

Chapter 2

Overview of Amorphous Carbon Films

Abstract Carbon, one of the most versatile elements around, manifests itself in a wide variety of allotropic forms that exhibit a diverse range of properties. Amorphous carbons form a big class of carbon allotropes. As the name suggests, amorphous carbons contain a certain degree of disorder (non-crystallinity) in contrast to the crystalline structures of diamond and graphite. The sp^3 content of amorphous carbon films is very important in achieving excellent properties such as high hardness and high density.

2.1 The Versatility of Carbon: Structure and Bonding

Carbon, one of the most versatile elements around, manifests itself in a wide variety of allotropic forms that exhibit a diverse range of properties. The reason for this extraordinary characteristic of carbon lies in its ability to exist in three types of hybridizations, namely sp^1 , sp^2 and sp^3 , as shown in Fig. 2.1 [1]. Carbon as an atom has four valence electrons, out of which two electrons occupy the 2s orbital, and the other two electrons occupy one 2p orbital each. All four valence electrons of carbon actively take part in bonding. In sp^3 hybridization, the 2s orbital and three 2p orbitals of carbon are hybridized to form four equivalent sp^3 hybrid orbitals of equivalent energies, arranged in a tetrahedral structure as shown in Fig. 2.1, with one electron occupying each hybridized orbital. These four orbitals can form strong C–C σ bonds when the sp^3 orbitals of adjacent carbon atoms overlap. In sp^2 hybridization, three electrons occupy three equivalent sp^2 hybridized orbitals arranged in a trigonal planar configuration, with the 2s orbital and two 2p orbitals taking part in hybridization. The third 2p orbital containing the last valence electron in this case remains unhybridized and at a higher energy level than the sp^2 hybridized orbitals. This orbital, known as a π orbital, is arranged perpendicular to the plane of the three sp^2 orbitals, as illustrated in Fig. 2.1. During bonding, the sp^2 orbitals form strong σ bonds, whereas the π orbital forms a comparably weaker π bond via a side-to-side overlap with another π orbital on the adjacent atom, causing the π electrons to be delocalized between the two adjacent atoms. Sp^2 bonding in carbon is typically depicted as a C=C double bond, where the double bond consists

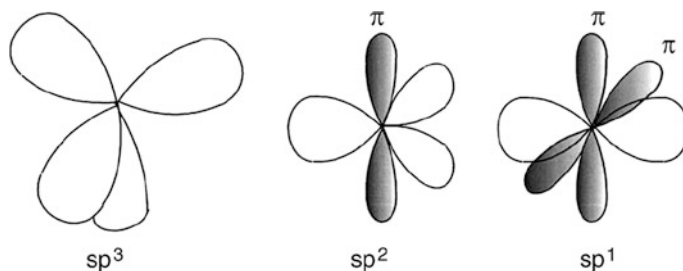


Fig. 2.1 The three possible hybridizations of carbon during bonding. Reproduced from Ref. [1] Copyright (2002), with permission from Elsevier

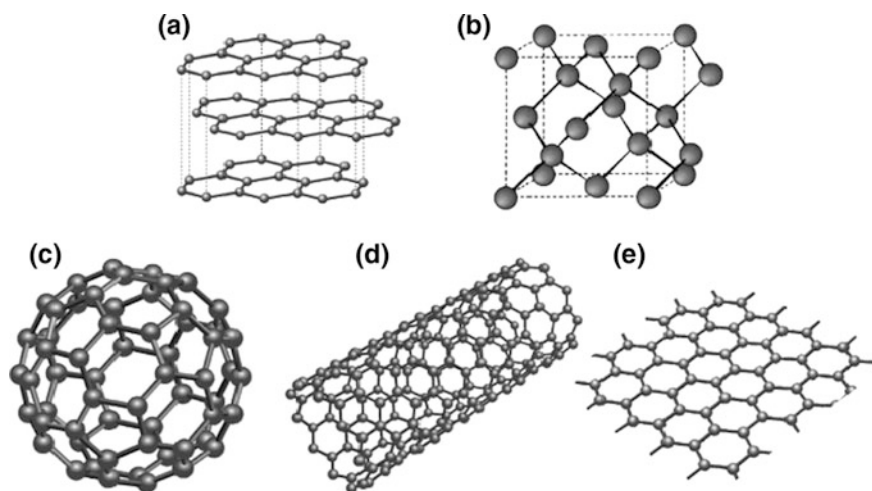


Fig. 2.2 Various allotropes of carbon. **a** Hexagonal crystalline graphite, **b** cubic diamond, **c** C_{60} fullerene, **d** carbon nanotube, and **e** graphene. Reproduced with permission from Ref. [2] Copyright © IOP Publishing. All rights reserved

of one σ bond and one π bond. Sp^1 bonding in carbon follows a similar trend, forming two equivalent sp hybridized orbitals with higher σ bond energy and two π orbitals with lower π bond energy, resulting in a $C\equiv C$ triple bond.

Consequently, carbon can be bonded to itself in any of the above configurations, resulting in different structures and ordering, as well as different mechanical, electrical and optical properties. Here two crystalline allotropes of carbon are compared—hexagonal crystalline graphite and diamond, and their crystal structures are shown in Fig. 2.2a and b respectively. In diamond, all carbon atoms are fully sp^3 bonded (all σ bonds) with each atom bonded to four other atoms arranged in a dense, tetrahedral crystalline network. Because of its high bond density and strong σ bonding, it not only exists as one of the hardest materials known, but it is also an excellent electrical insulator as all its electrons are involved in σ bonding.

Hexagonal crystalline graphite, on the other hand, consists of a highly ordered structure of carbon layers stacked above and below one another in an ABAB sequence as illustrated in Fig. 2.2a. Graphite contains pure sp^2 bonding, whereby within each layer, each carbon atom is bonded via σ bonds to three other atoms in hexagonal rings. At the same time, delocalized π bonding takes place above and below the carbon layer which extends throughout the entire plane. This means that the π electrons can move freely between the sheets of graphite. However, only weak forces of attraction (widely regarded as dispersive van de Waals interactions) are present between the graphite sheets, making it easy to slide the sheets across one another. Therefore, while graphite exhibits strong covalent bonding within the layers, it possesses low bulk hardness due to the weak interlayer interactions, and the extensive delocalization of electrons in graphite makes it a good electrical conductor.

Hence, it can be seen that the bonding and structure in carbon play an important role in contributing to its properties. In addition to the above examples, fullerenes (0D), carbon nanotubes (1D) and graphene (2D) are some important low dimensional form of carbon materials and possess mainly sp^2 -bonded carbon network, as shown in Fig. 2.2c–e respectively.

2.2 Introduction to Amorphous Carbon Films

Amorphous carbons form another big class of carbon allotropes. As the name suggests, amorphous carbons contain a certain degree of disorder (non-crystallinity) in contrast to the crystalline structures of diamond and graphite, as illustrated in Fig. 2.3. Amorphous carbons are usually deposited as films on a substrate,

Fig. 2.3 Typical structure of amorphous carbon. *Black atoms* represent sp^3 -bonded carbon atoms whereas *grey atoms* represent sp^2 -bonded carbon atoms in a disordered network. Reproduced with permission from Ref. [4] Copyright (2000) by the American Physical Society

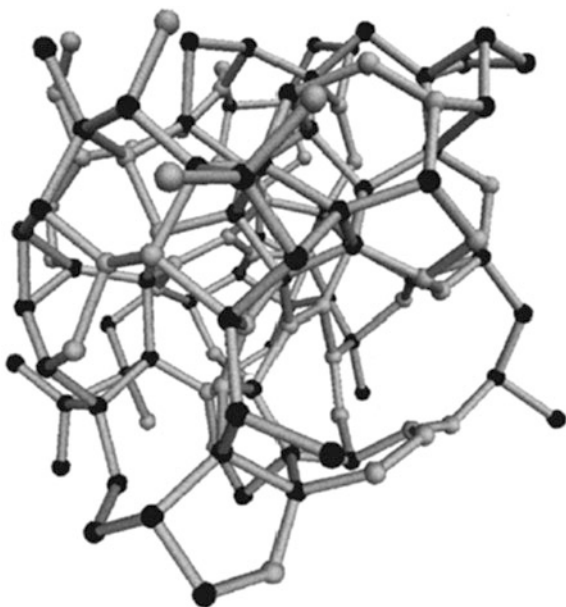
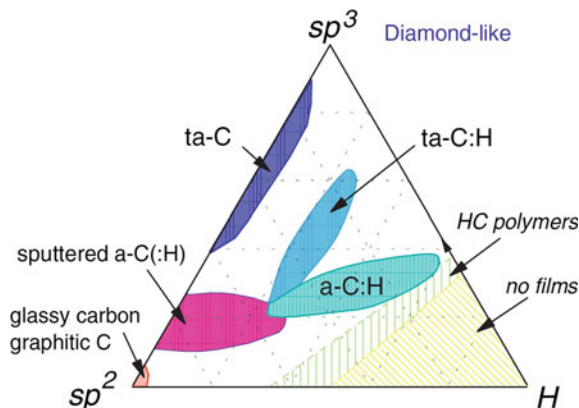


Fig. 2.4 Ternary phase diagram of the amorphous carbon-hydrogen system. Reproduced from Ref. [1] Copyright (2002), with permission from Elsevier



containing a mixture of sp^2 and sp^3 bonding with little evidence of sp^1 bonding being present [3]. Hence, they can be regarded as intermediate structures between graphite (fully sp^2) and diamond (fully sp^3), and exhibit some character of both, depending on their sp^2/sp^3 fractions. In the presence of hydrogen during amorphous carbon film deposition, the inclusion of hydrogen atoms in the carbon network to form hydrogenated amorphous carbon is possible, depending on the deposition conditions.

To illustrate the wide range of amorphous carbon film structures, Fig. 2.4 presents a well-known ternary phase diagram of the amorphous carbon-hydrogen system, with each side of the phase diagram representing the percentage of sp^2 carbon (sp^2C), sp^3 carbon (sp^3C) and hydrogen content, as depicted by the respective vertices [1]. The entire left side of the phase diagram shows the variation of sp^2C/sp^3C content for films with 0% hydrogen, also known as non-hydrogenated amorphous carbon films (hereon referred to as a-C films). At the bottom left vertex of the phase diagram with $\sim 100\%$ sp^2C bonding lie graphitic carbons such as char and soot, which exhibit similar properties to graphite, as well as glassy carbon. As the amount of sp^3C bonding increases, the a-C films start to exhibit more diamond-like character, i.e. an increase in hardness and density and a decrease in electrical conductivity. Hence, a-C films containing a significant amount of sp^3 bonding are usually termed as diamond-like carbon (DLC) [5]. As the sp^3 content in the film increases further to $\sim 70\text{--}90\%$, a special name of tetrahedral amorphous carbon (ta-C) is given to these films as a large fraction of the carbon atoms becomes tetrahedrally bonded in an sp^3 network [6, 7].

With the incorporation of hydrogen, hydrogenated amorphous carbon (a-C:H) films can be formed. This can be done for example by growing physical vapor deposition of carbon films in a hydrogen atmosphere, or by using hydrocarbon sources as a precursor for film growth in chemical vapor deposition processes [8, 9]. Softer a-C:H films can be obtained with $\sim 40\text{--}60\%$ H content, which are known as polymer-like a-C:H (PLCH) films. a-C:H films with intermediate hydrogen content (20–40%) possess relatively higher sp^3 C-C bonding than PLCH films and hence

better mechanical properties. These films are usually termed as hydrogenated DLC films. Tetrahedral a-C:H (ta-C:H), which is considered to be a special class of hydrogenated DLC films, contains $\sim 25\text{--}30\%$ hydrogen content and significantly higher sp^3 C-C bonding (up to $\sim 70\%$) [10]. a-C:H films with low hydrogen content of $10\text{--}20\%$ deposited by magnetron sputtering or by PECVD at high bias possess high sp^2 bonding and sp^2 clustering. Such films can be called as graphite-like a-C:H (GLCH) films [11]. While the inclusion of hydrogen aids in saturating the sp^2 C bonds in amorphous carbon to form sp^3 bonds with H, the sp^3 bonds of C-H are weaker than sp^3 C-C bonds, thus in general ta-C:H films have slightly lower hardness and lower density than ta-C films.

Similarly, other elements such as nitrogen and silicon can be incorporated to form alloyed amorphous carbon films with a range of properties, but they will not be discussed here. The primary interest of this work is on non-alloyed, non-hydrogenated a-C films.

2.3 Mechanism for sp^3 C Bond Formation and Its Importance

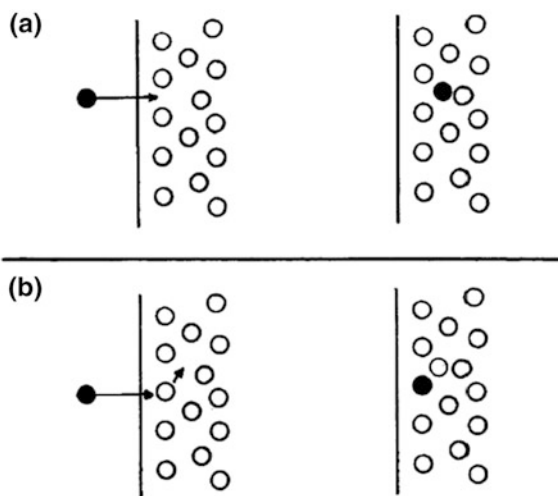
The sp^3 content of a-C films is very important in achieving excellent properties such as high hardness and high density. For example, the sp^3 content, bulk hardness and density of ta-C can reach up to $80\text{--}90\%$, $\sim 65\text{--}80$ GPa and ~ 3.3 g/cm³ respectively, which are very close to the bulk hardness and density values of diamond (~ 100 GPa and 3.5 g/cm³) with its mainly sp^3 -bonded carbon network. With increased sp^3 bonding in the a-C film, lower surface roughness can also be achieved [6]. Furthermore, a-C films with high sp^3 content have also been found to possess high thermal stability and a low amount of graphitization upon thermal annealing at high temperatures of up to ~ 1270 K [12]. Thus, sp^3 C-C bonding is a very important parameter in order to obtain high wear and corrosion resistance and high thermal stability in amorphous carbon films.

The sp^3 content in a-C films is known to be largely dependent on the energetics of the a-C film deposition process [3]. In processes such as thermal evaporation, the carbon species (ions or atoms) being deposited possess very low kinetic energies ($\sim kT$ which is 0.025 eV at room temperature), resulting in the formation of carbon films with very high sp^2 and very low sp^3 content ($\sim 1\text{--}12\%$ sp^3) [3, 7]. The reason for this observation is attributed to the insufficient energy required to promote the electron from the 2s to the 2p orbital for sp^3 hybridization [13]. DLC films can be deposited by more energetic processes such as sputtering, ion-assisted deposition, ion beam deposition and cathodic arc deposition, giving intrinsic kinetic energies of between $2.5\text{--}25$ eV.

Lifshitz et al. [14] proposed that the main growth mechanism of carbon films by carbon hyperthermal species (possessing energies of 1 to 1000 eV) is based on a subplantation model that can be used to explain the variation of sp^2/sp^3 bonding with energy. When the incoming carbon species interact with the growing carbon film

Fig. 2.5 Mechanism of film growth by subplantation.

a Penetration of energetic carbon species into the subsurface of the growing carbon film, and **b** preferential displacement of sp^2 -bonded carbon atoms into the film. Both mechanisms contribute to increasing the density and sp^3 content of the film. Reproduced from Ref. [15] Copyright (1993), with permission from Elsevier

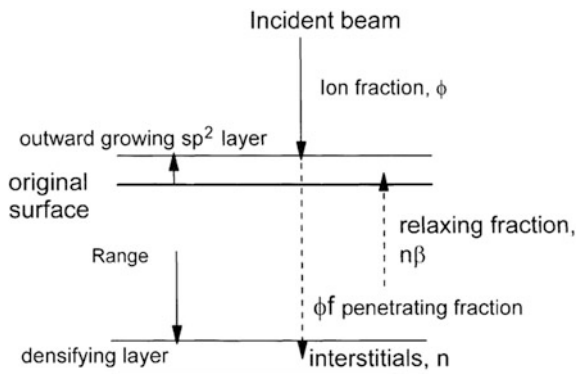


with sufficient energy, it is able to penetrate the subsurface of the film. This can result in either direct penetration trapping of the incoming carbon species into the film, or preferential displacement (knock-on) of the existing sp^2 bonded carbon as shown in Fig. 2.5. This effectively increases the density at the subsurface of the film, causing the transformation of bonding hybridization from sp^2 to sp^3 [15]. After subsurface penetration, some of the carbon atoms undergo a relaxation process towards the surface, forming a surface sp^2 -rich layer. This is illustrated in a schematic by Robertson in Fig. 2.6 [1], which shows the fraction of energetic ions being able to penetrate the surface by the subplantation process ($f\phi$) and the fraction of trapped interstitials relaxing towards the surface ($n\beta$). Thus the fraction of ions that remains at the interstitial sites and contribute to densification is expressed as $n = f\phi - n\beta$.

The subplantation mechanism requires a certain energy threshold of the arriving carbon species to be effected. At low energies (<10 eV), the carbon species do not have enough momentum to penetrate the growing carbon film, thus the occurrence of subplantation is negligible. Furthermore, very low displacement or mobility of the carbon species is observed, and the incoming carbon species are trapped as interstitials within the growing film, forming a disordered network. This results in the formation of highly sp^2 bonded graphitic films. With medium energies (~ 30 – 500 eV), the preferential displacement mechanism is effected which favors the formation of sp^3 bonding and reduces the number of graphitic sp^2 sites, hence a high sp^3 fraction can be achieved. However, if the energies are too high (~ 500 – 1000 eV), the growing carbon film can be easily damaged and amorphized. As such there is an optimum deposition energy range in the medium energy regime for each deposition process and tool to obtain DLC films with the highest sp^3C content.

Many groups have successfully attempted to create DLC films using processes in which the carbon species possess intrinsic energies in this range, such as ion beam deposition, ion-assisted deposition, laser ablation, cathodic arc deposition and sputtering [6]. However, to create highly sp^3 -bonded DLC films such as ta-C, C^+

Fig. 2.6 Diagram showing the fraction of incoming ions contributing to subsurface penetration, film densification as trapped interstitials, and relaxation towards the surface. Reproduced from Ref. [1] Copyright (2002), with permission from Elsevier



ions are commonly used as the species for film growth, because of the potential to moderate the energy of the arriving ions at the substrate by applying a suitable substrate bias. For example, the first reported DLC films were grown via an ion beam deposition method by Aisenberg and Chabot in 1971 by applying a substrate bias of -40 V [16]. By varying the ion energy, ta-C films with ~ 70 – 90% sp^3 bonding have been reported using ion energies within the range of ~ 20 – 300 eV [16, 17]. Presently, it is regarded that maximum sp^3 bonding can be achieved within an optimum energy range of ~ 80 – 120 eV [18–20].

2.4 Thickness Dependence of sp^3 Content in Ultrathin Amorphous Carbon Films

One of the challenges that arises when thickness is reduced for a-C/ta-C films is that the sp^3 content has been observed to be reduced significantly (especially at ~ 2 nm thicknesses and below), despite being grown under the same conditions [21]. It has been shown that in ta-C films, a layered structure involving three layers of different densities can be formed [22, 23]. For thicker films, the bulk layer contains the highest density, hence it can be inferred that its contribution to the overall sp^3 content is the highest. The other two layers, one at the substrate-film interface and another at the surface, have a lower density, which result in higher sp^2 bonding (lower sp^3 bonding) in these regions. The thicknesses of these layers can vary depending on the deposition conditions [22–24]. While the mechanism of formation of the sp^2 -rich interface layer is substrate dependent, the formation of the sp^2 -rich surface layer is suggested to arise due to the mechanism of the deposition process involving ion bombardment and deposition temperature [23]. When the thickness of the film decreases, the bulk layer correspondingly decreases, resulting in an increased contribution from the surface and interface layers. Therefore, this contributes to the overall reduction in the sp^3 content of the film. Nevertheless, Beghi et al. and Ferrari et al. suggested that FCVA-processed carbon films deposited at

optimum process conditions can have sp^3 bonding as high as $\sim 50\%$ at a thickness of 2 nm, which is still significantly higher than carbon films processed by magnetron sputtering and PECVD [22, 24].

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