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Review

Effects of Element Doping on the Structure and Properties of Diamond-like Carbon Films: A Review

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Abstract: Diamond-like carbon (DLC) films with excellent anti-friction and wear resistance, can effectively reduce the energy loss of tribosystems and the wear failure of parts, but the high residual stress limits their application and service life. Researchers found that doping heterogeneous elements in the carbon matrix can alleviate the defects in the microstructure and properties of DLC films (reduce the residual stress; enhance adhesion strength; improve tribological, corrosion resistance, hydrophobic, biocompatibility, and optical properties), and doping elements with different properties will have different effects on the structure and properties of DLC films. In addition, the comprehensive properties of DLC films can be coordinated by controlling the doping elements and their contents. In this paper, the effects of single element and co-doping of carbide-forming elements (Nb, W, Mo, Cr, Ti, Si) and non-carbide-forming elements (Cu, Al, Ag, Ni) on the properties of microstructure, mechanical, tribological, optical, hydrophobic, corrosion resistance, etc. of DLC films are reviewed. The mechanisms of the effects of doping elements on the different properties of DLC films are summarized and analyzed.

Keywords: DLC films; element doping; microstructure; mechanical properties; tribological properties; mechanism

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1. Introduction

Excellent lubrication can not only reduce the energy loss of tribosystems but also ensure the service life and reliability of moving parts [1]. DLC film is a carbon film hybrid with sp2-C and sp3-C, which is often used to improve the anti-friction and wear resistance of moving parts because it has the properties of diamond and graphite, that is, it has good wear resistance and self-lubricity [2–4]. In addition, it also has excellent optical properties, chemical inertness, and biocompatibility [5–7], and has broad application prospects in aerospace, biomedicine, micro-electro-mechanical systems (MEMS), and other fields [8–10]. Especially in the machinery industry, the application of DLC films in this field has been widely studied. For example, the application of DLC films to cutting tools can improve the wear resistance and self-lubrication properties, so as to improve the cutting performance and tool life [11]. Applying DLC films to piston rings and valve tappets of automobile engines can increase their wear resistance, reduce friction and improve fuel efficiency, and thus play a role in energy conservation and emission reduction [12,13]. Max Marian et al. [14] used Si-doped DLC film for the TEHL (thermo-elastohydrodynamically lubricated) cam/tappet component of the valve mechanism. Due to the low thermal diffusion coefficient of the DLC film, the increase in temperature resulted in a decrease in the viscosity and shear resistance of the lubricant. The results show that the application of Si-DLC film not only reduces the solid friction of the system but also reduces the fluid friction. Julia Kröner et al. [15] used metal-doped DLC films for deep-groove ball bearings, which significantly improved the wear resistance of the bearings. More than that, compared with the traditional lubricant, this self-lubricating solid carbon film does not contain sulfur, phosphorus, chlorine, or other hazardous elements to the environment. In addition to reducing environmental pollution, it also provides a solution for working conditions where lubricating oil and grease cannot be used.

However, the application of DLC films also faces a series of challenges. For example, due to the different thermal expansion coefficients between the film and the substrate, the epitaxial or structural mismatch between the film and the substrate, and the growth-induced stress, the DLC films have high residual stress [16], so that the adhesion strength between the DLC film and the substrate is dissatisfactory, which makes the DLC film prone to peeling off during work. In addition, DLC films have poor thermal stability. With the increase of temperature, sp3-C in DLC films changes to sp2-C and graphitization occurs, which leads to the deterioration of mechanical and tribological properties of DLC films, and when the operating temperature of DLC films reaches 300 °C, the excessive graphitization of DLC films will lead to lubrication failure [17,18]. These obstacles limit the popularization and application of DLC films. Therefore, reducing the residual stress, and improving the microstructure and the comprehensive properties are of great significance to the application and service life of DLC films. Researchers have explored various approaches to reduce the residual stress and enhance the comprehensive properties of DLC films, mainly including annealing, adding transition layers, and element doping modification measures. Among them, doping heterogeneous elements in DLC film is an effective method to reduce the residual stress of DLC film and increase its adhesion strength with substrates [19]. In recent years, the effects of element doping on the properties of DLC films and their mechanisms have attracted a lot of attention from researchers.

It has been found that doping elements with different properties, different doping content, and different preparation processes have different effects on the microstructure and properties of DLC films. For example, appropriate doping of some elements can improve the tribological properties of DLC films by increasing the hardness/elastic modulus ratio [20,21]; the doping of some elements can improve the optical properties of DLC films by forming nanocrystalline materials in the carbon matrix, that increase the optical coupling effect [22]; the doping of some elements can introduce antibacterial ions, improve the antibacterial properties of DLC films [23,24], and broaden the application fields of DLC films. Nevertheless, element doping does not always bring beneficial effects to DLC films. Generally, element doping will reduce the residual stress of DLC films [25–28], but also cause the hardness to decrease [29–33]. In addition, when the content of a doping element is inappropriate, not only the mechanical properties of DLC films will be reduced, but this can also cause the reduction of tribological properties, and even cause the rise of residual stress [21,34–37]. Therefore, it is necessary to understand the mechanisms of the effects of element doping on the properties of DLC films, optimize and match the parameters such as the type of doping elements, the content of doping elements, and the preparation processes according to the effect characteristics, so as to provide a basis for obtaining DLC films with better comprehensive properties.

This review focuses on the aspects of microstructure (structure and roughness), mechanical properties (residual stress, hardness, and elastic modulus), tribological properties, and other properties (corrosion resistance; hydrophobic, antioxidation, and antibacterial properties; conductivity and optical properties), and summarizes the effects of carbide-forming elements (Nb, W, Mo, Cr, Ti, Si), non-carbide-forming elements (Cu, Al, Ag, Ni) and co-doping of these elements on DLC films; the effects and mechanisms of doping elements to change the structure and properties of DLC films are discussed.

2. Microstructure

2.1. DLC Film Structure

A large number of studies have found that doping elements have a certain solubility in the carbon matrix, and they will dissolve in the carbon matrix when the content of doping elements in DLC films is small. When the carbon matrix has a high content of doping elements, the elements with different properties will present in different states in the carbon matrix. Carbide-forming elements will form carbides in the carbon matrix, which is determined by their strong reactivity with carbon, such as Nb [29,38–42], W [25,43–45], Mo [30,46–49], Cr [26,31,34,50–55], Ti [20,21,32,56–65], and Si [66–73] elements. Due to the low reaction activity of non-carbide-forming elements with carbon, they exist in the carbon matrix in the form of nanocrystals, such as Cu [22,33,74–80], Al [35,36,81–86], Ag [23,24,28,37,87–93], and Ni [94–98] elements. According to existing works, it is found that with the increase of the content of doping elements in the carbon matrix, the DLC film gradually transforms from an amorphous diamond-like carbon structure to an amorphous carbon structure containing dissolved elements, and finally into a nanocomposite structure composed of amorphous carbon and carbide or nanocrystals [20,33,43,99]. In addition, the grains formed in the carbon matrix may exhibit different growth processes with the change in the content of the doping element [25,39]. For example, Kan Zhang et al. [39] found that Nb would first form cubic NbC with a smaller grain size in the carbon matrix, and when the Nb content in the matrix further increased, the cubic NbC phase would transform into the hexagonal Nb_2C phase with a larger grain size. Due to the growth of such different grains, different phase structures or different grain sizes formed by them have a great impact on the mechanical properties and tribological properties of DLC films [42]. When overmuch carbide-forming elements are doped in the carbon matrix, a large number of carbides will be formed in the matrix, which will destroy the continuity of the carbon network structure [29,34,52,57], and eventually seriously deteriorate the properties of DLC films.

The preparation processes of DLC films also have effects on their structure, such as applying bias can increase the denseness of the structure of DLC films [41,42,82]. This is because the bias can endow particles with energy, and high-energy particles are more likely to penetrate the growth surface, thus increasing the local density of DLC films. Another effect of applying bias is to promote the conversion of sp2-C to sp3-C so that the film has a higher denseness [24,41,42,84], which is also conducive to improving the mechanical properties of the DLC film.

Effected by the preparation processes, the doping elements will form other structures besides nano-grains in the carbon matrix. For example, Wei Dai et al. [83] used a mixed ion beam system consisting of an anode layer ion source (LIS) and magnetron sputtering with a different bias to deposit Al-DLC films, and proper bias can make the microstructures of DLC films evolve from nano-grains to nano-stripes, as shown in Figure 1A. Fei Zhao et al. [32] used RF plasma-enhanced chemical vapor deposition (RF-PECVD) and an unbalanced magnetron sputtering process to prepare Ti-DLC films, and these films with embedded fullerene-like nanostructures, are shown in Figure 1B. Lili Sun et al. [100] used LIS and a rectangular DC magnetron sputtering system to prepare Cu/Cr-DLC films, and these films with “onion-like” structures, are shown in Figure 2A. Shanhong Wan et al. [97] prepared Ni-DLC films by pyrolyzing nickel nitrate and poly(phenycarbyne) (PPC) at atmospheric pressure, and Ni particles appear to be connected with each other in the form of a hexagon and are randomly distributed on the sub surface, as shown in Figure 2B. Wei Dai et al. [101] used LIS and a high-power impulse magnetron sputtering (HiPIMS) system to prepare Al/Cr-DLC films, and these Al/Cr-DLC films with alternating structures consisting of aluminum-poor and aluminum-rich structures, are shown in Figure 2C. Furthermore, these special structures have a great effect on the mechanical and tribological properties of DLC films. However, many studies [56,67,79,85,102] have adopted similar preparation processes to prepare DLC films but failed to obtain special microstructures such as fullerenes and onions, which indicates that besides the preparation processes, the factors affecting the microstructure of DLC films include substrate material, surface morphology, properties of doping elements, and deposition process parameters, etc. What factors affect the growth process of these doping elements, and the effect mechanisms and control rules are still unclear, and the research on the effect mechanisms and rules of different microstructures formed on the properties of DLC films are still insufficient.

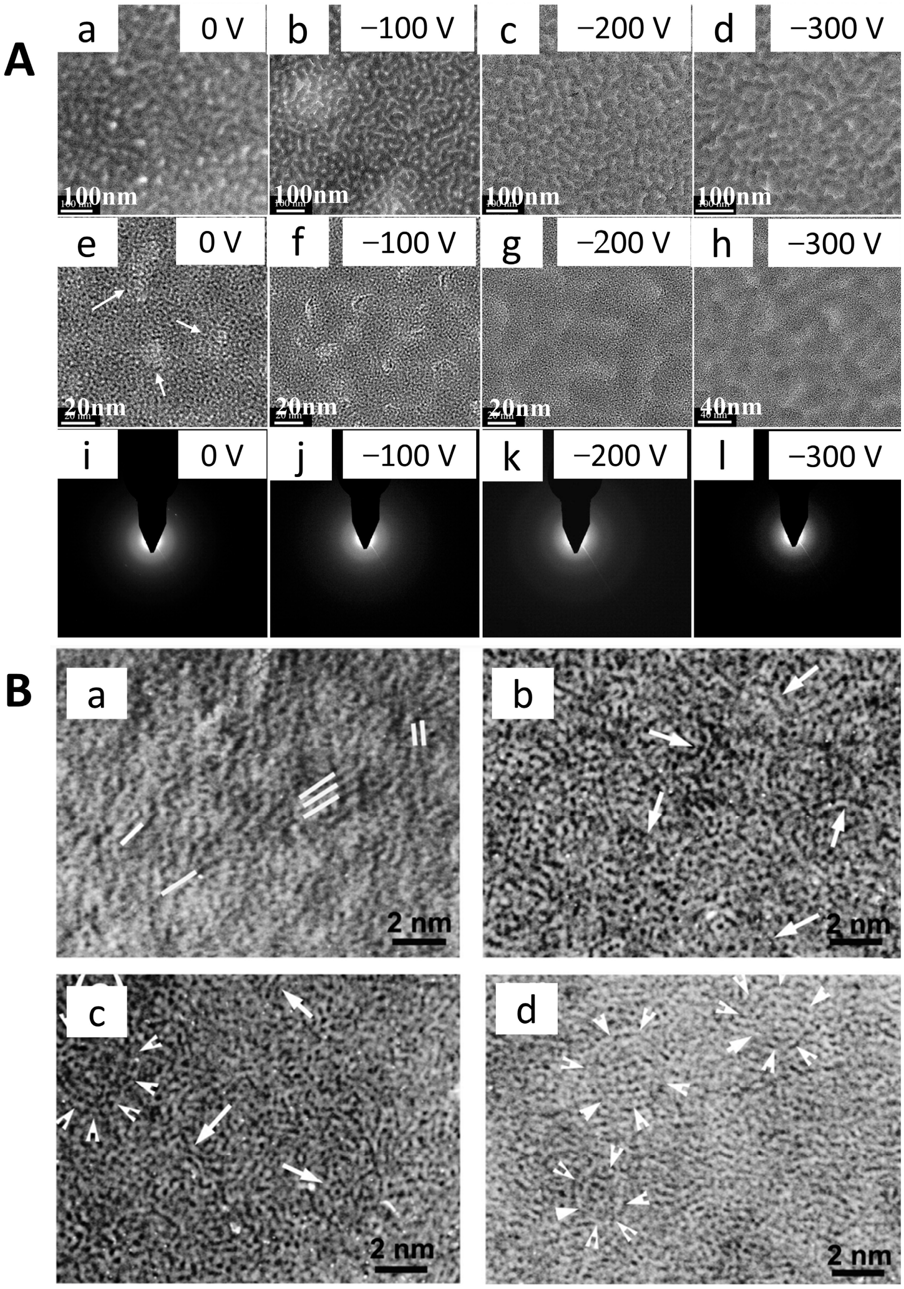

Figure 1. (**A**) TEM micrographs and electron diffraction patterns of DLC films prepared by different bias voltage [83]. (**a**–**h**) TEM micrographs and (**i**–**l**) electron diffraction patterns of the films as a function of bias voltage. There are grains exist in the DLC film which deposited at 0 V bias voltage. As the bias voltage changes to −100 V, the grain microstructure evolves into a nano-stripe structure. With the further increase of bias voltage, those nano-stripes become weak. Reprinted from Surface and Coatings Technology, Volume 229, Copyright (2013), with permission from Elsevier. (**B**) HRTEM plan-view images for the films. The arrows show the curved sheets or closed cage structures [32]. Ti−DLC films prepares by different CH_4/Ar ratios. CH_4/Ar= (**a**) 2/4; (**b**) 3/4; (**c**) 4/4; (**d**) 5/4. Reproduced from [Effect of microstructural evolution on mechanical and tribological properties of Ti-doped DLC films: How was an ultralow friction obtained, with the permission of AVS: Science and Technology of Materials, Interfaces, and Processing.

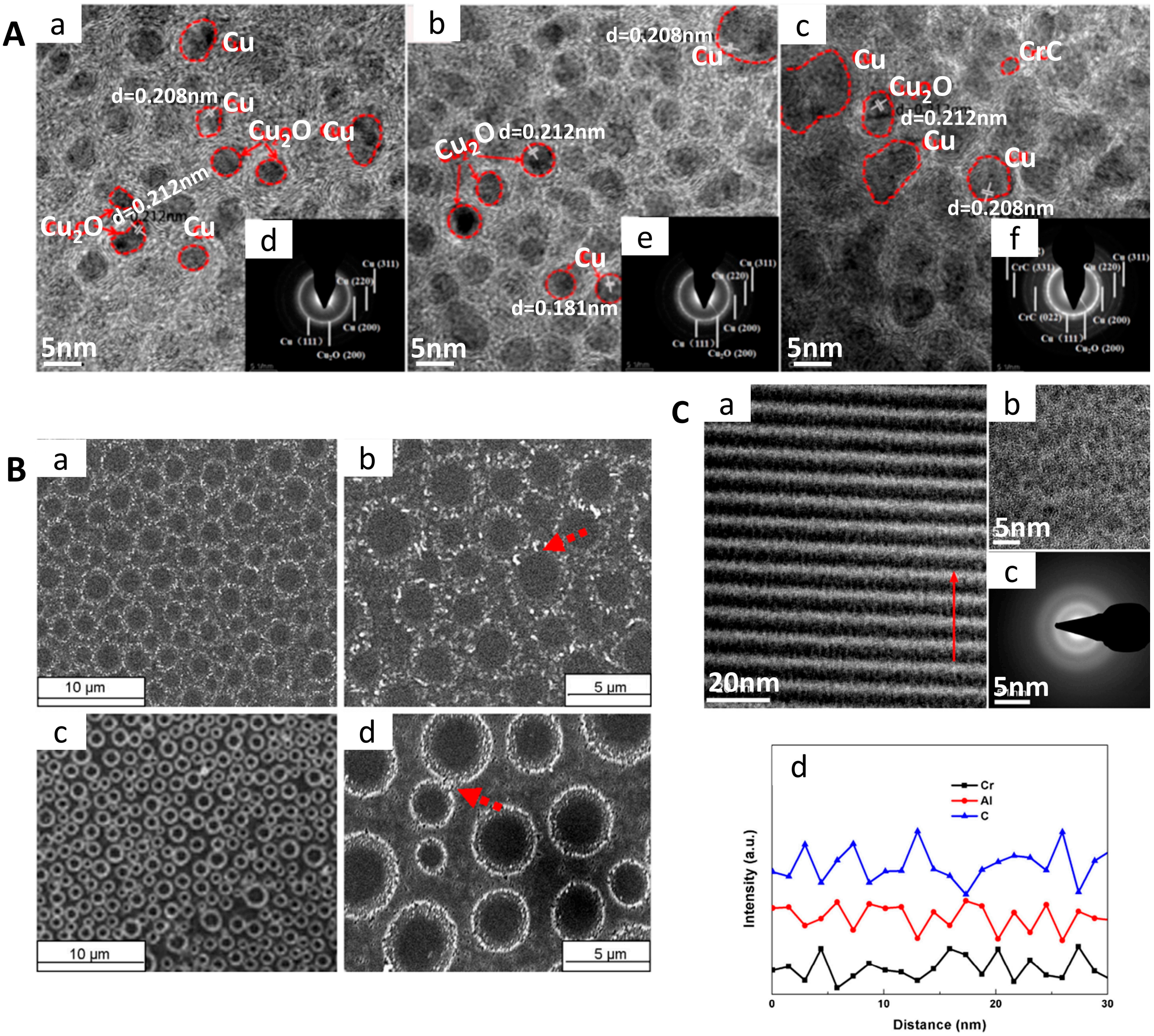

Figure 2. (**A**) Nanoclusters and curved planes forming onion-like structures. This figure shows that the amorphous carbon matrix consists of a number of nanoclusters and curved planes that form an onion-like structure. Both (**a**,**b**) contain Cu and Cu_2O nanoclusters, (**d**,**e**) are the corresponding diffraction patterns; (**c**) contains Cu, Cu_2O, and CrC nanoclusters, (**f**) is the corresponding diffraction patterns [100]. Reprinted from Diamond and Related Materials, Volume 68, Copyright (2016), with permission from Elsevier. (**B**) Ring-like patterns of Ni-DLC films. SEM images of ring patterns on the surface of Ni-DLC films. (**a**,**b**) 10%Ni-DLC film; (**c**,**d**) 20%Ni-DLC film [97]. Reprinted from Applied Surface Science, Volume 256, Copyright (2010), with permission from Elsevier. (**C**) Al-rich layer (white layer) and Al-poor layer (dark layer). (**a**) TEM micrograph; (**b**) the corresponding high magnification micrograph; and (**c**) the corresponding SAED pattern of the film deposited at the C_2H_2 fraction of 60%; (**d**) linescan EDX compositional measurement along the arrow in the (**a**) of (**C**) [101]. Reprinted from Applied Surface Science, Volume 388, Copyright (2016), with permission from Elsevier.

2.2. Roughness

The surface roughness of DLC films is mainly affected by the content of doping elements in the carbon matrix and their preparation processes. In general, the roughness of DLC films increases with the increase of the content of carbide-forming elements in the carbon matrix. This is because the number and size of carbides in the carbon matrix gradually increase and cluster on the surface of DLC films with the increase of the content of carbide-forming elements in the carbon matrix. The literature [59] reported the preparation of Ti-DLC films by magnetron sputtering, and the sputtering current was in a small range (0.3–1 A). With the increase of the sputtering current, the surface roughness of these films showed a trend of decreasing first and then increasing. However, the analysis shows that in the initial stage of element doping, the doping element dissolved in the carbon matrix leads to an increase in the density of the DLC film. Therefore, when the sputtering current is small, the roughness of the DLC film will decrease with the increase of the current. However, when the sputtering current reaches the critical value, the formation of carbides and the increase of their number and size lead to an increase in surface roughness. The effect of non-carbide-forming elements on the surface roughness of DLC films also follows this rule. Although the non-carbide-forming elements will not form carbides in the carbon matrix, with the increase of the content of doping elements in the carbon matrix, they gather in the carbon matrix and form larger particles on the DLC film's surface, resulting in the increase of the surface roughness of DLC films [76,77,82,88,89,96]. In general, the existing form of element doping with different content in DLC films and the change in their roughness is shown in Figure 3.

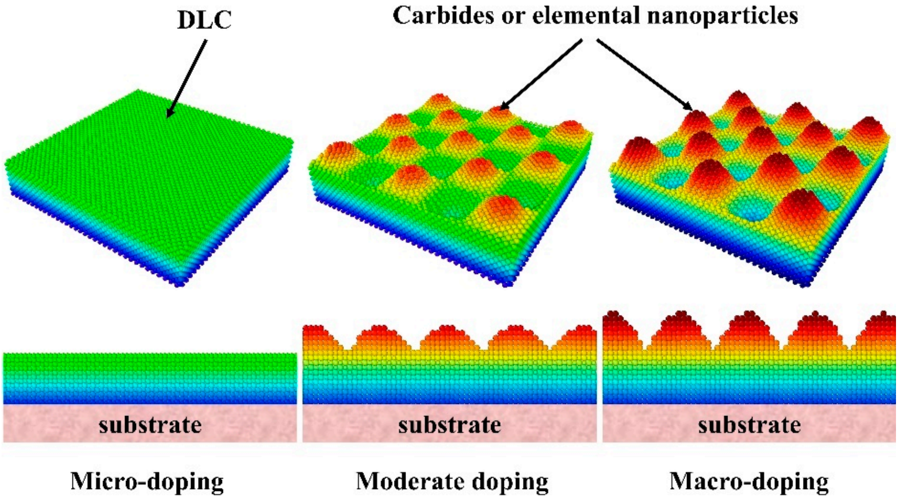

Figure 3. Morphological evolution of DLC films doped with different elements.

In terms of the effects of preparation processes on the surface roughness of DLC films, many studies have found that the appropriate bias can reduce the surface roughness of DLC films [41,84,103]. This is because the bias can increase the mobility of particles on the surface of DLC films, and the particles transfer from the wave peak to the trough [41], which makes the surface of DLC films more dense and smoother. However, the bias should not be too large, otherwise, it will cause an increase in roughness [82,84,103]. There are two explanations for the increase in surface roughness caused by excessive bias: (1) High bias substantially increases the plasma density, causing excessive etching of the film surface. In addition, the superfluous energy accelerates the atoms' diffusion and these atoms congregate again onto the surface, resulting in a coarser surface [82]. (2) High bias leads to increased collisions between particles, inducing an energy loss, and the particle diffusion capacity is reduced, eventually, merging them into larger particles on the surface of the film [84]. These phenomena show that surface roughness is mainly affected by the size of surface grains. It has also been found that the deposition time of DLC films prepared by electrodeposition has an effect on the surface grains' size of DLC films. With the increase of electrodeposition time, the average grain size of the DLC film's surface decreases, the density of DLC films increases, and the surface roughness decreases [95]. Some studies have found that if the doping elements in the carbon matrix reach a relatively high level, the surface roughness of DLC films will decrease instead [22,34,78]. This is because when the content of doping elements in the carbon matrix is high, the convex peaks on the surface of DLC films merge into larger aggregates, or concave valleys are filled, leading to a dense structure and a smooth film surface. However, the analysis shows that the surface roughness of DLC films is mainly affected by the preparation technology, compared with the literature [22,76,80], even DLC films with similar content of doping elements have a significantly different surface roughness under different preparation processes.

3. Mechanical Properties

3.1. Residual Stress

The residual stress has a great effect on the adhesion strength between the DLC film and the substrate. Generally, the higher the residual stress of DLC films, the lower the adhesion strength they have, which becomes one of the main obstacles to the application of DLC films. The residual stress of DLC films is mainly composed of thermal stress, internal stress, and external stress [104]. The thermal stress is mainly caused by the difference in the thermal expansion coefficient between the DLC film and the substrate. The internal stress is mainly related to the microstructure or morphology of DLC films, nevertheless, the preparation processes have a great effect on the microstructure or morphology of DLC films [105]. For example, in the deposition process of DLC films, the incident particles with higher energy will promote the diffusion of the adsorbed particles on the surface of DLC films, and the pressure wave generated by the collision of the incident particles can promote the growth of sp3-C, leading to the DLC film becoming more dense, which causes changes in the microstructure of the DLC films [106]. Compared with the sp2 phase, the sp3 phase has a longer bond length and higher disorder, which causes greater compressive stress, so the change of microstructure causes the change of internal stress. For the bond lengths of sp3-C and sp2-C, the quantum chemical bonding study by Pascal Vermeeren et al. [107] based on the Kohn-Sham molecular orbital theory showed that the bond length of the C-C bond is related to the steric (Pauli) repulsion between the substituents around the pertinent carbon atom, and the magnitude of the Pauli repulsion is related to the steric proximity of the substituents around the carbon atom. The Pauli repulsion increases with the number of substituents, and the higher coordination number of sp3 than sp2 indicates that it has higher Pauli repulsion due to more substituents, which also leads to the SOMO-SOMO (singly-occupied MO) orbital overlap of C reaching its maximum earlier in the case of sp3 hybridization. The point at which the SOMO-SOMO overlap reaches a maximum is usually considered an important factor in determining the equilibrium bond length [108,109], thus sp3-C has a longer bond length. The external stress is mainly caused by impurity pollution (such as H, O), which produces new phases with different molar volumes in the carbon matrix. In order to overcome the adverse effects caused by high residual stress, the methods of doping elements in the carbon matrix or adding a transition layer are usually adopted. Compared with adding a transition layer, doping heterogeneous elements in DLC films can better reduce the residual stress of these films and increase their adhesion strength to the substrate [56]. This is due to the transition layer merely alleviating the mismatch between the thermal expansion coefficient of the DLC film and the substrate, not only that, but the doping of heterogeneous elements can also release the internal stress of DLC films.

As atoms get closer together to each other, atomic orbitals overlap to form molecular orbitals [110]. During this period, if the electrons fill the bond state, they will increase the bond strength, conversely, if the electrons fill the anti-bond state, they will weaken the bond strength. When C atoms form molecular orbitals, electrons fill into bond states and form high-strength covalent bonds [111]. The high-strength covalent bonds lead to the distortion of bond angle and bond length, which is also the reason for the high residual stress of DLC films. It has been discussed that the microstructure and morphology of DLC films have an effect on their residual stress, and the doping of heterogeneous elements changes the structure of DLC films, which will inevitably lead to a change in the residual stress. For carbide-forming elements (for example, W [25], Cr [26], Ti [27]), when the doping elements are dissolved in the carbon matrix, the strain energy caused by bond angle distortion can be reduced, so as to reduce the residual stress of DLC films. As for the conclusion that the bond angle distortion causes the strain energy to increase, Ai Ying Wang et al. [112] used the first-principles calculation to show that when there is no doping, the C-C bond angle deviates from the equilibrium value of the tetrahedral bond, and the total energy of the system increases rapidly; when the W doping content is low, W dissolves in the carbon matrix, and W atoms are located in the center of the tetrahedron formed by four C atoms, which significantly reduces the total energy caused by bond angle distortion, thus helping to reduce the residual stress of the DLC film. The variation trend of the total distortion energy of C-C and C-W bonds with the disordered bond angle is shown in Figure 4.

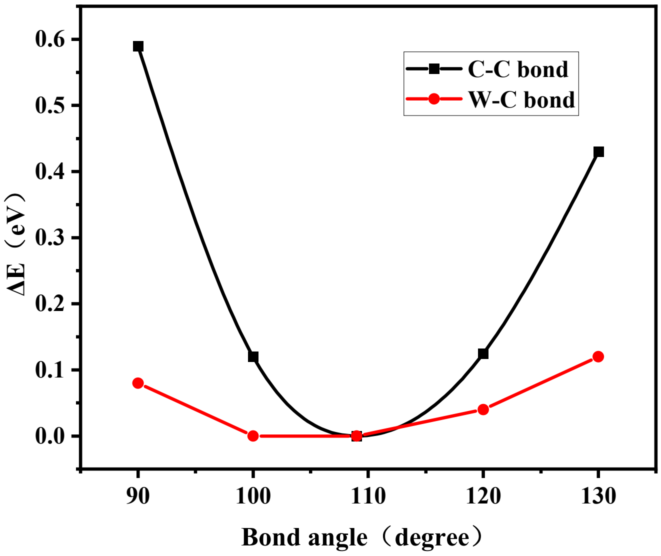

Figure 4. The variation of total energy of C-C and C-W bonds varies with the disordered bond angle [112].

It has been found that the non-carbide-forming element Cu is similar to that of the carbide-forming element W, and the deformation energy of bond angle distortion is closely related to the residual stress. The first-principles calculation based on density functional theory (DFT) shows that the energy change caused by the angular distortion of the Cu-C bond is much smaller than that of the C-C bond. Through the analysis of the partial density of state (PDOS) and charge distribution of the highest occupied molecular orbital (HOMO), as shown in Figure 5, it is found that the Cu-C bond shows anti-bonding characteristics because Cu does not react with C, so it has a small distortion energy change [77]. In addition, doping Cu element can also reduce the ratio of twisted bond angle and bond length in the DLC film, which significantly reduces the residual stress of the DLC film and increase the stability of the system. However, W is a carbide-forming element, which can reduce the residual stress of DLC films even without anti-bonding properties, indicating that appropriate element doping can play a role in reducing the residual stress of DLC films. The reason is that there is a weak covalent bond between some carbide-forming elements and carbon. XiaoWei Li et al. [113] analyzed the HOMO of Al, Ti, and C, as shown in Figure 6, and the result shows that: the charge between Al and C transfers around C, and the non-carbide-forming element Al and C show ionic characteristics; however, Ti and C show covalent bond characteristics, and there is only a small electron accumulation between Ti and C, and the strength of the Ti-C bond is far less than that of the C-C bond. This also may be the reason why carbide-forming elements can still reduce the bond-twisting strength and residual stress in DLC films although they have no anti-bonding properties. This phenomenon has been referred to by some researchers as “stress release hubs” [31,47,100] and “stress buffer sites” [28].

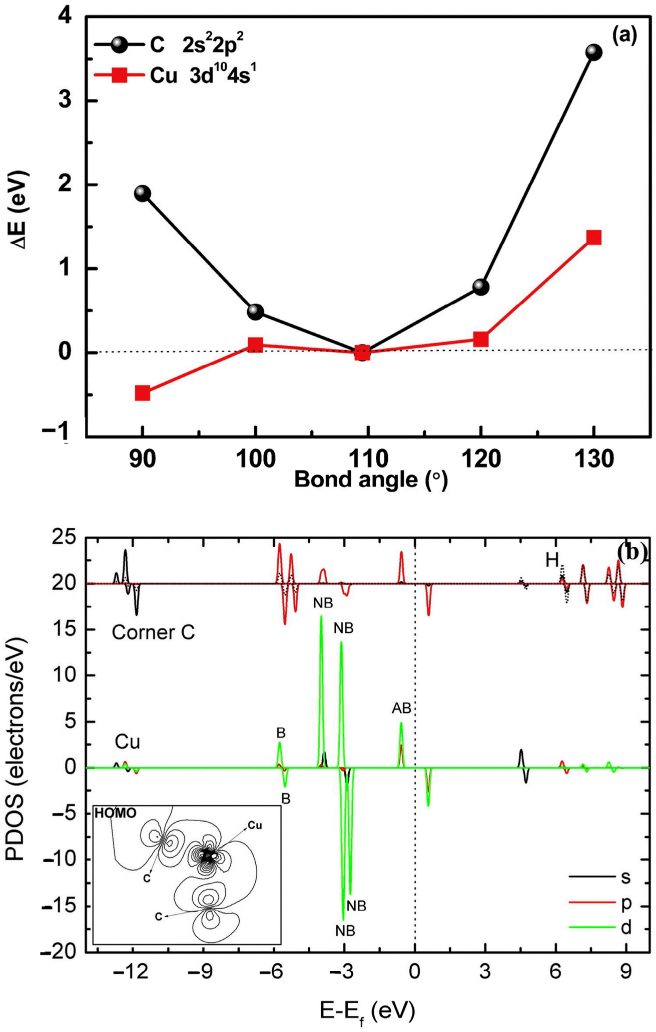

Figure 5. (**a**) Energy change via bond angle distortion in Cu-C and the pure C-C system; (**b**) PDOS projected on the central Cu and corner C atoms in the Cu-C system, in which the inset shows the charge density between the central Cu or C and corner C atoms for the HOMO passing through Cu and two corner C atoms [77]. B, NB, and AB stand for bonding, nonbonding, and antibonding, respectively [114]. Reprinted from Thin Solid Films, Volume 640, Copyright (2017), with permission from Elsevier.

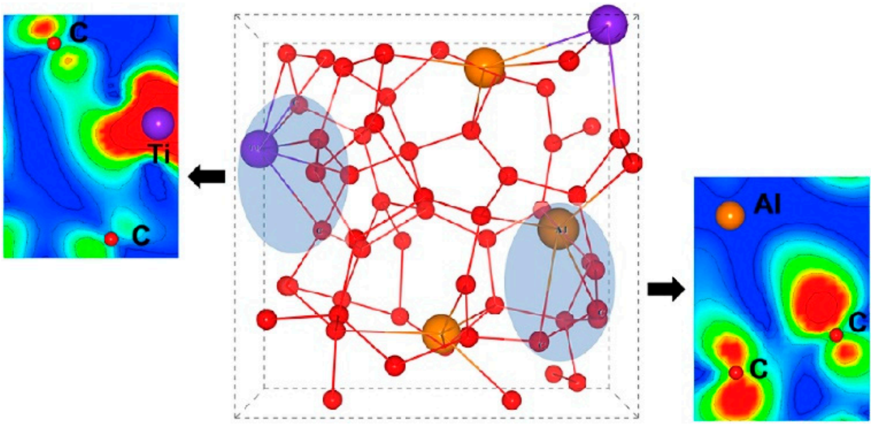

Figure 6. Contour plots of charge density of HOMO passing through Ti-C or Al-C bond [113]. Reprinted from Carbon, Volume 111, Copyright (2017), with permission from Elsevier.

The effects and mechanisms of micro-doping of elements on residual stress of DLC films are analyzed as mentioned above. With the increase of the content of doping elements in the carbon matrix, carbide-forming elements will form carbides, i.e., forming Y-C bonds with long bond length [100,115] (Y = Cr, W, Ti, Mo, Nb, etc.), which will lead to the rise of residual stress, but it is generally lower than that of undoped DLC film. The residual stress of DLC films varies with the content of carbide-forming elements in the carbon matrix as shown in Figure 7. In addition, carbide-forming elements doping can also promote the graphitization of DLC films [30,38,40,54,55], that is, sp3-C is transformed into sp2-C. Due to the chaotic distribution of sp3-C, this increases the degree of cross-linking of the carbon network and increases the distorted bond length and bond angle, leading to an increase in residual stresses of DLC films [91,113,116,117]. The increase of sp2 content in DLC films will reduce the disorder of bond length and bond angle and make the films more orderly [38,72], so the graphitization of DLC films can reduce the residual stresses.

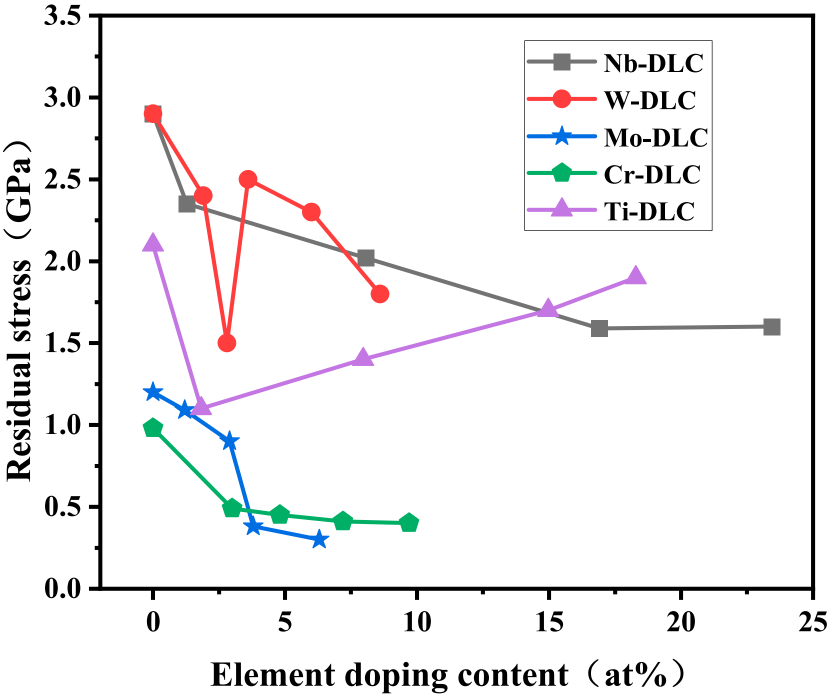

Figure 7. The general trends of residual stress change of DLC films with the content of doping elements. Nb-DLC [38]; W-DLC [25]; Mo-DLC [30]; Cr-DLC [52]; Ti-DLC [21].

Carbide-forming elements are easy to bond with carbon, and the formed carbides also have their growth process, and the transformation in the growth process will cause the change in residual stress. Kan Zhang et al. [39] found that with the increase of the content of C in DLC film, the carbides of Nb change from the hexagonal Nb_2C phase to the cubic NbC phase, as shown in Figure 8, and the size of carbide grains decreases, which increases the defect density in DLC film and leads to lattice deformation, thus rapidly increasing the internal stress of the DLC film. Ai-Ying Wang et al. [25,112] found that with the increase of the content of W in the carbon matrix, W gradually evolves from the dissolved state to the WC_{1-x} phase. As the length of the W-C bond is longer than that of the C-C bond, the bond angles are distorted or twisted, resulting in an increase in the residual stress, but it is still lower than that of undoped DLC film. With the further increase of W content, the WC_{1-x} phase gradually evolves into the crystalline α-W_2C phase, which further leads to the reduction of residual stress. This also indicates that the nanocrystals formed in the carbon matrix will also affect the change of residual stress. Furthermore, computer simulation results show that the average stress generated by the formed nanocrystalline grain boundary is 10–20% lower than that in the grain, and the stress in the grain increases with the increase of grain size [118]. As the nanoparticles embedded in the carbon matrix will form high-density interfaces and a high-volume fraction of grain boundaries, the residual stress of the DLC film can be alleviated by diffusion and the sliding of the grains' boundaries and interfaces [36,46,79,80,115,119]. Simultaneously, the sliding of the interface atomic plane will cause plastic deformation, and the residual stress will be released through this plastic deformation [118]. However, it is not that the smaller the grain size is, the more obvious the reduction of residual stress in DLC film is. Too small grain size will cause the anti-Hall-Petch effect, increase the defect density in DLC film, and lead to lattice deformation, as a result, rapidly increasing the internal stress of the DLC film [39].

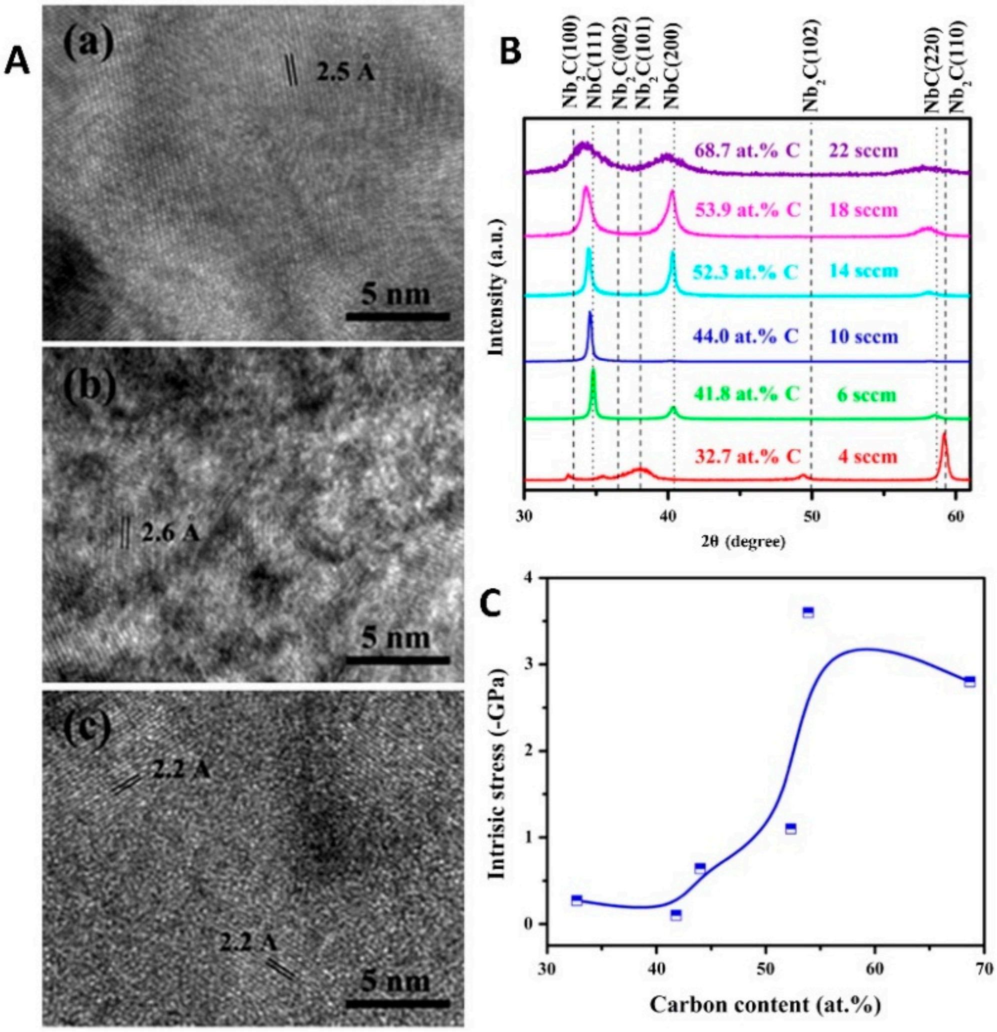

Figure 8. (**A**) High-resolution TEM image for NbC_x films. (**a**) 32.7; (**b**) 53.9; (**c**) 68.7 at.% carbon [39]. (**B**) XRD patterns in the Bragge Brentano (θ–2θ) configuration for NbC_x [39]. (**C**) Intrinsic stress for NbC_x film as a function of total carbon content in the films [39]. Reprinted from Vacuum, Volume 99, Copyright (2014), with permission from Elsevier.

As for the non-carbide-forming elements, they are similar to carbide-forming elements. When they are dissolved in the carbon matrix, they can significantly reduce the bond strength, bond orientation, and strain energy of bond angle distortion [33,79,90], thereby reducing the residual stress of DLC films. Similarly, non-carbide-forming elements can also increase the degree of order of DLC films by promoting graphitization, which reduces the residual stress [35,75,76,88,96,97].

Different preparation processes will affect the microstructure of DLC films, which will certainly cause a variation in residual stress. As discussed above, the shock wave generated by incident particles with higher energy can promote the generation of the sp3 phase, and many studies have found that higher energy can be given to the particle by applying bias to the substrate during the preparation of DLC films. Bias affects the change of residual stress of DLC films mainly through three aspects. Firstly, the particles with enough energy penetrate the growth surface, which increases the local density of the film and promotes the formation of the sp3 phase [41,84]. The bond angle and bond length of the sp3 phase are more disordered than the sp2 phase, which causes the residual stress of the DLC films to increase. Secondly, the enhanced shot peening effect due to high-energy particle bombardment caused by bias will lead to structural damage of the DLC film in a certain volume range, and as a result, the residual stress will be increased [84]. For example, for Nb-DLC films [39] and Al-DLC films [84] prepared under bias, the relative content of the sp3 phase in the carbon matrix increases with the increase of bias, and their compression stress also increases, as shown in Figure 9. Thirdly, the collision of particles with higher energy during deposition will cause the energy to be absorbed by DLC films, resulting in an increase in residual stress [42]. For example, P.P. Jing et al. [91] used high-power pulsed plasma vapor deposition technology to prepare Ag-DLC films, and with the increase of Ag content in the carbon matrix (0.4–2.99 at.%), the proportion of the sp3 phase in the matrix increased, and the residual stress of Ag-DLC films also increased. A.F. Yetim et al. [81] prepared Ti-DLC, Al-DLC, and V-DLC films by physical vapor deposition (PVD) technology. These doped-DLC films have a higher proportion of the sp3 phase than undoped DLC film and the residual stress also increased. However, the effect of bias on the residual stress of hydrogenated DLC films is different from the works aforementioned. Studies [82] have shown that the bias applied will weaken the vibration intensity of the C-H groups in DLC films, that is, the C-H bond is broken, causing the release of H. Because the existence of H can stabilize the sp3 phase in the DLC film, the release of H might cause the decrease of sp3 phase content, which also might lead to the I_D/I_G value decrease. A large number of studies [28,54,72] have shown that the increase in I_D/I_G reduced the residual stress in DLC films. However, the work [82] found that the residual stress still decreased when the I_D/I_G value was unchanged. Regarding the I_D/I_G value, it is related to the D-line and G-line in the Raman spectra, and it is the relative ratio of D-line and G-line intensity. Generally, the D-line is attributed to the breathing mode of the sp2-C ring, which is active in the presence of disorder, while the G-line is attributed to the stretching vibration of the C(sp2)-C(sp2) bond [120]. The I_D/I_G value increases with the increase of sp2-C content in the carbon matrix [121]. Some studies [28,35] show that the larger the I_D/I_G value of the DLC film, the higher the degree of graphitization. This will also have an effect on the mechanical properties, tribological properties, etc. of DLC films. Therefore, the increase in I_D/I_G is not the sole reason for the reduction of residual stress. As mentioned above, external stress is also an important part of residual stress, and H doping is likely to increase the residual stress by generating a new phase leading to volume expansion in the carbon matrix. Therefore, the release of H can also reduce the residual stress without changing the I_D/I_G value of the DLC film.

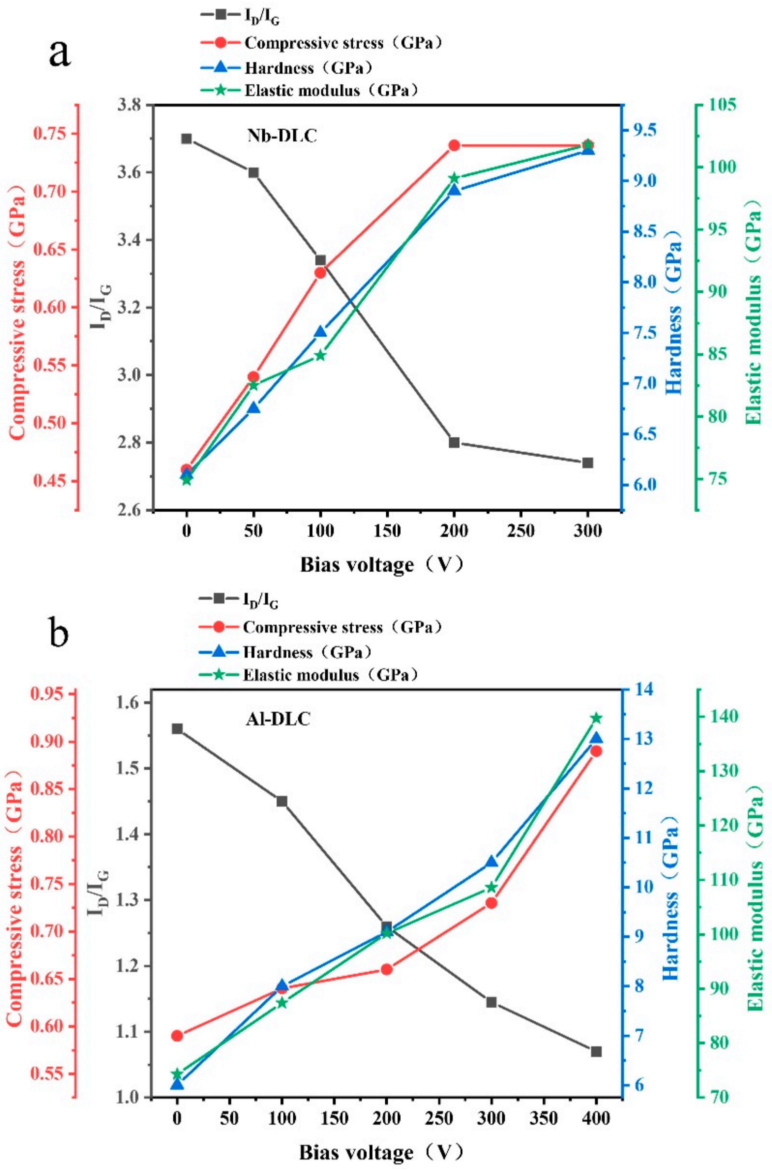

Figure 9. General effect trends of bias on I_D/I_G, compressive stress, hardness, and elastic modulus of DLC films. (**a**) Nb-DLC [41]; (**b**) Al-DLC [84] films.

3.2. Hardness and Elastic Modulus

In terms of the effect of micro-structure on the hardness and elastic modulus of DLC films, the sp3-C phase in DLC film has the properties of diamond and has high hardness and elastic modulus. However, the decrease of sp3-C phase content in DLC film means graphitization of the DLC film. Due to the low hardness of the graphite phase, the graphitization phase transformation of DLC film will reduce its hardness and elastic modulus. A large number of studies have shown that the doping of carbide-forming elements can promote the graphitization of DLC films, which leads to the reduction of the hardness and elastic modulus of DLC films. For example, Mo element doping can break the sp3-C bond or tetrahedral bond to promote graphitization of the DLC film, which leads to the reduction of hardness and elastic modulus [30]. The doping of carbide-forming elements such as W [43], Ti [62,65], Mo [46,47], Cr [52,54], and Si [72] can reduce the hardness and elastic modulus of DLC films by increasing the sp2 phase in the carbon matrix. This may be because the formation of carbides increases the sp2-C sites of DLC films, but the specific mechanisms by which they promote the graphitization of DLC films have not been systematically studied. The effect of non-carbide-forming elements doping on the hardness and elastic modulus of DLC films is similar to that of carbide-forming elements, for example, increasing the order degree by promoting the graphitization of DLC films [28,35,37,75,88,92] and disrupting the continuity of the carbon network [77,93] to reduce the hardness and elastic modulus. In addition, since the non-carbide-forming elements (such as Cu, Al, Ag, Ni) are generally soft in texture, the doping of these elements will increase the soft phase in the carbon matrix, resulting in a decrease in the hardness and elastic modulus of DLC films.

In terms of the effect of the preparation process on the hardness and elastic modulus of DLC films, according to different preparation processes, sometimes the doping of elements may also increase the content of the sp3 phase in DLC film, thus increasing the hardness and elastic modulus of the film. For example, Yefei Zhou et al. [21] prepared Ti-DLC films by ion beam-assisted enhanced unbalanced magnetron sputtering. When the Ti content is low (1.82 at.%), the hardness and elastic modulus of the Ti-DLC film are increased compared with the undoped DLC film. This is mainly because the micro-doping of Ti increases the local density of the DLC film and promotes the formation of sp3-C bonds. Wei Dai et al. [56] found a similar phenomenon in Ti-DLC films deposited by a mixed ion beam system consisting of a linear anodic layer ion source (ALIS) and DC magnetron sputtering. This is mainly because of the low bond energy of sp2-C, which can preferentially bond with Ti atoms to form nanocrystalline carbides, resulting in the reduction of sp2-C proportion. Some studies [35,52,85] adopt the same preparation processes as above, but the results show that with the increase of the content of doping elements in the carbon matrix, the content of the sp3 phase in DLC films decreases monotonically, and the hardness and elastic modulus also decrease. It can be summarized that the structure, hardness, and elastic modulus of DLC films are closely related to the preparation processes and conditions adopted. In combination with the reported effects of the preparation processes [20–98] on DLC films, the following general effects can be obtained. When DLC films are prepared by magnetron sputtering or pulsed laser deposition, element doping will generally promote the graphitization of these films. The combination of magnetron sputtering with plasma-enhanced chemical vapor deposition (PECVD) or plasma source ion implantation (PSII) generally does not increase the relative content of the sp3 phase of DLC films. The combination of magnetron sputtering technology and linear anode-layer ion source (LIS) presents an uncertain effect on the relative content of the sp3 phase of DLC films because elements of different properties produce different phenomena when using this method. For example, Wei Dai et al. [56] found that the relative content of the sp3 phase increased when Ti (3.78–23.57 at.% content) is doped into the carbon matrix, but the doping of Al (0.68–17.6 at.% content) element promoted the graphitization of the DLC film [35], which may be caused by the reduction of the sp2 phase due to the preferential combination of carbide-forming element Ti with sp2-C. For another example, Wei Dai et al. [34] found that the sp3/sp2 values of DLC films gradually increased with increasing the Cr content (1.49–40.11 at.%) in the carbon matrix, and their hardness also increased slowly and finally leveled off. However, these have not been compared with undoped DLC films, and further studies are needed to determine whether element doping under this preparation process can improve the mechanical properties of DLC films. As Wei Dai et al. [33] found, although the I_D/I_G values of DLC films showed a trend of increasing and then decreasing with increasing Cu content (0.94–47.6 at.%) in the carbon matrix, their hardness was always lower than that of undoped DLC film. Furthermore, the hardness and elastic modulus of the Si-doped DLC films prepared by this method by Jae-Il Kim et al. [71] are lower than the undoped DLC film. In addition, the application of bias in the process of DLC film preparation will generally increase the relative content of the sp3 phase of DLC films.

In terms of the effects of carbide-forming elements on the hardness and elastic modulus of DLC films, the hardness and elastic modulus are also related to the doping content of carbide-forming elements, which are mainly affected by the existence state of carbide-forming elements in the carbon matrix. Studies in the literature [27,29,52,57,58,62,100,122,123] show that the effects of carbide-forming elements doping content on hardness and elastic modulus of DLC films show the rules are as following: (1) When trace amounts of elements are doped in the carbon matrix, they dissolve in the carbon matrix, accompanied by the formation of a small amount of nanocrystalline carbides, which will destroy the continuity of the carbon network and lead to the reduction of the hardness of the DLC film (but the hardness will not decrease significantly at this time); (2) With the content of doping elements increases, the hard carbides formed in the carbon matrix help to inhibit the loss of hardness and elastic modulus of DLC films, and the hardness and elastic modulus of DLC films rise to a certain extent (but are generally lower than that of undoped DLC film); (3) If there is too high a content of doping elements in the carbon matrix, the formation of a large number of carbides will destroy the structure of DLC films, which will seriously deteriorate their mechanical properties. In general, the effects of carbide-forming elements doping content on the hardness of DLC films are shown in Figure 10. vspace-5pt

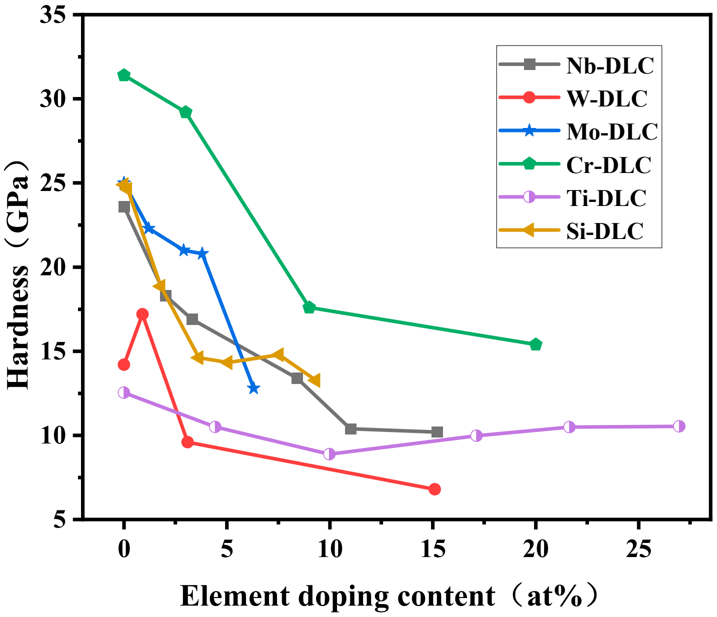

Figure 10. General changing trends of hardness of DLC films with carbide-forming elements doping content. Nb-DLC [29]; W-DLC [44]; Mo-DLC [30]; Cr-DLC [31]; Ti-DLC [57]; Si-DLC [67] films.

In terms of the effect of nanocrystalline structures formed by doping elements on the hardness and elastic modulus of DLC films, studies have found that the sliding of nanocrystals formed by doping elements in the carbon matrix will lead to the reduction of the hardness and elastic modulus of DLC films. For example, Wei Dai et al. [33] prepared Cu-DLC films by a combination of the linear ion source in the anode layer and DC magnetron sputtering. Although the relative content of the sp3 phase in DLC films increased, the hardness and elastic modulus of DLC films decreased due to the sliding of the ductile copper nanoparticles. Similar to grains sliding, the presence of dislocation motion also reduces the hardness of DLC films. In order to overcome the reduction of hardness and elastic modulus of DLC films caused by dislocations, J.B. Cai et al. [60] found that the preparation of multilayer DLC films could overcome this problem. In their work, a-C/a-C: Ti multilayer films are prepared by employing closed-field unbalanced magnetron sputtering technology. The TiC nanocrystals formed in the carbon matrix contribute to the formation of a local strain field, which increases the resistance to dislocation movement. Moreover, the interface in the multilayer can inhibit grain growth and block dislocation movement, resulting in higher hardness of the multilayer DLC films. Li Ji et al. [115] found that small-size nanocrystalline carbides formed in the carbon matrix could separate two–three atomic layers, which could prevent grain sliding and dislocation. In addition, the interfaces in these films are also places of energy dissipation and crack deflection, which can reduce cracks and propagation of cracks, and make DLC films possess good toughness and maintain good resistance to plastic deformation [124]. Some studies have also found that the hardness and elastic modulus of DLC films gradually increase with the decrease in grain size, which may be affected by the Hall-Petch effect [42]. Similarly, W.Q. bai et al. [58] found that if the TiC grains in Ti-DLC films become coarse, the hardening effect of nano-composite films will be reduced, leading to a decrease in the hardness of DLC films. However, the strength of a grain cannot increase indefinitely as its size decreases, so the Hall-Petch effect can only be adapted to grains within a certain size range [125]. Moreover, if only trace amounts of elements are doped, no grains of the doping element are formed in the carbon matrix, and the grains boundary strengthening effect is no longer applicable to this situation. Therefore, when the content of the doping element is lower than a certain critical value, that is, when the grain size is lower than the critical value of dislocation accumulation, the hardness (or strength) of DLC films may remain unchanged or only slightly decrease. This also explains why the hardness of DLC films can remain when trace amounts of elements are doped into the carbon matrix.

Besides preparation processes, microstructure, and local strain field caused by nanocrystals of doping elements, some other factors will also affect the hardness and elastic modulus of DLC films, such as the phase transition of carbides formed by carbide-forming elements in the carbon matrix. Kan Zhang et al. [39] found that with the increase of C element content in the carbon matrix, the carbides of Nb change from the hexagonal Nb_2C phase to the cubic NbC phase, and the hardness of hexagonal Nb_2C is higher than that of cubic NbC phase. Therefore, this phase transition reduces the hardness of DLC films. The effect of Si element doping on the hardness and elastic modulus of DLC films is controversial because the Si atom and C atom only form quadruple coordination covalent structure (Si-C) [66], that is, the Si atom and C atom only form the sp3 phase. Although this leads to the decrease of sp3-C, the overall sp3 phase (Si-C, Si-H) in the carbon matrix increases, and the hardness of DLC films also increase [68], as shown in Figure 11a. Studies [67] used the same preparation process as that of [68] to prepare Si-DLC films, but the results of the two studies are contradictory. The results of the study [67] showed that Si doping reduced the hardness and elastic modulus of DLC films, as shown in Figure 11b. Although the doping of Si can increase the sp3 phase of the carbon matrix, the sp3 bonds (Si-H bond, Si-C bond) formed by Si are weak, leading to the overall intermolecular structures of DLC films being weakened, thus reducing the hardness and elastic modulus. However, it may also be due to the different content of doping elements.

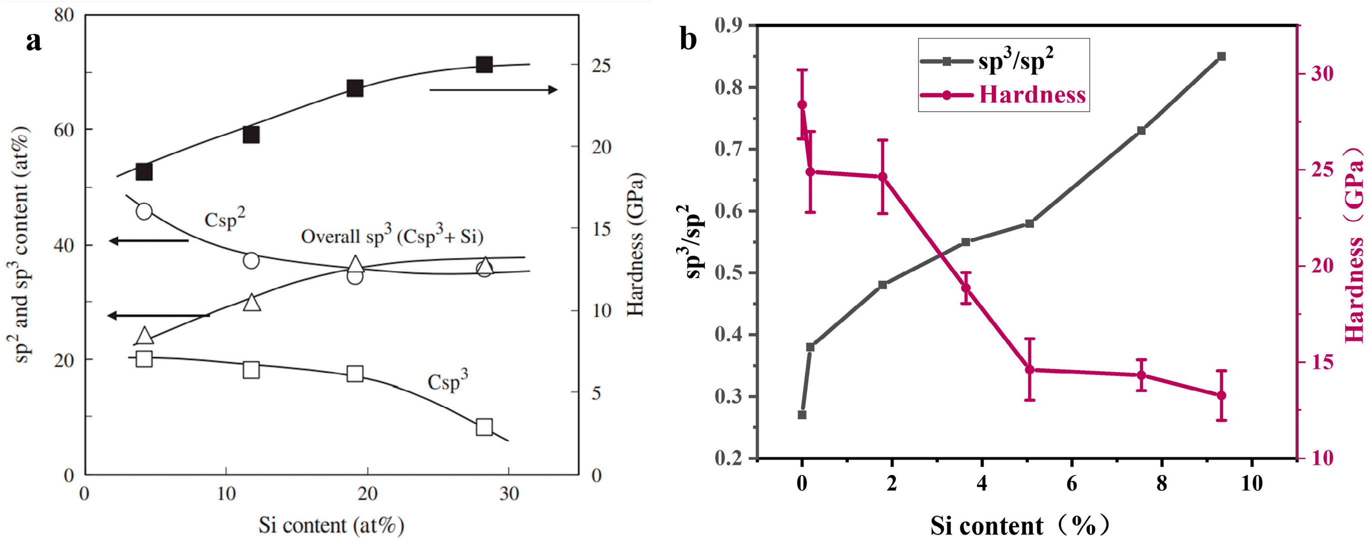

Figure 11. Relationship between hardness and sp3. (**a**) [68]; (**b**) [67]. Reprinted from Diamond and Related Materials, Volume 15, Copyright (2006), with permission from Elsevier.

From the aspect of single-element doping, it is found that both carbide-forming elements and non-carbide-forming elements have difficulty increasing the hardness and elastic modulus of DLC films while significantly reducing the residual stress. The general rules of single-element doping are as follows: when there is only a trace amount of element doping in the carbon matrix, DLC film can significantly reduce the residual stress while maintaining high hardness and elastic modulus [25,26,90]; when there is too high content of doping elements in the carbon matrix, the nanoparticles formed in the carbon matrix will destroy the continuous structure of the carbon matrix, deteriorate the mechanical properties of the DLC film, and even cause the rise of residual stress [21,34,52,62,77]. In order to overcome these shortcomings of single-element doping, researchers have also conducted many studies on the properties of multi-element doped DLC films, such as co-doping of carbide-forming elements (Cr/N [126], W/Ti [123,127], F/Si [102]), co-doping of carbide-forming elements and non-carbide-forming elements (Al/Ti [113,128,129], Al/Cr [101], Ti/Ag [115], Al/Si/Cr [99]). Compared with some DLC films doped with non-carbide-forming elements, the doping of the proper content of carbide-forming elements can improve the mechanical properties of DLC films. For example, Ya gang Zhang et al. [122] prepared Ni-DLC and Ni/B-DLC films by electrodeposition. Because B forms a hard B_4C phase in the carbon matrix, Ni/B-DLC film has a higher hardness than Ni-DLC film. Li Ji et al. [115] prepared a series of Ti/Ag-DLC films by magnetron sputtering while keeping the content of Ag in the carbon matrix (about 3.5 at.%) basically unchanged. Compared with the Ag-DLC film without doping Ti, when the content of Ti in the carbon matrix is 1.6 at.%, the TiC formed in the carbon matrix can compensate for the reduction of hardness caused by graphitization of the DLC film, and the Ti/Ag-DLC film has better mechanical properties in this case. In addition, the co-doping of appropriate carbide-forming elements can also improve the mechanical properties of DLC films. For example, Li Qiang et al. [123] prepared Ti/W-DLC films (0.3 at.% Ti) by co-sputtering W and Ti targets in a mixed atmosphere of methane and argon. Compared with Ti-DLC film without doping W, when the content of W in the carbon matrix is 2.6 at.%, the hardness and elastic modulus of the DLC film can be increased without significantly increasing the residual stress. For the co-doping of carbide-forming elements, if the mechanical properties of DLC films are to be improved, the doping content cannot be too large. If the content of carbide-forming elements in the carbon matrix is too high, a large number of carbides will be formed in the carbon matrix. Numerous studies have shown that the formation of a large number of carbides in the carbon matrix can seriously break the continuity of the carbon network [34,130]. Although there is the formation of hard carbides, the breakage of the carbon network will reduce the mechanical properties of DLC films, and the formation of a large number of longer metal-C bonds will also significantly increase the residual stresses in DLC films [19,123]. While the content of carbide-forming elements co-doping is small, although the formation of a small amount of carbide will also break the continuity of the carbon network, the formation of hard carbides will also offset the reduction of mechanical properties caused by the breakage of the carbon network [123], and even improve the mechanical properties of DLC films. In addition, the doped elements will also play the role of "stress release hub" [31,47], so a small amount of element doping will not cause a significant increase in residual stress. Therefore, the content of multi-element doping should also be appropriate. In the case of a low content of doping elements, an appropriate amount of carbide cannot be formed in the carbon matrix to compensate for the decrease of hardness and elastic modulus caused by the graphitization of the DLC films; when the carbon matrix has a high content of doping elements, the formation of overmuch carbides will destroy the carbon matrix structure, resulting in the reduction of mechanical properties of DLC films [100,123,127,130].

4. Tribological Properties

At present, there are three explanations for the excellent tribological properties of DLC films: (1) The high temperature generated on the friction surface during rubbing will promote the graphitization of the DLC film, increasing the sp2 phase with good lubrication properties, and thus making DLC films exhibit good anti-friction properties [59,60,75], as shown in Figure 12a. However, this friction reduction method will generally increase the wear of DLC films [85,89], unless the doping elements are combined with graphitized carbon to form micro-particles with friction-reducing effects, such as “rod-like debris” [75,90,91]. (2) Graphitized transfer film with low shear strength is formed during the rubbing of DLC films [35,36,39,82,93], as shown in Figure 12b. The formation of transfer film with good self-lubricity will also reduce the direct contact between tribo-pairs, which can significantly reduce the friction coefficient and wear rate of DLC films. (3) In terms of microscopic mechanism, the passivation of surface dangling bonds can also improve the tribological properties of DLC films. The sp2-C bonds will form π-π bonds interaction at the sliding interface and electrostatic forces and capillary forces caused by molecular species adsorbed on the surface will also cause friction in the tribosystems. However, the three σ bonds of the carbon atoms on the surface of DLC films will bind to their nearest carbon atoms, and the remaining σ bonds are likely to be exposed outside the surface as free-dangling bonds. The free-dangling σ bonds will interact with the atomic covalent bonds of the tribo-pairs, resulting in strong adhesion, which leads to high friction. Therefore, the physical or chemical passivation caused by the bonding between the dangling bonds on the surface of DLC films and the surrounding media (such as hydrogen, oxygen, water molecules, etc.) can play a role in reducing friction and wear [75,131]. Passivation of dangling bonds on the surface of DLC films is shown in Figure 12c.

The factors affecting the tribological properties of DLC films are not only the graphitization, surface passivation, and transfer film effects mentioned above, but also the microstructure, mechanical properties, and working conditions of the DLC film. Studies have shown that when elements are doped with appropriate content, the residual stress of the DLC film can be significantly reduced while maintaining good mechanical properties, the adhesion between the DLC film and the substrate can be increased, and the tribological properties of DLC films can be maintained while prolonging the life of the DLC film [20,44,47,58,91,98]. It has also been found that the amorphous nanoparticles formed in the carbon matrix can improve the toughness and bearing capacity of DLC films, and improve their tribological properties [32,101]. This also indicates that the tribological properties of DLC films cannot be determined by a single factor, and they can be improved through the cooperation of multiple factors. Therefore, according to the reports, further discussion will take place below.

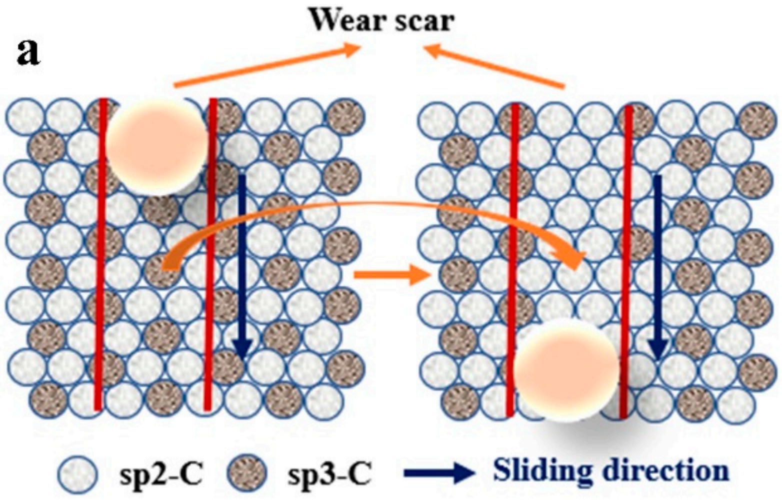

Figure 12. *Cont.*

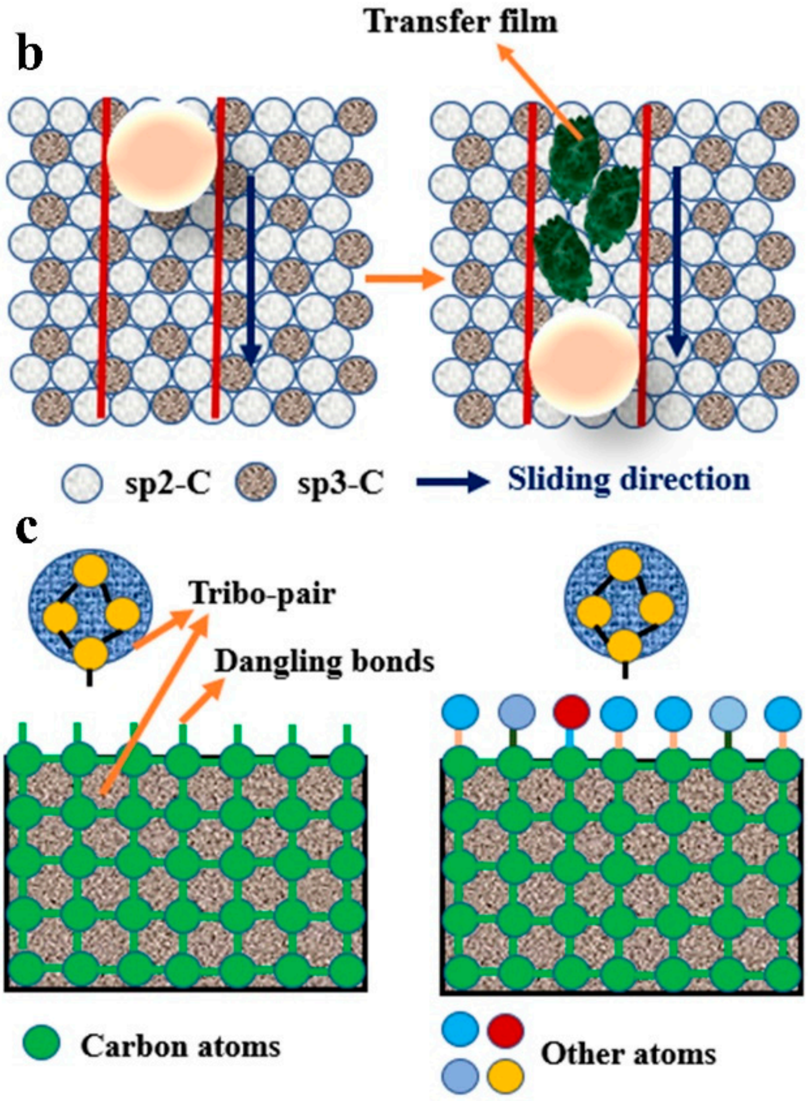

Figure 12. Schematic diagram of friction reduction and anti-wear mechanisms of DLC films. (**a**) Promoting graphitization of DLC films increases the lubricating sp2-C; (**b**) Low shear strength transfer film formation; (**c**) Passivation of surface dangling bonds.

4.1. Carbide-Forming Element Doping

Generally, the doping content of carbide-forming elements has great effects on the tribological properties of DLC films. When trace carbide-forming elements are doped, the doping elements are dissolved in the carbon matrix, which can not only effectively release the residual stress of DLC films, but also maintain their good mechanical properties [21,56]. The reduction of residual stress and good mechanical properties (such as high hardness and elastic modulus) are the key factors to improve the service life of DLC films and maintain good tribological properties. The reduction of residual stress can increase the adhesion between the DLC film and the substrate, and prevent cracks and spalling during rubbing, while the high hardness and elastic modulus of DLC films can reduce their wear [20,21,44,47,60]. For example, Guojia Ma et al. [61] prepared Ti-DLC film with a combination of reactive magnetron sputtering and PSII. Ti doping increased the hardness of the DLC film, and its wear resistance was also increased. For another example, Wei Dai et al. [26] prepared Cr-DLC films by DC magnetron sputtering. With the increase of Cr content in the carbon matrix, the hardness and elastic modulus of Cr-DLC films decreased, leading to an increase in their friction coefficient and wear rate. However, the effect of mechanical properties on the tribological properties of DLC films does not simply depend on the increase or decrease of hardness (H) and elastic modulus I but also depends on the comprehensive relationship between them. It was found that the H/E value can be used to characterize the wear resistance of materials [132]. If the doping of elements increases the H/E values of DLC films, they will improve the wear resistance and thus improve the tribological properties. As shown in Figure 13, under the doping of different elements, the wear rate of DLC films always decreases with the increase of H/E and increases vice versa.

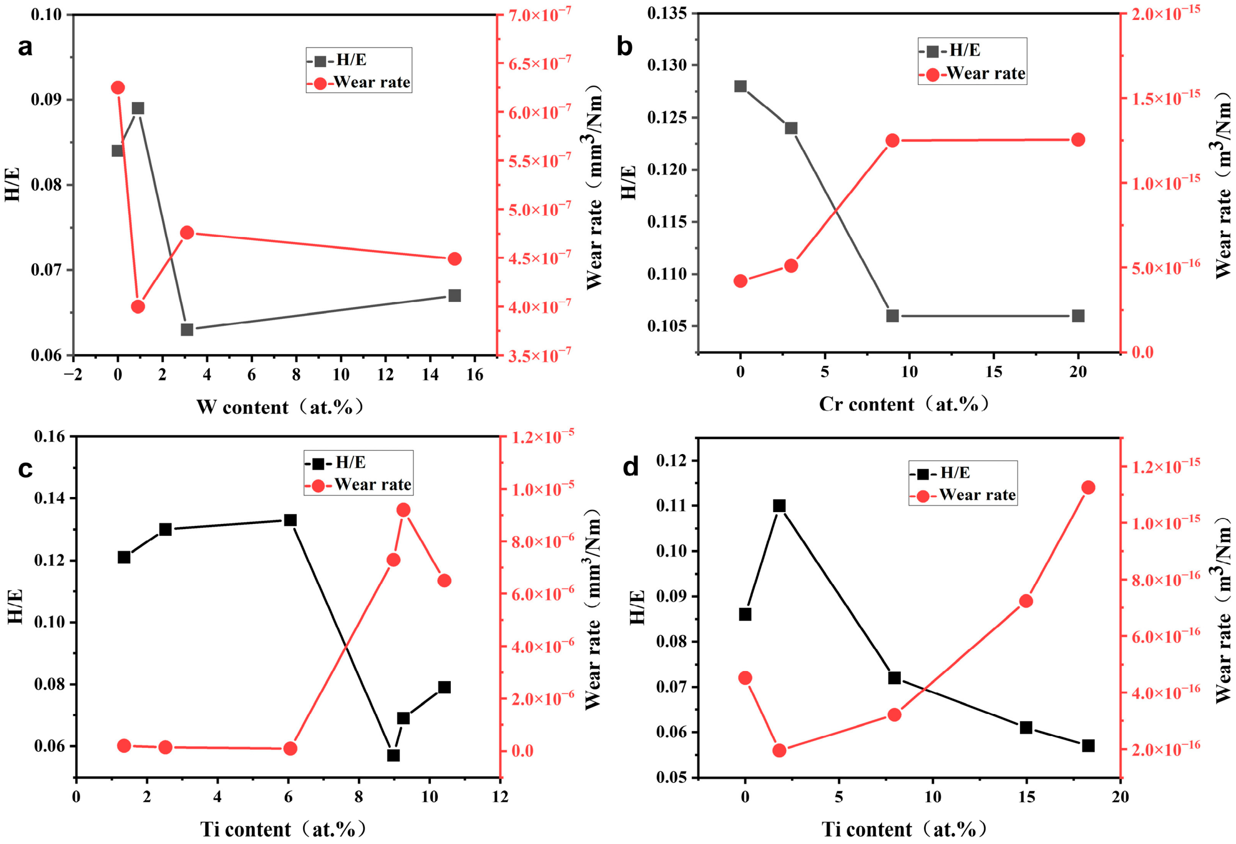

Figure 13. The wear rate variations of DLC films with H/E values. (**a**) [44]; (**b**) [31]; (**c**) [20]; (**d**) [21].

When the carbon matrix is doped with a high content of carbide-forming elements, a large number of hard carbides will be formed. On the one hand, the formation of a large number of carbides leads to the gradual transformation of the DLC film from an amorphous state to a film rich in hard carbides, which destroys the structure of the carbon matrix [21,56] and even seriously deteriorates the mechanical properties of the DLC film. Not only that, but the residual stress of the DLC film will also increase, leading to the easy peeling of hard particles from the substrate, and these act as abrasive particles during rubbing. Therefore, while high content carbide-forming elements are doped in the carbon matrix, the friction and wear of the DLC film will generally increase in the case of no special tribo-films being formed [29,38]. On the other hand, the high content element doping will cause more elements doped to be exposed to the friction surface and react with oxygen to form oxides during the rubbing operation, and the soft oxidized surface will lead to both adhesive and high friction, which will lead to abrasive wear and adhesive wear, resulting in a very unstable friction process [34,54]. The effect mechanisms of the content of carbide-forming elements on the tribological properties of DLC films can be illustrated as in Figure 14.

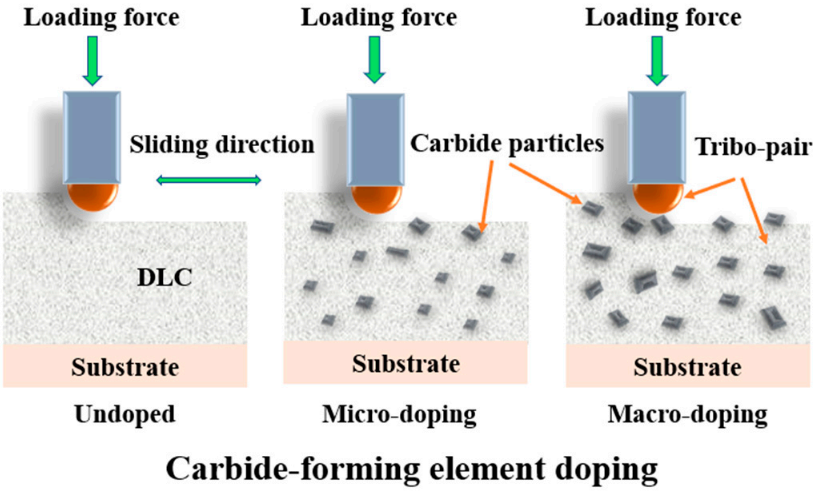

Figure 14. Friction mechanisms of DLC films doped with different contents of carbide-forming elements [21].

However, not all the effects of carbide-forming elements on tribological properties can be attributed to the above trends. Due to the complex friction environment, some carbide-forming elements can react with the surrounding media to form tribo-films with low shear strength, so as to improve the tribological properties of DLC films. For example, Jae-Il Kim et al. [71] doped Si element into ta-C (amorphous tetrahedral carbon film), and the doping of Si changed the film structure from ta-C to a-C:Si:H (hydrogenated amorphous carbon film). The low content of Si doping reduces the hardness of the DLC film and produces more wear debris during rubbing, which leads to abrasive wear and deteriorates the tribological properties of the DLC film. However, when the Si content reaches a certain level, the temperature rise during rubbing will lead to the chemical reaction between the frictional contact surface and water molecules, as shown below:

$$\text{ta-C:Si} + H_2O \rightarrow \text{ta-C}/SiO_x(OH)_y \qquad (1)$$

The low-friction silicon-rich tribo-films of silica sol are formed, which causes a decrease in the friction coefficient. However, the wear rate cannot be reduced due to the decrease in the DLC film hardness. When the Si content exceeds the critical point (about 20 at.%), the DLC film cannot persistently maintain good tribological properties. This is due to the excessive formation of wear debris. They believe that the formation and elimination of wear debris inside the friction interface should be kept in a stable state to stabilize the tribo-film on the wear track. Otherwise, the tribo-film is rapidly destroyed due to the lack of moisture, humidity, mechanical properties, and unstable chemical reaction. Thus, the DLC film cannot maintain good tribological properties for a long time. This indicates that according to the properties of the doping elements, the application environment suitable for the doped DLC films can be found, and vice versa.

Effected by the preparation processes of DLC films, doping elements may form nanostructures in the carbon matrix that improve their mechanical and tribological properties. For example, Fei Zhao et al. [32] prepared Ti-DLC films using hybrid RF-PECVD and unbalanced magnetron sputtering. When the doping content of Ti in the carbon matrix is low (~1.9 at.% and ~2.1 at.%, respectively), TiO_2 clusters form embedded fullerene-like nanostructures with high cross-linking and elastic energy storage capacity on the surface of DLC films, which increases their hardness and adhesion, and improves the toughness and bearing capacity of these DLC films. During rubbing, these structures can be transformed into a structure with low shear resistance, and prevent oxidation of the DLC film, which gives the DLC film better tribological properties. However, the transformation mechanism of the microstructure remains unclear.

In addition to the general operation conditions, the doping of some carbide-forming elements can improve the high-temperature tribological properties of DLC films [133]. Due to the DLC film having high residual stress and low adhesion to the substrates, the adhesion strength between the DLC film and the substrate will further deteriorate when the temperature rises, and the graphitization of the DLC film will be brought about by the temperature rise, which will decrease the wear resistance of the DLC film [52,61]. However, under the combined protection of low-stress and high-hardness carbides, the DLC film can maintain good tribological properties even at elevated temperatures when doped with the appropriate content of doping elements. Guojia Ma et al. [61] found that more TiC is formed in the carbon matrix at high temperatures (300–450 °C), which improved the adverse effect of graphitization of the sp3 phase on the wear properties of the DLC film. Yet, even in the case of an appropriate content of element doping, an excessive temperature will seriously increase the internal stress and reduce the adhesion and wear resistance of the DLC film. At higher temperatures, the deterioration of tribological properties is not only related to the destruction of the DLC film structure but also evaporates substances such as water molecules in the environment, which leads to insufficient passivation of the surface of the tribo-pairs and increases the interaction between atoms, thus reducing the tribological properties [134,135].

4.2. Non-Carbide-Forming Element Doping

By doping the non-carbide-forming elements into the carbon matrix, most of them improve the anti-friction properties by promoting the graphitization of DLC films and forming transfer films on the friction surfaces during rubbing [35,75,82,83,85,93]. For the doping of non-carbide-forming elements to promote the graphitization of DLC films, P.P. Jing et al. [136] used molecular dynamics simulation to reveal that during the deposition of DLC films, the film-forming particles are first deposited on the substrate in the Frank-van der Merwe mode, forming one or two atomic layers, and then shift to the Volmer-Weber mode. In the hybrid mode of the aforementioned two modes, the particles form an island-like structure, which forms loose columnar structures. The island atoms can undergo interlayer diffusion to fill holes and defects, resulting in a denser structure. However, when atoms cross the boundary of an island for interlayer diffusion, it decreases the coordination number of neighboring atoms, leading to the creation of Ehrlich–Schwoebel (ES) barriers [137,138]. Simulation results show ES barriers for interlayer diffusion of 0.60 eV and 3.46 eV for Ag and C, respectively, indicating that Ag atoms easily undergo interlayer diffusion. The interlayer diffusion of Ag atoms causes a decrease in the coordination number of neighboring atoms, which also leads to a shift from high to low coordination number of C atoms, i.e., sp3→sp2 rearrangement, and, eventually causes an increase in the graphitization content in DLC films. However, the mechanism of graphitization of DLC films caused by doping of non-carbide-forming elements such as Cu and Al still needs to be further studied. Although friction-induced graphitization reduces the friction coefficient of the tribosystems, it usually leads to an increase in the wear rate of DLC films [37,84]. However, not all non-carbide-forming elements doping conform to these conclusions, and the tribological properties of DLC films are also related to the preparation process and the content of doping elements. A. F. Ytim et al. [81] used the PVD process to prepare Al-DLC films, and the results show that Al doping increased the relative content of the sp3 phase and the denseness of these DLC films. Compared with undoped DLC film, Al-DLC films had higher hardness, and although the friction coefficients of the tribosystems are relatively high, the wear rates are reduced. Many studies have also found that in the preparation of DLC films, applying bias on the substrate can provide enough energy to the incident particles penetrating the subsurface and increase local density, leading to the conversion of the sp2-C bond to sp3-C bond, thus increasing the hardness, elastic modulus and other mechanical properties of DLC films [24,82–84]. Similarly, although these result in a high friction coefficient of the tribosystems, it greatly reduces the wear rate of the DLC film. Therefore, the mechanical properties of DLC films, such as hardness and elastic modulus, are closely related to their tribological properties. High hardness or high yield strength can reduce adhesion and deformation during rubbing and achieve better tribological properties [139].

Most doping non-carbide-forming elements tend to reduce the mechanical properties of DLC films, as the data shows in Table 1. Due to the tribological properties being affected by the mechanical properties of DLC films, the wear rate of DLC films increases significantly with the decrease in hardness and elastic modulus. According to the data of Ag-1 and Ag-2, under different preparation processes, with the increase of Ag content, the hardness of DLC films shows an opposite change trend, which also indicates that the preparation processes of DLC films have a great effect on their mechanical properties, thus affecting their tribological properties. From the data of Ag-1, it can be seen that even if the friction coefficient of the tribosystems increases, their wear rate decreases with the increase in hardness. As for the data of Al-2, by calculating the ratio of hardness to elastic modulus (H/E) of Al-DLC films, it is found that the H/E values decrease with the increase of Al content in the carbon matrix, and the wear rates show an opposite trend with the change of H/E values.

However, it can also be seen from the data of Cu-1 in Table 1 that the hardness and elastic modulus of Cu-DLC films decrease with the increase of Cu content, and the calculated H/E values also gradually decrease, but the wear rates of Cu-DLC films are greatly reduced because "rod-like debris" is formed on the wear surface of Cu-DLC films [75]. Weak interaction between Cu and C, which easily leads to the precipitation of Cu from the carbon matrix during rubbing and accumulates to form "rod-like debris", thus reducing friction and wear. Table 1 shows that the tribological properties of DLC films are affected by many factors. When one aspect of the properties deteriorates, the tribological properties of DLC films do not necessarily decrease by reason of the forming of phases with low shear strength.

Table 1. Properties data of DLC films doped with non-carbide-forming elements.

Doping Element and Preparation Method	Doping Content (at.%)	Hardness (GPa)	Elastic Modulus (GPa)	Residual Stress (GPa)	I_D/I_G	Friction Coefficient	Wear Rate ($mm^3/N \cdot m$)	Ref.
Al-1 Unbalance reactive magnetron sputtering	0	~22.5		~1.37	~1.69	~0.07	$\sim 4.9 \times 10^{-7}$	[36]
	0.37	~22.2		~1.34	~1.71	~0.068	$\sim 4.3 \times 10^{-7}$	
	2.3	~19.8		~0.73	~1.78	~0.06	3.1×10^{-7}	
	7.8	~9.9		~0.48	~1.94	~0.085	$\sim 2 \times 10^{-6}$	
	19.3	~6.2		~0.34	~2.15	~0.12	$\sim 2.5 \times 10^{-6}$	
Al-2 ALIS and magnetron sputtering	0	~24.6	~228	~2.65	~0.43	0.113	$\sim 1.5 \times 10^{-8}$	[35]
	0.68	~17.5	~155	~1.6	~0.94	0.089	$\sim 6.4 \times 10^{-8}$	
	6.93	~11.6	~127	~0.65	~1.23	~0.032	$\sim 7.6 \times 10^{-8}$	
	11.04	~11	~125	~0.7	~1.28	~0.026	$\sim 1.05 \times 10^{-7}$	
	17.6	~8.5	~118	~0.2	~1.41	0.024	$\sim 1.27 \times 10^{-7}$	
Cu-1 High-power impulse magnetron sputtering	0	~21.2	~140	~2.24	0.84	~0.125	$\sim 1.2 \times 10^{-7}$	[75]
	3.19	~19.5	~113	~1.8	0.93	~0.105	$\sim 4.6 \times 10^{-8}$	
	8.21	~17.4	~111	~1.75	1.06	~0.1	$\sim 4.1 \times 10^{-8}$	
	11.28	~15	~106	~1.3	1.10	~0.085	$\sim 1.9 \times 10^{-8}$	
Ag-1 High-power pulsed plasma vapor deposition	0	~8.6		~0.5		~0.12	$\sim 1.18 \times 10^{-6}$	[91]
	0.4	~8.8		~0.75		~0.17	$\sim 2.8 \times 10^{-7}$	
	2.41	~11		~0.83		~0.2	$\sim 1.1 \times 10^{-7}$	
	2.99	~12.8		~1.3		~0.15	$\sim 6 \times 10^{-8}$	
Ag-2 DC magnetron sputtering	0	12.9		2.3	1.5	0.1	$\sim 0.075 \times 10^{-6}$	[37]
	1.3	13.0		2.4	1.4	0.12	$\sim 0.1 \times 10^{-6}$	
	6.1	12.0		2.2	1.6	0.13	$\sim 0.13 \times 10^{-6}$	
	13.1	9.3		1.4	2.0	0.2	$\sim 0.19 \times 10^{-6}$	

Similarly, P.P. Jing et al. [91] prepared Ag-DLC films by employing high-power pulsed plasma vapor deposition, and also found “rod-like debris” on the friction surface, as shown in Figure 15. Compared with undoped DLC films, Ag-DLC films have lower friction coefficients and significantly lower wear rates. Due to the weak interaction between Ag and C, Ag is easily precipitated from the carbon matrix during rubbing. Moreover, the friction process promotes the release of H from the friction region, which accelerates the graphitization of the DLC film. “Rod-like debris” formed by the graphitized layer and migrating Ag not only reduced the direct contact between tribo-pairs but also changed the contact mode from sliding to rolling, which reduced the wear rate of the DLC film. Later, the work of [90] prepared Ag-DLC films by using high-power pulsed magnetron sputtering (HPPMS) and high-power pulsed plasma-enhanced chemical vapor deposition (HPP-PECVD). When Ag content in the carbon matrix is 3.2 at.%, the DLC film shows excellent wear resistance, which is also attributed to the formation of “rod-like debris”.

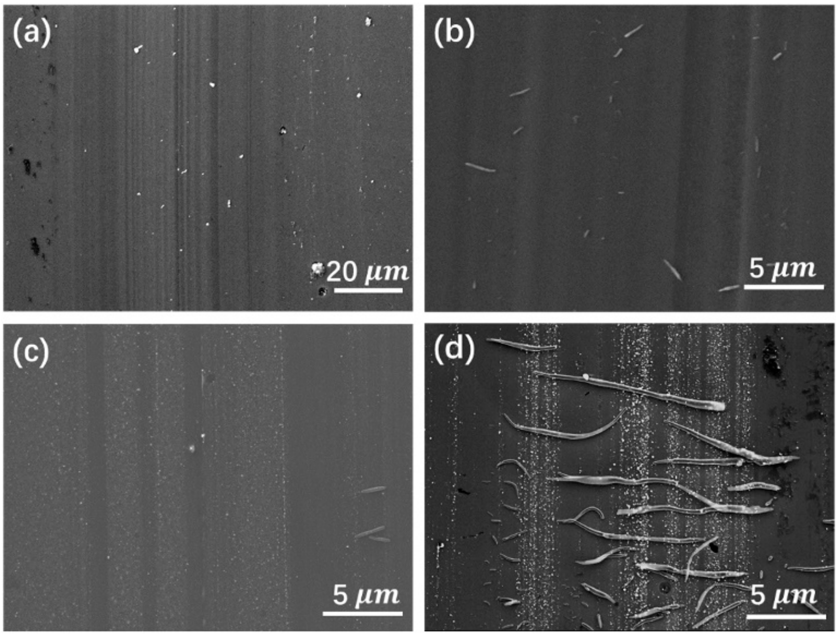

Figure 15. SEM image of wear track of Ag-DLC films [91]. (**a**) DLC film; (**b**): Ag-DLC film (0.40 at.% Ag); (**c**) Ag-DLC film (2.41 at.% Ag); (**d**) Ag-DLC film (2.99 at.% Ag). Reprinted from Vacuum, Volume 173, Copyright (2020), with permission from Elsevier.

Not only that, N.K. Maanninen et al. [37] also studied the properties of Ag-DLC films. Although no “rod-like debris” was found, SEM characterization showed that Ag gathered on the wear track of Ag-DLC films. This is mainly due to the low compatibility of precious metals with the carbon matrix. During rubbing, Ag diffuses on the friction surface, and Ag segregates in the subsurface layer, and finally accumulates in the wear track. This explains why P.P. Jing et al. [91] found “rod-like debris” in the wear track of Ag-DLC films. The structure of Ag-DLC film and the formation process of “rod-like debris” are shown in Figure 16. However, according to the literature [37], the precipitation of Ag cannot improve the tribological properties of the DLC film but leads to an increase in the friction coefficient and wear rate, which may be related to the differences in microstructure and mechanical properties of DLC films caused by different preparation processes. In contrast, it was found that the Ag-DLC films prepared by P.P. Jing et al. [91] by high-power pulsed plasma vapor deposition has higher hardness than the undoped DLC film, while the Ag-DLC films prepared by magnetron sputtering in reference [37] has a lower hardness than the undoped DLC film. This proves the close relationship among mechanical properties, preparation processes, and tribological properties of DLC films.

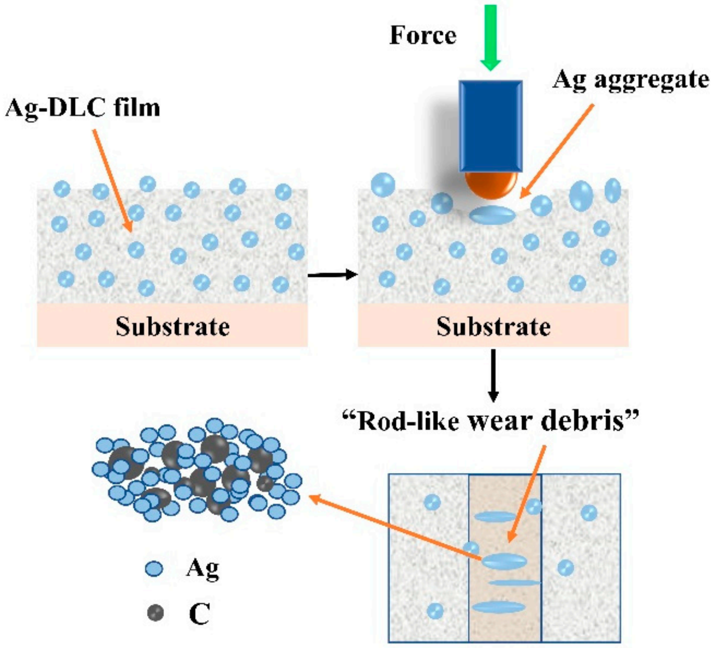

Figure 16. Schematic diagram of Ag segregation and the formation of "rod-like debris" during rubbing [37,91].

4.3. Multielement Doping

In general, carbides formed by carbide-forming elements in the carbon matrix are beneficial to improve the hardness reduction caused by graphitization of DLC films, but overmuch carbides easily act as abrasive particles during rubbing and increase wear. The doping of non-carbide-forming elements will reduce the hardness of DLC films, which will cause greater wear. However, during rubbing, DLC films doped with non-carbide-forming elements are prone to form transfer films with low shear strength or other tribo-films that helps to reduce the friction coefficient. Generally speaking, the doping of a single element has difficulty improving the comprehensive properties of DLC films. Researchers have tried to dope various elements in the carbon matrix and made use of their complementary effects to overcome these problems.

As discussed above, the doping of multi-elements can improve the mechanical properties of single-element doped DLC films, which can also improve the tribological properties of these films. For example, reference [122] reported that the doping of element B improved the hardness of Ni-DLC film, which also resulted in better tribological properties of Ni/B-DLC film. The doping of element B makes the structure of the DLC film smoother and more dense, and increases the microhardness and critical load of the DLC film. In addition, the formation of an appropriate amount of a hard B_4C phase stably embedded in the carbon matrix, can play a supporting and bearing role during rubbing, and improve the tribological properties of the DLC film. For another example, reference [115] reported that an appropriate content of Ti (1.6 at.%) doping improved the hardness and elastic modulus of Ag-DLC film, so that the Ti/Ag-DLC film had better mechanical properties, wear resistance, and plastic deformation resistance, eventually resulting in the DLC film having better tribological properties. For example, in the study of [123], under the condition that the content of Ti (0.3 at.%) in the carbon matrix remains unchanged when the doping content of W in the carbon matrix is 2.6 at.%, the hardness and elastic modulus of the DLC film can be increased without significantly increasing the residual stress, which gives the DLC film a low wear rate. Similarly, no matter whether it is co-doped with carbide-forming elements and non-carbide-forming elements, or co-doped with carbide-forming elements, under the condition that the content of one doping element remains unchanged, the content of the other doping elements should be appropriate, otherwise excessive element doping will deteriorate the tribological properties of DLC films. For example, Wei Dai et al. [99] studied DLC films doped with different Al, Si, and Cr content. The high content of doping elements leads to a large number of hard carbides formed in the carbon matrix. Although hard carbides increase the hardness and elastic modulus of the DLC film, they will cause abrasive wear during rubbing, resulting in a high friction coefficient and wear rate.

In addition to mechanical properties, the effect of multi-element doping on tribological properties is also similar to that of single-element doping, including graphitization transfer film, surface passivation, and interaction between doping elements and surrounding media. For example, Cuicui Kong et al. [129] prepared Al/Ti-DLC films using a deposition system consisting of a linear ALIS and DC magnetron sputtering. The results show that when the content of Al and Ti in the carbon matrix is 4.78 at.% and 10.06 at.%, respectively, the DLC film has better tribological properties. The reason is that the graphitized carbon of the DLC film forms a continuous and tight transfer film with TiC in the carbon matrix and Al_2O_3 formed by oxidation. In addition, the transfer film enriched with metal carbides and oxides can prevent the invasion and destruction of the cross-linked carbon network by oxygen, and prevent oxidative damage to the structure and properties of the DLC film. As a result, good tribological properties can be maintained.

In terms of the mechanism by which the passivation of dangling bonds on the surface of DLC films can improve the tribological properties, Yong Zhou et al. [128] prepared Al/Ti-DLC films by ALIS. The study found that when the Al and Ti content in the carbon matrix is 5.34 at.% and 1.83 at.%, respectively, the DLC film had better tribological properties. However, in the tribotest within 30 min, the friction process does not lead to graphitization of the friction surface of the DLC film, and no transfer film is formed on the friction surface, but the DLC film has a relatively smooth surface. As for the causes of smooth surfaces, Holmberg et al. [140] modeled and simulated the friction and wear properties of coatings, and pointed out that hydrogenation of dangling bonds on the surface of DLC films may be an important factor leading to smooth surfaces. In addition, some studies have found that the passivation of dangling bonds on the surface of thin films can improve their tribological properties [75,131]. Therefore, in reference [128], the better tribological properties of the Al/Ti-DLC film can be explained by the passivation of dangling bonds. The high temperature generated in the friction process leads to the fracture of the C-H bond on the friction surface, and the release of H and other gas-reactive substances leads to the formation of a passivation layer at the friction surface, which effectively reduces the interaction of atoms, thus having good tribological properties. Besides, Yang Wang et al. [141] carried out a molecular dynamic simulation of friction of DLC films in an H_2 environment. The H in the environment can continuously passivate the carbon exposed on the surface of DLC films, thus greatly reducing the surface adhesion and mechanical wear of DLC films.

The interaction between doping elements and surrounding media also affects the tribological properties of DLC films. Xubing Wei et al. [102] prepared a series of Si- and F-doped hydrogenated DLC films by planar cathode PECVD. The results show that the doping of Si and F can reduce the friction coefficient of these DLC films. On the one hand, the doping of Si can increase the oxygen content in DLC films and form silica-rich oxides on DLC film surfaces. On the other hand, the Si-OH group on the surface of DLC films can absorb water molecules and reduce the shear strength between the friction surfaces. However, the doping of F and Si will form -CF2 and -CF3 groups that reduce the structural density of the carbon network, as well as Si-H and Si-Si bonds with weak bond strength, which weaken the matrix of the DLC film and lead to a high wear rate [142].

5. Other Properties

5.1. Corrosion Resistance

The corrosion resistance of DLC films is closely related to their structure, and the dense structure of DLC films can prevent the penetration of corrosive media, which improves their corrosion resistance. It has been discussed above that applying bias can promote the transformation of sp2-C to sp3-C and increase the structural denseness of DLC films, and this structural transformation can also increase the corrosion resistance of DLC films. Sara Khamseh et al. [42] applied bias to the substrate when preparing Nb-DLC films by the PVD method. The results show that in the case of applying bias, the structure of Nb-DLC films became more dense with the increase of bias, and the corrosion resistance of the DLC film also increased. In addition, high sp3-C content is not the only way to increase the denseness of DLC films. For example, Sara Khamseh et al. [78] found that Cu doping reduced the content of sp3-C of the DLC film, but when the high-density Cu nanoparticles are embedded in the carbon matrix, it could also increase the density of the DLC film and prevent the corrosive medium from penetrating the substrate, thus improving the corrosion resistance of the DLC film. For another example, the doping of Ag and Al can reduce the defects and porosity in DLC films, which not only effectively prevents the penetration and corrosion of salt ions but also increases the obstruction of charge transfer at the interface between the DLC film and the substrate, thus improving the corrosion resistance of the DLC film [90,143]. Xiaowei Xu et al. [143] also found that when the DLC film has a high content of Al, it is conducive to the formation of Al corrosion products, which can fill the micropores caused by pitting in the defect area of the DLC film, prevent further corrosion of the DLC film, and thus improve the corrosion resistance of the DLC film. On the contrary, if the doping elements destroy the carbon network structure or lead to excessive graphitization of the DLC film, the corrosion resistance of the DLC film will be reduced. The destruction of the carbon network structure of the DLC film cannot effectively prevent the diffusion of a corrosive medium into DLC film, while the high electrical conductivity of graphitic carbon will increase the corrosion current, which will accelerate the diffusion of corrosive ions between the DLC film and the substrate interface, thus reducing the corrosion resistance of the DLC film. For example, N.W. Khun et al. [96] prepared Ni-DLC films by DC magnetron sputtering. Due to the poor stability of Ni in the salt solution, nickel chloride may be generated by Ni atoms through the following reactions:

$$\mathrm{Ni} + 2\mathrm{H}^{+} \rightarrow \mathrm{Ni}^{2+} + \mathrm{H}_2 \tag{2}$$

$$\mathrm{Ni}^{2+} + 2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Ni(OH)}_2 + 2\mathrm{H}^{+} \tag{3}$$

$$\mathrm{Ni}^{2+} + 2\mathrm{Cl}^{-} \rightarrow \mathrm{NiCl}_2 \tag{4}$$

This leads to the dissolution of the DLC film. Not only that, Ni doping destroys the cross-linking structure of the sp3-C bond and increases the relative content of the sp2-C phase in the DLC film, which will increase the electrical conductivity of the DLC film. The corrosion current increases with the increase of the DLC film conductivity and accelerates the dissolution of the DLC film. The accumulation of Ni will also destroy the cross-linking structure of the amorphous carbon matrix, and the metal-carbon interface formed in the DLC film increases the possibility of electrolyte penetration into the substrate, thus reducing the corrosion resistance of the DLC film.

The reduction of residual stress also plays an important role in improving the corrosion resistance of DLC films. Due to the high residual stress of DLC film, it is easy to peel off and internal cracks can easily occur in the DLC film, as shown in Figure 17a, which makes the corrosion medium easy to penetrate and leads to weak corrosion resistance. The reduction of residual stress will increase the combination strength of the DLC film with the substrate and reduce the tendency of cracks in the DLC film, thus improving the corrosion resistance of the DLC film. For example, P.P. Jing et al. [90] found that the doping of Ag reduced the residual stress of the DLC film, which not only inhibited the formation and propagation of cracks but also improved the adhesion stability between the DLC film and the substrate, effectively reducing the spalling corrosion of the DLC film.

The protective layer can also hinder the erosion of DLC films by corrosive media. Sara Khamseh et al. [42] prepared Nb-DLC films by using PVD and applying bias to the substrate. The results show that the corrosion resistance of DLC films increases with the increase of Nb content. Although bias can improve the corrosion resistance of DLC films by increasing their structural denseness, without bias, the content of Nb in the carbon matrix is higher and has better corrosion resistance. This is probably due to the formation of a passivation layer composed of NbC and Nb oxides on the DLC film surface at a high content of Nb, which improves the corrosion resistance of the DLC film. Xubing Wei et al. [102] found that Si doping on the one hand would increase the H content in the DLC film to promote the stability of the sp3-C structure. On the other hand, the oxygen content in the DLC film will be increased, which will lead to the formation of an insulating silicon oxide layer with good corrosion resistance on the surface of the DLC film, so that the DLC film has good corrosion resistance. Studies [50] have found that the doping of the Cr element will lead to the following reactions during electrochemical corrosion:

$$\text{cathode: } O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{5}$$

$$\text{anode: } Cr - 3e^- \rightarrow Cr^{3+}, Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3 \tag{6}$$

The formation of water-insoluble, colloidal $Cr(OH)_3$ can protect the DLC film from corrosion.

To sum up, the main mechanisms of element doping affecting the corrosion resistance of DLC films are as follows: (1) Carbides formed by doping elements and their oxidation products on the surface of DLC film form a more dense protective layer that is difficult to be corroded by electrochemistry, which slows down the corrosion process of DLC films, as shown in Figure 17b. (2) DLC film has high internal stress, high cracking tendency, and a certain number of structural defects. Therefore, another mechanism for element doping to improve its corrosion resistance is to reduce its residual stress, increase the density of the structure of the DLC film, and prevent the corrosion medium from diffusing into the DLC film for internal corrosion, as shown in Figure 17c. (3) The doping of some elements can stabilize the sp3 phase in the DLC film and reduce the relative content of the conductive sp2 phase, which can not only prevent the structure of DLC film from being destroyed but also reduce the corrosion current so that the DLC film has better corrosion resistance.

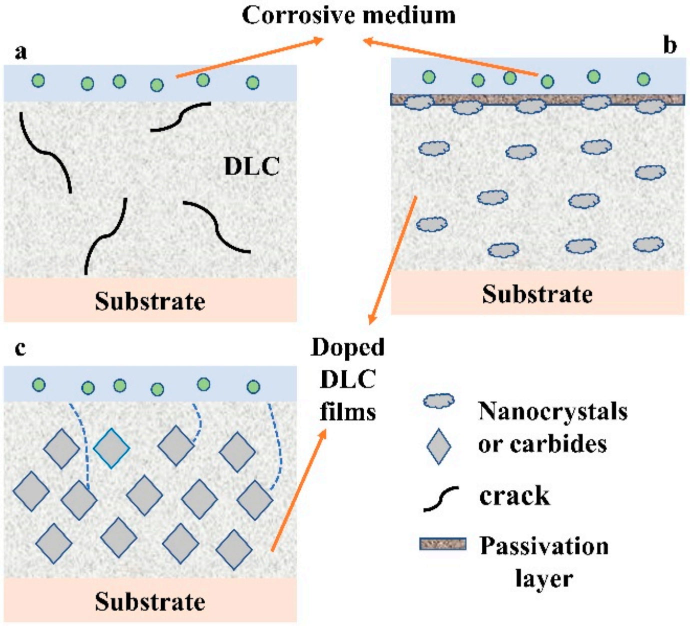

Figure 17. Influencing factors of corrosion resistance of DLC films. (**a**) Crack; (**b**) Passivation layer; (**c**) Dense structure [78].

5.2. Hydrophobic Properties

Surface morphology, surface energy, and surface chemicals have a great effect on the hydrophobic properties of DLC films. The study on the effect of element doping on the hydrophobic properties of DLC films can be mainly focused on two aspects: (1) The change of surface energy caused by the evolution of carbon bond hybridization; (2) The change of surface roughness. It has been shown that graphite surface has lower surface energy ($\sigma^{(001)}$ = 1.14 J/m^2) and a larger water contact angle (θ = 86 ± 2°) due to the absence of dangling bonds; the diamond surface has higher surface energy ($\sigma^{(111)}$ = 5.4 J/m^2) and a smaller water contact angle (θ = 39 ± 2°) due to more dangling bonds [144,145]. However, the sp3-C in the DLC film has the properties of diamond, so the DLC film with a high content of sp3-C will lead to more dangling bonds on the surface of the DLC film, which will lead to a high surface energy on the DLC film surface and a reduction in the hydrophobic properties of the DLC film [146]. Inversely, the DLC film with higher sp2-C content will have better hydrophobic properties. Similarly, if the dangling bonds on the DLC film surface are terminated, the surface energy of the DLC film can also be reduced, which can improve the hydrophobic properties of the DLC film. In addition, the surface roughness of DLC films mainly affects their hydrophobic properties by trapping air on the rough surface and forming an air film between the water droplets and the material to prevent the liquid from wetting the material. Masashi Miwa et al. [147] found that when the structures of surface rough peaks have an appropriate interval and height, they can capture enough air to construct the hydrophobic surface; otherwise, they cannot capture enough air, resulting in reduced hydrophobic properties.

The doping of some elements will increase the roughness of DLC films or change the hybrid state of carbon to improve the hydrophobic properties of DLC films. For example, Ji Cheng Ding et al. [86] prepared Al-DLC films by HiPIMS and pulsed direct current (PDC) sputtering and found that with the increase of Al content from 0 to 16.6 at.%, the water contact angle of Al-DLC films increased from 68.8° to 107.7°. On the one hand, the doping of Al increases the surface roughness of the DLC film, and the rough surface captures air to form a hydrophobic surface. On the other hand, Al doping increases the sp2-C content in DLC films, and the surfaces rich in sp2-C reduce the surface energy by reducing the dangling bonds on the DLC film surface, thus increasing the hydrophobic properties of the DLC film. However, this does not mean that the increase in I_D/I_G of DLC films will necessarily reduce the surface energy of DLC films or improve their hydrophobic properties. Keke Meng et al. [148] showed that the water contact angle and surface energy of DLC film exhibit non-monotonicity with I_D/I_G, that is to say, relying solely on the hybridization state alone cannot fully describe the surface wettability of DLC films, and the surface energy and water contact angle are also related to the content and type of sp2-C clusters and the degree of distortion of sp2-C rings. The sp2-C hybridization exists mainly as aromatic rings and olefinic chains and gathers into clusters by π-bonds. With the increase of sp3-C in DLC films, the sp2-C rings tend to break and form isolated C=C short chains instead of -CH$_n$-long chains, and the C=C bonds have strong polar interactions with water [149]. Therefore, the distortion of the sp2-C ring in DLC films and the reconstruction of the C=C bond increase the polar interactions on the surface of DLC films. Although the change of sp2-C content of DLC films will affect the surface energy of DLC films, it also depends on the type and distortion degree of sp2-C. Thus, the surface energy as well as the wettability of DLC films cannot depend only on the I_D/I_G value. Guojia Ma et al. [61] prepared Ti-DLC film (Ti content 5.3 at.%) by reactive magnetron sputtering and PSII. Due to Ti doping reducing the surface energy of the DLC film and increasing its surface roughness, the water contact angle of the DLC film increased from 70° (without doping) to 104.2°, and the hydrophobic properties of DLC film have been improved, as shown in Figure 18.

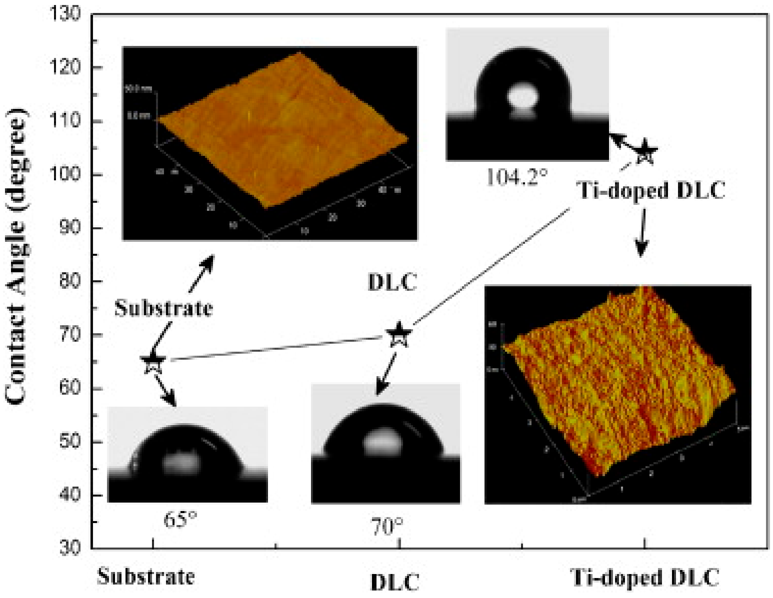

Figure 18. The changing trend of the water contact-angle on different samples and corresponding AFM pictures [61]. Reprinted from Applied Surface Science, Volume 258, Copyright (2012), with permission from Elsevier.

Since water is a polar molecule, its electric dipole is usually attracted by polar components on the solid surface, which will reduce the water contact angle, so the surface containing polar components shows poor hydrophobic properties. Nevertheless, the doping of some elements can reduce these polar components to improve the hydrophobic properties of the DLC film surface. Peng Guo et al. [80] and Lili Sun et al. [100] found that Cu doping could not only improve the hydrophobic properties of DLC films by increasing the content of sp2-C in the carbon matrix and increasing the surface roughness but also improve the hydrophobic properties of DLC films by forming Cu oxides on the surface of DLC films. This is mainly because the water molecule is attracted to polar components on the surface of DLC films, and polarity has a strong relationship with electronegativity, and the electron cloud will be biased towards the more electronegative atoms, showing the polarity. Nevertheless, Cu has low electronegativity, and its oxide has even lower electronegativity. Therefore, Cu doping and the generation of Cu oxide can reduce the surface energy by reducing the polar components on the surface of the DLC film, thus improving the hydrophobic properties of the DLC film.

Although the above studies have obtained the effect rules of surface energy and surface roughness on the hydrophobic properties of DLC films, there are still different understandings about the effect degree of surface energy and surface roughness on the hydrophobic properties of DLC films. Studies have shown that although the content of sp2-C in DLC film decreases, the hydrophobic properties increase with the increase of the roughness of the DLC film. For example, Ji Cheng Ding et al. [84] used HiPIMS and pulsed DC magnetron sputtering to prepare Al-DLC films. The results show that although the relative content of sp2-C in DLC films decreases due to Al doping, the hydrophobic properties of DLC films increase with the increase of their roughness. Therefore, it is inferred that reducing the surface energy by reducing the dangling bonds on the DLC film's surface by high sp2-C bonding has a minor effect on the hydrophobic properties of DLC films, while the roughness has a dominating effect on the hydrophobic properties of DLC films. However, some studies have shown that although the roughness of DLC films is reduced, the reduction of surface energy caused by the termination of dangling bonds on the DLC film's surface improves the hydrophobic properties of the DLC film. For example, Jae-Il Kim et al. [71] prepared Si-DLC films using trimethylsilane (TMS) as raw material and filtered cathode vacuum arc (FCVA) technology. The results show that, although Si doping reduces the surface roughness of DLC films, their surface energy is lower, which improves the hydrophobic properties of DLC films. It mainly contributed to the Si-, Si-CH_3, and CH_3 produced by the decomposition of TMS gas terminating the dangling bonds on the DLC film surface to further reduce the surface energy. In any case, the analysis shows that both the decrease in surface energy and the increase in roughness can improve the hydrophobic properties of DLC films.

5.3. Antioxidation Properties

Oxidation behavior will destroy the structure of DLC films, and promote their graphitization, resulting in the reduction of their mechanical properties [150,151]. However, there are not many studies on the mechanism of the effect of oxidation on the properties of DLC films, and there are relatively few studies on the antioxidation properties of DLC films by element doping. Li Ji et al. [49] prepared Mo-DLC film by unbalanced magnetron sputtering of molybdenum combined with plasma chemical vapor deposition and studied the effect of atomic oxygen (AO) irradiation on the properties of undoped DLC film and Mo-DLC film. It was found that doping Mo could improve the antioxidation degradation ability of the DLC film. The MoC particles formed in the carbon matrix can preferentially react with O, and form a MoO_3 protective layer on the DLC film surface to prevent O from invading and reacting with C, thus enhancing the oxidation resistance of the DLC film while maintaining its inherent structure and excellent properties. Cuicui Kong et al. [129] prepared Al/Ti co-doped DLC films by linear ALIS and DC magnetron sputtering. The doping of Al and Ti elements can form a “protective layer” containing metal carbide or oxide on the DLC film’s surface, which prevents O from invading and destroying the cross-linked amorphous carbon network. Moreover, the improvement of antioxidation properties can maintain good structure and mechanical properties of DLC films, and improve their tribological properties and service life.

5.4. Antibacterial Properties

Due to the advantages of good biocompatibility, corrosion resistance, and wear resistance, DLC films also have potential application value in the medical field, such as for artificial joints. Good antibacterial properties can reduce the adhesion of bacteria on human implants, so the antibacterial properties of DLC films are also important factors that must be considered when they are applied in the medical field. Studies on DLC films show that the antibacterial properties are mainly related to their surface energy, surface chemical composition, and surface roughness. In terms of the effect of surface energy on the antibacterial properties of DLC films, K. Baba et al. [23] prepared Ag-DLC films by combining reactive magnetron sputtering with PSII and tested the antibacterial properties with staphylococcus aureus. The results showed that Ag doping improved the antibacterial properties of DLC films. Because the Ag doping increases the water contact angle of DLC films, it indicates that the surface energy of DLC films decreases, and low surface energy is adverse to the adhesion of bacteria on the DLC film’s surface. Some studies [152,153] have shown that there is a linear relationship between bacterial adhesion and surface free energy, and the lower the surface free energy of the DLC film is, the less conductive to bacterial adhesion, thus improving the antibacterial properties. In addition, the doping of Ag also increases the relative content of sp2-C in DLC films, and studies [154,155] have shown that bacterial adhesion decreases with the decrease of the sp3/sp2 value. From the aspect of surface energy, it may be that the increase of sp2-C content reduces the surface energy of DLC films and reduces the adhesion of bacteria, thus showing better antibacterial properties. Hao Wang et al. [24] prepared Ag-DLC films by using the dual-targets HiPIMS. With the increase of Ag content in the carbon matrix, the I_D/I_G value of DLC films increased gradually, and the antibacterial properties of DLC films against escherichia coli and staphylococcus aureus also improved. This result shows that the antibacterial properties are closely related to the value of sp3/sp2 of DLC films. Although roughness is not a decisive factor affecting the antibacterial properties [23,156], it also has a certain effect on the adhesion of bacteria. Generally speaking, the rough surface has a larger surface area, which leads to more bacterial adhesion, and the bacterial adhesion decreases with the decrease of surface roughness. However, the contribution degree of surface energy and roughness to antibacterial properties has not been clearly explained.

In fact, in biomedicine, a large number of studies [157–159] have shown that Ag nanoparticles have high inactivation properties for many viruses and bacteria. The good antibacterial properties of Ag nanoparticles are closely related to the release of Ag ions, which can penetrate the bacterial cell wall and interact with the negative part of the bacteria, hinder bacterial growth, and cause bacterial death. In addition, the smaller the size of Ag nanoparticles, the easier they are to diffuse and penetrate bacterial cells, and the more significant the antibacterial properties there are. Therefore, the antibacterial properties of Ag-DLC films cannot be attributed solely to their adhesion properties to bacteria, which also indicates that chemical properties have a significant impact on the antibacterial properties of DLC films. C. Liu et al. [160] prepared DLC, N-DLC (N content 1~2 at.%) and Si-DLC (Si content 6~8 at.%) films by magnetron sputtering, and studied the adhesion of different DLC films to pseudomonas aeruginosa (ATCC 33,347). The results show that the higher the content of N in N-DLC film, the better the antibacterial properties of the DLC film, while the antibacterial properties of Si-DLC film increase with the decrease of Si content, and the effect of N doping on the antibacterial properties of DLC film is more prominent. It also reflects that the chemical properties of the DLC film surface have an important effect on the antibacterial properties. In addition, Mg, Cr, Co, and Ni elements all have good antibacterial properties [161], but there are relatively few studies on the antibacterial properties of DLC films doped with these elements.

5.5. Biotribological Properties

Some studies have shown that element doping can improve the biocompatibility of DLC films. For example, low-concentration Cr-doped DLC films are conducive to the differentiation of osteoblasts, while high-concentration Cr-doped DLC films are conducive to cell adhesion [162]. The doping of F reduces the adhesion of DLC films to platelets, which prevents the formation of thrombi, significantly improves their blood biocompatibility, and facilitates their application in medical devices [163]. These have led to a wide application in biomedical for DLC films, such as artificial heart valves [164], coronary stents [165,166], artificial joints [167], etc. Infection caused by multiple etiologies and aseptic loosening of endoprosthesis caused by wear particles of implant materials will shorten the service life of artificial joints [168]. In addition, metal ions released from metal prostheses promote toxic tissue reactions when they exceed certain toxicity limits in the human body [169], which is detrimental to biocompatibility, so the application of coatings with good biocompatibility and biotribological properties on the surface of artificial joints is an effective approach to improve their durability [170]. Coincidentally, DLC films have a low coefficient of friction and high hardness which provides unique advantages in artificial joints, and numerous studies have shown that the application of DLC films on the surface of artificial joint materials significantly reduces their wear [171–173]. Therefore, the study of the biotribological properties of DLC films is also particularly important.

In the study of biotribological properties of DLC films, Benedict Rothammer et al. [174] deposited ta-C film on CoCr, Ti64, and ultra-high molecular weight polyethylene (UHMWPE) substrates using the PVD technique. The cells adhere well to the film surface and the application of the films significantly reduces the wear of the tribopairs. These results indicate that ta-C film is beneficial to prolong the service life of the artificial prosthesis. However, the film is prone to crack on the UHMWPE substrate, and the crack extension may lead to the local failure of the film. A detailed explanation for the crack generation is provided by Benedict Rothammer et al.: the increase in temperature during film deposition leads to significant thermal expansion of the polymer, and greater shrinkage of the polymer substrate on cooling, so the substrate is under tensile stress at the film-substrate interface, and the film has high compressive stress due to the high sp3-C content. Therefore, under frictional cyclic stress, fracture and shear occur at the highest stress location within the film and at the film-substrate interface, which is also an important wear mechanism for DLC films in this application condition. For films, it is necessary to maintain high hardness to maintain wear resistance and prevent adhesive wear, but for softer substrates, it is necessary to reduce the hardness and internal stress of the film to accommodate the deformation of the softer substrate and to prevent surface fatigue. Then, the doped DLC films can be effectively utilized. As discussed above, trace amounts of elements doped in the carbon matrix can reduce the residual stress while maintaining the hardness of the DLC films, which is conducive to increasing the adhesion of DLC films to the substrate and reducing cracking. This conclusion can also be supported by the previous experimental biotribological studies of a-C:H:W and a-C:H by Benedict Rothammer et al. [175,176]. The results show that the doped DLC films not only present good adhesion to the substrate, good biocompatibility, and mechanical properties, but also the DLC films do not exhibit large wear particles, delamination or spalling, nor signs of cracking and fatigue, providing the possibility to extend the service life of the implants. In addition, A. Escudeiro et al. [177] prepared DLC and Zr-DLC films on Ti alloy substrates by magnetron sputtering and carried out biotribological experiments in simulated body fluids (composed of neonatal calf serum, sodium chloride, and deionized water). The results show that the doping of Zr improves the adhesion of DLC films to the substrate and decreases the surface defect density of DLC films, but the defect size is higher than that of undoped DLC films. However, Zr-DLC films exhibit poorer biotribological properties compared to undoped DLC films. During frictional cyclic stress, larger surface defects promote stress-induced corrosion cracks [178], and high frictional shear stress will lead to crack growth beneath the film, thus leading to delamination. Anna Jedrzejczak et al. [179] fabricated DLC, a-C:H:Si, and a-C:H:SiOx films on AISI 316L stainless steel substrates by using RF plasma-assisted chemical vapor deposition and carried out biotribological experiments in simulated body fluids as well as in bovine serum albumin. In contrast, the doping of Si does not significantly improve the biotribological properties of the DLC films, while the wear rate of the DLC films containing low concentrations of Si and O is significantly reduced.

In terms of the effect of different I_D/I_G values on the biotribological properties of DLC films, Dingding Xiang et al. [180] prepared a-C:Cr films on Co-Cr-Mo substrates using closed-field unbalanced magnetron sputtering and PECVD methods. The former prepared DLC films were named Cr-GLC due to their high sp2/sp3 ratio, i.e., high I_D/I_G value and the latter was named Cr-DLC, due to its low sp2/sp3 ratio, i.e., low I_D/I_G value. Compared with Co-Cr-Mo substrates, doped DLC films have better biocompatibility and are more favorable for cell adhesion. Biotribological experiments in three different simulated body fluids, neonatal calf serum, Ringer's, and Hanks, showed that the Cr-GLC films had lower friction coefficients and wear rates, and they attributed the better biotribological properties of the Cr-GLC films to their higher graphite content that slid more easily under shear force and that macromolecules and water molecules in the simulated body fluids are easily embedded in the graphite layer, making it easier for the graphite layer to act as a lubricant for interlayer sliding. In addition, Dipankar Choudhury et al. [181] prepared N-DLC films with a Zr:ZrN/Zr:DLC transition layer on Ti-6Al-4V substrate by unbalanced magnetron sputtering and conducted biotribological experiments in simulated body fluids (made of a mixture of globulin powder, bovine serum, and deionized water). Compared with Ti-6Al-4V, all DLC films have higher hardness and plasticity, significantly reducing the friction coefficient of the tribosystem, especially wear, and DLC films do not produce any visible debris. The comparative study between different DLC films shows that DLC films with larger I_D/I_G can improve the delamination strength of the film and further reduce the friction coefficient and wear rate, which helps to overcome the film delamination during rubbing.

In terms of ion irradiation to alter the surface properties of DLC films, Yuzhen LIU et al. [182] studied the effects of nitrogen ion irradiation on the biocompatibility and biotribological properties of DLC films. The results show that nitrogen ion irradiation increases the sp3 C-N bonds on the DLC film surface, which leads to polarization of the DLC film surface due to the difference of electronegativity between C and N and increases the unsaturation of the N bonds [183], which enhances the interaction between the DLC film surface and the surface functional groups of cell proteins, and thus increases cell adhesion. In addition, the depth of the DLC film surface pattern caused by ion irradiation should be moderate, too small is not enough to capture wear particles and provides a hydrodynamic effect; too large will increase an edge effect, which can lead to high friction.

In addition, P.P. Jing et al. [184] prepared Ag-DLC films on Co-Cr-Mo substrate by the HPP-PECVD method. Biotribological experiments in bovine serum albumin solution indicate that compared with undoped DLC film, the tribosystem containing Ag-DLC film has a lower friction coefficient and wear rate, which is mainly because the Ag+ ions released from the Ag-DLC film during rubbing promote the denaturation of proteins in solution and form a protein biofilm on the friction surface. The protein biofilm plays an important role in improving lubrication and reducing friction. Ag-DLC films are known to have good antibacterial properties [36,80], however, the Ag^+ ions released from the film promote protein denaturation, which is beneficial for biofilm formation to improve the biotribological properties, but it remains to be studied whether this will cause harm to the healthy reproduction of cells. These results also indicate that the relationship between antibacterial properties and biocompatibility should be considered when using metal-doped DLC films for artificial joints.

In conclusion, when DLC films are used in biomedical applications such as implants, their biocompatibility, frictional delamination due to high stress, corrosion cracks induced by cyclic stress, and abrasive particle flaking should be addressed to ensure the durable high performance of DLC films. Furthermore, antibacterial properties and biocompatibility should be comprehensively considered when metal-doped DLC films are used in artificial joints.

5.6. Electrical Conductivity, Optical, and Triboelectrification Properties

DLC films have a wide optical band gap, a high absorption rate in the visible regions, and high transmittance in the infrared regions and microwave frequency bands, so they have better optical properties. In addition, DLC films have good wear resistance, so they can be used for anti-reflection film and protective film on solar panels, and anti-reflection and protective films on optical lenses [185,186]. Neeraj Dwivedi et al. [79] prepared Cu-DLC films by DC sputtering and RF-PECVD. The results show that the prepared Cu-DLC films show 80–90% transmission in the near-infrared region, showing good optical properties. This is mainly due to the formation of Cu nanoparticles in the carbon matrix, and according to Harry A. Atwater et al. [187], metal nanoparticles in the material help to improve the optical absorption rate of the material. On the one hand, nanoparticles on the surface of the material can be used as subwavelength scattering elements to scatter light into a medium with a large dielectric constant, so that the light can be concentrated and folded into a thin absorption layer, thus increasing the absorption of light. On the other hand, local surface plasmons in metal nanoparticles embedded in the medium can capture light and couple it to the lower layer of the medium, increasing the effective absorption cross section and thus improving the optical properties of the material.

In addition, element doping can also reduce the resistivity of DLC films. For example, the W element can form conductive carbides in the carbon matrix to reduce the resistivity of the DLC film [45]. For another example, Cu doping reduces the optical bandgap energy of the DLC film, which reduces the energy required for electronic transition and improves the electrical conductivity of DLC films [76]. The doping of the Cu element also increases the sp2-C in the carbon matrix and the formation of the Cu-C chain, which also increases the electrical conductivity of DLC films. Some studies have shown that the conductivity of amorphous carbon is exponentially related to the change of sp2-C content, and electron transport can be considered as thermally activated conduction along the connection or chain of sp2-C atoms. Moreover, the increase of sp2-C can also reduce the activation energy of current transport and eventually lead to an increase in conductivity [188,189]. At present, the research on the electrical conductivity of doped DLC films and the effect of the change of electrical conductivity on DLC films are still insufficient. Moreover, the reduction of resistivity and the improvement of optical properties of DLC films will broaden their applications in the field of optoelectronics.

Based on the various excellent properties of DLC films, they have been widely studied in the field of optics and electronics, etc., such as metal semiconductors [190], cathode material for field emission displays [191], sensors [192,193], etc. For example, Takumi Iwata et al. [194] used DLC films on the oil film pressure sensors on the main bearing surfaces of the engines, which improved the durability of the sensors under high rotation and high loads. At present, there is much interest in the application of DLC films for energy generation and harvesting due to their excellent optical and other properties. For example, Naim Aslan et al. [195] found that Ag-DLC films have photovoltaic properties, photoresponsive, photosensitivity, and electrical properties that are enhanced with the intensity of external light. In addition, Ag-DLC films also exhibit diode properties, indicating that DLC films have great potential for applications in solar energy and detectors. Sholpan Nauryzbekova et al. [196] based on finite-difference time-domain simulations in Lumerical's DEVICE Multiphysics Simulation Suite concluded that the use of DLC in combination with porous silicon significantly reduces the light reflection from Si solar cells compared to pristine Si, and therefore improves the efficiency of Si solar cells. Maryam Hekmat et al. [197] found that Ag-DLC films with double layers and with different sizes of Ag nanoparticles significantly enhanced light trapping and increased their short-circuit current compared to single-layer Ag-DLC films, thus improving the performance of silicon solar cells.

However, what is more exciting is the application of DLC films in triboelectric nanogenerators (TENGs) systems, which are based on the triboelectric charging of solids [198]. This effect is influenced by the electron affinity, configuration, temperature, and surface properties of the triboelectric material [199,200]. DLC films have high resistivity [144], high defect state density and a wide band gap from the semiconductor to the insulator (1–4 eV), low electron mobility (10^{-11}–10^{-12} cm^2/V) [201], and also a low coefficient of friction and high wear resistance, which together make DLC films become promising and durable triboelectric materials.

In the study of TENGs based on DLC triboelectric materials, Shreeharsha H et al. [202] introduced DLC films into TENG systems and showed that TENG based on H-DLC film with higher hardness and polytetrafluoroethylene (PTFE) dielectric pairs produced higher output than other conventional dielectric pairs (e.g., Al/PTFE, polyimide (Kapton®)/PTFE, and Kapton/Al), while F-DLC film paired with Kapton produced higher TENG output compared to H-DLC film. In addition, the formation of a transfer film on the friction surface and the graphitization of the DLC film during rubbing reduce the TENG output of the system. The transfer layer partially covers the contact of the PTFE surface, as a result, the polarity difference between the dielectric materials is reduced, and the contact of the triboelectric pair is also decreased. Furthermore, the graphitization of DLC film caused by friction heat reduces its resistivity [203] which greatly reduces the overall dielectric properties of the DLC film, thus reducing the TENG output of the system. Later, Shreeharsha H et al. [204] carried out further studies on the application of DLC films in TENG systems. H-DLC films have a lower work function, lower electron affinity, and positive surface potential, and release electrons to become donors. (The work function is a description of the surface electron polarity of the material [199]). However, F-DLC film and PTFE have high work function and negative potential, attract electrons during contact charging, and have high electron affinity to be used as an acceptor. Therefore, the F-DLC/H-DLC film triboelectric materials pair can also be used in TENG systems, and it has been shown that the F-DLC/H-DLC film pair has the highest TENG output at low rotational frequencies. Moreover, the frictional charge is believed to be present not only on the outermost surface but also penetrate in the depth direction. In contrast, DLC films and PTFE do not have any mobile ions, which suggests that the charge is transferred by electrons, and that also confirms that electrons can penetrate the film up to several microns [205], indicating that film thickness also has effects on TENG output. Studies on the effects of DLC film thickness on TENG output show that low-thickness film causes low inductive voltage and low TENG output, which may not produce a sufficient amount of frictional charge. If the thickness of the DLC film is too high, the distance to the electrode increases, thus reducing the induced voltage and leading to a reduced TENG output despite a good frictional charge. In addition, and more importantly, at high loads, the output of the Al/PTFE dielectric pair is highly unstable due to wear of the PTFE and causes a drop in output current, while the H-DLC/PTFE dielectric pair exhibits stable output and excellent durability. Mang Gao et al. [206] studied the effects of H-DLC and Si-DLC (Si content 0–26.1 at.%) films as dielectric materials for TENG on their output and durability. With increasing Si content, the structures of Si-DLC films are more disordered and the doping of Si can generate more dangling bonds on the surface of DLC films [207], which may provide more electron-giving sites, which is favorable for TENG charge accumulation [208,209]. The doping of Si can also decrease the electron emission potential barrier of DLC film, which leads to lower work function [210]. The experimental results show that Si-DLC films have a lower work function, which contributes to their higher electron emission. In addition, the dielectric constant of Si-DLC films increases with the increase of Si content, while the high dielectric constant of the triboelectric material improves the output performance of TENG. Compared to H-DLC films, Si-DLC films exhibited higher TENG output under both dry and water-lubricated conditions, and Si-DLC-based TENG under non-immersed water-lubricated conditions increased the output voltage by more than 2.5 times compared to dry conditions due to the stronger positive charge of water. A transfer layer of PTFE was observed on the Si-DLC film and the H-DLC film tested under dry conditions, which reduced the output of the TENG. Under water-lubricated conditions, Si-DLC can effectively reduce the formation of PTFE transfer film on its surface, thus maintaining a stable and high yield, and the Si-DLC films exhibited better durability than the H-DLC films.

In conclusion, DLC films have great application prospects in TENGs. Although the application of DLC films can improve the durability of TENG systems, further studies should be focused on overcoming their graphitization during rubbing, tribofilm removal, and other adverse effects on TENG output. In addition, more attempts are also meaningful to find more effective triboelectric material pairs based on the nature of DLC films.

6. Conclusions and Prospect

In general, element doping has significant effects on the microstructure and properties of DLC films, which is an effective way to reduce residual stress and improve the various properties of DLC films. An appropriate content of element doping can significantly reduce the residual stress and increase the adhesion between the DLC film and the substrate without dramatically reducing the mechanical properties of DLC films, and also improve the tribological, hydrophobic, corrosion resistance, and antibacterial properties, etc. of DLC films, which broadens the application fields of DLC films. However, whether there are carbide-forming elements or non-carbide-forming elements, the doping content should not be too high, otherwise it may not only fail to reduce the residual stress but also damage the structure of the carbon matrix and deteriorate the mechanical and tribological properties of the DLC film. Although doping heterogeneous elements can improve the structure and properties defects of DLC films to varying degrees, it is difficult to improve the comprehensive properties of DLC films simply by doping elements. Generally, it is difficult to improve the mechanical properties of DLC films by single-element doping while reducing the residual stress, while multi-element doping also faces this problem. However, compared with single-element doping, the complementary effect between different elements can be used to coordinate the various properties of DLC films when multi-element doping is carried out. The mechanism of element doping to reduce the residual stress and improve various properties of DLC films mainly includes:

(1) Element doping can reduce the residual stress of DLC films by promoting the graphitization of DLC films and forming nanocrystals in the carbon matrix as "hubs" for stress release;

(2) Element doping can improve the tribological properties of DLC films by improving their comprehensive mechanical properties, forming tribo-films on the friction surfaces, and generating antifriction products by reacting with the surrounding media;

(3) Element doping can increase the density of DLC films by forming nanocrystals in the carbon matrix, forming a corrosion-resistant protective layer on the surface of DLC films, and reducing the residual stress to reduce the cracks and propagation in DLC film, so as to improve the corrosion resistance of DLC film;

(4) Element doping can improve the hydrophobic properties of DLC films by changing the surface roughness to form hydrophobic surfaces that are easy to trap air, promoting the graphitization of DLC films to reduce the number of dangling bonds on the surface which reduces the surface energy, and reduces the polar molecules on the DLC film surface;

(5) Element doping can form nanoparticle "elements" in the carbon matrix that increase the optical coupling, thus improving the optical properties of DLC films;

(6) Element doping can improve the antibacterial properties of DLC films by adjusting the roughness and surface energy of DLC films to reduce bacterial adhesion and release antibacterial ions.

Although a lot of progress has been made in the study of element doping modification and properties enhancement of DLC films, in order to improve their application ability in complex environments, better coordination and optimization of the comprehensive properties of DLC films are still the direction of future efforts. In addition, DLC films are prone to oxidation in air, which leads to the reduction of their mechanical and anti-wear properties. It is urgent to further understand their oxidation failure mechanism and protective measures. Finally, the preparation processes of DLC films are complex and expensive, and the existing technology is difficult to mass produce. Therefore, in addition to the properties research of DLC films, there is a great space for research on the preparation processes and methods of DLC films.

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