

Classification of Diamond-like Carbons

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Abstract Diamond-like carbon (DLC) is an amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C:H) thin film material with a high fraction of sp^3 carbon bonding. It is generally prepared by a deposition process which involves energetic ions. The sp^3 bonding is metastable compared to sp^2 bonding, unless it is stabilised by C–H bonds. The various types can be classified according to their fraction of sp^3 bonding and hydrogen (H). DLC variants alloyed with other elements such as Si, metals or B, N and F are also found.

Keywords sp^3 , hydrogen content, density, ion beam, deposition, a-C:H, ta-C, alloys

1 Introduction

Diamond-like carbon (DLC) is an amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C:H) thin film material with a high fraction of metastable sp^3 carbon bonding [1,2]. It is generally prepared by a deposition process which involves energetic ions. These ions give rise to the sp^3 bonding, which is metastable compared to sp^2 bonding, unless it is stabilised by C–H bonds. The ion-induced process is distinct from plasma polymerisation, where the C sp^3 bonding arises from a condensation of C–H groups with the evolution of molecular H_2 . DLC can be alloyed with other elements such as Si, metals or B, N and F. This chapter focuses first on the unalloyed material and then mentions the alloyed varieties.

2 Phase Diagram

The types of DLC can be displayed on a ternary phase diagram, as shown in Fig. 1. This shows the fraction of sites in the alloy that are C sp^3 , C sp^2 or hydrogen (H). The diagram was first derived by Jacob and Moller [3]. Note that here the total

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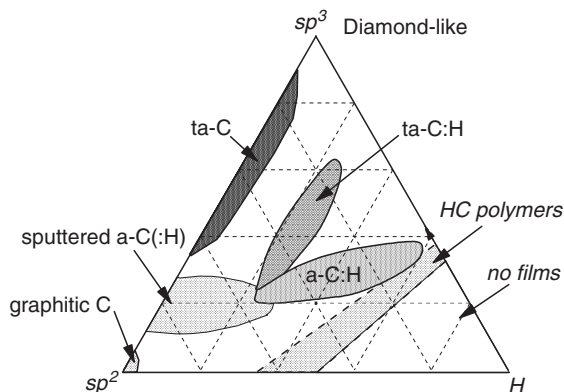


Fig. 1 Ternary phase diagram of the C, H system [2]

fraction of atoms adds up to 1. One should be careful with cases quoting the sp^3 fraction (of C only), or the H/C ratio instead of the H/(C + H) ratio.

The phase diagram consists of three main regions. The first region is H-free a-C along the left axis. The sp^2 a-C is typically glassy carbon, or a-C made by pyrolysis of hydrocarbon polymers or by evaporation, and is not DLC. An a-C of higher sp^3 content, but still without H, is typically made by sputtering, and is a DLC. The modern variants of sputtering, including unbalanced magnetron sputtering can create DLCs with quite large sp^3 contents. At even higher sp^3 content, there is a specific type of a-C designated as tetrahedral amorphous carbon or ta-C. This is made from ion or plasma beams with a high ion fraction and a narrowly defined ion energy. These methods include mass selected ion beam (MSIB) deposition, filtered cathodic vacuum arc (FCVA) and pulsed laser ablation deposition (PLD) [4–7]. Deposition occurs at room temperature.

The second region of the phase diagram is the bottom right of the figure, where the H content is so large that the material cannot form a fully connected network, but only gas molecules [3]. The boundary line of this region is defined by the compositions of C_2H_2 on the sp^2 -H axis and $(CH_2)_n$ on the sp^3 -H axis.

In between these regions lies the region of a-C:H materials. a-C:H is produced typically by plasma-enhanced chemical vapour deposition (PECVD) of hydrocarbon molecules, or by the reactive sputtering of graphite in an atmosphere including H or by ion beam deposition from a hydrocarbon gas precursor [8–13]. The typical PECVD or sputtering process will produce an a-C:H which lies in the region indicated as a-C:H. This can range from the material with only 20–25% H content up to those with very high H contents of ~60% of the total number of atoms.

As PECVD has advanced, it is possible to create the so-called high-density plasmas, such as by electron cyclotron resonance (ECR), inductively coupled plasma (ICP), the plasma beam source (PBS) or electron cyclotron wave resonance

(ECWR). These methods produce more dense a-C:Hs which we call highly tetrahedral hydrogenated amorphous carbon or ‘ta-C:H’ [14,15]. The high-density plasmas are achieved by operating at a pressure lower than the usual PECVD and by using magnetic fields to give long electron path lengths, which encourages a high plasma ionisation. As conventional PECVD processes improve, the zones of a-C:H and ta-C:H begin to merge.

3 Diamond-like Character

The ‘diamond-like’ character of DLC films obviously arises from its C–C sp^3 bonds. The DLC is an amorphous phase and atomically, it is a random network [2,16]. The mechanical properties of this network can be considered as an alloy of different bonding components, C–C sp^3 , C–C sp^2 and C–H bonds. The Young’s modulus, hardness and general diamond-like quality arise from the C–C sp^3 bonds. The C–C sp^2 bonds do not contribute much. The C–H bonds do not link up the network, so mechanically they are just like a dangling bond, and contribute nothing to mechanical properties [16]. Thus, the Young’s modulus is found to depend monotonically on the mean C–C coordination number, or in other words, the C–C sp^3 fraction [17]. It is found that the density of a-C varies linearly on the C–C sp^3 fraction [18] (see Fig. 9).

It is found that the Young’s modulus varies with the ion energy involved in deposition in a standard way. For H-free a-C, the modulus and sp^3 content pass through a maximum at an ion energy of about 100 eV, as in Fig. 2(a). For lower and

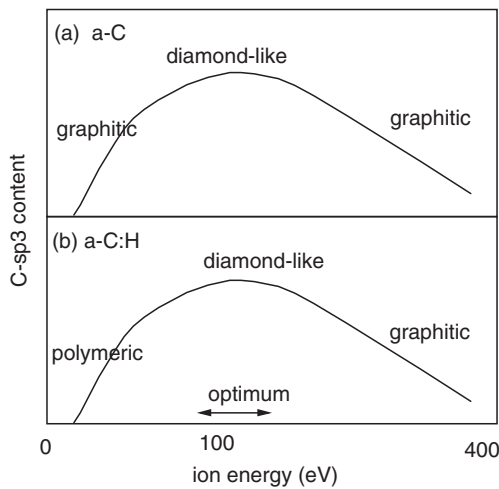


Fig. 2 Schematic variation of fractional diamond-like character of (a) a-C and (b) a-C:H with deposition ion energy

higher ion energies, the sp^3 content is less, the sp^2 content is larger and the films are more graphitic. For a-C:H films, the variation is similar. The maximum generally occurs at an ion energy of about 100 eV (Fig. 2(b)). At the optimum, the C sp^3 fraction is a maximum (but not necessarily so high). But at lower ion energies, the films contain many C(sp^3)–H bonds and they are more ‘polymeric’. At higher ion energies, the sp^2 fraction increases and the films are more graphitic. Thus there is a difference in structure at low ion energies, between a-C and a-C:H. The actual sp^3 and H contents were determined by nuclear magnetic resonance (NMR) in a-C:H films [12,13].

4 Deposition Process

The sp^3 bonding which characterises DLC arises from the ion-assisted nature of the deposition process. This means that, to zeroth order, the resulting a-C or a-C:H depends primarily on this ion energy [8]. Strictly, it depends on the energy per incident C ion [19]. Thus, for a-C:H, it also depends somewhat on the precursor hydrocarbon molecule, C_nH_m .

There are two aspects to this. Firstly, the sp^3 content in pure a-C arises from the subplantation process, which depends on the ion energy [20]. Secondly, the H content of the a-C:H is lower than that of the precursor hydrocarbon species. H is lost due to ion bombardment, and this depends primarily on the ion energy.

The subplantation process creating sp^3 sites in a-C occurs as follows [19,20] (Fig. 3). Normally, when atoms are added to a solid, they add to the surface, and may diffuse about on the surface to find the lowest energy position. In subplantation, the incoming C ion has enough energy to pass through the outer layer of the film, enter

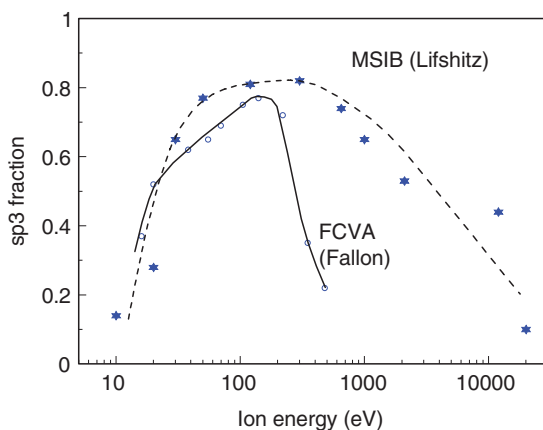


Fig. 3 The subplantation process of an energetic carbon ion into a C film. Subplantation of a diatomic C species into the film, with the breaking of the C_2 species

the film and cause subsurface growth. This gives rise to a local densification. Now DLC, like diamond, is metastable. The density of sp^3 diamond is $\sim 50\%$ higher than that of sp^2 -bonded graphite. By analogy, the coordination of atoms in a-C follows the local coordination. Any surface growth of a-C will be unconstrained, normal to the film surface and will be in the lowest energy state, which is sp^2 . But, subplantation will give rise to more dense, metastable zones, where the bonding will convert into sp^3 . The mean coordination will be similar to that in bulk ta-C.

The sp^3 content and thus density depends in a standard way on the ion energy [19]. The maximum sp^3 content occurs at an ion energy per C ion of 100 eV. A lower ion energy results in a greater fraction not subplanting, but sticking to the other surface as sp^2 . A higher ion energy also results in a lower sp^3 content. This occurs because the excess ion energy allows atomic relaxation around the implanted atom and a reversion of some sp^3 sites to the sp^2 ground state. The exact nature of this process is still debated. Roughly, it involves a thermal spike, which results in diffusion of the excess C atoms to the surface [19]. However, molecular dynamics simulations show that the real process is more complex than this simple, continuum description [21].

A similar process will occur in the formation of a-C:H and ta-C:H [14]. In addition, the ion bombardment will cause the loss of H, primarily by the displacement of H from C-H bonds to form H_2 molecules, which then leave the network [22,23]. This happens within the ion range of the incident CH_x^+ ion. Now, H loss in a-C:H involves a different process than in a-Si:H. a-Si:H with a lower H content is promoted by using a H-diluted silane plasma [24]. Atomic H from this plasma abstracts H from Si-H bonds [25], which leaves as H_2 . The reduced H content eventually leads to the formation of microcrystalline Si which contains only $\sim 1\%$ H, compared to the typically 10% H in a-Si:H [24].

The opposite situation seems to occur in a-C:H, which when grown in H-diluted plasmas seems to have similar or higher H content than a-C:H grown from pure hydrocarbons [26,27]. H abstraction can occur, but it does not seem to lead to a lower H content. Presumably, as atomic H abstracts an H, it also adds an H to the resulting C dangling bond, as shown in Fig. 4, on the right. Thus the main process remains the displacement of H from C-H bonds by incident ions, shown in Fig. 4, on the left.

The overall result is that for a-C:H, the H content and sp^3 content decline monotonically with increasing hydrocarbon ion energy [2,8,12], as shown in Fig. 5. Displacement yields increase with ion energy. The hardness and diamond-like nature of the a-C:H go through a maximum, but this is a maximum of C-C bonded content, not that of a simple C sp^3 . This is because at 0 eV, the C sp^3 content is at a maximum. However, it is all bonded to H atoms. As the ion energy increases, the H content decreases. The sp^3 content does not decrease as fast. Thus, there comes an ion energy where the C-C bonded fraction, excluding the C-H bonds, reaches a maximum. This is the composition of maximum modulus and hardness. For even higher ion energies, the sp^3 content decreases too much, and the C-C content and modulus now decreases. This is summarised in Fig. 6.

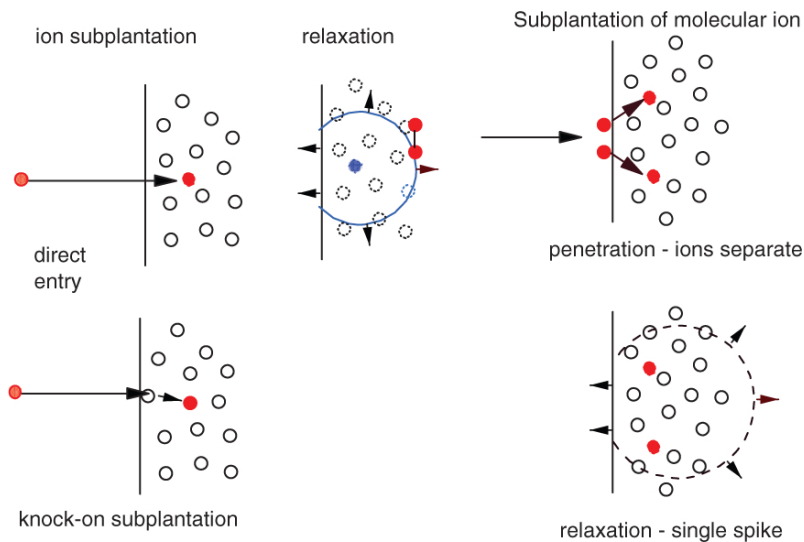


Fig. 4 Processes leading to loss and gain of hydrogen in a-C:H films

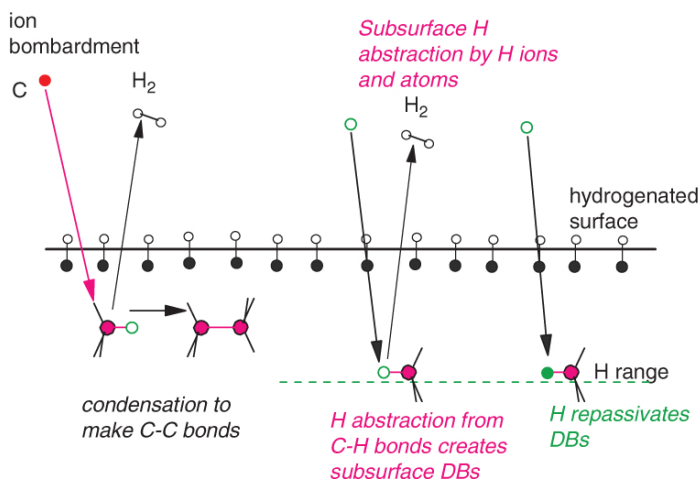


Fig. 5 Experimental dependence on sp^3 content, H content, mass density and optical band gap on the bias voltage for PECVD a-C:H films, deposited from methane or benzene

Generally, many applications would desire films with the maximum modulus or hardness. Thus, these would use ion energies around 100eV. There are other cases though. For ta-C, in the FCVA method, ions leave the cathode with an ion energy of about 30eV, unless an explicit bias voltage is attached to the substrate. This so-called floating potential is enough to give a high sp^3 content, and is often used.

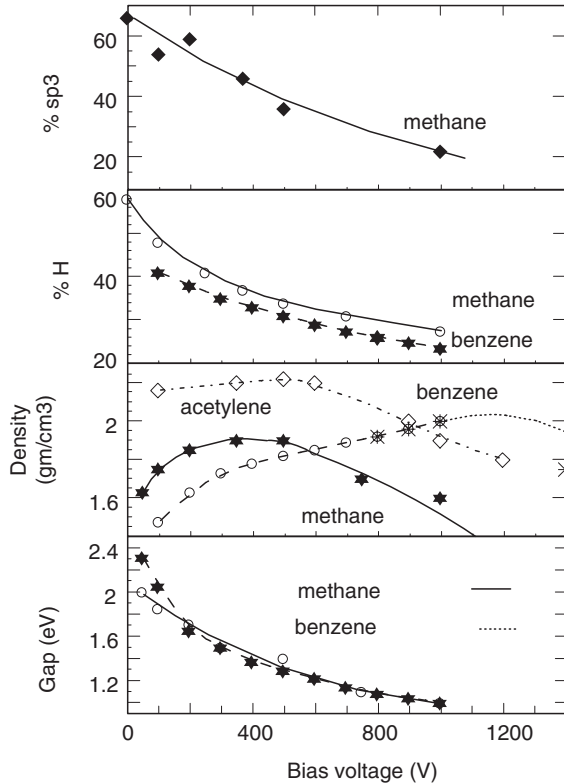


Fig. 6 Variation of the sp^3 fraction with the ion energy for ta-C deposited by an early cathodic arc [4] and by mass-selected ion beam deposition [6]

5 Growth Rates in PECVD

The precursor molecule for a-C:H growth is generally chosen with regard to the film growth rate. The growth rate is found to be strongly correlated to the ionisation potential of the molecule [8], as seen in Fig. 7. Unsaturated molecules with low ionisation potentials such as acetylene give much higher growth rates than methane.

Acetylene is also favoured by many workers because it has the lowest H content (along with benzene) of the usual precursor molecules, and thus the H content of the resulting a-C:H film also tends to be lower [19]. This gives the densest films (see Fig. 8). As the Young's modulus is related to the fraction of C-C bonding, lowering the H content tends to raise modulus, and thus hardness, for a given sp^3 content.

A disadvantage of acetylene as source gas is that it is impure, with about 1% impurity, compared to the highly pure availability of electronic grade methane.

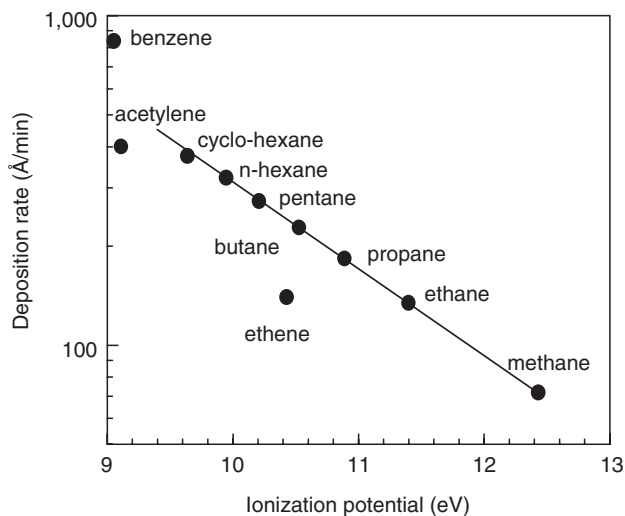


Fig. 7 Variation of PECVD growth rates of a-C:H on the ionisation potential of the precursor species

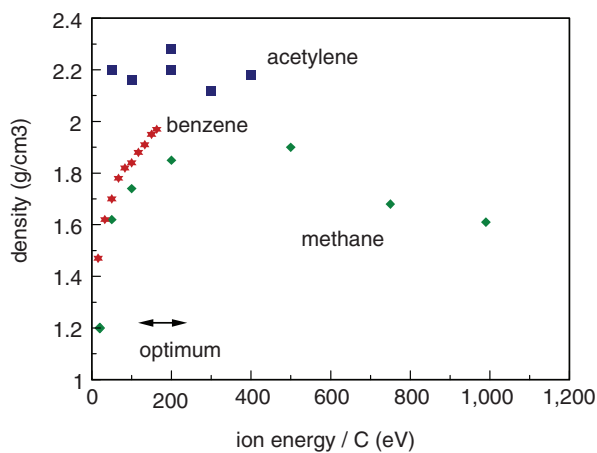


Fig. 8 Variation of a-C:H density with ion energy per C ion, for various precursor molecules

A second reason not to use acetylene is to access high ion energies. It is the ion energy per C atom that matters. Thus, one might want to deposit at a high ion energy of say 500 eV per C in order to reduce stress. An ion energy per C atom requires 500 eV for methane but 1,000 eV for acetylene. The former is experimentally easier, cheaper and safer.

An unusual combination is to deposit a-C:H from methane at a high ion energy (600–1,200 eV). This situation leads to the so-called superlow friction films of a-C:H which have been widely studied by Erdemir et al. [28–33]. The high ion energy may allow thicker films, due to stress relaxation, as discussed shortly. For methane, the ion energy per C atom is the same as the nominal value. Thus the ion energy is well over the optimum of value of 100 eV corresponding to maximum sp^3 content. Thus the C bonding is partly graphitic. But the high ion energy also leads to an implantation of much of the H atoms of the incident methane, so that the film has an unusually higher H content, for a-C:H films of this sp^2 content. This combination of high H content and higher sp^2 content is unique to methane as precursor. This also leads to be high surface H content, which appears to lead to very low friction coefficients. The friction processes of a-C:H and of diamond have been modelled by Harrison [34,35].

6 Stress

A second situation is the desire for thick films. The main disadvantage of DLC and ion beam methods is that they lead to films with a large intrinsic compressive stress. This stress causes delamination in thicker films. There is a maximum thickness of the film before it delaminates [2].

There are a number of methods to minimise this effect, such as using an adhesion layer of Si, a graded adhesion layer, multi-layered or metal alloying. Another method is to use high-energy pulsed deposition as in the plasma ion implantation immersion (PIII) process. In this case, the film is deposited with a mean ion of say 100 eV, but it is also subjected to short ($\sim 10 \mu\text{s}$) pulses of much higher bias voltage of 1,000 eV or more. The high-energy ions cause a stress relaxation [36,37]. It appears that the high-energy ions allow some atomic relaxation which relieves the stress. A small amount of the sp^3 sites convert to sp^2 , but not too many, so the overall diamond-like character remains. This process will work for both ta-C and a-C:H, in principle.

7 Density: sp^3 Plot

There are two typical variations of density with sp^3 content. The first, for H-free a-C, is a linear variation [18], expected from Vegard's law for an alloy. The second is for a-C:H. If it is ta-C:H prepared only from high-density plasma sources, the density increases monotonically with sp^3 content up to considerable sp^3 contents. Often, the density reaches a maximum, then the H content rises too rapidly and the large molecular size of C–H groups causes the density, which passes through a maximum, to fall at high sp^3 values (Fig. 9).

Raman has recently been found to be able to follow these trends in local bonding [38,39]. This is described in detail in Chapter 2. It was found that the width of the

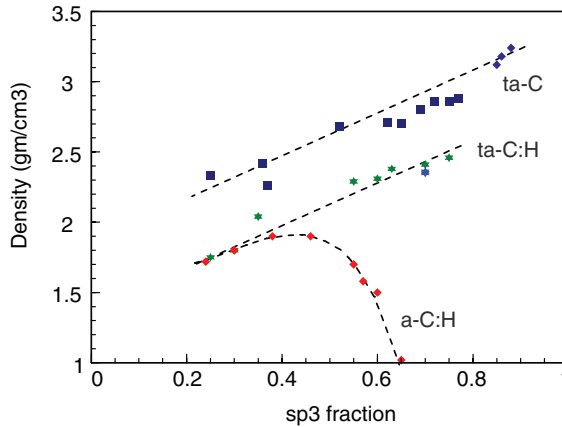


Fig. 9 Variation of the mass density derived from XRR or EELS with the total C sp^3 fraction, for ta-C, ta-C:H and a-C:H films

Raman G peak (FWHM of G) was proportional to the density, for most a-C's. It was also found that the dispersion of the wave number of the G peak with varying excitation energy (G dispersion) was proportional to the sp^3 content. Thus, a plot of G width versus G dispersion mirrors the dependence of density on sp^3 content shown in Fig. 9.

8 Alloyed DLCs

The properties of DLCs have been of sufficient interest that groups have naturally extended the range of materials by alloying with various other elements [40–45] (see Chapters 9, 12, 13, 19 and 24 for further details). The motivation for this is varied and the problem of compressive stress has been a major limitation. This led to the study on the effect of alloying with various transition metals, such as Ti, Cr and Al. Al in particular was found to reduce the stress, and thus allow growth of thicker films. These can be referred to as a-C:Me or a-C:H:Me, respectively. Graded layers have been employed. Alloying with transition metals is also motivated by a need to increase the mechanical toughness of the films. DLC is a rather brittle ceramic. Alloying with carbide-forming metals make it tougher due to the formation of nanosized carbide inclusions. Addition of Si to a-C:H is also found to lower stress and reduce the friction coefficient in humid conditions [44].

The second motivation for alloying with other elements is to modify the surface energy. Addition of F lowers the surface energy considerably. Si, N and B modify it. These can be referred to as a-C:X or a-C:H:X, respectively [42]. Films, with the addition of N in particular, have been extensively studied due to the interest in the hypothetical compound C_3N_4 in which C is sp^3 bonded and N is sp^2 bonded [43].

However, this effort is now declining, as it appears that this material cannot be prepared in the desired state.

9 Conclusions

The various forms of DLC is an amorphous carbon (a-C) or hydrogenated amorphous carbon (a-C:H) have been classified. They are materials with a high fraction of sp^3 carbon bonding [1,2]. They are prepared by a deposition process which involves energetic ions. These ions give rise to the sp^3 bonding. The ion-induced process is distinct from plasma polymerisation, where the C sp^3 bonding arises from a condensation of C–H groups with the evolution of molecular H_2 . DLC can also be alloyed with other elements such as Si, metals or B, N and F, in which case they are referred to as a-C:Me, a-C:H:Me, a-C:X or a-C:H:X, respectively.

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