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Pokročilé (bio) senzorické prvky na bázi diamantu

Advanced diamond-based (bio) sensors

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Summary

Development and implementation of specific materials for (bio-) sensors is one of the most rapidly developing fields in micro-electronic. Synthetic diamond thin films exhibit an extraordinary combination of intrinsic properties which make it an attractive material for label free investigation and monitoring of (bio-) molecules and complex biological systems. The diamond thin film becomes widely used as a functional layer whose surface is morphologically and chemically tailored to specific requirements.

Hydrogen terminated intrinsic diamond films reveal a phenomenological property - induced p-type surface conductivity which has been used for fabrication of optically transparent electronic devices including impedance elements and field effect transistors.

This study draws on research conducted by employing diamond functional films for optical and electronic (bio-) sensoric uses and point out fundamental technological and physical principles for detection of (bio-) materials.

Souhrn

Vývoj a implementace nových materiálů pro (bio-) senzoriku jsou akcelerovány přirozeným požadavkem pro dynamicky se vyvíjející obor mikroelektroniky. Syntetické diamantové vrstvy vykazují výjimečnou kombinaci intrinzických vlastností, což předurčuje jejich využití ke studiu a monitorování (bio-) molekul a komplexních biologických systémů. Vodíkem terminovaný povrch intrinzického diamantu vykazuje fenomenologickou vlastnost – indukovanou povrchovou vodivost p-typu, která se využívá pro realizaci opticky transparentních impedančních elektronických prvků a tranzistorů řízených elektrickým polem. V současné době se použití diamantových vrstev, jako funkčního materiálu s morfologicky a chemicky definovaným povrchem, stává realitou.

Předložená práce se věnuje využití diamantových vrstev pro (bio) senzorické aplikace a technologickým a fyzikálním principům detekce jednotlivých (bio) materiálů.

Klíčová slova

diamant, nukleace, chemická depozice z par plynů, tenká vrstva,
povrchová elektrická vodivost, planární impedanční prvek,
tranzistor řízený polem, senzor molekul plynů a biomolekul,
senzor růstu buněk

Keywords

diamond, nucleation, chemical vapor deposition, thin film,
surface electrical conductivity, planar impedance element,
field effect transistor, sensor of gas molecules and biomolecules,
sensor of cell growth

Content

1. Introduction

Over the last several years reports in the literature have pointed out the advantages of smart and (bio-) functional materials for interdisciplinary fields as material engineering, (bio-) electronic or (bio-) sensoric, chemistry and physics, life science and regenerative medicine, etc. However, these multifunctional materials have to exhibit extraordinary combination of intrinsic properties such as high reflection vs. transition, high mobility of charge carriers vs. insulating properties, chemical/thermal/radiation and mechanical resistance, hardness, flexibility, long-term stability, selectivity and sensitivity, biocompatibility, etc.

Rapidly developing field of (bio-) sensors expects the implementation of specific materials according to a form of sensed domain and a type of signal to be produced and distributed. Such materials are used not only as mechanically passive substrates (a concept similar to photoluminescence measurements) but also as active devices, i.e. electro-opto-mechanical complex systems known as Micro-Electronic Mechanical Systems (MEMS) or Lab-on-Chip devices.

The fabrication of novel (bio-) sensors often requires not only implementation of extraordinary materials but also the development of new procedures for self-assembled (nano-) structuring, respectively semiconductor based technologies and multidisciplinary-related processes including (bio-) chemistry, nano-manipulation, biological protocols and others.

Diamond thin films represent a class of multi-functional materials which morphological, chemical, optical and electronic properties are tailorable on demand for above mentioned applications. This work reviews diamond properties, continues with nucleation and techniques, and points out representative diamond based (bio-) sensors at the end.

2. Diamond Thin Films

2.1. Diamond Properties

The element carbon occurs in various *allotropic* forms, each with characteristic intrinsic properties predefined by its prevalent atom bonding type. Diamond belongs to the cubic Fd3m-O7h space group. The diamond structure has a face-centered cubic lattice with two atoms per primitive unit cell. Each carbon atom is tetrahedrally coordinated to four other carbon atoms via sigma bonds of sp^3 hybrid atomic orbitals, with a C-C bond energy of 711 kJ/mol [1]. For diamond, the cubic edge “*a*” is 3.5667 Å at 0 °C and the bond length is 0.154 nm [2].

Its strong chemical bond lead to a unique combination of physical (high thermal conductivity), mechanical (hardness, Young’s modulus, wear resistance, high acoustic velocity), chemical (chemical inertness, high affinity for covalent bonding with specific organic molecules), optical (high transparency in wide optical range) and electrical properties (wide band gap semiconductor – tuneable electronic behaviour) [3]. Only briefly, chemical inertness of diamond is required for fabrication of electronic devices working in harsh environments (acids, high temperature, etc.). Its low relative permittivity (5.5) is a very useful property for microwave devices among semiconducting materials. The large energy bandgap (5.45 eV) of diamond designates it as a very suitable material for high temperature electronic devices. Combination of high mobility, breakdown and thermal conductivity results in the largest Johnson's and Keys' figures of merit by far. These figures of merit combine electrical (e.g. carrier mobility, breakdown voltage) and thermal (heat dissipation) properties of materials to indicate their relative capability to handle a power or speed in comparison to Si, GaAs or β-SiC.

2.2. Diamond Synthesis

Diamond nucleation: The diamond thin film growth on non-diamond substrates (silicon, quartz, AlN, etc.) is not a trivial issue due to the high surface energy of diamond and its metastable character of the sp^3 hybridization. Firstly, such substrates have to be pretreated (nucleated) to compensate differences in surface energies of the substrate and diamond [4]. Various nucleation techniques have been developed and optimized in accordance to substrate properties, especially its mechanical stability (stiffness and hardness), shape and geometry, chemical reactivity or even electrical conductivity. Figure 1 summarizes nucleation techniques developed up to day. Technological details including their advantages and disadvantages can be found in book chapters [5,6] and review papers [7,8].

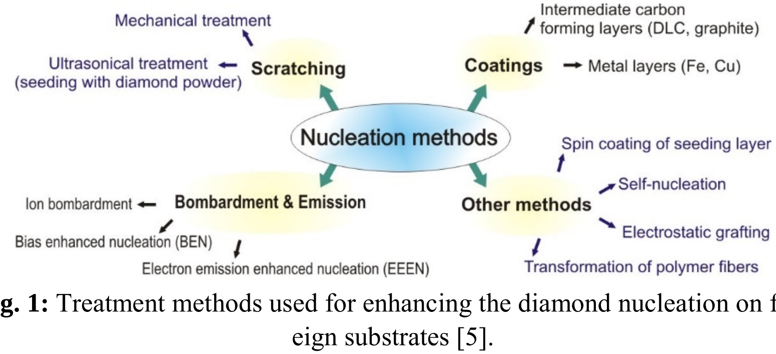

Fig. 1: Treatment methods used for enhancing the diamond nucleation on foreign substrates [5].

Diamond growth: The chemical vapor deposition (CVD) of diamond thin films includes several steps: a) the activation of gases into radicals by appropriate source of energy, b) gas phase chemical reactions between the activated species, c) transport of the gas species to the substrate, and d) reactions on the substrate [9]. The CVD process is often provided at temperatures 400÷1000 °C and at pressures < 20 kPa from a gas mixture of diamond-forming growth species (CO_x, CH_4, C_xH_y, etc.) and a powerful selective etchant (e.g. hydrogen, oxygen, fluorine, etc.) in order to remove the non-diamond carbon phases from the growing diamond film [8,10]. In the hydrogen rich ($H_2 > 90\%$) gas mixture, molecular hydrogen is dissociated to atomic hydrogen and initializes a set of chemical reactions – i) selective etching of non-diamond carbon phases, ii) diamond surface stabilization and iii) production of methyl radicals (CH_3) known as the main growth species. The gas activation is provided by external heating (chemical reactions driven by the hot filaments as Ta, W, Mo) and oxy-acetylene flame process, or by plasma activation at DC, radiofrequency or microwave frequency.

Today, where a large number of various CVD techniques demonstrate a successful diamond growth on various substrates, the hot filament CVD (HF CVD) and microwave CVD techniques are the most used processes over the world.

3. Hydrogen and Oxygen Terminated Diamond Surface

The diamond surface reveals a distinct feature – its surface can be covalently terminated with different atoms (molecules). Such termination can be easily visualized by wetting angle (CA), i.e. either highly hydrophobic or hydrophilic properties. The water contact angle can vary from extremely low values (<5°) up to as high as values of 110° (super-hydrophobic surface) and is controlled on the atomic level by the diamond surface termination (Fig. 2). Among of variety of atomic or molecular terminations, there are two typical diamond surface terminations known as oxygen and hydrogen terminated diamond surface. As discussed below, both these terminations tailor wetting properties and surface conductivities.

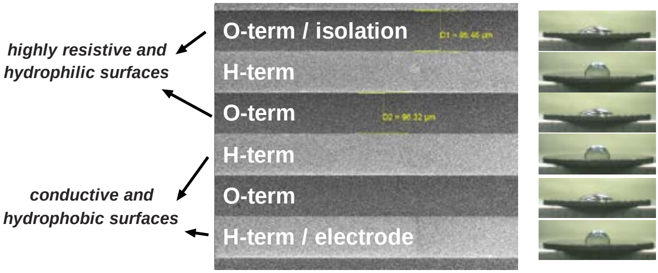

Fig. 2: Scanning electron microscopy of oxygen (O-term) and hydrogen (H-term) terminated diamond surfaces (on the left) and appropriate contact angle images (on the right).

3.1. Hydrogen Termination

The hydrogen terminated diamond surface is hydrophobic with the contact angle varied from 60 to 110° depending on the size of crystals, their orientation and surface morphology. It is naturally built during the diamond CVD. The hydrogen-terminated diamond surface induces a hole accumulation in a close proximity to the surface [11]. The *two-dimensional hole gas channel* is generated without any dopant atoms. The hole accumulation mechanism is under controversial discussion. [12]. Due to electronegativity differences of hydrogen and carbon (2.1 vs. 2.5, respectively), formed C–H dipoles and adsorbates are essential for hole accumulation (Fig. 3). The C–H dipoles lead to the spontaneous polarisation, and after exposing such surface to ambient air, the surface conductivity occurs due to the surface transfer doping effect [13,14].

The first diamond electronic device based on the induced p-type conductivity should be dedicated to the work of Kawarada [15] who presented the diamond based metal-semiconductor field effect transistor (FET). Above mentioned findings on H-terminated diamond inspired scientific and industrial community for continued effort on developing FETs and (bio-) sensors.

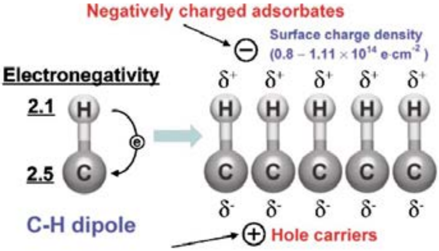

Fig. 3: Model for hole accumulation layer at diamond surface [12].

3.2. Oxygen Termination

The diamond surface terminated with oxygen results in a hydrophilic surface (contact angle <10°) keeping electrically-insulating properties. Oxygen termination can be achieved by UV/ozone treatment [16], wet chemical treatment or by dry plasma treatment [17].

Generally, O- and H-terminated surfaces are not resolvable under the optical microscope. However, after their exposing to electron irradiation (e.g. like in scanning electron microscopy, SEM), contrast between O- and H-terminated diamond surface becomes well resolvable (see Fig. 2). The H-terminated diamond surface are represented by brighter regions (strips) in the SEM image due to the negative electron affinity (NEA). Thus, H-terminated strips can emit electrons easier than the oxygen terminated surface (darker strips in Fig. **2**) [18]. The H-terminated diamond patterns are represented by brighter regions in the SEM image due to the NEA.

Last but not least feature of the H- and O-terminated diamond surfaces is their specific applications in life science and tissue engineering. In other words, the O- and H-terminated diamond patterns control the cell adhesion (SAOS-2, MG63 and MSC, etc.). It was found that the degree and selectivity of adhered cells is driven by dimensions of H-/O-terminated patterns and by the presence of fetal bovine serum (FBS), i.e. by protein conformation on these surfaces [19,20]. Fig. 4 shows fluorescence images of SAOS-2 cells cultivated on H-/O-terminated diamond patterns. The cells strongly prefer O-terminated patterns. The optimal patterned cell selectivity was observed for low *initial* cell concentrations (2 500 cells/cm^2). Employing higher *initial* concentrations (>10 000 cells/cm^2) resulted in the colonization of less favorable H-terminated diamond surface. To notice both these terminations exhibit the same surface roughness and crystal size.

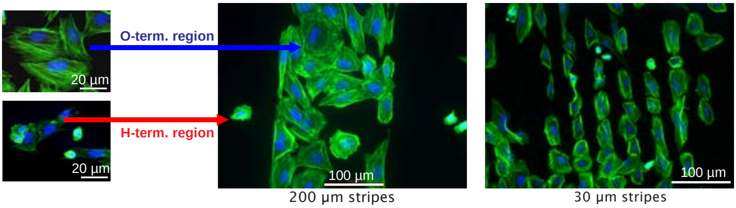

Fig. 4: Fluorescent microscopy images of osteoblastic cells (SAOS-2) cultivated in McCoy's medium supplemented with 15% FBS for 2 days on H-/O-terminated stripes [21].

It can be concluded that biocompatibility and semiconducting properties with a functional surface make diamond an attractive material for merging studies on biological systems. The preliminary works on the diamond functionalization with DNA or proteins motivated research on developing the diamond based biosensors employing the p-type surface conductivity induced even on the intrinsic diamond [22,23].

4. Diamond as Functional Coating for (bio-) Sensors

Diamond exhibits extraordinary combination of intrinsic properties which make it promising material for interdisciplinary oriented community – material engineering, thin film physics, plasma chemistry, civil engineering, life science, etc. Especially its induced p-type surface conductivity is promising for fabrication of advanced optical elements, electronically active devices or (bio-) sensoric uses.

Representative examples of such devices and their functionalities are summarized in the following sub-chapters.

4.1. Optical Elements for Infrared Spectroscopy

Monocrystalline germanium is well-established material in infrared (IR) spectroscopy. However, like many other IR transparent materials - Ge possesses several drawbacks as low chemical and mechanical resistance, high reflectivity, or limited surface functionalization. Similar limitations exhibit also gold or aluminum mirrors which are also used in IR spectroscopy. To minimalize such limitations, the diamond coating should be employed as a protective and functional layer which morphology can be further tailored (structured) to increase its surface area and thus, enhance the sensitivity for IR detection/recognition of adsorbed molecules. Schematic drawings and representative diamond morphologies are shown in Fig. 5 [24]. The SEM images reveal a uniform surface morphology for all layer types, i.e. fully closed flat (albeit nanocrystalline), columnar, or porous-like layers. The columnar diamond layer was fabricated by top-down strategy using metal mask and reactive ion etching. The porous diamond layer was fabricated by bottom-up strategy at optimized plasma chemistry (80% of CO_2 in the CH_4+H_2 gas mixture). The diamond character of structured coatings was confirmed by Raman measurements which revealed a sharp peak centered at about 1330 cm^{-1} – the sp^3 coordinated carbon.

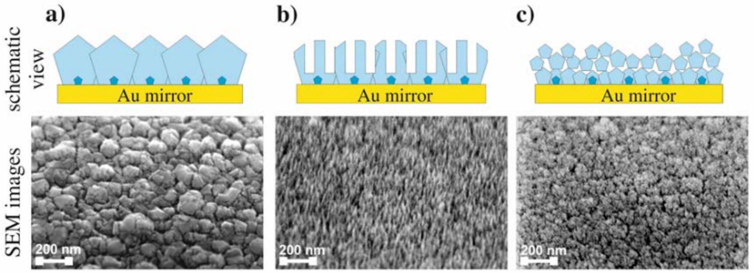

Fig. 5: Schematic drawings and corresponding SEM images of the diamond layers with a) flat, b) nano-columnar, and c) nano-porous surface morphologies [24].

Diamond coated optical elements were used for the grazing angle reflectance (GAR) IR characterization of fetal bovine serum proteins adsorbed on the O-terminated diamond surface [24]. In spite of the different processing and structuring, all diamond layers (films) showed good stability, uniformity, and optical properties, including a good reflectivity of the gold mirrors. Gold mirrors coated with nanostructured diamond were used as IR optical elements to study the interactions of a small amounts of organic molecules with diamond. Even 3 nm thin layers of protein molecules adsorbed from FBS solution were well recognized by IR measurements. The signal gain, defined as the IR intensity ratio of structured to the flat surface, was about 500% and 600% for nano-columnar and nano-porous diamond layers (Fig. 6), respectively. The enhanced sensitivity was attributed to the increased surface area of the nanostructured coating.

Technological progress in the low temperature (<400°C) growth allowed the diamond deposition on temperature sensitive materials (Au, Ge, Al, amorphous Si, glass, etc.) and ATR prisms using a large area linear antenna microwave plasma CVD system [25,26]. The Ge ATR prism was preserved and stabilized by a thin amorphous silicon interlayer (thickness less 30 nm). The absorbance spectra measured with ATR IR setup exhibited a good enough resolution and sensitivity to ultra-thin protein layer (3 nm). Wider spectral window of the germanium optical element in comparison to silicon, allowed the IR analysis in the 900–4000 cm^{-1} spectral region. In comparison to the transmission IR regime with KBr pellets, the newly developed diamond-coated Ge ATR prism significantly simplified and speeded up the IR analysis.

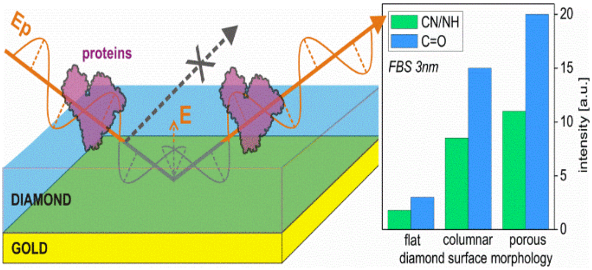

Fig. 6: Schematic view of GAR IR measurements (on the left) and comparison of GAR IR intensities of C=O and CN/NH bands in FBS proteins with 3 nm layer thicknesses on the diamond layers with flat, nano-columnar and nano-porous surface morphologies [24].

4.2. Field Effect Transistors - FETs

Planar Field Effect Transistor: The hydrogen-terminated surface induces a two-dimensional surface conductivity (see subsection 3.1) after its exposure to air where a water (mono-) layer is absorbed. New equilibrium conditions result in the charge transfer (i.e. transport of electrons) from the diamond bulk to this interface [27,28]. The remaining holes are accumulated below the diamond surface and give rise to the p-type conductivity of otherwise intrinsic highly resistive bulk diamond films.

In the early beginning, FETs devices were fabricated on monocrystalline diamond (monoD) [29]. However, monoD is limited in the volume (approx. 5x5x8 mm^3). Therefore, there was a technological demand on FET devices working on thin diamond films. The “Pie” and “Corbino” diamond FETs were fabricated employing standard semiconductor processes including optical lithography, evaporation of metals, plasma functionalization, etc. [30]. Fig. 7 shows digital photos and current-voltage characteristics of fabricated FETs. The I-V characteristics clearly confirm the modulation of p-type channel current with the bias voltage (U_{GS}). The drain-source current (I_{DS}) considerably increases with the increase of U_{GS} to -3.5 V. The diamond FET exhibited low leakage currents, and full channel pinch-off was achieved at U_{GS} = -1 V. However, microcrystalline diamond films are rough, and their high root-mean-square surface roughness (≥ 1 µm) is not compatible with technological requirements of optical lithography and other semiconductor processes. Therefore, the growth of thinner and more flat nanocrystalline diamond films became preferable [31].

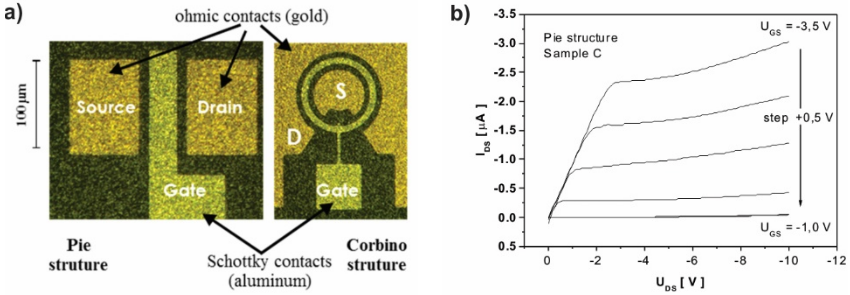

Fig. 7: a) Digital photo of diamond FET structures and b) source to drain *I-V* measurements *vs*. gate bias for the “Pie” structure [30].

Detection of (bio-) Molecules: Discovery that the current flow of diamond-based FETs is sensitive to ion concentrations [32] has drawn attention on development a variety of chemical and biological sensors. The diamond solution-gated (SG) FET uses the H-terminated surface without the need of protective dielectric layer (SiO_2, Si_3N_4, etc.). The diamond-based SGFETs has been introduced by Kawarada et al. [33] who used an Ag/AgCl electrode as the gate (reference) electrode immersed in the electrolyte. The idea of binding large molecules (such as enzymes, proteins, DNA) to the diamond surface was mentioned as a promising concept for achieving a selective response to special substances. However, authors did not elaborate the SGFET performance for biosensoric applications.

Studies published later, especially focused on the covalent grafting of DNA [22], proteins, antibodies and other functional molecules [34,35] to the diamond surface have stimulated works on the diamond SGFETs for biosensoric applications [23,36].

Yang and Hamers used undoped (intrinsic) nanocrystalline diamond thin films for fabrication of biologically sensitive SGFETs. The diamond film was hydrogen terminated by radiofrequency plasma. Then, its surface was modified with human immunoglobulin G (IgG) through a multi-step process [37], see Fig. 8a. Sputtered gold electrodes were used as ohmic contacts (source and drain), the active channel area was 0.5x3 mm^2, and the embedded platinum electrode was used as the gate (Fig. 8b). SGFET electrical characteristics revealed nearly identical dependences for buffer solution without/with anti-IgM antibody confirming its minimal (or no) effect on the transistor characteristics.

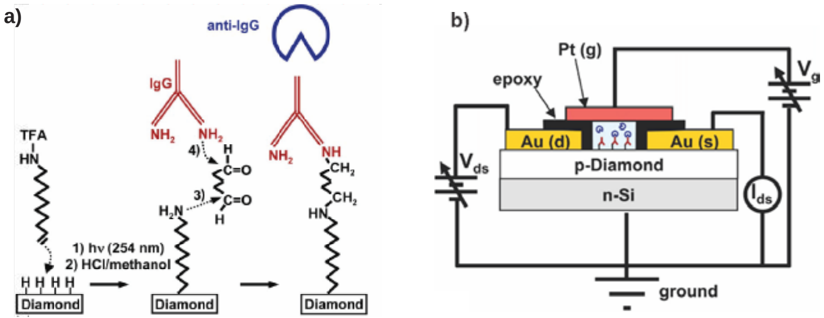

Fig. 8: a) Overview of the chemistry for linking human IgG to the diamond surface and b) schematic view of the diamond-based SGFET [37]. V_g - gate voltage (U_G), I_{ds} - source-drain current (I_{DS}).

The ability of the SGFET to selectively detect the anti-IgG antibody was confirmed after exposing the diamond channel to anti IgG (134 mg/ml), i.e. an antibody which binds strongly to the surface-tethered IgG. After adding anti-IgG , I_{ds} currents decreased by approx. 25%, Fig. 9a. The diamond SGFET transfer characteristics before and after exposing the transistor to anti-IgG molecules are shown in Fig. 9b. As expected, the highest differences in source-drain currents by ~30% were found for the highest gate voltage (V_g = -6 V).

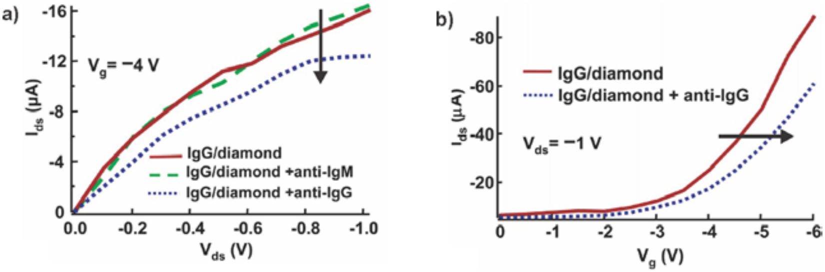

Fig. 9: a) Current-voltage and b) transfer characteristics of the diamond-based SGFET before and after its exposure to the anti-IgG [37].

Hartl et al. have functionalized undoped nanocrystalline diamond FET channel with the enzyme catalase [23]. Provided cyclic voltammetry measurements confirmed (bio-) chemical activity of covalently bonded enzymes to the diamond surface. The direct electron transfer between the enzyme's redox centers and the diamond electrode was confirmed by I-V measurements. The fabricated diamond FET channel exhibited a linear response to different H_2O_2 concentrations with a sensitivity of about 70 µA/mm^{2}M. The detection limit was as low as 0.3 mM H_2O_2. Noticeable was the transistor functionality after its storage for 8 weeks – the bio-functionality of the catalase enzyme after a certain period was still active. For these experiments, the SGFETs were stored at 4°C in a buffer solution to minimize the enzyme bio-degradation.

4.3. Gas Sensor

The operating principle of diamond gas sensors is based on the modulation of induced surface conductivity due to a set of reactions with adsorbed gas molecules. First study employed the Pd/intrinsic diamond/boron doped-diamond configuration for the detection of H_2 [38]. Later on, the same configuration was used to detect benzene and toluene [39]. The use of undoped monocrystalline diamond for detection of reducing (NH_3, CO, H_2) and oxidising gases (O_2, NO_2, HCl) was presented in work [40]. Furthermore, diamond was plasmatically structured to nano-cones to increase the adsorption layer and finally, to improve the sensor response and detection limit [41]. Nevertheless, most of such devices have been realized on monocrystalline diamonds.

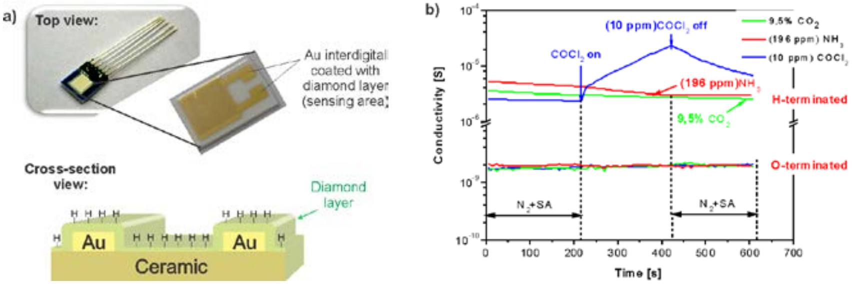

Fig. 10: a) Digital photo of diamond layer/metal interdigitated electrodes/insulating ceramic sensor and its schematic cross-section view. b) Time dependence of surface conductivities of O- and H-terminated diamond films [42].

As an alternative solution, the sandwich structure of intrinsic H-terminated diamond layer/metal interdigitated electrodes/insulating ceramic has been presented [43]. The new design used built-in interdigitated electrodes (IDEs) in the diamond layer (Fig. 10a). Impedance gas measurements are shown in Fig. 10b. As clearly observed, the oxygen terminated diamond surface does not exhibit any response to the testing gases. On the other hand, the hydrogen terminated sensor show a positive response to the testing gases: humidity, carbon dioxide (CO_2), ammonia (NH_3), and phosgene ($COCl_2$). Moreover, the H-terminated diamond layers exhibited a peculiar selectivity towards phosgene as the oxidizing gas. It was observed that the diamond surface conductivity increased up to 31 times for $COCl_2$ concentration increase from 5 to 20 ppm. A good enough sensitivity of diamond sensor to phosgene was attributed to the phosgene dissociation in the monolayer of water adsorbed on the diamond and consequent enhanced charge transfer due to the multiplication effect of the increased H_3O^+ concentration.

It was found that the nano-columnar diamond morphology increased the surface-to-volume ratio and resulted in enhanced sensitivity of the H-terminated diamond sensing element. The sensor response, defined as the relative variation in the surface conductivity due to the presence of a specific gas, increased up to 4344 in 20 ppm of phosgene for the nano-columnar diamond sensor in comparison to the flat diamond film [44]. These results indicate that the H-terminated diamond device has prospects as the gas sensing element for industrial uses, especially for $COCl_2$ detection. It should be expected that some gases should display a similar charge transfer multiplication effects.

4.4. Electrical Monitoring of Cell Growth

Non-invasive label-free techniques for *in vitro* monitoring of cell growth are of high interest due to simplicity, fast response in real time and excluding experiments on animals. Presently, there are two analytic approaches which employ either *optical* or *electronic* signal processing [45]. Both these approaches reached the state of the art in a transducer type which converts a stimulus-induced cellular response into a quantifiable signal (i.e. biosensor signal) [46]. From the broad family of electronic systems, diamond based impedance and field effect transistor devices are the most used devices for real-time monitoring of biosignals during the cell growth.

Impedance Sensors for Cell Monitoring: Impedance measurements seem to be one of the simplest and still a powerful method for monitoring cellular signals [47]. As presented by many reports, the monitored impedance signal is sensitive not only to ionic currents but also to cell growth stages (i.e. cell attachment, spreading, shape, proliferation, differentiation and communication) [48–51]. The typical impedance sensors use gold interdigitated electrodes which are deposited on an electrically isolating material (glass, ceramic, plastic, etc.). In some cases, gold electrodes may limit optical monitoring of cultivated cells from the sensor backside.

Electrodes made of intrinsic diamond are optically transparent and provide a suitable biocompatible substrate for cell cultures. The IDEs were provided in the form of H-terminated surface regions ("combs") as in-plane conductive electrodes and they were separated by O-termianted surface regions [52]. Such planar interdigitated electrodes monitored cells cultivation. Fig. 11 shows the time dependence of impedance measured at 1 kHz for sensor seeded with human osteoblast-like MG 63 cells (16 000 cells/cm^2). For comparison, the time dependence of the cell index on Au electrodes by xCELLigence sensor is added as the reference measurement together with the background measurement (i.e. sensor part loaded with the pristine cultivation medium without the cells). The values of impedance as well as cell index increase with time and follow nearly the same profile. The impedance increase in the first hours should be attributed to the coverage of the electrodes with osteoblast-like MG 63 cells (Fig. 11). However, the exact correlation of cell growth with the impedance changes is not a trivial issue, especially when the patterned cell colonization is dominated by their spreading.

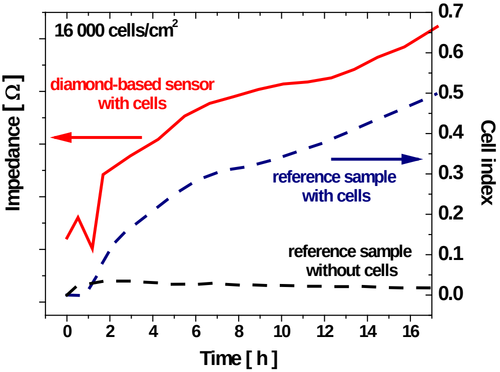

Fig. 11: Time dependence of impedance at 1 kHz and corresponding reference measurements with xCELLigence sensor [52].

FET Sensors for Cells Monitoring: The solution-gated field effect transistors are proposed as more suitable biosensor devices due to simple miniaturization (scaling down), higher signal-to-noise ratio, better signal stability and amplifying the measured signal. The first ion-sensitive FET has been introduced as the silicon-based chemical sensor [32]. However, the silicon based FET devices had to use the dielectric protective layer for their proper functionality. In contrast to the Si FET, the diamond FET does not employ the dielectric layer.

The first diamond FET cell biosensor is related to the work of Rezek et al. [53]. The SGFET was fabricated from H-terminated nanocrystalline diamond films. The size of diamond crystals was 150 nm and the surface roughness was approx. 30 nm, as determined from tapping mode AFM across the area of 1x1 μm^2. The diamond sample was processed by metallization steps and passivated by the polymer layer. Openings in the polymer layer (60x60 μm^2) were made to expose the H-terminated channel (20x60 μm^2) to cells. Like the gate, the Ag/AgCl reference electrode was used. It was observed that exposing the transistor channel to FBS proteins (i.e. the part of the cultivation medium) decreases the surface conductivity. In comparison to the reference conditions (i.e. device loaded with McCoy's 5A medium), the transistor transfer characteristic reflected the negative gate potential shift of −45 mV for the FBS medium. Then SAOS-2 cells were added and an additional negative gate potential shift by -78 mV was observed. In this case, the cells were well spread across the whole area. Proteins, as well as cell membranes, have a negative net charge at pH 7.4. Thus, the direct contribution of electrostatic effect from the adsorbed proteins or cell on the channel current modulation was refused due to observed an opposite effect – the decrease of the channel current. The decrease of channel current was attributed to sticking of proteins (or biomolecules) to a close vicinity of the diamond surface and repelling the counter-ions, and thus to the concentration decrease of holes in the surface conductive channel. A similar effect was observed after adsorbing lipid bilayers to the diamond FETs [54].

5. Conclusions

Diamond, especially in the form of a thin film layer, is a promising functional material for (bio) sensoric applications. Electronic surface properties of intrinsic undoped diamond films can be simply controlled by covalently bonded atoms, especially by hydrogen or oxygen atoms. It was successfully demonstrated that the diamond coatings can be used as the protective and functional layer for advanced optical elements used in IR measurements, namely the GAR substrates and ATR prisms.

The undoped hydrogen-terminated diamond thin films revealed electronic functionality even for the film consisting of nano-sized crystals (<150 nm). The morphologically structured H-terminated diamond IDEs were used as the sensing element to detect reducing and oxidizing gases. The multiplication sensing effect has been observed for phosgene.

Finally, the optically transparent planar diamond electrodes were used as IDEs for real-time impedance measurements of cultivated cells. Electrical measurements provided on the SGFETs confirmed the surface channel modulation by the presence of proteins and living cells. The sensitivity of induced p-type surface conductivity to surrounding environment has opened attention on a variety of chemical and biological sensors, microfluidic systems for in vitro cultivation and testing new drugs, or for providing cytotoxic experiments.

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Ing. Alexander Kromka, Ph.D. - Curriculum vitae

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Date of birth: 6.5.1971 Location: Nitra, Slovak Republic

1990-1995 study of electronic at the Department of Microelectronics, Faculty of Electrical Engineering and Information Technology, Slovak Technical University, Bratislava, Slovakia (Ing.)

1995-2001 PhD study with the main focus on the growth of diamond thin films by a hybrid hot filament CVD technique at the Department of Microelectronics, Faculty of Electrical Engineering and Information Technology, Slovak Technical University, Bratislava, Slovakia (Ph.D.)

Work experience:

1995 (3 months) final MSEE project at the Faculty of Electrical Engineering and Information Technology, TU Ilmenau, Germany

1998 – 1999 technician at the Department of Physics, CUHK Hong Kong

2000 – 2001 research assistant at the Depart. of Microelectronics, KME, Bratislava. Slovakia

2001 – 2002 postdoc at the Institute of Electron Devices and Circuits, EBS, Ulm, Germany

2002 – 2003 postdoc at the Institute of Physics, ASCR, Prague, Czech Republic

2003 – 2005 researcher at rho-best coating plc. (rho-best plc), Innsbruck, Austria

2005 – 2008 visiting researcher at the Institute of Physics, ASCR, Prague, Czech Republic

2008 (3 months) visiting scientist at the Institute IMO IMEC, Hasselt-Belgium

2009 – 2013 Purkyně Fellowship and Team leader at the Inst. of Physics, ASCR, Prague, Czech Republic

2014 – present Group leader in Diamond and Carbon nano-Structures Laboratory, at the Institute of Physics, CAS, Prague, Czech Republic.

Selected stays abroad:

Several long period stays at well recognized research groups and labs including: Angstrom labs (Uppsala, Sweden), CEA List (Paris, France), NIMS and AIST (Tsukuba, Japan), IMOIMEC (Hasselt, Belgium), Uni Innsbruck (Innsbruck, Austria), City Uni HK (Hong Kong), KIST (Wanju-gun Jeonbuk, Korea), TU Wien (Austria), INES (Lisbon, Portugal), ILC & STU & SAV (Bratislava, Slovakia), Uni Tokyo (Tokyo, Japan), TU Ilmenau (Ilmenau, Germany).

Field of interest:

Diamond CVD, Low temperature large area microwave plasma, High-power/high-pressure microwave plasma CVD process, Reactive ion etching, Nucleation, Diamond nucleation from polymer composites, Graphene, CNT, Polymer composites, Biosensors, Artificial substrates for life science, Microfluidic systems, Composite materials, Surface functionalization, Raman, Nanotechnology.

Awards:

2015 diploma from Hungarian Academy of Science for skilled leading of the student Maria Domonkos.

2014 1st place in poster session at international conference NANOCON 2014 with the contribution „FABRICATION OF 3D DIAMOND MEMBRANES FOR MICROFLUIDIC SYSTEMS„ (Brno, Czech republic) (http://www.nanocon.eu/cz/).

2002 Honorable letter of the dean of faculty* for skilled leading of the student Tibor Daniš (ŠVOČ 2002), *Prof. Ing. František Janíček, Ph.D. – dean of the Faculty of electrical Engineering and Information Technology, Slovak Technical University, Ilkovičova 3, 812 19 Bratislava, Slovak Republic (2002).

2001 Werner von Siemens Excellence Award – 1st place for PhD Thesis (13 December, 2001)

2000 Honorable letter of the dean of faculty* for skilled leading of the student František Balon (ŠVOČ 2000), *Prof. Ing. František Janíček, Ph.D. – dean of the Faculty of electrical Engineering and Information Technology, Slovak Technical University, Ilkovičova 3, 812 19 Bratislava, Slovak Republic (10th May 2000).

1999 Award of the Slovak Association of Mechanical Engineers and the Slovak Union for Quality and Innovation for the Excellently Solved Scientific and Technological Project, presented at the 7th Conference and Exhibition on News in Technology (NOVTECH ’99), organized by MŠ SR, MP SR, MH SR, ÚSRSVT SR, SAV, ÚPV SR and ZSVTS, Žilina, Slovak Republic (24. 26. November 1999).

1999 Award of the Slovak Central Institution of Electrical Engineers for outstanding presentation at the Second Conference on Electrical Engineering and Information Technology for PhD students, Bratislava, Slovak Republic (9th September 1999).

1996 Honorable letter of the dean of faculty* for excellently written master thesis, *Prof. Ing. Viktor Smieško, Ph.D. – dean of the Faculty of electrical Engineering and Information Technology, Slovak Technical University, Ilkovičova 3, 812 19 Bratislava, Slovak Republic (3rd January 1996).

Grants and projects (principal investigator/co-investigator):

15-01687S (01/2015 - 12/2017) - A. Kromka, Fyzikální ústav AV ČR, Allotropes of carbon: microbiological studies (GACR).

P108/12/0910 (01/2012 - 12/2014) - A. Kromka, Fyzikální ústav AV ČR, Fabrication, structuring and treatment of nanocrystalline diamonds for antibacterial studies (GACR).

P108/11/0794 (01/2011-12/2013) - L. Kubinova, Fyziologický ústav AV ČR, Visualization of collagen production in osteogenic cells cultivated on nanocrystalline diamond films (GACR).

FR-TI2/736 (2010-5/2014) - J. Jiruse, TESCAN, Modular Scanning Electron Microscope (MPO).

TA01011740 (01/2011-12/2014) – A. Pijak, SVCS Process Innovation, Hybrid high-density low-temperature microwave plasma sources in matrix configuration suitable for growth of advanced materials and their (nano) composites on 2D and 3D substrates (TACR).

M100100905 (06/2009-05/2012) - A. Kromka, Fyzikální ústav AV ČR, Study of interaction of (bio) molecules with synthetic diamond surfaces with Uppsala University (GAAV).

P108/12/G108 (01/2012 - 12/2018) - V. Svorcik, Vysoká škola chemicko-technologická v Praze, Preparation, modification, characterization, materials, radiation(GACR).

Purkyně Fellowship (01/2009-12/2013) - A. Kromka Fyzikální ústav AV ČR, Growth of diamond and carbon nanostructures (Academy of Sciences of the Czech Republic).

Pedagogical activities:

Member of PhD study council Electronics P2612V / 2612V015 (since 02/2013). Participating in lectures at KFE CVUT 34 NSE - New trends in electronic, at FJFI ČVUT - Selected chapters in nanoelectronics, at TU Liberec - Chapters from nanoelectronics. Since 2013 participating at lectures at FSv CVUT – Nanotechnology (D62ZNT, guarantee prof. RNDr. Pavel Demo, CSc.).

Supervised 4 Diploma students and 6 PhD students from Czech and Slovak Universities so far.

Author and co-author of 170 papers in the refereed impacted international journals, 8 papers in non-impacted journals, 6 book chapters, 16 papers in conference proceedings, 5 patents, 3 model utilities (CZ) and 2 industrial procedures (CZ).

Author and co-author of 12 invited keynote and plenary lectures at International Conferences.
The publications received more than 1200 citations (Scopus, auto-citations excluded), Hirsch factor, H=22 (WOS, August 2016).

Selected book chapters:

1. T. Izak, O. Babchenko, S. Potocky, Z. Remes, H. Kozak, E. Verveniotis, B. Rezek, A. Kromka: Low temperature diamond growth, chapter 13 in book: Nanodiamond, Royal Society of Chemistry 2014, ISBN 978-184-973-639-8, pp. 290-342.
2. A. Kromka, O. Babchenko, T. Izak, S. Potocky, M. Varga, B. Rezek, A. Sveshnikov, P. Demo: Diamond nucleation and seeding techniques for tissue regeneration, chapter 10 in book Diamond based materials for biomedical applications, Woodhead Publishing Series in Biomaterials No. 55, Edited by R Narayan, University of North Carolina, USA ISBN 0 85709 340 1, ISBN-13: 978 0 85709 340 0, pp. 206-255.

Selected publications

1. A. Kromka, J. Janík, F. Balon, M. Kubovič, I. Červeň, V. Dubravcová: Comparison of diamond nucleation in DC and AC substrate bias mode, Thin Solid Films 433 (1-2) (2003) 73-77.
2. A. Kromka, T. Daniš, F. Balon, J. Janík, M. Vaněček: Influence of nucleation parameters on growth of diamond thin films by hybrid hot filament CVD, Diamond and Related Materials 12 (3-7) (2003) 356-360.
3. V. Malcher, A. Mrska, A. Kromka, A. Satka, J. Janik: Diamond film coated on WC/Co tools by double bias-assisted hot filament CVD, Current Applied Physics 2 (3) (2002) 201-204.
4. A. Kromka, B. Rezek, M. Kalbacova,V. Baresova, J. Zemek, C. Konak, M. Vanecek: Diamond seeding and growth of hierarchically structured films for tissue engineering, Advanced Engineering Materials 11 (7) 2009 B71-B76.
5. A. Kromka, O. Babchenko, H. Kozak, B. Rezek and M. Vanecek: Role of polymers in CVD growth of nanocrystalline diamond films on foreign substrates, phys. stat. sol. b 246 (11-12) (2009) 2654-2657.
6. A. Kromka, O. Babchenko, H. Kozak, K. Hruska, B. Rezek, M. Ledinsky, J. Potmesil, M. Michalka, M. Vanecek: Seeding of polymer substrates for nanocrystalline diamond film growth, Diamond and Related Materials 18 (5-8) (2009) 734-739 (doi: 10.1016/j.diamond.2009.01.023).

7. A. Kromka, O. Babchenko, B. Rezek, K. Hruska, A. Purkrt, Z. Remes: Comparison between chemical and plasmatic treatment of seeding layer for patterned diamond growth, in Diamond Electronics and Bioelectronics - Fundamentals to Applications III, edited by P. Bergonzo, J.E. Butler, R.B. Jackman, K.P. Loh, M. Nesladek (Mater. Res. Soc. Symp. Proc. Volume 1203, Warrendale, PA, 2010), 1203-J17-53.
8. A. Kromka, O. Babchenko, T. Izak, K. Hruska, B. Rezek: Linear antenna microwave plasma CVD deposition of diamond films over large areas, Vacuum 86 (6) (2012), pp. 776-779.
9. S. Potocky, M. Čada, O. Babchenko, T. Ižák, M. Davydova, A. Kromka: Perspectives of linear antenna microwave plasma and growth of various carbon nano-forms, physica status solidi b 250 (12) (2013) 2723-2726.
10. A. Kromka, O. Babchenko, M. Kratka, B. Rezek: Diamond Films Deposited by Oxygen-Enhanced Linear Plasma Chemistry, Advanced Science, Engineering and Medicine 5 (6) (2013) 509-514.
11. T. Izak, O. Babchenko, M. Varga, S. Potocky, A. Kromka: Low temperature diamond growth by linear antenna plasma CVD over large area, physica status solidi b 249 (12), (2012) 2600–2603.
12. A. Kromka, B. Rezek, Z. Remes, M. Michalka, M. Ledinsky, J. Zemek, J. Potmesil, M. Vanecek: Formation of continuous nanocrystalline diamond layer on glass and silicon at low temperatures, Chemical Vapor Deposition 14 (2008) 181–186.
13. S. Potocky, A. Kromka, J. Potmesil, Z. Remes, Z. Polackova, M. Vanecek: Growth of nanocrystalline diamond films deposited by microwave plasma CVD system at low substrate temperatures, physica status solidi (a) 203 (12) (2006) 3011-3015.
14. P. Kulha, A. Kromka, O. Babchenko, M. Vanecek, M. Husak, O. A. Williams, K. Haenen: Nanocrystalline diamond piezorezistive sensor, Vacuum 84 (1) (2010) 53-56.
15. A. Kromka, M. Kubovič, F. Balon, J. Janík, V. Dubravcová: Investigation of MESFET structures based on polycrystalline diamond films grown by modified HF CVD technique, Journal of Electrical Engineering 54 (3-4) (2003), pp. 96-99 (ISSN 1335-3632).
16. H. Kozak, A. Kromka, O. Babchenko, B. Rezek: Directly grown nanocrystalline diamond field-effect transistor microstructures, Sensor Letters 8 (2010) 482-487.

17. A. Kromka, M. Davydova, B. Rezek, M. Vanecek, M. Stuchlik, P. Exnar: Gas sensing properties of nanocrystalline diamond films, Diamond and Related Materials 19 (2010) 196-200.
18. S. Stehlik, T. Izak, A. Kromka, B. Dolenský, M. Havlik, B. Rezek: Sensitivity of diamond-capped impedance transducer to Tröger's base derivatives, ACS Applied Materials & Interfaces, 4 (8) (2012) 3860–3865.
19. T. Izak, K. Novotná, L. Bačáková, B. Rezek, A. Kromka: H-terminated diamond as optically transparent impedance sensor for real-time monitoring of cell growth, physica status solidi b 250 (12) (2013) 2741–2746.
20. V. Smilauer, O. Babchenko, S. Potocky, A. Kromka: Hydration of plasma-treated alumosilicate binders, Acta Polytechnica 54 (2014) 348-351.
21. A. Kromka, J. Čech, H. Kozak, A. Artemenko, T. Ižák, J. Čermák, B. Rezek, M. Černák: Low temperature hydrogenation of diamond nanoparticles using diffuse coplanar surface barrier discharge at atmospheric pressure, physica status solidi b 252 (11) (2015) 2602–2607.
22. J. Beranova, G. Seydlová, H. Kozak, O. Benada, R. Fišer, A. Artemenko, I. Konopásek and A. Kromka: Sensitivity of bacteria to diamond nanoparticles of various size differs in gram-positive and gram-negative cells, FEMS Microbiology Letters 351 (2) (2014) 179-186.