

Chapter 2

Diamond and Diamond-Like Carbon

Zahra Khalaj, Mahmood Ghoranneviss, Elnaz Vaghri, and Oana Ponta

Abstract A carbon allotrope is classified as “diamond” according to several parameters including the types of chemical bonds, type of crystal network, or range of crystal dimensionality. This chapter is a review on two major allotropes: diamond and diamond-like carbon, which are mostly produced by CVD technique. A detailed description of these techniques, as experienced by our group, is given. The importance of preparing the support for depositions and monitoring the process parameters is argued by the quality of carbon allotrope deposits, evidenced by a variety of physical measurements and microscopic images.

2.1 Introduction

Carbon is one of the most important natural elements in the periodic table, having more than one million different compounds in different forms. There exist four valence electrons in a carbon atom, two in 2s subshells and two in the 2p subshell. The atomic arrangement makes the carbon to exist with different allotropes such as diamond, diamond-like carbon, graphite, fullerene, carbon nanotubes, and carbon nanowalls and different material properties (Vaghri et al. 2012; Shams et al. 2012). This chapter is a review on two major allotropes, diamond and diamond-like carbon, that can be produced by chemical vapor deposition (CVD) techniques. Nanodiamond films (NDF) and nanocrystalline diamonds (NCD) possess high thermal

Z. Khalaj (✉) • M. Ghoranneviss • E. Vaghri
Plasma Physics Research Center, Science and Research Branch,
Islamic Azad University, Tehran, Iran
e-mail: khalaj.z@gmail.com

O. Ponta
Department of Condensed State Physics and Advanced Technologies, Faculty of Physics,
Babes-Bolyai University, Cluj, Romania

conductivity, large bandgap, excellent hardness, high electrical resistivity, and low friction coefficient (Takano et al. 2005; Yamazaki et al. 2008a, b). These properties promise outstanding applications of NCDs in electronics, optics, mechanics, etc. (Sharda et al. 2001). In addition, during the last decades, diamond-like carbon films have been intensively studied and utilized in many fields of industry, owing to their remarkable characteristics. Due to the excellent properties, very close to that of diamond, this allotrope was called diamond-like carbon (DLC). These films are extremely hard and mainly consist of sp^2 and sp^3 carbon networks.

2.2 Carbon Allotropes

Carbon is unique among all the elements, having four valence electrons and four vacancies in its outer shell, with an electron ground state $1s^2 2s^2 2p^2$.

There are three types of hybridization in allotropes of the carbon:

sp -type hybridization: one s-orbital hybridizes with one of the p-orbitals to make two sp -hybridized orbitals. The angle between these new orbitals is 180° and the carbon atom bounds by a diagonal symmetry.

sp^2 -type hybridization: one s-orbital is mixed with two of the p-orbitals to form three hybridized orbitals with a trigonal symmetry; the angles between them are 120° .

sp^3 -type hybridization: one s-orbital of a carbon atom is hybridized with all the three p-orbitals of the carbon atom to form four new orbitals with a tetrahedral symmetry and with 109.5° angles between them.

Combination of the above hybridized states allows the formation of several allotropic forms such as graphite, diamond, diamond-like carbon, and spherical cages also called fullerenes.

Figures 2.1, 2.2, 2.3, and 2.4 show some types of carbon allotropes produced by the authors using Plasma Enhanced Chemical Vapor Deposition (PECVD) and Hot Filament Chemical Vapor Deposition (HFCVD) techniques.

2.3 History of the Diamond

It is thought that the first diamond has been discovered by human beings more than 3,000 years ago. The word “diamond” comes from ancient Greek word “adamas,” which means “invincible,” referring to the extreme hardness of the material. After scientists discovered that diamond is an allotrope of carbon, many groups attempted to produce this rare and valuable material synthetically. General Electric Company was the first group who succeeded to heat carbon up to $3,000^\circ\text{C}$ under a very high pressure. After optimization of the growth process, they named it high-pressure high

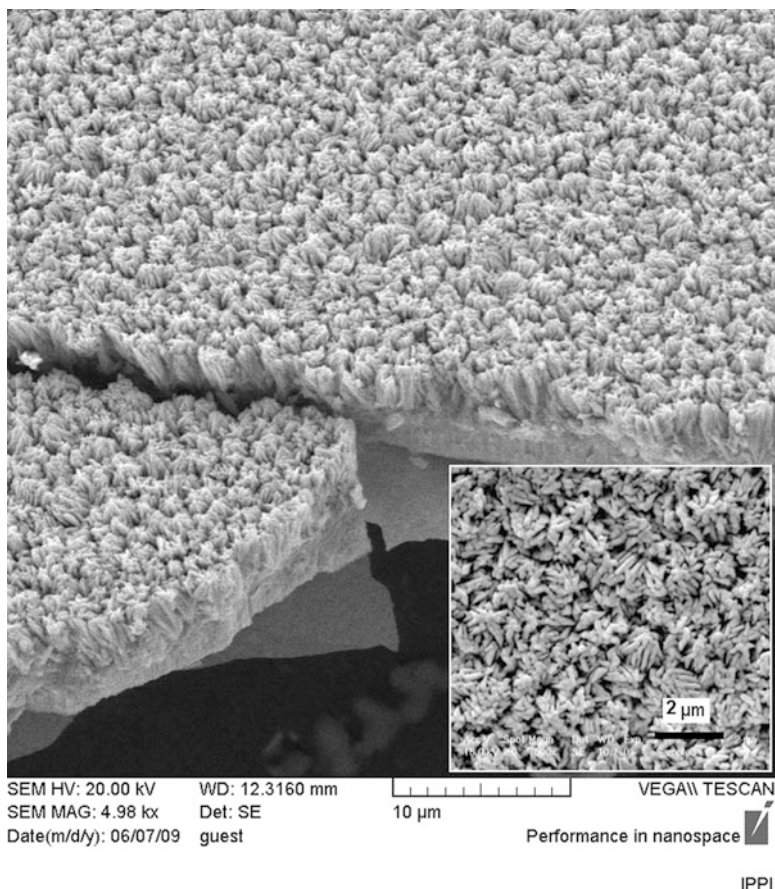


Fig. 2.1 Self-assembled cone-like carbon synthesized on gold coated silicon substrate using ammonia as an annealing gas and a mixture of CH_4/H_2 with 5% flow ratio as a reaction gas by HFCVD technique

temperature (HPHT) method. Scientists tried to grow diamonds as pure as possible. Next, the chemical vapor deposition (CVD) technique was proposed to grow the diamond at lower pressure and temperature.

In diamond lattice, each carbon atom is tetrahedrally coordinated, forming strong bonds to its four neighbors using sp^3 hybridized orbitals, with equal angles of 109.28° to each other. Each tetrahedron combines with four other tetrahedra forming a strongly bonded, uniform, three-dimensional, entirely covalent crystalline structure with the bond length of 0.154 nm. Due to its outstanding properties, diamond is the unique material with various applications in life and technology. It is the hardest of all natural materials and the highest thermal conductivity.

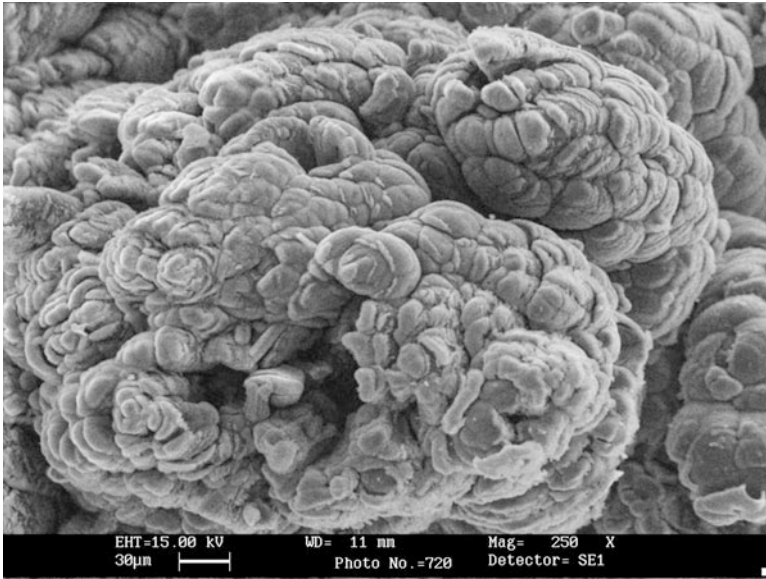


Fig. 2.2 SEM image of the DLC synthesized using PECVD technique

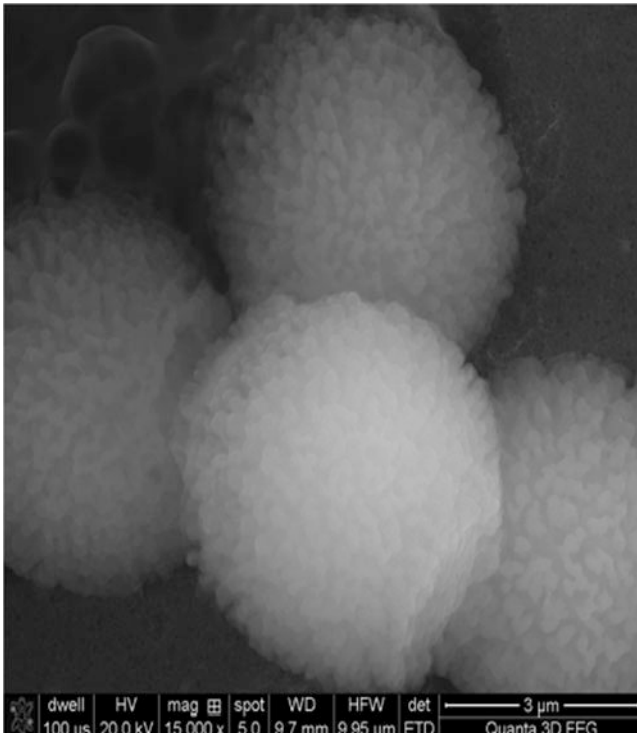


Fig. 2.3 Carbon microspheres synthesized by PECVD technique

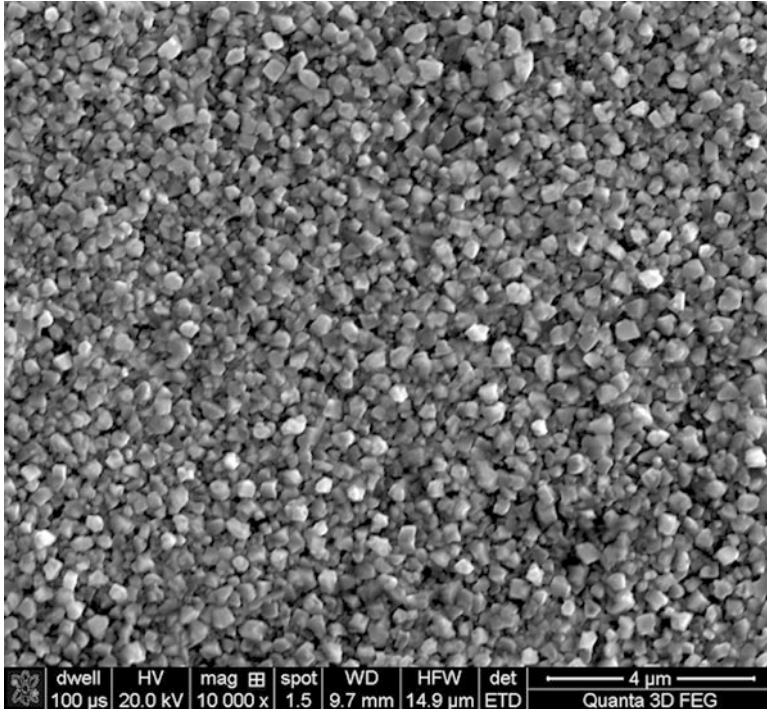


Fig. 2.4 Diamond thin film deposited on high-purity nickel substrate by PECVD technique

2.4 Quality of the Diamond Films

By developing the chemical vapor deposition (CVD), nanocrystalline diamonds (NCDs) and nanocrystalline diamond films (NDFs) became the topic of wide research (Khalaj et al. 2009, 2012; Khalaj and Ghoranneviss 2012; Atefi et al. 2012; Gupta et al. 2002; Yamazaki et al. 2008a, b; Melo et al. 2007; Tallaire et al. 2006; Zhoutong et al. 2008; Arnault et al. 1999; Donato et al. 2001). Nanocrystalline diamond films can be grown in a variety of conditions, using different chemical vapor deposition techniques at relatively low pressures and high nucleation densities. The quality and purity of nanostructures in CVD techniques are very important. There are some ways for increasing the quality and quantity of these deposits. To achieve a high nucleation density, several approaches are available.

2.4.1 *Role of Interlayer and Catalyst Layer*

The nucleation and growth of diamond coating on non-diamond substrates (e.g., silicon, steel, and Al) can be dramatically improved with different surface treatments (Fu et al. 2000). There are several methods to enhance the diamond nucleation, including mechanical and chemical treatment processes such as using interlayer or catalyst layer. In this case, the interlayer might act as an adhesion layer and makes a good reactive surface for adsorbing the carbon. Furthermore, using a catalyst layer can increase the rate of diamond nucleation and provide a diffusion barrier to increase the carbon concentration for diamond nucleation. Using suitable catalyst (e.g., gold or silver nanoparticles) can enhance the diamond nucleation and, therefore, increase the quality of the films (Khalaj and Ghoranneviss 2012). In addition, a homogenous distribution of the catalyst nanoparticles could lead to a dense film of the diamond.

2.4.2 *Role of Etching Treatment*

Another effective way to enhance the diamond nucleation is the chemical or physical etching treatment of the substrate (Khalaj et al. 2010). The etching process can be a wet or a dry one, depending on whether the material removed enters the liquid or gas phase, respectively (Ohring 2002). While wet etching techniques dominate in micromechanics, up to micrometer range, dry etching becomes interesting with decreasing structure size and it plays a key role in diamond growth. Due to the dependence on the etching rate (involving the mobile phase, chemical reactions at solid state surface, or removal of reaction products) of the thickness of the diamond deposit, it is important to calculate the etching rate (r_{etch}) for each sample, $r_{\text{etch}} = d_{\text{etch}} / t_{\text{etch}}$, where d_{etch} is the removed thickness of the layer and t_{etch} is the duration of etching (Ohring 2002).

Different research groups have investigated various parameters, treatments, and CVD techniques with the aim of enhancing the diamond nucleation and increasing the deposit quality (Gruen 1999; Buhler and Prior 2000; Liang et al. 2006; Khalaj et al. 2012). Producing a high quality and controllable growth of the diamond is very important for industrial applications. Using different etching gases, such as hydrogen, nitrogen, and ammonia, has different effect on diamond nucleation. By our experience (Khalaj et al. 2010), the quality of the diamond deposits was higher in case we used hydrogen as an etching gas. Depending on the experimental conditions, good quality diamond films or diamond single crystals were obtained.

An example of the morphology and the Energy dispersive X-ray analysis (EDS) from the surface of the high-quality diamond film synthesized on nickel substrate is shown in Fig. 2.5. The substrate is polished with 1 μm diamond paste and etching treated by hydrogen before inserting the reaction gases. Hydrogen-etching

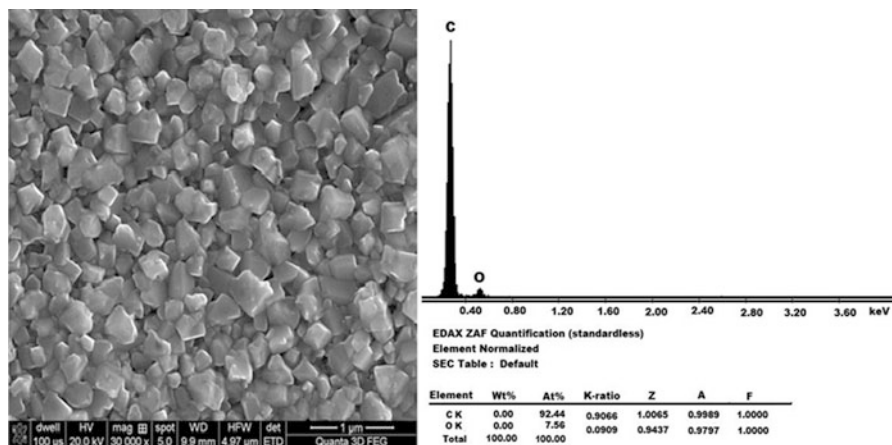


Fig. 2.5 High nucleation density of a diamond film obtained by seeding high-purity nickel (99.99 %) substrate with 1 μm diamond paste. The film was produced by our group using CH_4/H_2 mixture with flow ratio 8 % by plasma-enhanced CVD system

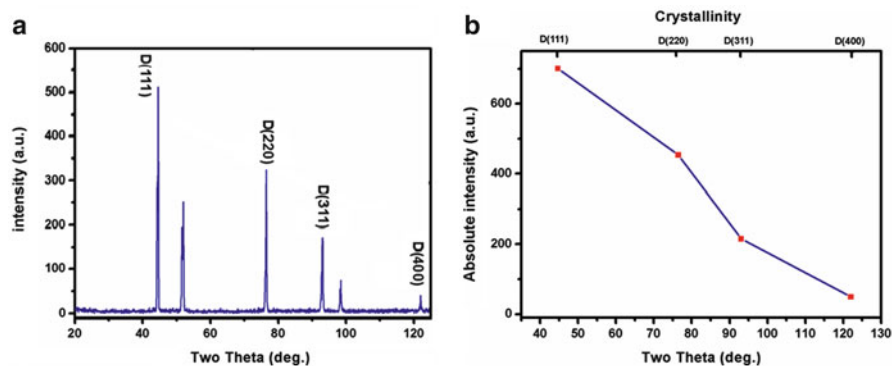


Fig. 2.6 (a) The XRD pattern for synthesized diamond film on Ni substrate by PECVD system and (b) two-theta diagram versus intensity and crystallinity, respectively

treatment helps to produce dense diamond film with high-purity crystallite structure in comparison with virgin substrate with no etching treatment.

The crystalline structure of this film was measured using X-ray diffraction (XRD). The XRD patterns were recorded with a Shimadzu XRD – 6,000 diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation. Crystallographic identification was accomplished by comparing the experimental XRD patterns with standard inorganic crystal structure data JCPDS. Based on the spectra in Fig. 2.6, four diffraction peaks were found in the spectra for the typical SEM image, at different two-theta values. One can observe the spectrum is dominated by $2\theta = 44.44^\circ$, 76.34° , and 92.91° which could be identified with reflections from (111), (220), and (311) plane of

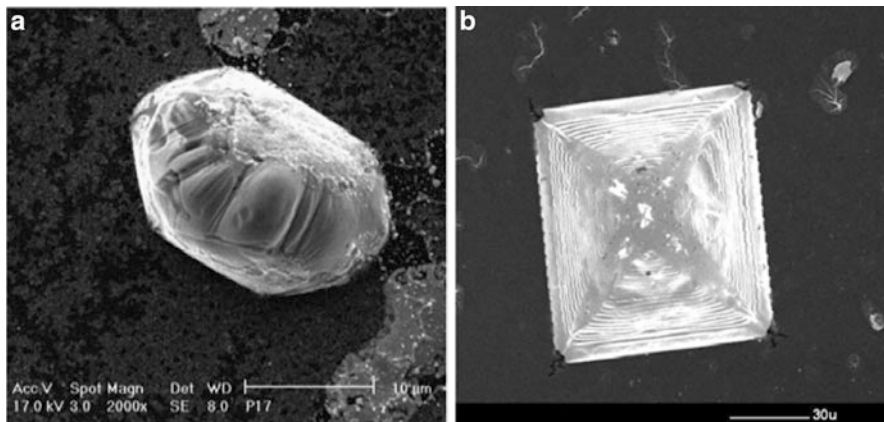


Fig. 2.7 Diamond single crystals grown on selected area: (a) gold coated silicon wafer and (b) silicon

diamond. The last peak with lower intensity exhibits at 121.70° which is indexed to the diffraction from (400) crystal planes of diamond. The full width half maximum (FWHM) of the diamond peaks shows the sharp peaks with small FWHM which indicate high crystal quality.

In addition, one can see an obvious pattern for two-theta versus absolute intensity and crystallinity. Due to the intensity and FWHM of each peak, the quality of the crystallites varies with changing the two theta. Therefore, it is clearly seen that the quality of the crystallites orientation decreases by increasing the two-theta degree on diamond coated nickel substrate.

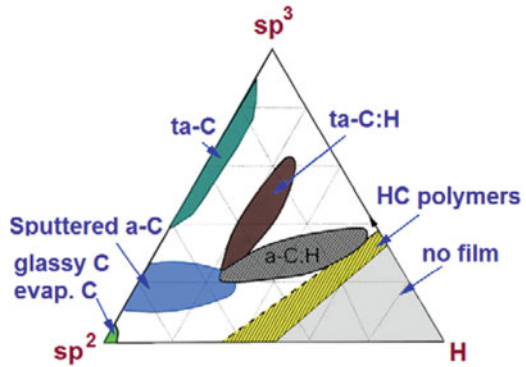
2.4.3 Selective Growth

One of the important methods in controllable diamond production is the selective growth method (Khokhryakov and Palyanov 2006; Tran et al. 2010; Li et al. 2003, 2010). A good quality of CVD diamond depends on the controllable growth in selected area that can make the diamond more applicable. Figure 2.7 shows the microcrystalline diamond with different crystallite structure grown on selected area.

2.5 Diamond-Like Carbon Films

A great variety of materials are formed from carbon, ranging from crystalline to amorphous structures. Diamond-like carbon (DLC) films consist of a random network of sp^2 and sp^3 carbon sites with varying amount of hydrogen dispersed

Fig. 2.8 Ternary phase diagram of the C, H system displaying composition of DLC films



within the lattice (Donnet et al. 1999, 2000). The sp^2 -bonded carbon controls the optical properties of DLC films like bandgap and infrared refractive index while the sp^3 -bonded carbon controls the mechanical properties like hardness, coefficient of friction, and Young modulus (Robertson 2002).

Aisenberg and Chabot (1971) were the first who prepared DLC films using carbon ions in argon environment. A first model of DLC structure was proposed by Robertson (1986, 2001, 2002). Angus and Jansen (1988) developed a model describing DLC as a dense film phase of a random covalent carbon network. Based on the existence of hydrogen in these films, a material can be categorized as follows:

1. Hydrogenated amorphous carbon (a-C: H) is the common form of DLC; these films contain a moderate content of sp^3 carbon and 10–40 % H (Lifshitz 2003). The a-C: H films or DLC films can be divided into two different forms, the hard a-C: H and the soft one. The hard a-C: H consists of a fraction of sp^2 bonds and sp^3 bonds and low hydrogen amount whereas the soft a-C: H has a higher hydrogen amount.
2. Hydrogenated tetrahedral amorphous carbon (ta-C: H) films with a high sp^3 content and relatively low hydrogen content.
3. Hydrogen-free form of amorphous carbon (a-C) film is another important form of DLC; it has a significant fraction of sp^2 bonds.
4. Tetrahedral hydrogen-free amorphous carbon (ta-C) contains up to 90 % sp^3 -hybridized bonds (Lifshitz 2003). Figure 2.8 represents various forms of DLC by a ternary diagram.

The three corners of this diagram are related to diamond, graphite, and hydrocarbons. The a-C: H film is located at the center of the phase diagram and shows various amounts of sp^3 , sp^2 , and H contents. Research on diamond-like carbon films has been devoted to find both optimized conditions and characteristics of the deposited films on various substrates. Depending on the deposition conditions, DLC films can be totally amorphous or include micro- or nanocrystalline diamond. Figure 2.9 shows a sample of DLC structures without crystalline orientation.

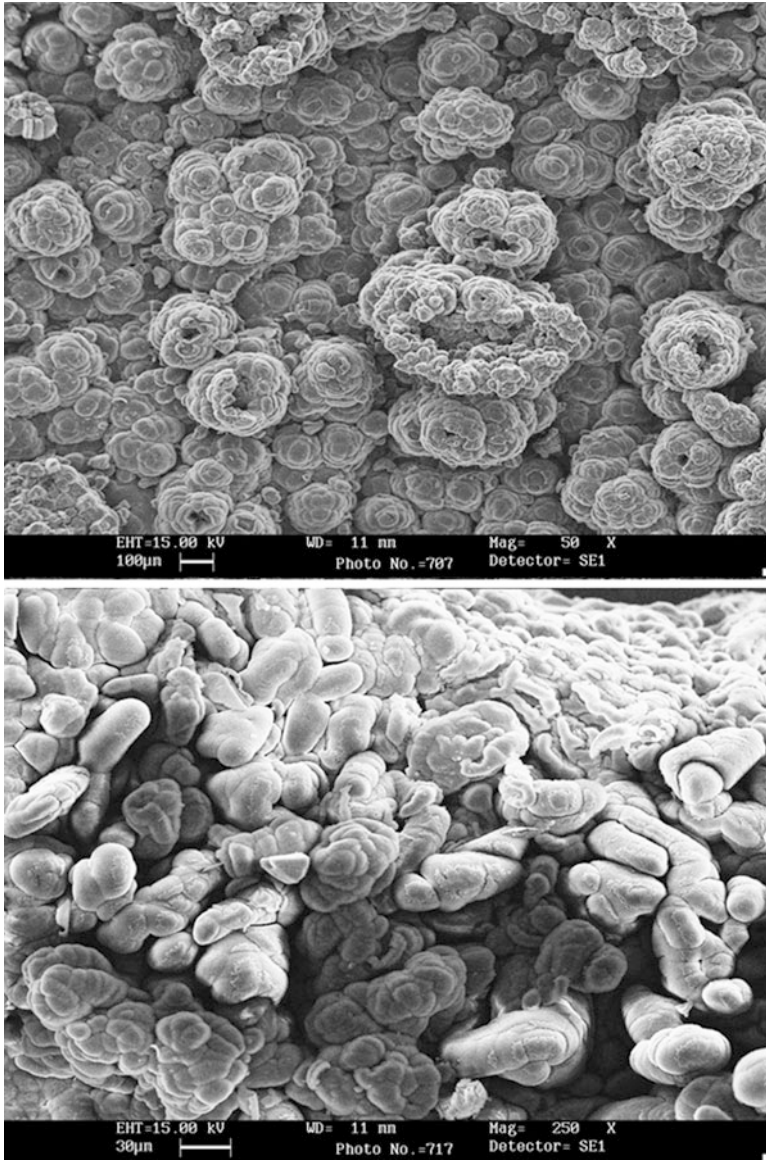


Fig. 2.9 Typically SEM images of diamond-like carbon synthesized by our group

2.6 Properties and Applications

Since their first preparation, in the early 1970s (Aisenberg and Chabot 1971), DLC films have attracted a considerable interest from both academic and industrial communities owing to their extraordinary properties such as: low friction coefficient,

high wear resistance, chemical inertness, optical transparency, high hardness, and biocompatibility (Nakazawa et al. 2010) that make them reliable to use in various fields of science and technology. DLC coatings have found biomedical applications such as contact lenses, medical wires, arterial stents, orthopedic pins, surgical scalpels, and dental instruments (Yin et al. 2008; Robertson 2002; Donnet et al. 1999; Donnet and Grill 1997; McHargue et al. 1991; Shirakura et al. 2006; Morrison et al. 2006; Ishihara et al. 2005). One of the significant properties of DLC is the high mechanical hardness; thus, they are commonly utilized in industry as protective, nonabrasive, and corrosion-resistant coating. Other applications include antireflection optical windows and lubricant coatings in micro-electromechanical devices (Cho et al. 2005; Singh et al. 2006; Piazza et al. 2005; Ferrari 2004; Robertson 2001; Dearnaley and Arps 2005; Grill 1999, 2003; Vaghri et al. 2011). In addition, DLC coating would increase the surface hardness and its longevity, therefore, it can be used for harden the internal wall of the Tokamak reactors (Vaghri et al. 2011). However, adhesion of DLC films to metallic substrates, especially stainless steel, is the major concern related to these films.

2.7 Quality of DLC Films

The presence of a high internal compressive stress in DLC films is the main drawback of these films leading to crack and poor adhesion to the substrate (Grill 1999, 2003; Silva et al. 2011; Chiba and Tada 2012) which results in production of low-quality DLC films with no application. The internal stress of DLC films is composed from the intrinsic stress and thermal stress. The intrinsic stress appears during the growth process while the thermal stress is caused by difference in thermal expansion coefficient between the film and base material (Ji et al. 2008). Many attempts have been made to increase the adherence of diamond-like carbon coatings to the substrate such as incorporation of elements into the film and/or introducing interlayer between films and substrates (Ji et al. 2008; Azzi et al. 2010; Chen and Lin 2009; Ahmed et al. 2009). Dwivedi et al. (2012) investigated the growth and characteristics of Cu-incorporated DLC films. Their experimental results illustrated that copper incorporation into DLC matrix relaxed the residual stress and considerably improved the temperature-dependent electrical transport. Gayathri et al. (2012) reported the growth of DLC films with different transition metal ($M = \text{Cr, Ag, Ti, Ni}$) interlayers. They found that chromium interlayer reduces the internal stress significantly compared to titanium, nickel, and silver. Ban and Hashegawa (2002) found that the incorporation of silicon into DLC films reduced the internal stress. Other parameters influencing on DLC adhesion to the substrates include: chemical bonding between the DLC coating and substrate, contamination, roughness of the substrate, and physical properties (Koski et al. 1996; Morshed et al. 2003). Surface roughness and morphologic variations have direct influence on layer adhesion to the substrate. We can decrease the surface roughness by selecting a suitable intermediate layer and roughness of the coatings. In view to produce a

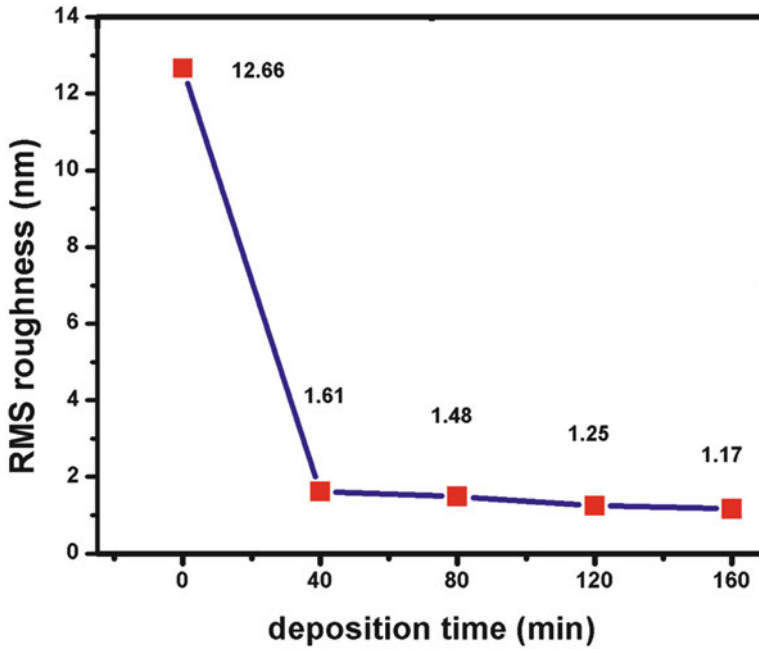


Fig. 2.10 Variation in the roughness of Ni coating on AISI 304L substrates at different deposition times

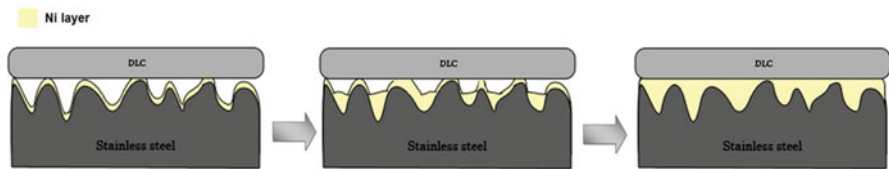


Fig. 2.11 The contact mechanism of a DLC sliding on a Ni-coated stainless steel with different surface roughness

high quality of DLC, we used nickel as an intermediate layer (Khalaj et al. 2012) and investigate the effect of surface roughness on the deposit quality. Decreasing in the nickel layer roughness (see Fig. 2.10) resulted in a DLC better adhesion to the stainless steel substrate (probably due to a higher degree of chemical bonding and good friction coefficient of Ni layer which is compatible with the model in Fig. 2.11).

The root-mean-squared roughness (R_{rms}) of surface is one of the most important parameters for the characterization of the surface structure (Eskusson et al. 2008). An illustration of the roughness and morphology of the surface of the stainless steel coated by nickel is given in Fig. 2.12.

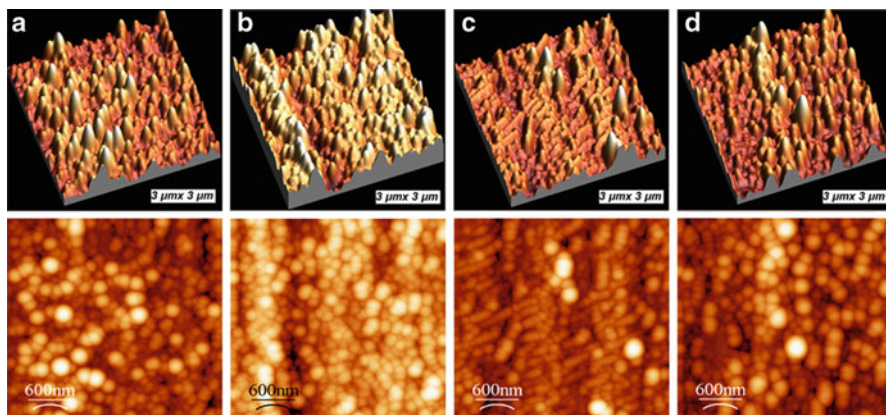


Fig. 2.12 2D and 3D AFM images of the stainless steel coated by Ni at different deposition time: (a) 40 min, (b) 80 min, (c) 120 min, and (d) 180 min, respectively

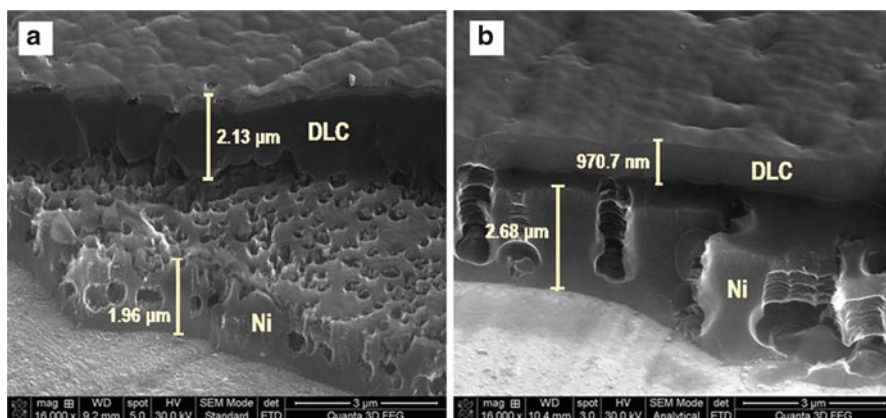


Fig. 2.13 Typical cross-section SEM images of DLC deposits on stainless steel coated by Ni at 40 min (a) and 180 min (b)

For a more detailed morphological analysis there was performed a cross section using high-current ion column. Quanta 3D FEG's high-current Focused Ion Beam (FIB) enables fast material removal. Automated FIB sectioning recipes enable accurate cross-sectioning and low damage sample cleaning. Figure 2.13 shows the minimum and the maximum thickness of the Ni layer in coatings.

Forming an intermediate layer between the DLC film and substrate releases the thermal stress by diminishing the mismatch of thermal expansion coefficients while incorporation of elements into the film releases the intrinsic stress by adjustment of film composition and structure (Ji et al. 2008).

2.8 Deposition Techniques

A wide variety of chemical and physical vapor deposition methods have been developed for the deposition of the diamond and DLC films. Different types of CVD techniques are used to produce diamond and diamond-like carbon films, and they can be grouped into four main categories based on the activation process: (1) plasma activation, (2) thermal activation, (3) laser ablation, and (4) combustion. Similarly, physical vapor deposition (PVD) techniques have also been attempted in the last years. In this part, we introduced two of the most applicable CVD techniques for producing DLC and diamond films: plasma-enhanced chemical vapor deposition and hot filament chemical vapor deposition, designed by Plasma Physics Research Center (PPRC) engineering group.

2.8.1 PECVD Technique

Two of the most common techniques used for the deposition of DLC films are Dc- and Rf-PECVD methods. Possibility of deposition on a large area and at low temperature is the main advantage of the PECVD technique; it provides using a wide variety of substrate materials, with great industrial importance (Eskusson et al. 2008). The central part of our PECVD system is a cylindrical process chamber with a diameter of about 30 cm consisting of a base and a cap. On the top of the cap, the Dc-/Rf-source is flanged. The chamber can be opened for substrate handling by vertical shifting the aluminum cap on top. The substrate is placed on a furnace right under the anode. The temperature of the substrates is monitored by a thermocouple. Figure 2.14 shows the schematic diagram of our PECVD system.

The PECVD process is based on the disintegration of a carbonaceous gas into species such as ions, radicals, and atoms near the substrate surface. In this way, a wide range of substrate material can be used. Most of the researches used Rf-discharge to produce DLC (Whitmell and Williamson 1976; Bubenzer et al. 1983; Dhawan et al. 2003; Li et al. 2003, 2010). It is generally considered that DLC is not possible with DC discharge due to deposition of dielectric films, the electrode exposed to the plasma gradually becoming covered with an insulator (Angus and Jansen 1988). Although a DC discharge may be initiated, it will quickly extinguish as the electrons accumulate on the insulator and recombine with the available ions. Using hydrogen dilution could avoid covering the target with a hydrocarbon gas. In addition, DC-PECVD is suitable for DLC coating because of the low stress values of deposits in comparison to Rf-PECVD method (Ferrari 2004).

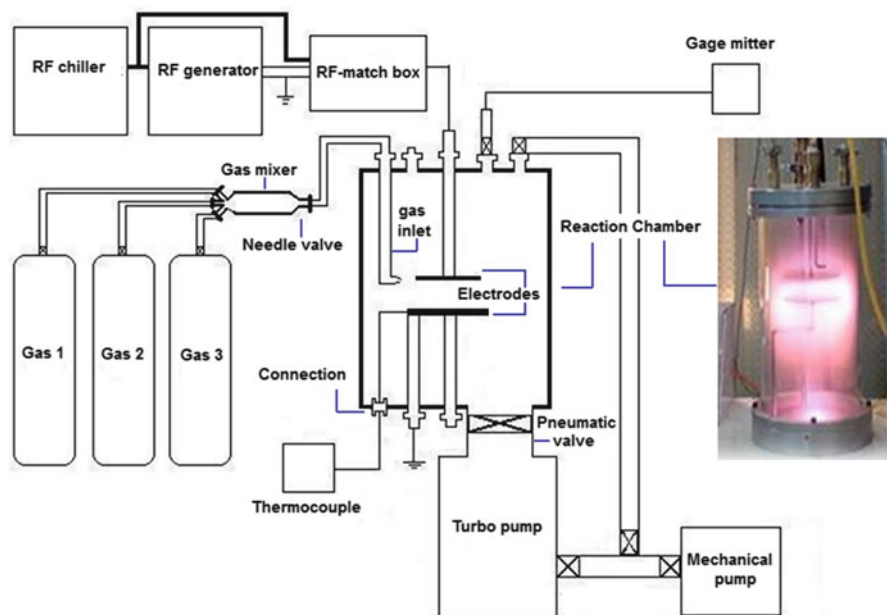


Fig. 2.14 The schematic diagram of the PECVD system designed and fabricated by S. Shams and M. Ghoranneviss (Registered in: State Reg. Org. for Deeds and Real-Estates, Industrial Property General Office, Iran, Serial No: A/89-020594)

2.8.2 HFCVD Technique

The Hot filament chemical vapor deposition (HFCVD) system is used for growing diamond films and other carbon allotropes (Shahsavari et al. 2011; Atefi et al. 2011). This system consists of a horizontal stainless steel (S.S.316) cylinder as a reaction chamber, a furnace, and filament. Figure 2.15 shows the schematic diagram of our HFCVD system. Tungsten wires were used as filaments which electrically heated to over 2,000 °C during the reaction. The substrate is placed on a substrate holder right under the filament, where the distance between the filament and substrate is adjustable. Due to the high degree of ionization occurring by the hot filament, this system is much more suitable for diamond growth. Production of other carbon allotropes is also possible using optimum experimental condition. In order to obtain diamond nano- and microstructures, the substrate is introduced into the reaction chamber and it will evacuate to 10^{-6} Torr as a base pressure. The source gas and dilution gas are fed into the system through a steel nozzle.

Diamond can be deposited from a large variety of precursors including methane, aliphatic, and aromatic hydrocarbons. These compounds generally decompose into stable primary species such as the methyl radical (CH_3) that is considered the dominant species in generating the growth of CVD diamond.

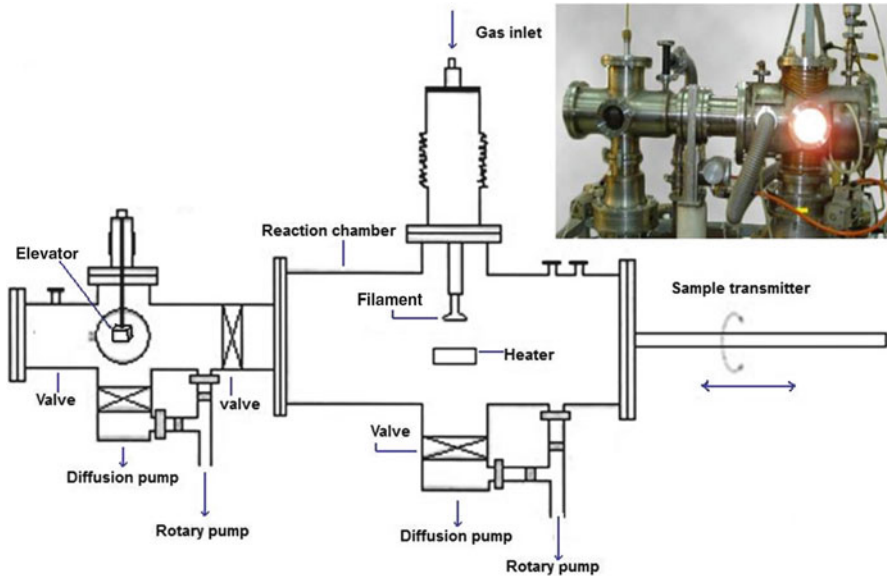


Fig. 2.15 The schematic diagram of the HFCVD system fabricated by Plasma Physics Research Center group

The stable hydrogen diatomic molecule (H_2) dissociates at low pressure and the temperature over $2,000\text{ }^\circ\text{C}$ to free atoms. The rate of recombination to diatomic molecule is rapid, the half-life of atomic hydrogen being only 0.3 s (Hugh O. Pierson 1999). Atomic hydrogen plays an essential role in the surface and plasma chemistry of diamond deposition as it contributes to the stabilization of the sp^3 dangling bonds found on the diamond surface plane (Yasuda et al. 1990). Unlike molecular hydrogen, atomic hydrogen is extremely reactive and helps to remove the graphite selectively by etching the deposits. Although the hydrogen etching occurs simultaneously in graphite and diamond, its effect on graphite is 20 times as fast as it etches diamond. This process is very important and sensitive in producing high-quality diamond films.

References

- Ahmed SF, Moon M-W, Lee K-R (2009) Effect of silver doping on optical property of diamond like carbon films. *Thin Solid Films* 517:4035–4038
- Aisenberg S, Chabot R (1971) Ion-deposition of thin films of diamond like carbon. *Appl Phys* 42:2953–2958
- Angus J, Jansen F (1988) Dense “diamond like” hydrocarbons as random covalent networks. *Vac Sci Technol A* 6:1778–1782

- Arnault JC, Demuyneck L, Speisser C, Le Normand F (1999) Mechanisms of CVD diamond nucleation and growth on mechanically scratched Si (001) surfaces. *Eur Phys J B* 11:327–343
- Atefi H, Ghoranneviss M, Khalaj Z, Diudea MV (2011) Effect of different substrate temperature on growth of nano crystalline diamond by HFCVD technique. *Studia Univ Babes-Bolyai Chemia* 56:133–140
- Atefi H, Khalaj Z, Ghoranneviss M (2012) Deposition and characterization of nano crystalline diamond on different substrates by plasma enhanced CVD technique. *Studia Univ Babes-Bolyai, Chemia* 57:51–58
- Azzi M, Amirault P, Paquette M, Klemberg-Sapieha JE, Martinu L (2010) Corrosion performance and mechanical stability of 316L/DLC coating system: role of interlayers. *Surf Coat Technol* 204:3986–3994
- Ban M, Hasegawa T (2002) Internal stress reduction by incorporation of silicon in diamond-like carbon films. *Surf Coat Technol* 162:1–5
- Bubbenzer A, Dischler B, Brandt G, Koidl P (1983) Rf plasma deposited amorphous hydrogenated hard carbon thin films: preparation, properties, and applications. *J Appl Phys* 54:4590–4595
- Buhler J, Prior Y (2000) Study of morphological behavior of single diamond crystals. *Cryst Growth* 209:779–788
- Chen K-W, Lin F-J (2009) The study of adhesion and nanomechanical properties of DLC films deposited on tool steels. *Thin Solid Films* 517:4916–4920
- Chiba K, Tada M (2012) Buffered internal stresses in diamond-like carbon films reinforced with single-walled carbon nanotubes. *Thin Solid Films* 520:1993–1996
- Cho S-J, Chung J-W, Lee K-R (2005) Characterization of the mechanical properties of diamond-like carbon films. *Diam Relat Mater* 14:1270–1276
- Dearnaley G, Arps JH (2005) Biomedical applications of diamond-like carbon (DLC) coatings. A review. *Surf Coat Technol* 200:2518–2524
- Dhawan A, RoyChowdhury S, De PK, Sharma SK (2003) Corrosion behaviour of amorphous Ti48Cu52, Ti50Cu50 and Ti60Ni40 alloys investigated by potentiodynamic polarization method. *Bull Mater Sci* 26:609–612
- Donato MG, Faggio G, Marinelli M, Messina G, Milani E, Paoletti A, Santangelo S, Tucciarone A, Verona Rinati G (2001) High quality CVD diamond: a Raman scattering and photoluminescence study. *Eur Phys J B* 20:133–139
- Donnet C, Grill A (1997) Friction control of diamond-like carbon coatings. *Surf Coat Technol* 94:456–462
- Donnet C, Fontaine J, Le Mogne T, Belin M, Héau C, Terrat JP, Vaux F, Pont G (1999) Diamond-like carbon-based functionally gradient coatings for space tribology. *Surf Coat Technol* 120:548–555
- Donnet C, Fontaine J, Grill A, Le Mogne T (2000) The role of hydrogen on the friction mechanism of diamond-like carbon films. *Tribol Lett* 9:137–142
- Dwivedi N, Kumar S, Malik H, Sreekumar C, Dayal S, Rauthan CMS, Panwar OS (2012) Investigation of properties of Cu containing DLC films produced by PECVD process. *Phys Chem Solids* 73:308–316
- Eskusson J, Jaaniso R, Lust E (2008) Synthesis of DLC films by PLD from liquid target and dependence of film properties on the synthesis conditions. *Appl Phys A* 93:745–749
- Ferrari AC (2004) Diamond-like carbon for magnetic storage disks. *Surf Coat Technol* 180:190–206
- Fu Y, Yan B, Nee Lam L (2000) Effects of pre-treatments and interlayers on the nucleation and growth of diamond coatings on titanium substrates. *Surf Coat Technol* 130:173–185
- Gayathri S, Krishnan R, Ravindran TR, Tripura Sundari S, Dash S, Tyagi AK, Raj B, Sridharan M (2012) Spectroscopic studies on DLC/TM (Cr, Ag, Ti, Ni) multilayers. *Mater Res Bull* 47:843–849
- Grill A (1999) Diamond-like carbon: state of the art. *Diam Relat Mater* 8:428–434
- Grill A (2003) Diamond-like carbon coatings as biocompatible materials an overview. *Diam Relat Mater* 12:166–170
- Gruen DM (1999) Nanocrystalline diamond films. *Ann Rev Mater Sci* 29:211–259

- Gupta S, Weiner BR, Morell G (2002) Electron field emission properties of microcrystalline and nanocrystalline carbon thin films deposited by S-assisted hot filament CVD. *Diam Relat Mater* 11:799–803
- Ishihara M, Suzuki M, Watanabe T, Nakamura T, Tanaka A, Koga Y (2005) Synthesis and characterization of fluorinated amorphous carbon films by reactive magnetron sputtering. *Diam Relat Mater* 14:989–993
- Ji L, Li H, Zhao F, Chen J, Zhou H (2008) Adhesion studies of diamond-like carbon films on 202 stainless steel substrate with a silicon interlayer. *Eng Mater* 373–374:151–154
- Khalaj Z, Ghoranneviss M (2012) Investigation of metallic nanoparticles produced by laser ablation method and their catalytic activity on CVD diamond growth. *Studia Univ Babes-Bolyai Chemia* 57:21–28
- Khalaj Z, Taheri SZ, Laheghi SN, Eslami PA (2009) Diamond growth on aluminium substrate by HFCVD using different etching gasses. *Iran Phys J* 3(1):19
- Khalaj Z, Ghoranneviss M, Nasirilaheghi S, Ghoranneviss Z, Hatakeyama R (2010) Growth of nanocrystalline diamond on silicon substrate using different etching gases by HFCVD. *Chin J Chem Phys* 23:689–692
- Khalaj Z, Ghoranneviss M, Vaghri E, Saghaleini A, Diudea MV (2012) Deposition of DLC film on stainless steel substrates coated by nickel using PECVD method. *Acta Chim Slov* 59:338–343
- Khokhryakov AF, Palyanov YN (2006) Revealing of dislocations in diamond crystals by the selective etching method. *Cryst Growth* 293:469–474
- Koski K, Hölsä J, Ernoult J, Rouzaud A (1996) The connection between sputter cleaning and adhesion of thin solid films. *Surf Coat Technol* 80:195–199
- Li Y, Li Q, Wang F (2003) The electrochemical corrosion behavior of TiN and (Ti, Al)N coatings in acid and salt solution. *Corros Sci* 45:1367–1381
- Li YS, Pan TJ, Tang Y, Yang Q, Hirose A (2010) Selective synthesis of diamond and CNT nanostructures directly on stainless steel substrates. *Diam Relat Mater* 20:187–190
- Liang X, Wang L, Yang D (2006) The structural evolution of nanocrystalline diamond films synthesized by r.f. PECVD. *Mater Lett* 60:730–733
- Lifshitz Y (2003) Pitfalls in amorphous carbon studies. *Diam Relat Mater* 12:130–140
- McHargue CJ, Tzeng Y, Yoshikawa M, Murakawa M (1991) In: Feldman A (ed) *Applications of diamond films and related materials*, Materials science monographs. Elsevier, New York, p 113
- Melo LL, Moro JR, Castro RM, Corat EJ, Trava Airoldi VJ (2007) A comparative study of diamond growth on tungsten wires by using methane and graphite as the carbon source. *Surf Coat Technol* 201:7382–7386
- Morrison ML, Buchanan RA, Liaw PK, Berry CJ, Brigmon RL, Riester L, Abernathy H, Jin C, Narayan RJ (2006) Electrochemical and antimicrobial properties of diamond like carbon–metal composite films. *Diam Relat Mater* 15:138–146
- Morshed MM, McNamara BP, Cameron DC, Hashmi MSJ (2003) Effect of surface treatment on the adhesion of DLC film on 316L stainless steel. *Surf Coat Technol* 163–164:541–545
- Nakazawa H, Sudoh A, Suemitsu M, Yasui K, Itoh T, Endoh T, Narita Y, Mashita M (2010) Mechanical and tribological properties of boron, nitrogen–coincorporated diamond-like carbon films prepared by reactive radio–frequency magnetron sputtering. *Diam Relat Mater* 19:503–506
- Ohring M (2002) *Materials science of thin films: deposition and structure*, 2nd edn. Academic Press, USA
- Piazza F, Grambole D, Schneider D, Casiraghi C, Ferrari AC (2005) Protective diamond-like carbon coatings for future optical storage disks. *Diam Relat Mater* 14:994–999
- Pierson HO (1999) *Principles, technology, and applications*, 2nd edn, CVD diamond growth. Noyes, Norwich, pp 93–95
- Robertson J (1986) Amorphous carbon. *Adv Phys* 35:317–374
- Robertson J (2001) Ultrathin carbon coatings for magnetic storage technology. *Thin Solid Films* 383:81–88
- Robertson J (2002) Diamond-like amorphous carbon. *Mater Sci Eng R* 37:129–281

- Shahsavari F, Ghoranneviss M, Khalaj Z, Diudea MV (2011) Effect of atalyst layer thickness on growth of CVD diamond. *Studia Univ Babes-Bolyai Chemia* 56:141–148
- Shams S, Khalaj M, Ghoranneviss M (2012) How plasma species affect the structural and morphological properties of mwcnts. *Studia Univ Babes-Bolyai Chemia* 57:167–176
- Sharda T, Rahaman MM, Nukaya Y, Soga T, Jimbo T, Umeno M (2001) Structural and optical properties of diamond and nano–diamond films grown by microwave plasma chemical vapor deposition. *Diam Relat Mater* 10:561–567
- Shirakura A, Nakaya M, Koga Y, Kodama H, Hasebe T, Suzuki T (2006) Diamond–like carbon films for PET bottles and medical applications. *Thin Solid Films* 494:84–91
- Silva WM, Trava-Airoldi VJ, Chung YW (2011) Surface modification of 6150 steel substrates for the deposition of thick and adherent diamond–like carbon coatings. *Surf Coat Technol* 205:3703–3707
- Singh RA, Yoon E-S, Kim HJ, Kong H, Park S-J, Lee K-R (2006) Friction behaviour of diamond–like carbon films with varying mechanical properties. *Surf Coat Technol* 201:4348–4351
- Takano Y, Nagao M, Takenouchi T, Umezawa H, Sakaguchi I, Tachiki M, Kawarada H (2005) Superconductivity in polycrystalline diamond thin films. *Diam Relat Mater* 14:1936–1938
- Tallaire A, Achard J, Secroun A, De Gryse O, De Weerd F, Barjon J, Silva F, Gicquel A (2006) Multiple growth and characterization of thick diamond single crystals using chemical vapour deposition working in pulsed mode. *Cryst Growth* 291:533–539
- Tran DT, Fansler C, Grotjohn TA, Reinhard DK, Asmussen J (2010) Investigation of mask selectivities and diamond etching using microwave plasma–assisted etching. *Diam Relat Mater* 19:778–782
- Vaghri E, Khalaj Z, Ghoranneviss M (2012) Preparation and characterization of diamond-like carbon films on various substrates by PECVD system. *Studia Univ Babes-Bolyai Chemia* 57:143–150
- Vaghri E, Khalaj Z, Ghoranneviss M, Borghei M (2011) Characterization of diamond: like carbon films synthesized by DC–plasma enhanced chemical vapor deposition. *Fusion Energy* 30:447–452
- Whitmell DS, Williamson R (1976) The deposition of hard surface layers by hydrocarbon cracking in a glow discharge. *Thin Solid Films* 35:255–261
- Yamazaki K, Furuichi K, Tsumura I, Takagi Y (2008a) The large–sized diamond single–crystal synthesis by hot filament CVD. *J Cryst Growth* 310:1019–1022
- Yamazaki K, Furuichi K, Tsumura I, Takagi Y (2008b) The large–sized diamond single–crystal synthesis by hot filament CVD. *Cryst Growth* 310:1019–1022
- Yasuda T, Ihara M, Miyamoto K, Genchi Y, Komiyama H (1990) Gas phase chemistry determining the quality of CVD diamond. In: Spear K, Cullen G (eds) *Proceedings of the 11th international conference on CVD*. Electrochemical Society in Pennington, Pennington, pp 134–140
- Yin Y, Hang L, Xu J, McKenzie DR, Bilek MMM (2008) Surface adsorption and wetting properties of amorphous diamond–like carbon thin films for biomedical applications. *Thin Solid Films* 516:5157–5161
- Zhoutong H, Shumin Y, Qintao L, Dezhang Z, Jinlong G (2008) Selective growth of diamond by hot filament CVD using patterned carbon film as mask. *Nucl Sci Technol* 19:83–87