time period of two months. During this time period, the sensor has been periodically checked for more than 30 measurements in penicillin solution of different concentrations followed by

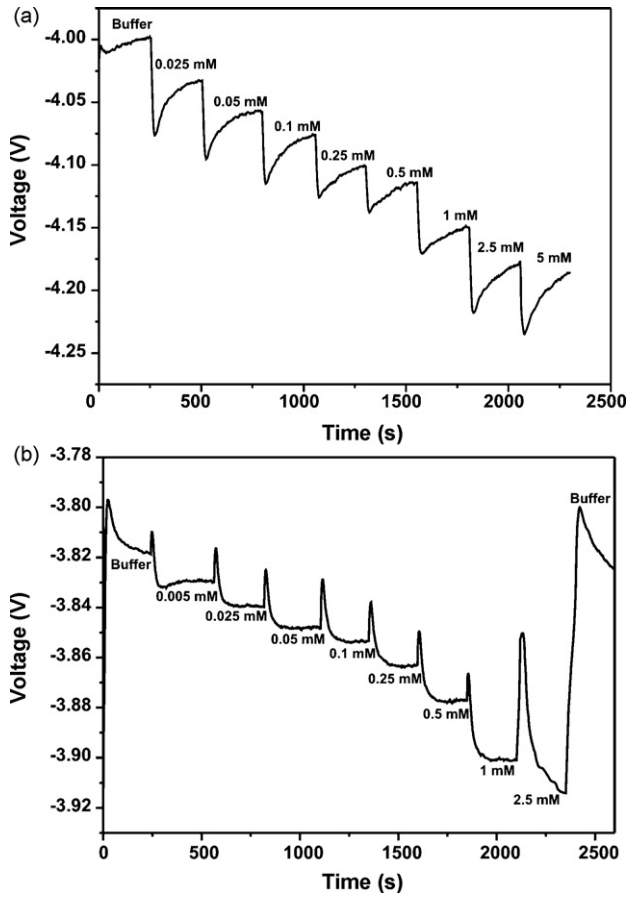


Fig. 4. Typical ConCap response of the developed NCD-based penicillin sensor with freshly immobilised enzyme penicillinase (a) and after two months enzyme immobilisation (b).

rinsing in buffer solution. Fig. 4 shows a ConCap response of freshly prepared (a) and after two months after the enzyme immobilisation (b). The corresponding calibration curves of the developed penicillin biosensors are presented in Fig. 5. The freshly prepared sensors show a high penicillin sensitivity of 65–70 mV/decade in the linear concentration range from 0.025 to 2.5 mM penicillin G. With increasing penicillin concentration from 0.025 to 5 mM, the concentration of the H^+ ions resulting from the penicillin hydrolysis is increased, too. As a result, the voltage that is necessary in order to adjust the constant capacitance raise. Even after two months the recorded sensor output voltage directly correlates with the respective penicillin concentration in the solution with a low detection limit of 5 μM. However, the penicillin sensitivity was approximately two times smaller (32 mV/decade in the linear range of 0.005–2.5 mM penicillin G) than that of the freshly prepared sensor. This could be due to washing out of the enzymes from the sensor surface during storage as well as frequent measurement and rinsing steps. Dependent on the penicillin concentration, the response time ($t_{90\%}$) of the EDIS biosensor was about 2–4 min, which is higher than that of penicillin-sensitive field-effect transistors with Ta_2O_5 gate (0.5–3 min) reported in (Poghossian et al., 2001a).

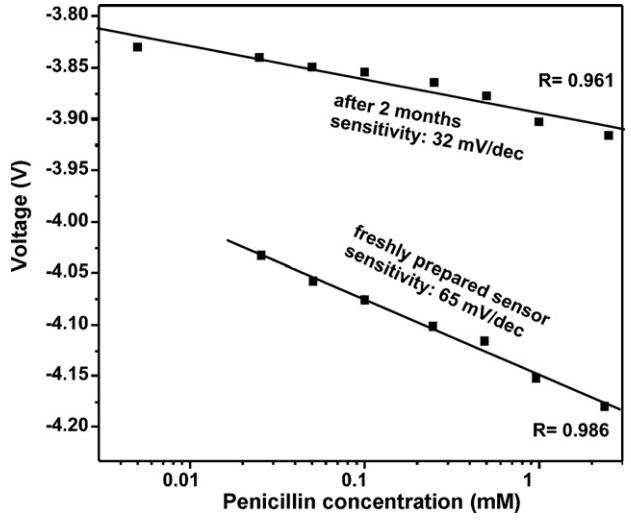


Fig. 5. Calibration curve of the developed penicillin biosensor.

3.3. Label-free electrical detection of charged macromolecules with EDIS sensor

Due to their simplicity and possibility of preparation of functional ultra-thin films with a nanoscale control of thickness, layer-by-layer (LbL) adsorbed PE multilayers are very suitable as model system for fundamental investigations of both molecular interactions at the solid/liquid interface and the label-free electrical detection of charged macromolecules (DNA, proteins, etc.) by means of field-effect devices. In addition, PE multilayers are very attractive as stimuli-responsive materials for drug release systems, biosensor and actuator fields (see e.g., Glinel et al., 2007).

Recently, the possibility of field-effect detection of PE layers with capacitive Si-SiO_2 and Si-SiO_2-Ta_2O_5 structures (Poghossian et al., 2006b, 2007a, 2007b, 2008) as well as Si thin-film resistors has been demonstrated (Neff et al., 2006a, 2006b, 2007). In the present work, the EDIS structure with O-terminated NCD film is used for a label-free electrical monitoring of the formation of PE multilayers in order to extend the functional capabilities of NCD films for multi-parameter sensing.

3.3.1. Functionalisation of O-terminated EDIS sensors with PE multilayers

Polyelectrolytes are linear macromolecule chains having a large number of charged groups when dissolved in water. The multilayers of PAH/PSS were obtained by using the LbL assembly technique (see e.g., Decher et al., 1998; Schönhoff, 2003; Schönhoff et al., 2007; Klitzing, 2006) by sequential adsorption of PAH and PSS from the respective PE solution. The PSS and PAH polyelectrolytes in powder form with an average molecular weight (Mw) of about 70000 were purchased from Sigma–Aldrich. The PAH is a weak PE and the degree of charging of its amine group depends on the pH of the aqueous solution. It is approximately fully charged at neutral and acidic solution, and is neutral at pH values above ten (Smith et al., 2004). The PSS is a kind of strong PE that totally dissociates in aqueous solutions and therefore, is fully negatively charged in a wide pH range as it liberates Na^+ ions (Smith et al., 2004). Usually, the dissolution of PAH and PSS changes the pH value of the electrolyte solution. Therefore, the pH of both PAH and PSS solutions was adjusted to the same value of pH 5.4 by titrating with NaOH and HCl.

During the experiment, the EDIS sensors were consecutively exposed to the respective PE solution for a time necessary for the adsorption of each single monolayer, followed by rinsing in electrolyte solution. We started the formation of the PE multilayer onto O-terminated NCD with positively charged PAH. In order to achieve a reproducible adsorption and sensor signal, the pH value and conductivity of PE solutions have been controlled before and after PE adsorption with a Mettler-Toledo MPC 227 pH/Conductivity Meter.

3.3.2. Label-free field-effect monitoring of the adsorption of charged PE

To obtain a picture according to which way the characteristics of the functionalised EDIS structures are affected by the number of PE layers, dynamic ConCap measurements have been performed during the whole multilayer formation. The ConCap measurement allows an in situ observation of the charge and potential changes at the interface, induced by the adsorption of each PE layer. As an example, Fig. 6 shows a typical ConCap response for a bare O-terminated EDIS sensor and an EDIS sensor functionalised with 15 PE layers. In this experiment, the bare EDIS sensor was first equilibrated in buffer solution, then the PAH solution (50 μM PAH, 0.1 M NaCl, pH 5.4) was applied to the sensor, and the sensor signal was recorded for about 5 min, followed by rinsing the measuring cell and the sensor surface with buffer solution and measurement in buffer solution (0.1 M NaCl, pH 5.4) for about 3 min. In the next step, the PSS solution (50 μM PSS, 0.1 M NaCl, pH 5.4) has been applied to the sensor surface and the ConCap response was recorded for about 5 min, again. These procedures were repeated until the 15 PE layers have been deposited. Thus, the sensor signal was monitored continuously during the whole PE multilayers build-up.

As can be seen from Fig. 6, the adsorption of negatively charged PSS shifts the potential towards the direction of a more negative surface charge (corresponding to a more positively sensor signal due to the feedback control in the ConCap mode), whereas the adsorption of the positively charged PAH shifts the sensor signal into the direction corresponding to a more positive charged insulator surface (the observed signal changes after each rinsing step are probably due to the remove of loosely attached PE macromolecules). Thus, the molecular layers induce an interfacial potential change resulting in alternating changes in the flat-band voltage of the EDIS structure and consequently, in a kind of zigzag curve of the signal changes as a function of the PE layer number (see Fig. 6, inset graph). Moreover, the potential shifts have a tendency to decrease with increasing the number of PE layers. For example, potential shifts decrease from originally 35 to 40 mV for an EDIS structure with first PE layers to 2–4 mV for an EDIS structure with 14–15 PE layers, respectively. Similar effects have been observed for Si thin-film resistors (Neff et al., 2006a, 2006b, 2007) and capacitive Si-SiO_2 structures functionalised with PE multilayers (Poghossian et al., 2007b, 2008), and were explained by the mechanism based on a screening of PE charges by mobile ions within the PE film (Neff et al., 2006b, 2007) and an ion- and/or proton-concentration redistribution within the PE multilayer induced by the charge of the outermost layer (Poghossian et al., 2007b, 2008).

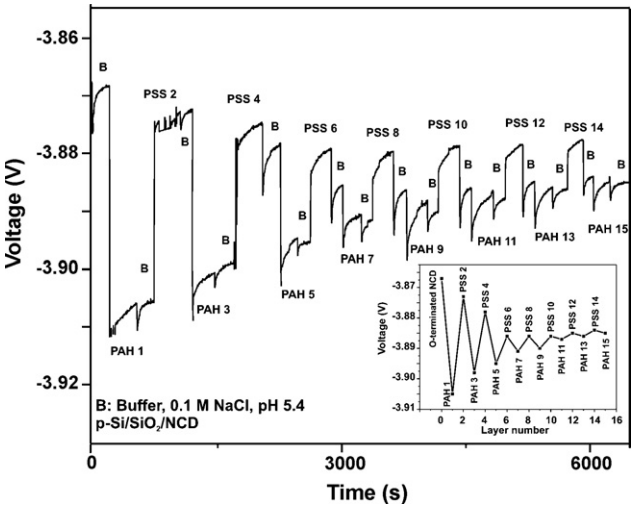


Fig. 6. Label-free electrical detection of charged PE multilayers with an EDIS sensor: ConCap response and the signal changes as a function of the PE layer number (inset graph).

4. Conclusions

The obtained results demonstrate the feasibility of EDIS structures with O-terminated NCD films as transducer material for multi-parameter sensing of different (bio-)chemical quantities, namely, pH value and penicillin concentration as well as charged macromolecules by using PE multilayers as model system. The immobilisation of biomolecules, like DNA and proteins on NCD films, for extending the biosensor capabilities of the EDIS platform, will be subject of our future studies.

Acknowledgements

The authors thank A. Besmehn and H.P. Bochem for technical support. Part of this work was supported by the School for Life Sciences of the Transnational University Limburg (IWT-SBO project "CVD diamond: a novel multifunctional material for high temperature electronics, high power/high frequency electronics and bioelectronics").

References

Bajaj, P., Akin, D., Gupta, A., Sherman, D., Shi, B., Auciello, O., Bashir, R., 2007. Biomed. Microdevices 9, 787–794.
Cane, C., Götz, A., Merlos, A., Gracia, I., Errachid, A., Losantos, P., Lora-Tamayo, E., 1996. Sens. Actuators B 35–36, 136–140.
Christiaens, P., Abouzar, M.H., Poghossian, A., Wagner, T., Bijnens, N., De Ceuninck, W., Williams, O.A., Daenen, M., Haenen, K., Schöning, M.J., Wagner, P., 2007. Phys. Stat. Sol. (a) 204, 2925–2930.
Daenen, M., Williams, O.A., D'Haen, J., Haenen, K., Nesladek, M., 2006. Phys. Stat. Sol. (a) 203, 3005–3010.
Dankerl, M., Reitinger, A., Stutzmann, M., Garrido, J.A., 2008. Phys. Stat. Sol. (RRL) 2, 31–33.
Decher, G., Eckle, M., Schmitt, J., Struth, B., 1998. Curr. Opin. Coll. Interface Sci. 3, 32–39.
Denisenko, A., Jamornmarn, G., El-Hajj, H., Kohn, E., 2007. Diamond Relat. Mater. 16, 905–910.
Garrido, J.A., Härtl, A., Kuch, S., Stutzman, M., Williams, O.A., Jackmann, R.B., 2005. Appl. Phys. Lett. 86, 073504.
Glinel, K., Dejugnat, C., Prevot, M., Schöler, B., Schönhoff, M., v Klitzing, R., 2007. Coll. Surf. A 303, 3–13.
Hal, R.E.G., Eijkel, J.C.T., Bergveld, P., 1996. Adv. Colloid Interface Sci. 69, 31–62.
Hamers, R.J., Butler, J.E., Lasseter, T., Nichols, B.M., Russell, J.N., Tse, K.-Y., Yang, W., 2005. Diamond Relat. Mater. 14, 661–668.
Kanazawa, H., Song, K.-S., Sakai, T., Nakamura, Y., Umezawa, H., Tachiki, M., Kawarada, H., 2003. Diamond Relat. Mater. 12, 618–622.
Kawarada, H., Araki, Y., Sakai, T., Ogawa, T., Umezawa, H., 2001. Phys. Stat. Sol. (a) 185, 79–83.
Klitzing, R., 2006. Phys. Chem. Chem. Phys. 8, 5012–5033.
Kondo, T., Honda, K., Tryk, D.A., Fujishima, A., 2005. J. Electrochem. Soc. 152, E18–E23.
Liu, F.B., Wang, J.D., Liu, B., Li, X.M., Chen, D.R., 2007. Diamond Relat. Mater. 16, 454–460.
Nebel, C.E., Rezek, B., Shin, D., Watanabe, H., Yamamoto, T., 2006a. J. Appl. Phys. 99, 033711.
Nebel, C.E., Rezek, B., Shin, D., Watanabe, H., 2006b. Phys. Stat. Sol. (a) 203, 3273–3298.
Nebel, C.E., Shin, D., Rezek, B., Tokuda, N., Uetsuka, H., Watanabe, H., 2007. J. R. Soc. Interface 4, 439–461.
Neff, P.A., Naji, A., Ecker, C., Nickel, B., von Klitzing, R., Bausch, A.R., 2006a. Macromolecules 39, 463–466.
Neff, P.A., Wunderlich, B.K., Lud, S.Q., Bausch, A.R., 2006b. Phys. Stat. Sol. (a) 14, 3417–3423.
Neff, P.A., Wunderlich, B.K., v Klitzing, R., Bausch, A.R., 2007. Langmuir 23, 4048–4052.
Poghossian, A., Schöning, M.J., Schroth, P., Simonis, A., Lüth, H., 2001a. Sens. Actuators B 76, 519–526.
Poghossian, A., Thust, M., Schroth, P., Steffen, A., Lüth, H., Schöning, M.J., 2001b. Sens. Mater. 13, 207–223.
Poghossian, A., Schöning, M.J., 2006a. In: Grimes, C.A., Dickey, E.C., Pishko, M.V. (Eds.), Encyclopedia of Sensors, vol. 9. American Scientific Publishers, Stevenson Ranch (USA), pp. 463–534.
Poghossian, A., Abouzar, M.H., Sakkari, M., Kassab, T., Han, Y., Ingebrandt, S., Offenhäusser, A., Schöning, M.J., 2006b. Sens. Actuators B 118, 163–170.

Poghossian, A., Abouzar, M.H., Amberger, F., Mayer, D., Han, Y., Ingebrandt, S., Offenhäusser, A., Schöning, M.J., 2007a. Biosens. Bioelectron. 22, 2100–2107.
Poghossian, A., Ingebrandt, S., Abouzar, M.H., Schöning, M.J., 2007b. Appl. Phys. A 87, 517–524.
Poghossian, A., Abouzar, M.H., Schöning, M.J., 2008. IRBM 29, 149–154.
Rezek, B., Watanabe, H., Shin, D., Yamamoto, T., Nebel, C.E., 2006. Diamond Relat. Mater. 15, 673–677.
Rezek, B., Shin, D., Watanabe, H., Nebel, C.E., 2007. Sens. Actuators B 122, 596–599.
Rubio-Retama, J., Hernando, J., Lopez-Ruiz, B., Härtl, A., Steinmüller, D., Stutzmann, M., Lopez-Cabarcos, E., Garrido, J.A., 2006. Langmuir 22, 5837–5842.
Schönhoff, M., 2003. Curr. Opin. Coll. Interface Sci. 8, 86–95.
Schönhoff, M., Ball, V., Bausch, A.R., Dejugnat, C., Delorme, N., Glinel, K., v Klitzing, R., Steitz, R., 2007. Coll. Surf. A 303, 14–29.
Schöning, M.J., Poghossian, A., 2006. Electroanalysis 18, 1893–1900.
Smith, R.N., McCormick, M., Barrett, C.J., Reven, L., Spiess, H.W., 2004. Macromolecules 37, 4830–4838.
Song, K.-S., Sakai, T., Kanazawa, H., Araki, Y., Umezawa, H., Tachiki, M., Kawarada, H., 2003. Biosens. Bioelectron. 19, 137–140.
Song, K.-S., Degawa, M., Nakamura, Y., Kanazawa, H., Umezawa, H., Kawarada, H., 2004. Jpn. J. Appl. Phys. 43, L814–L817.
Song, K.-S., Zhang, G.-J., Nakamura, Y., Furukawa, K., Hiraki, T., Yang, J.-H., Funatsu, T., Ohdomari, I., Kawarada, H., 2006a. Phys. Rev. E 74, 041919.
Song, K.-S., Nakamura, Y., Sasaki, Y., Degawa, M., Yang, J.-H., Kawarada, H., 2006b. Anal. Chim. Acta 573, 3–8.
Thavarungkul, P., Davan, S., Kanatharana, P., Asawatreratanakul, P., 2007. Biosens. Bioelectron. 23, 688–694.
Theije, F.K., Reedijk, M.F., Arsic, J., van Enckevort, W.J.P., Vlieg, E., 2001. Phys. Rev. B 64, 085403.
Vermeeren, V., Bijnens, N., Wenmackers, S., Daenen, M., Haenen, K., Williams, O.A., Ameloot, M., vandeVen, M., Wagner, P., Michiels, M., 2007. Langmuir 23, 13193–13202.
Williams, O.A., Douheret, O., Daenen, M., Haenen, K., Osawa, E., Takahashi, M., 2007. Chem. Phys. Lett. 445, 255–258.
Yang, W., Hamers, R.J., 2004. Appl. Phys. Lett. 85, 3626–3628.
Yang, J.-H., Song, K.-S., Kuga, S., Kawarada, H., 2006. Jpn. J. Appl. Phys. 45, L1114–L1117.