Sensing the charged macromolecules with nanocrystalline diamond-based field-effect sensor

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1. Introduction

Artificially grown diamond thin films have been recognised as an extremely attractive material for electronic devices which could replace silicon in the future. Due to the outstanding properties such as a superior chemical inertness, a large electrochemical potential window, the possibility of operation in a chemically harsh environment without passivation of the surface that is required for Si-based sensors, and its biocompatibility, diamond is also favoured as transducer material for chemical and biological sensing, in particular, for the detection of molecular interactions at the solid/liquid interface [1]. Moreover, the carbon composition, which is the basis of all organic matter, might allow a direct coupling of biological recognition elements onto the diamond surface and thus, offers a new challenge in creating interfaces to biological systems.

Most of diamond-based field-effect (bio-)chemical sensors have been realised on polycrystalline or monocrystalline diamond films using a transistor structure (see, e.g. [2,3]). Recently, we have introduced a field-effect capacitive EDIS (electrolyte-diamond-insulator-semiconductor) structure as platform for (bio-)chemical sensing [4]. In contrast to transistor structures, EDIS sensors are simple in layout, easy and cost-effective in fabrication. A feasibility of this platform has exemplarily been demonstrated by realising a pH-sensitive EDIS sensor, where nanocrystalline diamond (NCD) films with hydrogen (H)- and oxygen (O)-terminated surfaces serve as pH-sensitive transducer material.

In this work, the possibility of a label-free electrical detection of layer-by-layer adsorption and binding of charged macromolecules onto NCD surfaces using an EDIS structure is demonstrated for the first time. The positively charged polyelectrolyte (PE) PAH (Poly (allylamine hydrochloride)) and negatively charged PSS (Poly (sodium 4-styrene sulfonate)) have been used as a model system.

2. Experimental

Undoped NCD thin films (100-500 nm thickness) were grown on p-Si-SiO_2 (50 nm) substrates by a microwave plasma-enhanced chemical vapour deposition from a standard mixture of methane and hydrogen [4,5]. To obtain an O-terminated surface with insulating properties, the diamond surfaces were treated in an oxidising boiling mixture of H_2SO_4 and KNO_3. The results of XPS (X-ray photoelectron spectroscopy) analysis have shown that the O1s/C1s atomic concentration ratio for the O-terminated NCD films is about 10 at.%. The SEM (scanning electron microscopy) micrograph in Fig. 1 demonstrates an example of the morphology of a 100 nm and a 500 nm thick NCD film, respectively. The average grain size for the 100 nm thick NCD film is around 100 nm.

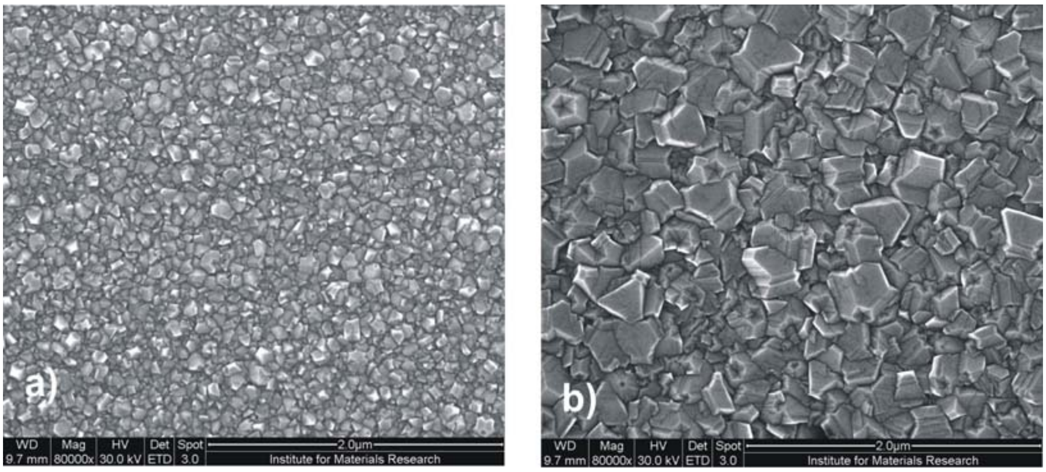

Fig. 1. Scanning electron micrograph of a 100 nm (a) and 500 nm (b) thick NCD film.

The PE multilayer (maximum number of PE layers was 6) was obtained using the layer-by-layer technique by consecutive adsorption of PAH and PSS from the respective PE solution (50 µM PSS or PAH, unbuffered 0.1 M NaCl, pH 5.3). The thickness of the multilayer consisting of three PAH/PSS double layers was ~12 nm, i.e. 2 nm/per layer. For the details of PE adsorption, see [6-8].

The EDIS sensors functionalised with a multilayer of charged macromolecules have been characterised by capacitance-voltage method and constant-capacitance method [9]. The measurement set-up, the layer structure as well as the simplified equivalent circuit of the EDIS sensor functionalised with charged macromolecules is presented in Fig. 2. For operation, a d.c. (direct current) polarisation voltage is applied via the reference electrode to set the working point of the EDIS sensor, and a small a.c. (alternating current) voltage (10-50 mV) is applied to the system in order to measure the capacitance of the sensor.

3. Results and discussions

Fig. 3 shows typical *C-V* curves for an EDIS sensor as-prepared and after the adsorption of each PE layer. As it can be seen, the adsorption of an additional PE layer shifts the *C-V* curve of the original EDIS structure along both the capacitance and voltage axis.

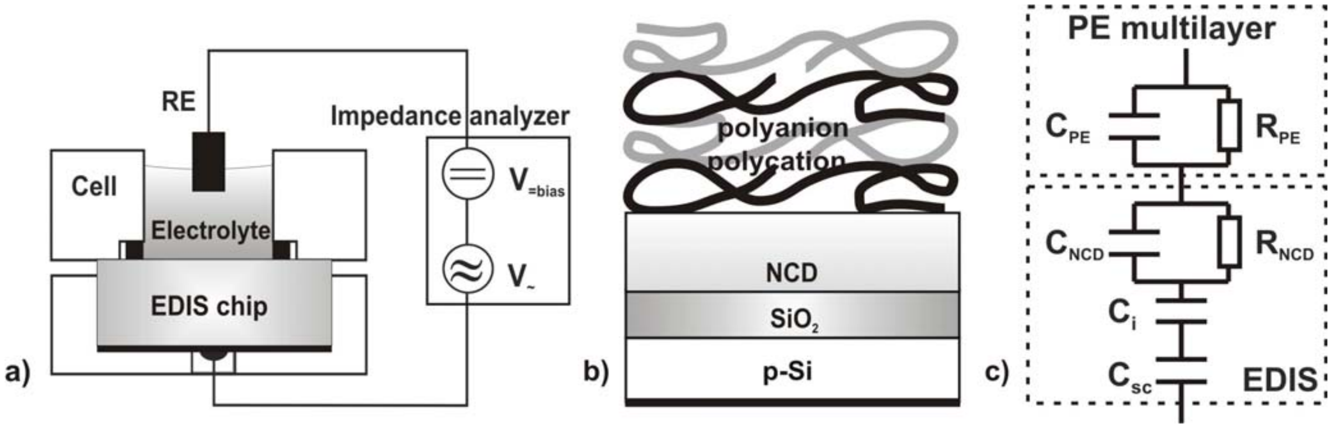

Fig. 2. Measurement set-up (a), schematic cross-section of a PE layer structure (b), and simplified equivalent circuit of the EDIS sensor functionalised with charged macromolecules (c). RE: reference electrode; C_{PE}, C_{NCD}, C_i and C_{SC} are capacitances of the PE multilayer, the NCD, the gate insulator and the space-charge region in the semiconductor, respectively; R_{PE} and R_{NCD} are resistances of the PE layer and the NCD, respectively.

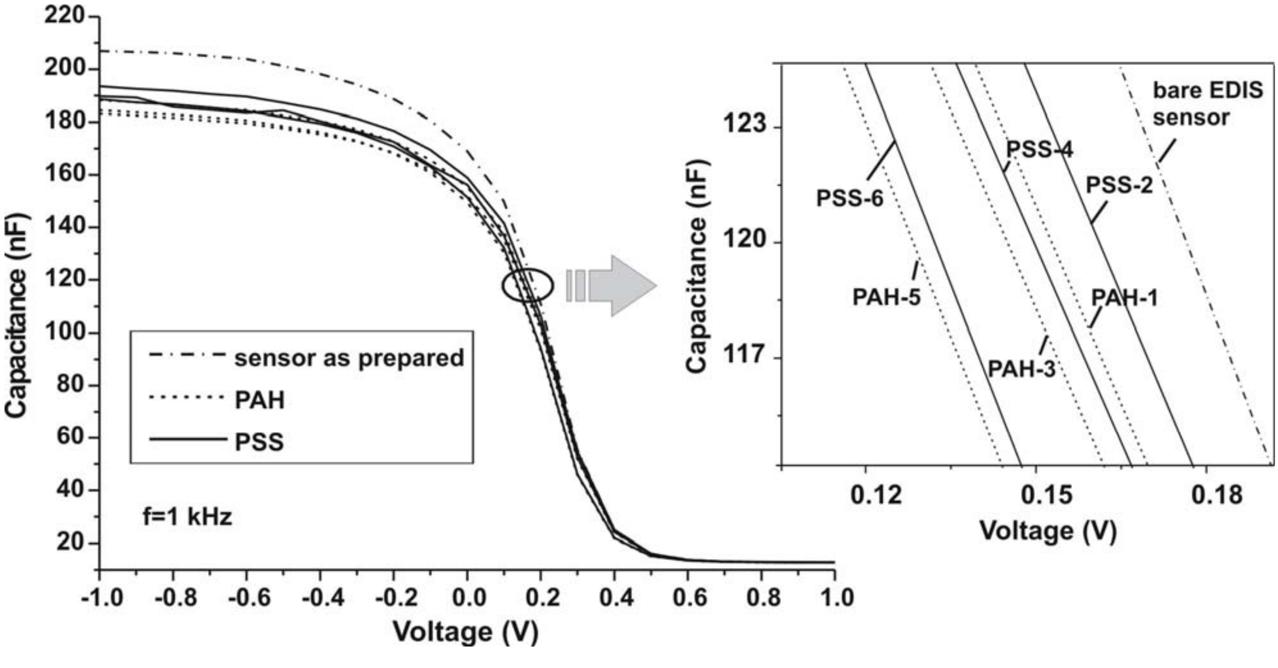

Fig. 3. Typical *C-V* curves for the EDIS sensor as prepared and after the adsorption of positively charged PAH and negatively charged PSS layer, respectively.

Small changes (5-10%) in the maximum capacitance of the *C-V* curve in the accumulation range are due to an additional series impedance of the molecular layer [9]. Alternating potential shifts (4-24 mV) have been observed along the voltage axis after the adsorption of each PSS and PAH layer onto the NCD surface. These shifts can clearly be recognised from the zoomed graph in the depletion region

(~60% of the C_{max}). The direction of the shift depends on the sign of the charge of the terminating polyelectrolyte layer. In case of the adsorption of the positively charged PAH, the potential shifts into the direction as for an additional positively charging of the NCD surface. Consequently, the direction of the potential change after adsorption of the negatively charged PSS corresponds to the case as if the NCD surface would have been additionally negatively charged. This indicates that the molecular layer may also induce an interfacial potential change (that is in series to the applied gate voltage) at the electrolyte side and/or gate-insulator side of the molecular layer, resulting in alternating changes of a flat-band voltage of the EDIS structure. Similar changes in the flat-band voltage have also been observed after adsorption of PAH and PSS onto a p-Si-SiO_2 or p-Si-SiO_2-Ta_2O_5 structure [6,8]. Nevertheless, the mechanism of signal generation is not yet clear in detail.

4. Conclusions

The obtained results demonstrate the feasibility of EDIS structures for a label-free electrical detection of charged macromolecules. The immobilisation of biomolecules, like DNA (deoxyribonucleic acid) and proteins on NCD films for extending the biosensor capabilities will be subject of future works.

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