

Introduction of Diamond-like Carbon Coatings

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1.1 Introduction

Carbon materials have attracted immense attention due to their exceptional mechanical strength and unique functionalities [1]. Among carbon materials, diamond-like carbon (DLC) has been extensively examined for its versatile structure and

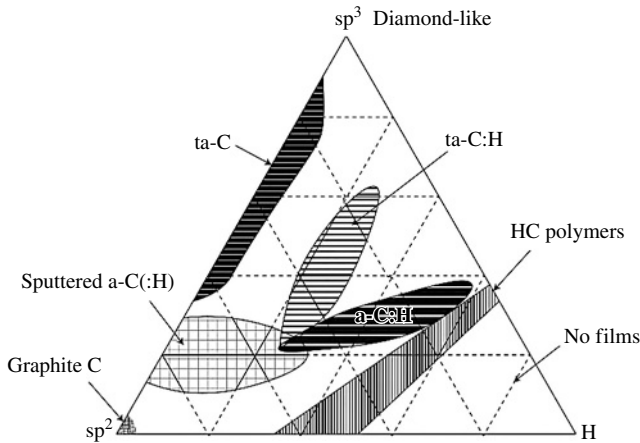


Figure 1.1 Ternary phase diagram that describes various parameters of DLC materials. Source: Reproduced from [6] / with permission of ELSEVIER.

multifunctional capabilities [2]. The term DLC is generally utilized to define a type of carbon-based materials containing a mixture of (graphitic) sp^2 - and (diamond) sp^3 -hybridized phases. DLC can contain 0–50% hydrogen atoms depending on the deposition methods employed [3]. However, the DLC coatings can be formed without hydrogen incorporation. Narayan et al. showed the formation of hydrogen-free DLC films with high sp^3 bonding and superior mechanical properties by pulsed laser deposition (PLD) [4]. The ternary phase diagram of DLC structures, as proposed by Robertson, is shown in Figure 1.1 [5]. Regions designated as a-C, ta-C, and a-C:H refer to pure carbon, tetrahedral amorphous carbon, and hydrogenated carbon with the corresponding extent of hydrogenation, respectively. Due to the variable fractions of sp^2 - and sp^3 -hybridized states, DLC structures show excellent mechanical strength, resistance to wear, resistance to corrosion, reduced friction coefficient, and unique functional properties [2, 4]. Thus, DLC materials have been a popular choice of coating materials for applications in mechanical and transportation industries, biomedical implants and devices, storage devices, and optical products. Some of the significant properties of different classes of carbon materials are summarized in Table 1.1 [6].

Several approaches have been developed for processing DLC films, such as both chemical vapor deposition (CVD) and physical vapor deposition (PVD) techniques. Among PVD techniques, ion beam deposition, PLD, and magnetron sputtering are widely explored for the deposition of DLC films [7]. Ion beam deposition facilitates the deposition of high-quality coatings at near-room temperature. However, the deposition rate is too low; the substrates require complex manipulation methods for uniform deposition, limiting the practical application of this approach [8]. Sputtering is employed as another popular technique to deposit DLC films with variable sp^2 content. Even so, the low ion energies associated with

Table 1.1 Important physical characteristics of carbon materials currently in use.

	Mass density (g cm ⁻³)	Hydrogen content (at. %)	Number density (1 cm ⁻³)	Hard/soft
Diamond	3.51	0	0.29	Superhard
Graphite	2.25	0	0.19	Soft
ta-C	3.2	1	0.27	Superhard
a-C:H	2.3	11	0.21	Hard
Polystyrene	1.05	50	0.16	Soft

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sputter deposition result in the poor mechanical strength of the coatings, making them unsuitable for high-strength applications [9]. On the other hand, PLD yields smooth DLC coatings with high sp³ content, but it has not yet been developed for the large-scale manufacturing of DLC, and it is often challenging to produce uniform coatings using this technique [10]. Among the CVD techniques, the plasma-enhanced chemical vapor deposition (PECVD) process has been commonly utilized for the growth of DLC films with high uniformity, conformal coverage, and reasonable deposition rates [11]. The PECVD also enables the growth of strain-free and adherent DLC coatings with high levels of mechanical strength and resistance to wear and corrosion [11–13]. Thus, it is highly preferred for the large-scale manufacturing of DLC coatings. A schematic showing the PECVD chamber used in the growth of DLC films is provided in Figure 1.2 [13].

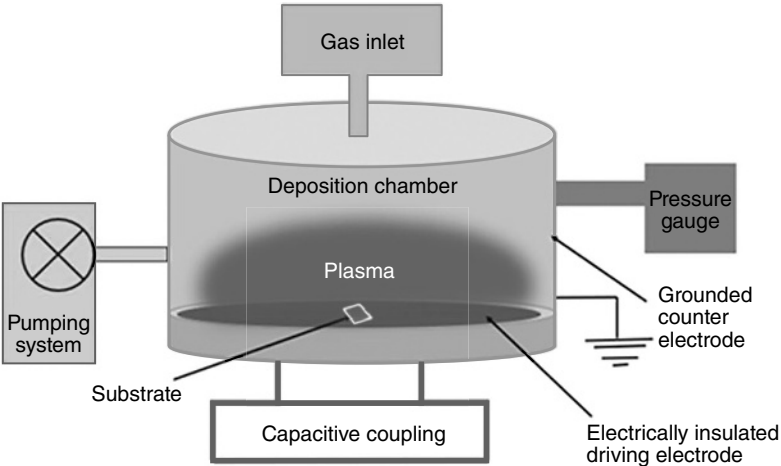


Figure 1.2 Schematic showing the PECVD instrument utilized for the deposition of the DLC films [13] / John Wiley & Sons/CC BY 4.0.

DLC structures are doped with several elements and compounds to improve their functionality [14]. Metals and semiconductors such as Mo, Cu, Cr, Ag, Ti, Ni, Al, W, and Si and compounds such as ZnO and W_2C have been reported to have doped to improve the performance of DLC coatings [13–17]. Among them, silicon (Si) is highly preferred as a dopant material, as it is known to reduce the internal stresses in the coating, enhance the adhesion of the coating to the underlying substrate, and improve the thermal stability of DLC structures [13, 18, 19]. Si-incorporated DLC (Si-DLC) is also shown to have a low friction coefficient, improved resistance to wear, and improved resistance to corrosion [18]. In addition, Yang et al. noted that Si-DLC coatings are biocompatible and inhibit microbial activity, expounding their applications to implantable medical devices [13]. This chapter gives an overview of several doped and undoped DLC coatings and their applications in mechanical and transportation, biomedical devices, electrical devices, and optical products. The limitations of DLC coatings are discussed briefly, and quenched carbon (Q-carbon) is introduced as an emerging, superior alternative for coating materials that are currently in use.

1.2 DLC Coatings for Mechanical and Transportation Applications

The unique combination of high hardness, reduced friction coefficient, resistance to wear, and resistance to corrosion in DLC materials have made them an unambiguous choice for protective coatings in the mechanical and transportation industry [2, 6]. Since their discovery in the 1950s, DLC coatings were first investigated for their unique scratch resistance properties [20]. In 1973, Aisenberg and Chabot reported that the cutting characteristics of paper cutting blades may be significantly improved by coating them with DLC films [21]. The wear tests revealed that the coefficient of friction is reduced on the coated blades. Since then, DLC coatings have been commonly used to enhance the performance of machines and mechanical tools. Moreover, due to their sophisticated structural properties, gears, bearings, and the inside of the automotive engines are coated with DLC to reduce wear, reduce friction, and the need for lubrication. Thus, it helps improve fuel efficiency and reduce the maintenance costs of the vehicle [22]. Some of these structural applications of DLC coatings are discussed in this section.

1.2.1 DLC Coatings for Lubricants

DLC is a popular choice of coating for mechanical and transportation applications, as it is a material that is able to provide high resistance to corrosion, low friction, and high hardness under dry sliding conditions with a coefficient friction as low as 0.01–0.5 based on the environmental conditions the DLC coating is subjected to [5, 23]. For instance, hydrogenated coatings perform

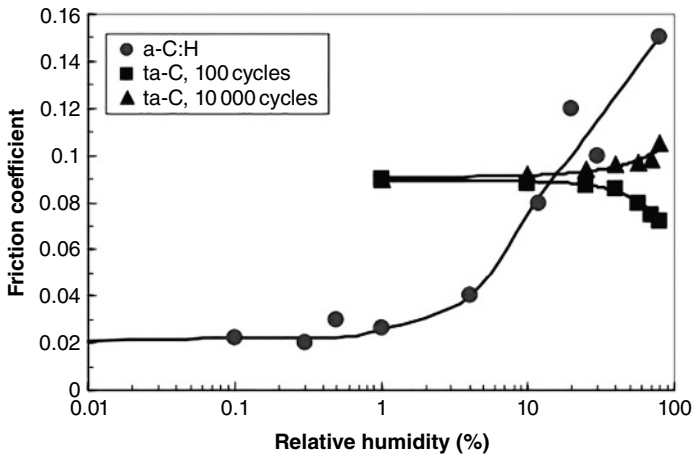


Figure 1.3 Changes in frictional coefficient with relative humidity for a-C:H and ta-C coatings. *Source:* Reproduced from [25] / with permission of IOP Publishing.

better in an inert environment. In contrast, hydrogen-free DLC is preferred in humid environments where a friction coefficient as low as 0.1 can be achieved for an extended period [5, 24]. The variation of the coefficient of friction with relative humidity for hydrogenated and nonhydrogenated DLC coatings is shown in Figure 1.3 [25]. Another class of DLC coatings, which is referred to as near-frictionless carbon, is associated with the lowest possible friction coefficient of any known material (~ 0.005) due to the passivation of the contact surface achieved by hydrogenated carbon atoms in DLC [25–27]. As such, the hydrogen content and chemical bonding in the coatings have a significant impact on the coefficient of friction. However, fabricating a single type of DLC to achieve low friction in both dry and humid environments is quite challenging. To address this issue, a new class of DLC coatings called diamond-like nanocomposite (DLN) coatings was developed [28, 29]. The structure of DLN materials consists of two amorphous interpenetrating networks with minimal bonding between them. Mutual stabilization within these networks reduces the coating residual stress, improves adhesion, and inhibits graphitic carbon growth at elevated temperatures [25, 28–30]. Furthermore, DLN provides a low friction coefficient and can adapt to dry and humid environments, expounding the mechanical applications of DLC coatings [25, 29].

1.2.2 DLC Coatings for Pipelines, Tubes, and Molds

In addition to a low coefficient of friction, DLC coatings show low wear rates ranging from 10^{-7} to 10^{-9} $\text{mm}^3 \text{Nm}^{-1}$ [31]. However, specific test conditions (e.g. temperature, relative humidity, and dopant materials) are known to influence

the wear properties of DLC coatings. For instance, the water vapor condensed on the contact zone in humid conditions can inhibit the dry lubricating effect of DLC and prevent the formation of transferred layers, leading to an increase in wear [31, 32]. Similarly, working temperature has a significant impact on the wear rates of DLC coatings. Gharam et al. have shown that the wear rate increases from a value of $0.5 \times 10^{-5} \text{ mm}^3 \text{ Nm}^{-1}$ to a value of $8.5 \times 10^{-5} \text{ mm}^3 \text{ Nm}^{-1}$ from room temperature to 100 °C and then gradually decreases to 400 °C [33]. Thus, several strategies, such as element doping, surface implantation, and surface thermal treatments, have been employed to overcome these challenges. Among them, doping is found to be a promising technique to enhance the mechanical and transportation properties of DLC [34]. DLC structures have been doped with various elements such as N, Mo, Cu, Cr, Ag, Ti, Ni, Al, W, and Si and various compounds such as W_2C and Mo_2C [14–18, 34]. One of the studies showed that co-doping DLC structures with Ti and Ni significantly reduced the internal stresses in the film, improving the durability of the coatings [35]. In another study, Wei et al. have shown that the metal interlayers of Cr, Ti, and Al in DLC led to a significant enhancement in the adhesion of these coatings by stabilizing the sp^2 clusters and thus decreasing the graphitization in the DLC structures [36]. Damasceno et al. observed a similar effect in the incorporation of Si into DLC [18]. Additionally, Kim and Lee's work showed that Si-DLC films resulted in a significant reduction in wear rate and a reduction in friction coefficient, leading to improved tribological properties in the film [37]. Figure 1.4 shows the variation of wear rate in Si-DLC films with varied concentrations of Si [38]. The sample with the highest Si content showed a significant reduction in the wear rate as well as an increase in the elastic modulus of the film. In addition, co-doping N/Si and O/Si in DLC was shown to elevate the thermostability of these structures [39]. Furthermore, Si prefers to create sp^3 bonding within DLC, increasing the sp^3/sp^2 ratio in the films. The increase in the sp^3 content in the films stabilizes the DLC structure, enhancing the strength of these coatings [40]. Thus, Si has been a popular choice of dopant materials to enhance the multifunctional capabilities of DLC coatings for mechanical applications [18, 19, 37–40].

1.3 DLC Coatings for Medical Applications

DLC is one of the oldest and most popular forms of carbon-based materials to be employed for biomedical applications [41]. In the 1990s, Thomson et al. reported that DLC coatings are biocompatible [42]. Since then, they have been widely studied for various biomedical applications due to their versatile

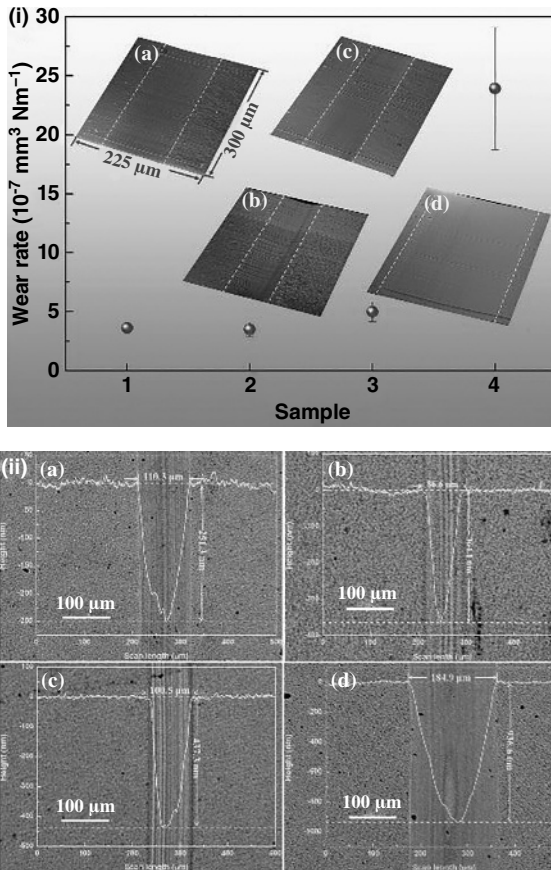


Figure 1.4 (i) 3D and (ii) 2D morphologies and profiles of wear rates for Si-DLC films with varied concentrations of silicon. *Source:* Reproduced from [38] / with permission of ELSEVIER.

properties. In addition to biocompatibility, DLC materials exhibit high resistance to corrosion, improved tribological properties, antimicrobial activity, and anti-inflammatory action, making them an ideal choice for biomedical implants and devices [43]. DLC films can be deposited on several types of substrates at relatively low deposition temperatures; this characteristic makes this class of carbon-based materials technologically and commercially important. Thus, it has been a popular choice of coating for orthopedic, cardiovascular, and dental implants [41–43].

1.3.1 DLC Coatings for Orthopedics

The life of prosthetic joints is severely shortened due to their tendency to wear and corrosion over time [44]. Therefore, DLC coatings have attracted interest in orthopedic applications because of their low friction coefficient, improved resistance to wear and corrosion, and biocompatibility [43]. In one of the studies, it was demonstrated that the DLC-coated femoral head Ti-6Al-4V alloy showed enhanced wear resistance as compared to the wear rate of uncoated stainless steel, alumina, titanium, and zirconia implants [45]. In another study, Tiainen et al. demonstrated that the wear rate of DLC-coated metal-polyethylene hip joints was reduced by 10^6 times smaller than that of metal-polyethylene joints or metal-metal joints [46]. Dowling group reported improved biocompatibility in DLC-coated hip joints with high sp^3 content, achieved by doping DLC with Si [47]. Similarly, Sheeja et al. showed that the corrosion resistance and hardness of Co-Cr-Mo alloy (orthopedic implant material) was significantly increased by coating it with Si-DLC [48]. In another study performed by Mitura and others, DLC-coated orthopedic screws showed no signs of corrosion or inflammation even after 52 weeks [49]. On the contrary, there are also reports on the failure of DLC-coated orthopedic implants. DLC-coated knee joint implants showed excessive wear and spallation when paired with ultrahigh molecular weight polyethylene [50]. In a similar study, Taeger et al. found that the DLC-coated Ti-6Al-V femoral head failed faster than the alumina femoral head, indicating a need for the development of a biomaterial with enhanced functionalities having superior wear, toughness, and adhesion [51].

1.3.2 DLC Coatings for Antimicrobial Performance

Microbial biofilms are ubiquitously increasing the risk of medical device infection [52]. As such, treatment related to medical device infections often requires the removal and replacement of devices, increasing healthcare costs and mortality [52]. DLC coating acts as a simple yet powerful antimicrobial layer by preventing the adhesion of microbes to the surface of the implants [46]. Yang et al. demonstrated that oxygen plasma-treated Si-DLC is hydrophilic, exhibits a lower negative zeta potential value, and showed antifungal behavior against *Candida albicans* (Figure 1.5) [13]. In another study, Robertson and others reported that Ge-doped DLC significantly reduced the formation of *Pseudomonas aeruginosa* biofilms on SS316 substrates [53]. Bociaga et al. opine that the antimicrobial response of Si-DLC is promising but needs further investigation [54]. A recent report on the antibiofilm characteristics of prosthetic meshes coated with several metal-containing DLC thin films showed significant antimicrobial activity against five microbial species. They propose that

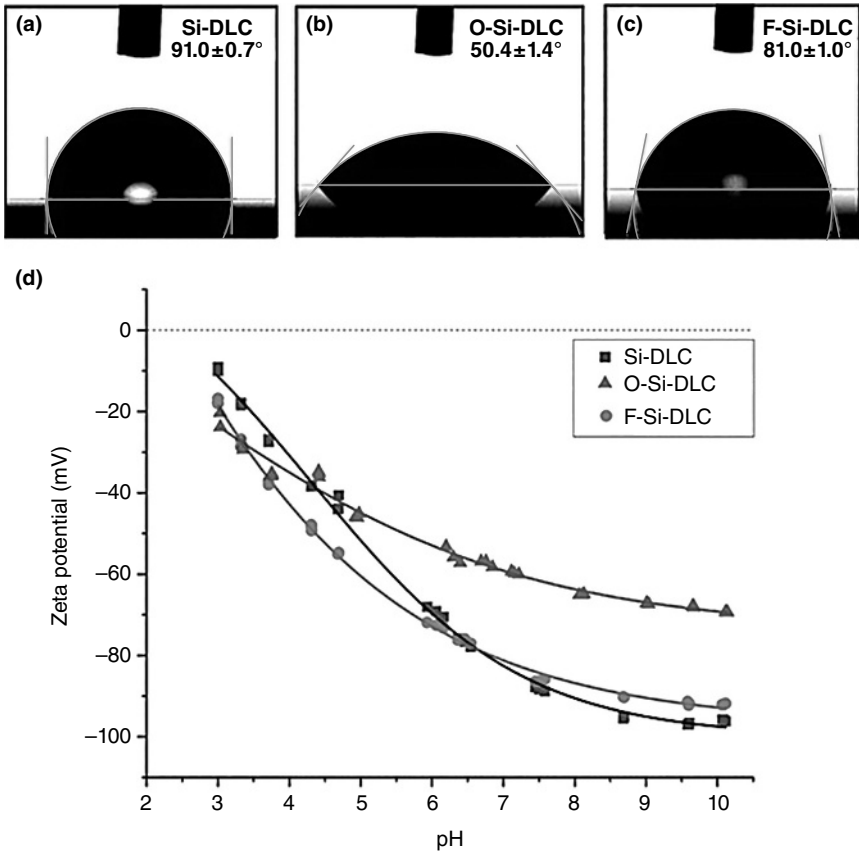


Figure 1.5 The water contact angle values for (a) Si-DLC, (b) oxygen plasma-treated Si-DLC (O-Si-DLC), (c) fluorine-terminated Si-DLC (F-Si-DLC), and (d) zeta potential values of Si-DLC, O-Si-DLC, and F-Si-DLC coatings versus the electrolyte solution pH values [13] / John Wiley & Sons/CC BY 4.0.

modified DLC coatings are a suitable choice of biomedical coatings because of their biocompatibility, mechanical strength, and antimicrobial activity [55].

1.3.3 DLC Coatings for Cardiovascular Implants

One of the primary requirements of a cardiovascular implant is that it should not activate plasma enzymes in order to prevent thrombosis. As such, early studies on DLC-coated heart implants showed a tendency to prevent platelet activation and coagulation of blood [56]. Cheng et al. have reported improved hemocompatibility in Ti-doped DLC due to its hydrophobicity and smooth surface [57]. In another study, researchers have shown that incorporating Si into DLC improves

endothelial cell attachment while reducing the adhesion of platelets at the same time [58]. They showed that the results were even better when Si-DLC films were treated with fluorine. All these findings showed that functionalized DLC coatings may be utilized for cardiovascular devices such as stents and heart valves. In addition, Gutensohn et al. showed that DLC-coated stents were resistant to corrosion, while noncoated stents released metal ions into the human plasma within four days of implantation [59]. In another study, Choi and others have shown that catheters coated with silver-doped DLC were highly effective in preventing bacterial infection while preventing the adhesion of platelets [60]. They believe that a greater focus should be placed on employing DLC coatings on cardiovascular devices owing to their multifunctional capabilities.

1.4 DLC Coatings for Electrical and Optical Devices

Due to their unconventional and excellent photoelectronic performance, broadband transparency, and ease of synthesis, DLC materials are among the emerging coating materials for electrical and optical devices [61]. The optical bandgap of DLC materials is governed by the amount and the size of sp^2 graphitic clusters because the sp^2 structure has one π bond [62]. As such, the bandgap value of DLC may be suitably tuned by controlling the sp^2/sp^3 content in the films. Similarly, the electrical conductivity of DLC structures may be increased by several orders of magnitude by increasing the sp^2 content and through the incorporation of metals within the films [61, 63]. Due to this precise manipulation of their optical and electrical functionalities, DLC materials are being evaluated for their applications in devices such as micro-electromechanical systems (MEMS), batteries, field emitters, and antireflective coatings in infrared (IR) devices [61].

1.4.1 DLC Coatings for MEMS

MEMS technology consists of miniaturized devices, including electronic and mechanical components grown through microfabrication techniques [25]. It is widely explored as a feasible option to automate devices for various applications [7, 25]. Owing to their tunable electronic properties and the ability for wafer-scale integration of electric circuits, Si-based materials are a popular choice for the MEMS devices currently in use [25]. However, the fabrication of Si microelectronic systems is not economical and requires state-of-the-art facilities to ensure their proper growth and integration of circuits. Moreover, the poor mechanical strength and low fracture toughness of Si make this process even more challenging [64]. This phenomenon has led to the search for new and efficient material

systems for use in MEMS. As such, polymers (e.g. polymethylmethacrylate and polydimethylsiloxane) are being explored due to their suitability [7, 25]. Among the prospective candidates for MEMS devices, diamond and DLC are the most promising due to their unusual mechanical properties and tunable electrical and optical properties that are otherwise not possible in Si-based materials [25]. Due to their very high tensile and fracture strength, Young's modulus, increased resistance to wear, and reduced coefficient of friction, DLC coatings are deemed suitable for high-frequency MEMS applications. In addition, the low coefficient of thermal expansion and very high thermal conductivity of DLC make them suitable candidates for packaging devices and thermal actuators that require efficient heat dissipation [25]. Moreover, the chemical inertness, mechanical strength, biocompatibility, and hydrophobicity of DLC make them a popular choice for coating materials for applications in bio-MEMS, such as biosensing and implantable medical devices [65]. Thus, DLC can be exploited as a promising structural material to provide unique features that are otherwise not possible with the existing materials and also as a coating material in order to enhance the functional properties of MEMS devices [25].

1.4.2 DLC Coatings for Nonvolatile Storage, Low-K Dielectrics, and Field Emitters

The tunable electrical properties achieved by controlling the sp^2 -hybridized states in DLC structures have enabled their applications in nonvolatile storage devices [7, 62]. As such, the high density of electronic trap states in DLC that are otherwise detrimental for electronic devices is being explored to create nonvolatile digital information storage devices [66]. Gerstner et al. observed a reduction in resistance as well as an increase in the capacitance of DLC structures after a negative bias was applied. They showed that the effects are reversible after the application of a positive bias [67]. They describe a two-state conduction mechanism where electron hopping and Pool–Frenkel conduction were observed in the high resistance states and low resistance states, respectively. Memory devices with high retention times as high as one year were designed by defining the binary states corresponding to the low and high resistance states. Another promising application of DLC coatings is its potential use as a low-K material that can be used for back end of the line circuits to upgrade their performance [61, 68]. Even though the dielectric constant of DLC materials is significantly higher (5.6) than SiO_2 (4.0) that is currently used, Grill et al. have shown that the dielectric constant of DLC can be modified to lower values (2.7–3.8) than SiO_2 by controlling the deposition conditions [68]. Furthermore, the outstanding mechanical properties, good adhesion, and high thermal stability of DLC coatings make them futuristic candidates for low-K dielectrics [25, 61]. Since the 1990s, DLC

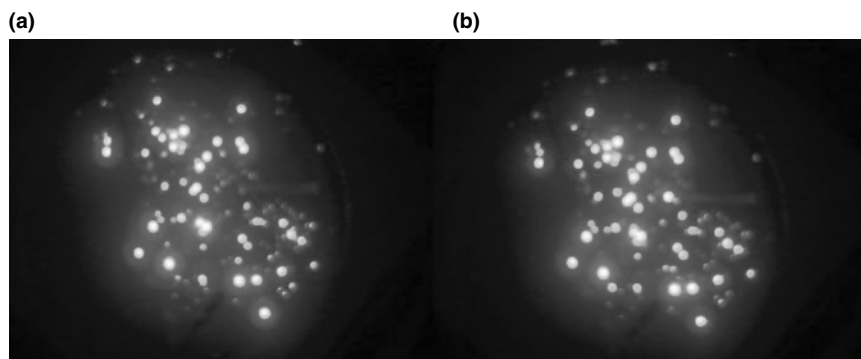


Figure 1.6 The emission images obtained from the patterned DLC coating: (a) initial image and (b) image after three hours. *Source:* Reprinted with permission from Ref. [73].

coatings have been considered for field emitter applications and have been shown to enhance the field emission performance of traditional Spindt-type emission tips [69]. Oh et al. have shown that the nitrogen-incorporated DLC coatings reduced the turn-on voltage by 45% and simultaneously increased the emission current (from a value of $160 \mu\text{A}$ to a value of $1520 \mu\text{A}$) [70]. Furthermore, the functionalization of the DLC-coated tips by plasma etching in hydrogen and oxygen also demonstrated a significant reduction in threshold voltage and an increase in the emission current [71]. More recently, the Narayan Research Group has shown that the field emission properties of Q-carbon (a new allotrope of carbon) outweigh the performance of DLC-coated field emitters with a turn-on electric field as low as $\sim 2.38 \text{ V } \mu\text{m}^{-1}$ and a substantial emission current density of $\sim 33 \mu\text{A cm}^{-2}$, which was associated with (a) the sp^2/sp^3 mixture in Q-carbon and (b) a large local field enhancement because of the unique diamond tetrahedral microstructure and the local geometry that is absent in DLC coatings [72]. Figure 1.6 illustrates the temporal evolution of field emission in DLC coatings, revealing a notable decline in both the total emission current and the emitting area over a three-hour period [73].

1.5 DLC Coatings for Optical Applications

DLC is one of the most popular antireflective coatings for IR optics that are made from ZnSe, ZnS, or Ge because of its IR transparency [74]. DLC coatings are also utilized to protect ZnS IR windows when it is used with a GeC intermediate layer [75]. He et al. have demonstrated that DLC protective coatings can enhance durability and also improve the functionalities of organic photoconductors [76].

The antiwear properties and low deposition temperatures of DLC coatings make them suitable for protection against abrasion caused by polycarbonate sunglasses. Thermal imaging systems use DLC coatings as a barrier against deterioration of the surface of Al mirrors [76]. In addition to their uses as protective optical coatings, DLC is also being explored for the fabrication of optical components [61]. Soares et al. have demonstrated the facile patterning of DLC with hard masks, such as SiO_2 and Al, by etching in oxygen plasma [77]. In conjunction with IR transparency, this expands the applications of DLC coatings for the recording of IR diffractive optical components that exhibit excellent pattern quality and precise surface control. DLC coatings are also being explored as candidates for photovoltaic applications. A high optical absorption coefficient obtained by increasing the sp^3 fraction in DLC structures was exploited for absorbing a significant amount of solar energy [78]. As such, a photovoltaic effect was observed in Si-DLC coatings, where the reverse current rose by three orders of magnitude on exposure of the structures to AM1 light (when compared to the undoped DLC coatings) [78].

1.6 Emerging Applications of DLC Coatings

DLC materials have been the number one choice of coatings for cutting tools, automotive parts, and biomedical implants due to their outstanding strength as well as resistance to corrosion. In this regard, efforts involving DLC coatings have mostly focused on enhancing their mechanical properties in the recent past. However, due to their multifunctional capabilities and extended product life, DLC coatings are being explored for various applications such as energy storage, innovative smart textiles, and polymers [6, 7]. In addition, recent advancements in machine learning and materials informatics have revolutionized data-driven materials development and viable manufacturing of technologically and commercially important materials with enhanced performance and durability. This approach has enabled the virtual optimization of DLC coatings to improve their structural and functional properties by saving cost and energy resources [7]. Thus, materials informatics has a strong potential to aid the sustainable production of DLC coatings by uplifting their capabilities [79].

1.6.1 DLC Coatings for Energy Storage Applications

Carbon materials are given significant attention for energy storage applications because of their structural and electrochemical stability, electrical conductivity, and durability [80]. Among them, DLC is being explored for use in Li-ion batteries (LIBs) due to its lithium-ion trapping characteristics and electronic conductivity [81]. The electrical properties of DLC can be suitably tuned by modifying the deposition conditions, post-processing treatments, and concentration of the doping elements.

Due to their superior structural stability, DLC coatings are known to resist the dendrite growth in LIB and provide a three-dimensional conducting environment for Li^+ ions [81]. As such, Cho et al. have demonstrated the increased capacity of up to 50 cycles in DLC-coated cathodes, whereas uncoated cathodes failed after 7 cycles [82]. In another study, Zhang et al. showed that the cyclic efficiency associated with lithium electrodes increased by up to 60% after 50 cycles when coated with DLC [83]. Figure 1.7 presents a comparative analysis of the cyclic performance of as-fabricated and laser-annealed carbon-based electrodes with varying sp^2 content, indicating enhanced capacity in the laser-annealed electrodes [84]. DLC coatings have also been shown to lower the contact resistance of current collectors, enhancing the performance of LiFePO_4 (LFP) composite cathodes. Onsurd et al. reported a considerable increase in the rate capability up to 89% in LFP cathodes with an area capacity of 1.7 mAh cm^{-2} upon cycling at 5C [85]. Thus, DLC coatings have shown promising features for battery applications, particularly for LIBs. Even so, there is a need for more statistical data to understand the potential use of DLC coatings for energy storage applications and to ensure consistent and comparable results across different studies [81].

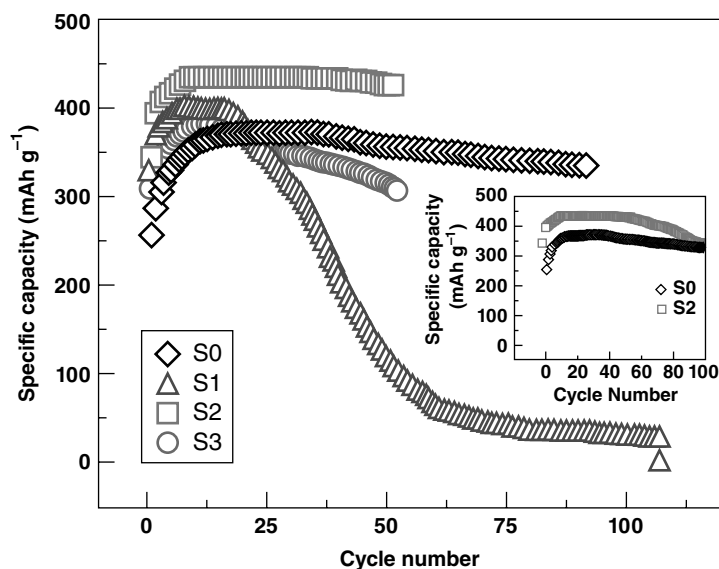


Figure 1.7 Cyclic characteristics of the reference electrode (S0) and laser-annealed carbon electrodes (S2) at the optimized parameters for the anodes in LIB. The results indicate enhanced capacity in the annealed sample when compared to the reference sample in LIB. S1 and S3 are laser-treated samples before optimization. The inset indicates the specific capacity of the optimized laser-annealed samples and reference electrode for 100 cycles. *Source:* Reproduced from [84] / with permission of ELSEVIER.

1.6.2 DLC Coatings for Polymers and Textiles

Smart textiles have revolutionized the field of the textile industry due to their ability to sense and react to external stimuli [86]. Several Kevlar and chromic materials, as well as polymer composites, are used to fabricate smart textiles [86, 87]. Specifically, carbon-based materials are being explored as a popular choice for next-generation smart textiles due to their peculiar properties. Among them, DLC coatings are particularly preferred due to their intrinsic strength, flexibility, and toughness, contributing to innovations in textile industries [88]. The superhydrophobic properties, flame resistance, and antimicrobial properties of DLC materials make them suitable candidates for next-generation smart textiles, self-cleaning windows, and applications that necessitate a reduction of drag in fluid flow [88]. Cortese et al. demonstrated the development of DLC-coated cotton textiles that exhibited superhydrophobic properties and used it as a membrane for filtration applications [89]. Additionally, DLC-coated cotton has been shown to exhibit a significant improvement in flame resistance, with a nearly twofold increase in resistance to flame propagation compared to pristine cotton [90]. Furthermore, Juknius et al. reported the development of DLC/silver nanocomposite thin film deposited on synthetic silk textiles for smart bandage applications [91]. They showed that incorporating DLC into the composite increased the efficiency of Ag^+ ion into aqueous media, enhancing the antimicrobial efficiency of the bandage by up to 50% compared to silver composite without DLC. As such, the emerging applications of DLC materials in polymers and textiles hold immense potential for transforming industries such as healthcare, energy, and consumer goods. As research and development continue to advance, DLC coatings are anticipated to play a vital role in shaping the future of smart materials. Figure 1.8 illustrates the potential smart applications of DLC coatings in textiles [88].

1.6.3 Optimizing DLC Coatings Through the Utilization of Artificial Intelligence Tools

DLC coatings are highly preferred for several applications because of their versatile, multifunctional capabilities. It should be noted that the deposition of high-quality DLC coatings is primarily controlled by the growth kinetics and balancing the energy per unit carbon atom/ion [4]. Moreover, the optimization of DLC production is contingent upon deposition methodology, technological specifications, and system configurations, which can entail over 50 combinations of chamber pressure, bias voltage, gas flow rate, deposition temperature, and other variables, enabling a need for a systematic approach [79]. The field has evolved through four generations: (i) experimental optimization of parameter-to-property relationships; (ii) multiparameter optimization using hybrid experimental methods and statistical approaches;

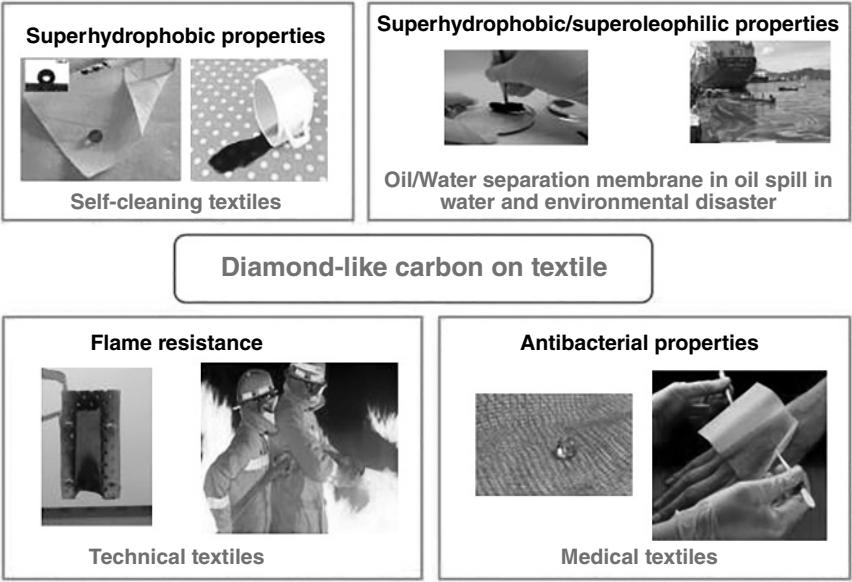


Figure 1.8 Potential innovative applications for DLC-modified textiles [88].

(iii) integration of statistical methods with artificial intelligence (AI) approaches; and (iv) AI-driven multiparameter and multiproperty optimization with predictive capabilities [92]. The current generation is expected to revolutionize DLC development, addressing the challenges of emerging markets and complex environments such as robots, fusion reactors, electric vehicles, and extraterrestrial vehicles. However, the limited data points generated by the experimental studies for developing the DLC modeling techniques are insufficient for training the AI models [79, 92]. Virtual data sets are being created by augmenting sparse experimental data through interpolation and extrapolation to address this issue. This approach necessitates comprehensive experimental studies covering a wide range of parameters to generate a substantial and reliable data set for model verification [79, 93]. A comprehensive data set would enable the development of accurate AI models that can predict DLC properties and behavior with high reliability [93].

1.7 Limitations of DLC Coatings

DLC materials are an unambiguous choice for coating materials due to their exceptional mechanical strength, corrosion resistance, and multifunctional capabilities. Because of their unique combination of structural and functional properties, DLC

materials are a popular choice of coatings in various sectors, including biomedical implants, electrical and optical devices, energy storage, next-generation textiles, and smart polymers. However, current fabrication techniques have limitations, including difficulty reproducing precise structures, toxicity, and defects [2, 7]. Furthermore, high-temperature annealing processes and decreased mechanical strength at elevated temperatures reduce the practicality and lifespan of DLC coatings [94]. Therefore, there is a pressing need for a novel coating material that offers a unique combination of economic viability, reproducibility, mechanical strength, chemical inertness, biocompatibility, and enhanced functionalities that surpass the performance of DLC coatings.

1.8 Q-Carbon as a Superior Coating Material

Q-carbon is a newly discovered allotrope of carbon that exhibits unusual structural and functional characteristics [95]. Q-carbon is comprised of randomly packed tetrahedra; it exhibits a very high sp^3/sp^2 ratio at its interface, making it the hardest known material to date [95, 96]. The Raman spectra and the microstructure of Q-carbon nanostructures are provided in Figure 1.9 [96]. Because of its unique structure, Q-carbon exhibits a higher number density of covalently bonded carbon atoms, making it up to 70% higher in hardness than diamond. Thus, it provides ultrahard coatings, which are harder, tougher, and more adherent than diamond and DLC structures [97]. As such, the Narayan Research Group at NC State University, Raleigh, USA, has developed a process for growing Q-carbon/diamond composite protective coatings that can be applied to practical substrates like sapphire, Si, glass, steels, and WC-Co, offering prospective opportunities for superhard coatings [97, 98–102]. In addition to its high hardness and toughness, Joshi et al. demonstrated that Q-carbon is biocompatible with superior antimicrobial properties [102]. They have shown that Si-incorporated Q-carbon inhibited the formation of biofilms up to 80%, making it a promising material for biomedical applications. Q-carbon is conventionally grown by the PLD and subsequent pulsed laser annealing of DLC thin film with a nanosecond pulsed excimer laser source [97, 98]. Recently, we have shown that Q-carbon can be grown with wafer-scale integration on substrates as big as 6" in diameter, enabling the industrial-scale production of Q-carbon with controlled thickness and properties [103].

In addition to its fascinating structural properties, Q-carbon demonstrates robust room-temperature ferromagnetism; it exhibits magnetization as high as 20 emu g^{-1} and T_c of ~ 757 K, making it an excellent candidate for targeted drug delivery applications [104]. When compared to DLC coatings, Q-carbon shows superior field emission potential due to its unique sp^2/sp^3 mixture in the emitter, as well as the presence of a semimetallic alpha-carbon matrix in the material [72].

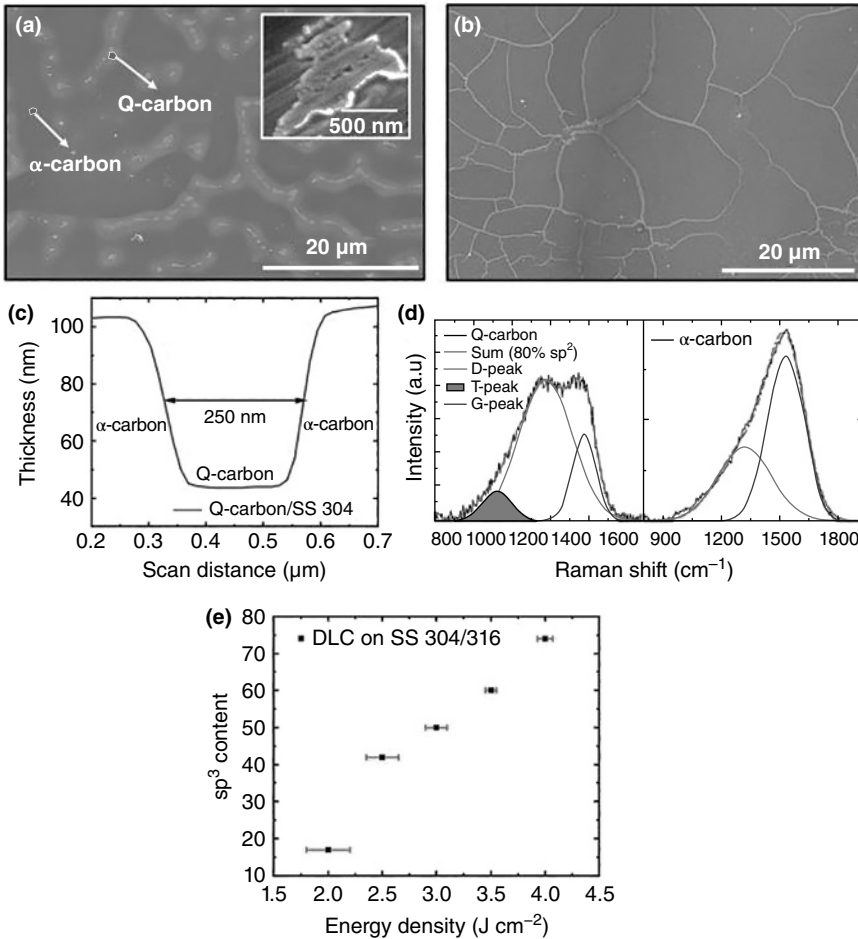


Figure 1.9 (a) Scanning electron microscope (SEM) image that shows the formation of Q-carbon on 304 SS; inset shows a high-resolution image of Q-carbon in alpha-matrix, (b) SEM image of Q-carbon, (c) surface roughness data for Q-carbon, (d) Raman spectroscopy data for Q- and alpha-carbon, and (e) relationship between the sp^3 content of the DLC and the laser energy density utilized during deposition. *Source:* Reproduced from [96] / with permission of ELSEVIER.

Q-carbon-based field emitters display exceptional performance, featuring (i) hysteresis-free emission, (ii) high emission stability, (iii) high current density operation without defect generation, and (iv) long-term reliability over successive emission measurements [72]. Unlike DLC, Q-carbon is highly resistant to radiation damage, withstanding ion radiation that induces extreme atomic displacements and electronic excitations [72, 105]. The Q-carbon anodes have shown

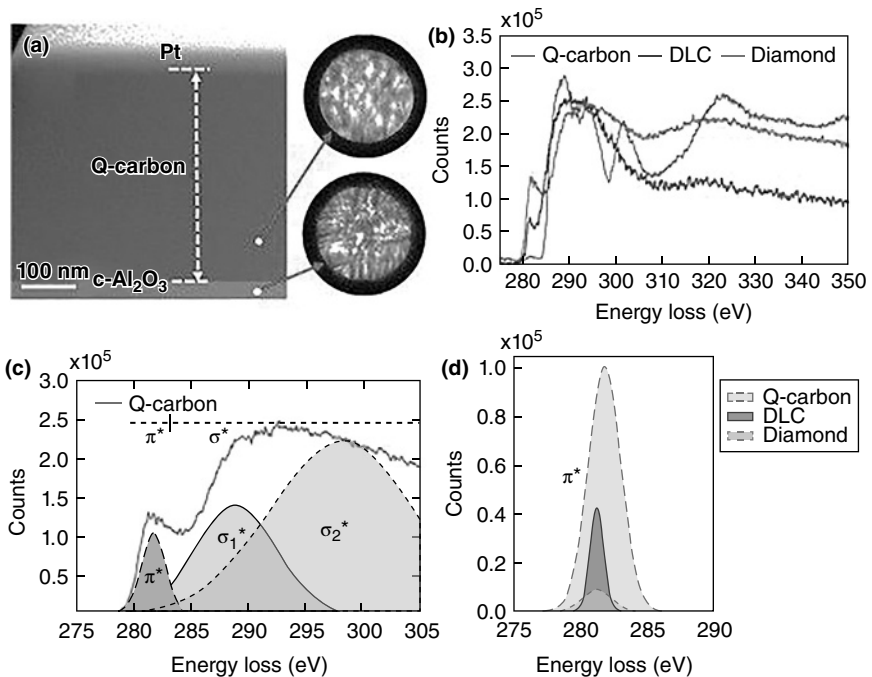


Figure 1.10 (a) High-angle annular dark-field image of Q-carbon on c-sapphire with the Ronchigram pattern, which demonstrates the amorphous and crystalline nature of Q-carbon and c-sapphire, respectively, (b) EELS results from Q-carbon, as-deposited DLC and diamond, (c) representative fitting routine obtained from Q-carbon EEL spectrum, and (d) the fitted π^* peaks that show an increase in the density of the electronic states in Q-carbon when compared to DLC and diamond. *Source:* Reproduced from [104] / with permission of American Chemical Society.

superior power, performance, and cyclability in lithium as well as sodium-ion batteries. This characteristic is attributed to the higher trapping efficiency of Li and Na ions, increasing from 1/6 in graphite to 1/2 in Q-carbon with its unique diamond tetrahedral structure [84, 106]. Figure 1.10 presents a comparative analysis of the electron energy loss spectra (EELS) of diamond, DLC, and Q-carbon, revealing an unexpected enhancement in the π^* region (EELS) of Q-carbon [104]. It is attributed to an increase in unpaired spin electron density, which is 80% higher than in DLC. This phenomenon is associated with the remarkable magnetic and optoelectronic properties of Q-carbon, which are absent in diamond and DLC. The unique electronic structure of Q-carbon is responsible for its fascinating characteristics, making it an ideal substitute for DLC coatings. Thus, Q-carbon is a versatile material with extraordinary properties, finding practical applications in nearly every technological domain. With its ability to overcome

the limitations of existing carbon materials, we envision Q-carbon as a superior alternative to DLC coatings, poised to revolutionize various technological fields in a wide range of applications.

1.9 Summary

Carbon materials have gained prominence in the twenty-first century due to their outstanding mechanical strength and tunable functional characteristics. DLC is a type of carbon-based material known for its versatile structure and multifunctional capabilities. DLC materials contain a variable mixture of sp^2 - and sp^3 -hybridized C–C bonds, with or without hydrogen atoms embedded in their structure. As such, the variable structure of DLC provides excellent mechanical strength, reduced friction coefficient, biocompatibility, resistance to wear, and resistance to corrosion, making them suitable for protective coating applications. Several techniques have been explored to grow conformal DLC coatings at low cost. Among these approaches, PECVD is widely utilized for the industrial-scale growth of strain-free and adherent coatings on intricate geometries. DLC structures are doped with various metals and compounds to add new functionalities and improve their performance. Si is widely used to dope with DLC structures, as it enhances adhesion, reduces internal stresses, and improves thermal stability in the coatings. This chapter describes DLC coatings and their applications in mechanical and automotive industries, biomedical devices, MEMS, dielectrics, and optical devices. Some emerging applications in energy storage, polymers, and smart textiles are also explored. In addition, the limitations of DLC coatings are discussed, and Q-carbon is introduced as a superior alternative to DLC materials, thereby providing an overview of the current coating technology. The Q-carbon coatings with enhanced hardness, toughness, and adhesion stand to revolutionize the field of high-performance coatings and take this field to the next level.

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