Polycrystalline Diamond Thin Films for Advanced Applications

Irena Kratochvilova

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Abstract

The technological achievements in diamond thin film synthesis over the past decade subsequently led to the utilization of outstanding diamond properties and development of a wide range of applications in various fields of engineering. However, since most chemical vapour deposition (CVD) diamond films are polycrystalline, their characteristics strongly depend on their microstructure. As the number of possible applications for polycrystalline CVD diamond increases, there is constant development and enhancement of the film properties. Polycrystalline diamond in the form of thin films delivers further advantages over thicker polycrystalline layer, e.g., smoother surface, less deposition time and less light absorption. Furthermore, besides the relevant diamond properties, the suitability for applications also depends on various material parameters such as substrate nature, substrate dimensions, possibility of non-planar geometries, surface morphology, electrical conductivity, capability of device fabrication, electrochemical properties and cost.

Keywords: chemical vapour deposition polycrystalline diamond films, boron-doped polycrystalline diamond film, zirconium alloys protection against corrosion, water splitting

1. Introduction

Due to unique combination of mechanical, thermal and optical properties, manmade diamond is commonly used nowadays in a number of industrial applications. After decades of research and gaining general knowledge, new foreseen applications can be realized through improvements of diamond properties. Achievements in the preparation of synthetic
diamond, in the form of thin films, allow for further research aimed at the development of modern applications.

A method, allowing preparation of polycrystalline diamond (PCD) films (Figure 1) under low-pressure and low-temperature regimes, was coined with the development of chemical vapour deposition (CVD). CVD apparatus is shown in Figure 2. A polycrystalline diamond film is formed during heteroepitaxial growth when the CVD deposition is carried out on a non-diamond substrate. The growth is achieved using small diamond crystal seeds dispersed onto a substrate. Due to eventual coalescence of different crystallites grown on variously oriented seeds (nucleation sites), a continuous PCD film with a columnar structure is formed. Such columnar structure is primarily made of diamond grains (crystallites) held together by thin layers of amorphous and graphitic inclusions located within the so-called grain boundaries. Overall, the PCD film thickness, the size of diamond grains at the surface and its roughness are determined at the moment when growth process is terminated [1].

The technological achievements in the synthesis of diamond thin films over the past decade subsequently led to the utilization of outstanding diamond properties and development of a wide range of applications in various fields of engineering. However, since most CVD diamond films are polycrystalline, their characteristics strongly depend on their microstructure. As the number of possible applications for polycrystalline CVD diamond increases, there is constant development and enhancement of the films properties. Polycrystalline diamond in the form of thin films delivers further advantages over thicker polycrystalline layer, e.g., smoother surface, less deposition time and less light absorption. Furthermore, besides the relevant diamond properties, the suitability for applications also depends on various material parameters such as substrate nature, substrate dimensions, possibility of non-planar geometries, surface morphology, electrical conductivity, capability of device fabrication, electrochemical properties (given by the $sp^3$/sp$^2$ ratio) and cost. Due to benefits of CVD
diamond films over single-crystalline form (low-cost, large area products), a variety of
applications already available expanded beyond classical mechanical use of diamond. These
include CVD polycrystalline diamond for optical, electronic and electrochemical applica-
tions, CVD diamond grades suitable for thermal management as well as PCD films for a
number of further advanced applications [1–6].

In this chapter, new technological applications of polycrystalline diamond films are present-
ed. First, we illustrate electrical applications of diamond films. The electrical properties of
diamond films can be tuned by addition of dopants, resulting in p-type or n-type conductiv-
ity. Additionally, the electrical characteristics can be modified through surface termination
with hydrogen, which gives rise to p-type surface conductivity. The origin of this effect is in
strong covalent bonding between C and H that leads to the formation of two-dimensional
surface layer for holes, spanning up to several nanometres below the diamond surface.
Conducting microcrystalline, nanocrystalline and ultrananocrystalline diamond films features
certain advantages and actively used as electrode material in electrochemistry. That includes
chemical stability in aggressive media, optical transparency and wide working potential
window. Therefore, diamond film electrodes nowadays find widespread use in various
electroanalytical applications, e.g., chemical sensing, in vivo monitoring of bioactive spices,
water purification and detection of organic pollutants.

Photoelectrochemical (PEC) cells for water splitting can offer a potentially inexpensive route
for molecular hydrogen-fuel generation. In the frame of such application, nanocrystalline
diamond has a potential to be utilized in PEC systems as a protective and electrically active
coating for water oxidation. A unique diamond deposition technology allowing low tempera-
ture growth (ca. 450°C) was employed to fabricate boron-doped nanocrystalline diamond
films on silicon solar cells. The goal of the study was to identify the properties of diamond
films suitable for PEC application and to reveal the influence of diamond deposition process
on the quality of silicon solar cells. Nanocrystalline boron-doped diamond (BDD) films possess
grain boundaries containing a small fraction of non-diamond carbon impurities [4].

In the study of Ashcheulov et al. [4, 5], the conductivity of BDD polycrystalline films that were
synthesized by microwave plasma-enhanced chemical vapour deposition on quartz sub-
strates was studied. Conductivity is a complex physical quantity and in the case of BDD films
there are many parameters that influence charge transport: (i) size of the diamond grains—the
conductance of BDD films containing bigger grains is higher than the conductance of BDD
films containing smaller diamond grains (for the same B content), (ii) diamond grain boun-
daries, (iii) setting of B defects and specific morphology of the layer changed by B addition
and (iv) diamond grain surface layer can have specific setting and concentration of B defects.
Boron-doped diamond is presently the subject of considerable interest as a promising electrode
material [5]. This is a consequence of several technologically important properties that
distinguish it from common electrode materials used in electrochemistry, such as gold or
platinum. Polycrystalline BDD films possess physical properties similar to those of bulk
diamond, which includes outstanding hardness, high hole mobility, high thermal conduc-
tivity and excellent resistance to radiation damage. Also, there is little evidence of degradation
of BDD electrochemical activity with time. Due to these unique characteristics, to date, BDD
electrodes are employed in a vast array of electrochemical applications. Additionally, then doped with high concentration of boron atoms, BDD films possess metallic conductivity and can also be optimized for light transparency [4, 5].

Nanocrystalline diamond layers were examined as anticorrosion protection of zirconium alloys nuclear fuel rods, operated in all commercial light-water and heavy-water nuclear reactors. Various corrosion tests were primarily focused on determining the ability of diamond layer to withstand emergency situations in nuclear reactors. The deposition of a polycrystalline diamond layer was carried out using linear antenna microwave plasma-enhanced chemical vapour deposition (LA-MW PECVD) apparatus (Figure 2) [1].

2. Doped nanocrystalline and epitaxial diamond layers for photovoltaic applications

It was showed that for hydrogen fuel generation based on water electrolysis by means of a light-driven photoelectrochemical process, boron-doped diamond is considered very promising material for electrodes [4]. The hydrogen produced using solar energy has been denominated as solar fuel. In essence, the photoelectrochemical process mimics photosynthesis by splitting water into $\text{H}_2$ and $\text{O}_2$. Nevertheless, water splitting cannot be achieved by sunlight directly because the water molecule cannot be electronically excited by sunlight photons. PEC water splitting is described by semiconductor’s absorption of light photons with energies greater than its band-gap energy. Once photoexcited electrons and holes are generated in the conduction and valence bands, respectively, they separate and migrate towards the surface sites where they reduce and oxidize adsorbed water to produce gaseous oxygen and hydrogen. It has been demonstrated that various materials and composite structures can be utilized as photoelectrodes in PEC water-splitting processes. However, there are still obstacles to direct water splitting using PEC cells based on single absorber material: (i) lack of efficient light absorption due to wide band gap of semiconductors, (ii) efficiency reduction caused by...
overpotential and insufficient band alignments and (iii) corrosion of the semiconductor. Moreover, high cost of light-absorbing materials and co-catalysts (e.g., Pt, RuO$_2$ and IrO$_2$), which can split water with reasonable efficiencies prohibited their use on a large scale and over large areas required for light harvesting. Thereby, to raise the conversion efficiency, new low-cost and effective absorber materials and material compositions should be developed.

Silicon (Si) is an appealing material for photochemical processes due to a large number of photons that can be absorbed and converted. Further, Si is one of the most abundant elements in the Earth’s crust. Thereto, Si is an attractive candidate for water-splitting platforms because of its prevalence in photovoltaic (PV) industries and predominance in electronics. Moreover, Si surpasses the majority of common semiconductor materials: the 1.1 eV band gap of Si allows effective light absorption from the UV to the near-infrared wavelengths region, thus resulting in a higher photocurrent and conversion efficiency.

Enabling Si as a photoelectrode for practical solar-fuel production from water mimics natural photosynthetic systems, where light absorption and catalytic reaction do not happen on the same material. Although, Si exhibits significant advantages over wide band-gap semiconductors (TiO$_2$, Fe$_2$O$_3$, WO$_3$, etc.) utilized in PEC devices, it has seldom been used in photocatalytic applications. The main reason is the significant corrosion of Si in non-acidic electrolytes; therefore, the realization of PEC device based on Si must account for its inherent corrosion. Recently, Si has been integrated as one of the main components of a novel concept of unwired macroscopic PEC device based on silicon solar cell of a standard structure (n-Si, p-Si and p$^+$-Si). In such system, p$^+$ side of Si solar cell is coated with corrosion resistant/conductive indium tin oxide (ITO) layer and catalyst for triggering the oxygen evolution reaction (OER). This approach enables fabrication of Si-based PEC devices with solar-to-fuel (STF) conversion efficiencies exceeding 10%. However, the scarcity and declining availability of indium forces to look for alternative corrosion resistant and electrically conductive material solutions.

Boron-doped diamond is presently the subject of considerable interest as a promising electrode material [4, 5]. This is a consequence of several technologically important properties that distinguish it from common electrode materials used in electrochemistry, such as gold or platinum. Polycrystalline BDD films possess physical properties similar to those of bulk diamond, which includes outstanding hardness, high hole mobility, high thermal conductivity and excellent resistance to radiation damage. Also, there is little evidence of degradation of BDD electrochemical activity with time. Due to these unique characteristics, to date BDD electrodes are employed in a vast array of electrochemical applications. Additionally, then doped with high concentration of boron atoms, BDD films possess metallic conductivity and can also be optimized for light transparency. It has been recently shown that a large potential window of BDD can be tuned by the fabrication of sp$^2$-abundant polycrystalline BDD films. Also, it has been reported, that BDD electrodes can be successfully utilized for disinfection of wastewater. On the whole, the above-mentioned properties make BDD electrodes an ideal candidate for implementation in PV-assisted electrochemical systems for solar-fuel generation by water decomposition and wastewater treatment.
Essentially, due to the favourable alignment of Si and BDD valence bands, a system based on Si solar cell and BDD electrode integrated in a PV-PEC device could be developed. Similarly to already reported PV-PEC systems with ITO layer, the rear side of the Si solar cell (p-type side) immersed into water has to be protected by electrically conductive and non-corrosive material, thus BDD layer acting as an anode has the capacity to render such demand.

Overall, this approach circumvents problems caused by the intrinsic properties of Si, such as corrosion in aqueous solution, minimizes the cost that is about one-third of the total PV system cost and could provide higher conversion efficiency as opposed to classical PEC systems.

Figure 3. Schematic representation of the water-splitting system based on Si solar cell equipped with boron-doped diamond electrode deposited on the p-side of the Si solar cell with closed circuit on the externally wired cathode.

A schematic representation of the concept of the light-driven water-splitting process realized by PV-assisted PEC cell equipped with BDD electrode is illustrated in Figure 3. Here, the Si solar cell is responsible for the incident light absorption upon which photogenerated carriers are swept across the pn-junction. Due to a large band gap of highly boron-doped diamond films, set into contact with the p-side of Si, electrons are reflected and prohibited to move towards the BDD surface. Meanwhile, due to metallic doping of the BDD film, the Fermi level lies below the diamond valence band maximum that enables photogenerated hole carriers to pass freely through the BDD layer. Hence, holes are permitted to enter the water or electrolyte solution. Thus, the BDD film is responsible for water oxidation process and PV Si/BDD device could operate as photoanode, whereas the n-side of Si could be protected by a transparent glass layer may be further connected by a wire to a secondary electrode (cathode) that can be kept in a separate compartment to assist the separation of hydrogen and oxygen gases. Additionally, various OER and hydrogen evolution reaction catalysts can be deposited on the BDD surface and on the cathode, to facilitate the overall water-splitting process. Finally, due
to the fact that commercially available single-junction Si solar cell is able to deliver potential of only \( \sim 0.7 \) V, which is not sufficient for triggering the water-splitting reaction \((1.23 \) V), a tandem or a triple-junction of the c-Si solar cells connected in series would be necessary.

3. Conductivity of boron-doped polycrystalline diamond films: influence of specific boron defects

Diamond, as a carbon-based material, seems to be an exceptional choice for many applications, holding many promises due to its excellent properties, such as chemical inertness, wide electrochemical potential window and surface tunability by surface functionalization. Boron-doped diamond is a p-type semiconductor with \( E_g \sim 5.5 \) eV. Boron acceptor level in semiconducting diamond is about 0.36 eV from the valence band (EVB). Upon the metallic doping, the Fermi level (EF) shifts towards the valence band of diamond. Crystalline diamond has a strong and rigid isotropic structure due to its cubic crystal symmetry—\( sp^3 \)-hybridized carbon atoms are bound by strong covalent bonds. Crystalline diamond is insulator with large band gap (more than 5 eV). Dopant atoms in the diamond matrices (usually boron or nitrogen) can strongly change electrical conductivity. The most widely used dopant is boron, conferring a p-type semiconducting character to diamond. The boron source can be a volatile compound introduced into the reactant gases, such as trimethyl borate or B2H6, or solid boron located near the substrate during the growth of the diamond film. The boron doping level is often in the range of \( 10^{18} \)–\( 10^{20} \) atoms/cm\(^3\) or a B/C ratio of about \( 10^5 \) to \( 10^3 \). Boron-doped diamond has randomly oriented microcrystallites with facets and grain boundaries characteristic of a polycrystalline material. B in a diamond lattice acts as an electron acceptor providing the diamond p-type semiconducting properties. The acceptor level introduced by B is quite deep 0.37 eV from the top of the valence band. At higher doping levels, conduction occurs by nearest neighbour and variable range hopping of holes between ionised B sites. Further addition of B results in a layer with conductivity comparable to metallic materials.

In the study of Ashcheulov et al. [5], the conductivity of boron-doped polycrystalline films was studied. BDD films were prepared by microwave plasma-enhanced chemical vapour deposition. Diamond is prepared by the decomposition of a mixture of methane (or other carbon-containing species) at pressures from 0.01 to 100 mbar and substrate temperatures of 250 to 800°C. If the chemical reaction takes place in an ionized plasma, the ionized gas requires much less energy (lower temperatures) to react. Ionization energy is generally provided by a high-frequency field.

Concerning BDD film conductivity, the following factors are important: (i) size of the diamond grains—BDD films containing bigger grains have bigger conductivity (for the same B content); (ii) grain boundaries with non-diamond carbon impurities; (iii) structures of boron defects and setting of the material; (iv) the surface of each diamond grain can have a higher concentration of B, allowing specific conduction. Resistance of boron-doped diamond layers as a function of boron concentration is shown in Figure 4.
Using a combination of theoretical and experimental techniques (plane-wave density functional theory, NDP, resistivity and Hall effect measurements, AFM, Raman spectroscopy), B defect location, vibration states, conductivity, free hole concentration inside the grains and hole mobility were investigated in [5]. Based on the analysis of specific structural, bond, interactions, charge localization parameters and spins, an explanation of the complex influence of specific B defects on the system charge transport mechanisms was set out:

- When the concentration of B in the PCD film is low, hopping conduction using the excited level of B defects is predominant. When the concentration of boron atoms in the diamond lattice is high enough so the wave functions of B overlap and form an impurity band passing to the top of the valence band metal-like conductivity behaviour of the material is reached.

- High boron concentration in diamond lattice can support complex defects (B dimers in deformed lattice). B dimers have high acceptor energy so electrons excitation from top of the valence band is very improbable. The impurity states do not merge with the valence band, and free carrier concentration is reduced. Moreover, due to compensated spins of 2s and 2p electrons in B dimmers, the probability of charge hopping is also reduced.

4. Protection of zirconium nuclear fuel cladding by polycrystalline diamond film of nanosize thickness

A 300 nm thick polycrystalline diamond layer has been used for the protection of zirconium alloy nuclear fuel cladding against undesirable oxidation with no loss of chemical stability and preservation of its functionality [2, 3, 6].
Reaction of fuel claddings with hot water steam triggered explosions of hydrogen gas in nuclear power reactors on several occasions, including the recent Fukushima accident. The probability of such accidents can be drastically lowered if the surface of the fuel claddings is coated with a suitable protective layer. In this chapter, we demonstrate that the 300 nm polycrystalline diamond layer on the surface of a Zr cladding rod improves the chemical stability of the cladding material while preserving its functionality.

Zirconium alloys are used in all commercial light-water (PWR, BWR and VVER) and heavy-water (CANDU) nuclear reactors. Nuclear fuel cladding (NFCs) are typically produced from zirconium alloys (with a common subgroup trademarked Zircaloy2), a material with very low absorption cross-section of thermal neutrons, high ductility, hardness and corrosion resistance [1–4]. Zircaloy2 serves faultlessly under standard operation conditions of the plant sealing the uranium oxide fuel pellets. Normal operating temperatures in the reactor is about 300°C. In the case of some accident at temperatures above 800°C the so-called high-temperature corrosion begins; in this case, the peeling of the oxide layer previously protecting the metal from oxidation occurs, which can result in mechanical failure of the system. It is strongly exothermic and high auto-catalytic reaction between zirconium and steam, during which the dissociation of steam molecules occurs and causes the formation of zirconium dioxide, hydrogen and releases a large amount of heat. The result of the reaction is not only the formation of hydrogen, which, as a combustible gas, is a serious risk in the case of a severe accident (like in recent Fukushima accident), but also the release of large quantities of heat, which further complicates the core cooling and strengthens the further course of the high-temperature oxidation of zirconium alloys. Finally, there is also the degradation of the fuel cladding, one of the protective barriers that may lead to its failure and subsequent leakage of highly radioactive fission products from nuclear fuel into the primary circuit. Many protective materials have been applied on the Zr alloys surfaces, but without any significant success. Just by applying a homogenous polycrystalline diamond layer on the surface of Zircaloy2, the Zircaloy2 cladding was successfully protected against undesirable changes and processes in the nuclear reactor environment. The layer of polycrystalline diamond will also prevent the reaction between zirconium and steam. The deposition of polycrystalline diamond layer was carried out using LA-MW PECVD apparatus. In our recent work we demonstrated success: the 300 nm composite polycrystalline diamond layer with high crystalline diamond content and low roughness can protect zirconium alloy’s nuclear fuel cladding against undesirable oxidation and consolidate its chemical stability while preserving its functionality. After ion beam irradiation (10 dpa, 3 MeV Fe2+), the diamond film still showed satisfactory structural integrity with both sp3 and sp2 carbon phases— it was confirmed by Raman spectroscopy (Figure 5). The zirconium alloys under the carbon-based protective layer after hot steam oxidation test (1100°C, 30 min) differed from the original zirconium alloy’s material composition only very slightly—the diamond coating increases the material resistance towards high-temperature oxidation by forming a protective composite structure. We also found that the presence of the PCD coating blocks hydrogen diffusion into the Zr surface and protects Zr material from degradation. By more closely monitoring the oxidation rate and phase change of PCD-coated Zircaloy2 fuel cell rods as a function of temperature, we found that even at temperatures above 850°C (Zr beta phase that is more opened for oxygen/hydrogen...
diffusion) the Zircaloy2 surface could be effectively protected against hot steam corrosion. PCD anticorrosion protection of Zr nuclear fuel rods can significantly (30%) prolong life of Zr material in nuclear reactors even above phase transition.

![Graph showing Raman spectra comparison](image)

**Figure 5.** Comparison of Raman spectra of the PCD coating (black curve) and PCD after ion beam irradiation (red curve). Both sp² and sp³ C (1332 cm⁻¹ in Raman spectra) phases were present in the PCD layer.

After hot steam oxidation (950°C), a high level of structural integrity of the PCD layer was observed. Both sp² and sp³ C (1332 cm⁻¹ in Raman spectra) phases were present in the protective PCD layer. A greater relative weight gain of oxidized unprotected Zircaloy2 compared to that of the oxidized PCD-coated Zircalloy2 samples was supported by a thicker oxide layer of unprotected samples measured by impedance spectroscopy. The PCD layer blocks the hydrogen diffusion into the Zircaloy2 surface thus protecting the material from degradation. Hot steam oxidation tests confirmed that PCD-coated Zircaloy2 surfaces were effectively protected against corrosion. PCD film surface coating can prolong the service life of Zr nuclear fuel claddings in nuclear reactors.

Even under standard operating conditions in nuclear reactors (400°C hot water vapour), the polycrystalline diamond layer retains its original properties and participates both in the removal of heat released during the reactor operating mode, and further protects the coated surface against undesirable chemical reactions and changes in the composition of the structure related to the diffusion of hydrogen atoms from dissociated water molecules to zirconium alloy—as shown in Figures 6 and 7. The polycrystalline diamond layer further reduces especially adverse high-temperature chemical reactivity of the zirconium alloy surface, thereby also reducing high-temperature dissociation of water vapour molecules and subsequent formation of zirconium dioxide and explosive hydrogen. In the case of temperature-induced changes in zirconium alloy, the layer will benefit from the mixed nature of the protective carbon layer, which besides crystalline diamond grains with sp³-hybridized carbon also contains flexible amorphous phase sp² from hybridized carbon capable of good adapta-
tion to volume changes/expansion of the metal substrate without compromising the protective layer integrity (Figure 8).

Figure 6. Comparison of Raman spectra of the PCD coating (black curve) and after hot steam oxidation (blue curve). Hot steam oxidation causes sp² transition of the layer.

Figure 7. The 488 nm Raman spectra of PCD covered Zr alloy sample after 6 days in 400°C hot vapour/reactor testing. Spectra were taken from various parts of the tube. Both sp² and sp³ C (1332 cm⁻¹ in Raman spectra) phases were present in the PCD layer.
5. Conclusions

From carbon nanomaterials especially polycrystalline diamond films have attracted more and more interest due to their unique electrical, optical and mechanical properties, which make them widely used for different applications. Diamond survives high temperatures, does not degrade over time and (important for the nuclear fuel cladding) has perfect neutron cross-section properties. Moreover, polycrystalline diamond layers consisting of crystalline (sp³) and amorphous (sp²) carbon phases could have suitable thermal expansion. Polycrystalline diamond films can be used in a wide range of applications: high boron- and phosphorus-doped nanocrystalline diamond layers that can have a significant impact in the industrial use of diamond in electrochemical applications. Boron-doped nanocrystalline diamond-coated silicon solar cells can be used for direct photoelectrochemical water splitting with high effectivity. In such a system, boron-doped diamond electrodes are responsible for water decomposition. Diamond could also be considered as a prospective material for electrodes and organic solar cells. Diamond layers were used as anticorrosion protection for zirconium alloys applied in nuclear reactors. Polycrystalline diamond anticorrosion protection of Zr alloys can significantly prolong life of Zr material in nuclear reactors even at temperatures above Zr phase transition temperatures. Zr alloy’s oxidation and hydrogenation lead to limitation criteria in justifying fuel rod operability—rods containing even non-irradiated nuclear fuel must be fired due to Zr alloy surface destruction by oxidation/corrosion in reactor. Thus, the protection of zirconium fuel rods’ surfaces against corrosion in nuclear reactors’ environment can protect nuclear fuel to important extent.
Author details

Irena Kratochvilova

Address all correspondence to: krat@fzu.cz

Institute of Physics, Academy of Sciences Czech Republic v.v.i, Prague, Czech Republic

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