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

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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

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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).

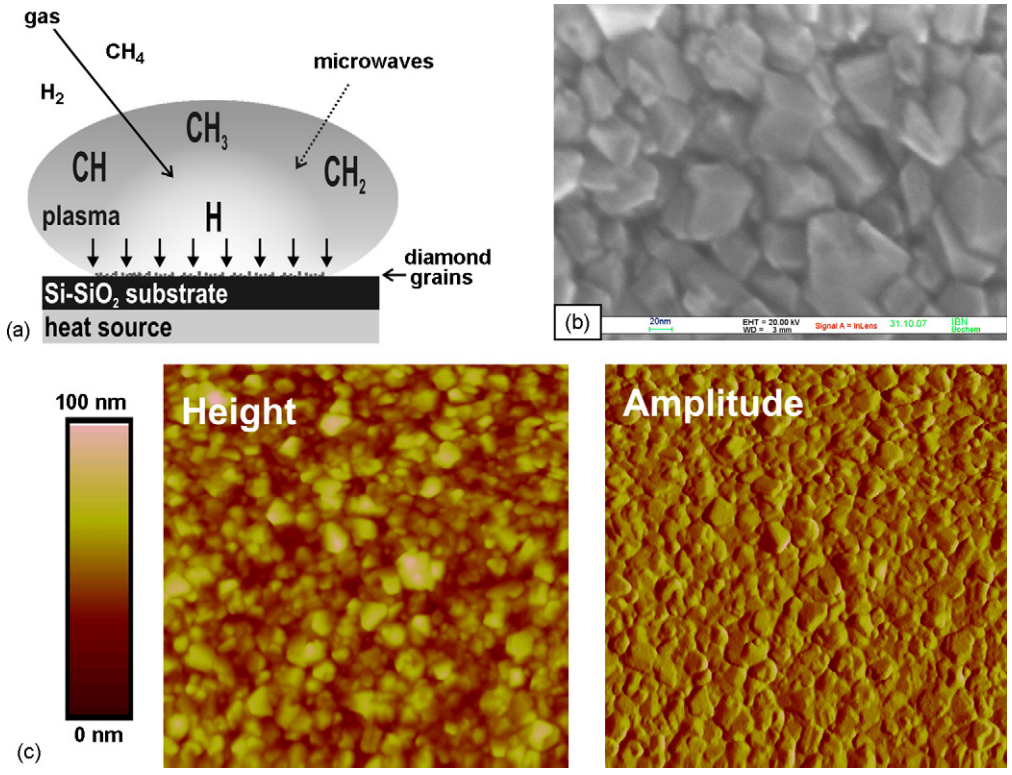

Fig. 1. (a) Schematic of the NCD growth process by a microwave plasma-enhanced chemical vapour deposition from a mixture of methane (CH_4) and hydrogen (H_2). (b) SEM picture of the surface morphology of a 100 nm thick NCD film deposited on a *p*-Si-SiO_2 substrate. (c) AFM image of a 100 nm NCD film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