Non-destructive Characterisation of Carbon Films

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Abstract The availability of reliable characterisation tools for carbon films down to a few atomic layers' thickness is one of the most decisive factors for technology development and production. In particular, non-destructive techniques are preferred. This chapter reviews the use of x-ray reflectivity, surface acoustic waves, and Raman spectroscopy to characterise carbon films in terms of density, thickness, layering, elastic constants, roughness, structure, and chemical composition. Raman spectroscopy, in particular, allows to probe of most of the materials properties, even if indirectly. The use of atomic force microscopy (AFM) will be considered to assess the basic growth mechanism of carbon films. The measurement of thermal conductivity of carbon films will also be reviewed.

1   Introduction

The availability of reliable characterisation tools for carbon films down to a few atomic layers' thickness is one of the most decisive factors for technology development and production. In particular, non-destructive techniques are preferred.

Rather than reviewing all possible methods suitable to assess carbon films, here I focus on x-ray reflectivity, surface acoustic waves, and Raman spectroscopy. For carbon films, the combination of these methods allows a full structural characterisation in terms of density, thickness, layering, elastic constants, roughness, structure, and chemical composition. Raman spectroscopy, in particular, allows the assessment of most of the materials' properties, even if indirectly. I will also show how atomic force microscopy (AFM) can be used to study the basic growth mechanism of carbon films. Finally, I will review the thermal conductivity of carbon films.

Many other techniques are utilised in literature, for example, EELS, NMR, XANES, and XPS/X-AES. These are either destructive, or require isotope enhancement

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or preferentially probe the samples surface. As such they will not be considered in detail here. However, the calibration of some of the correlations presented is done with EELS, NMR, or XPS, as highlighted in the text.

2   Properties of Carbon Films

The great versatility of carbon materials arises from the strong dependence of their physical properties on the ratio of sp^2 (graphite-like) to sp^3 (diamond-like) bonds. There are many forms of sp^2-bonded carbons with various degrees of graphitic ordering, ranging from microcrystalline graphite to glassy carbon. In general, an amorphous carbon can have any mixture of sp^3, sp^2 and even sp^1 sites, with the possible presence of hydrogen and nitrogen. The compositions of nitrogen-free carbon films are conveniently shown on the ternary phase diagram (Fig. 1a).
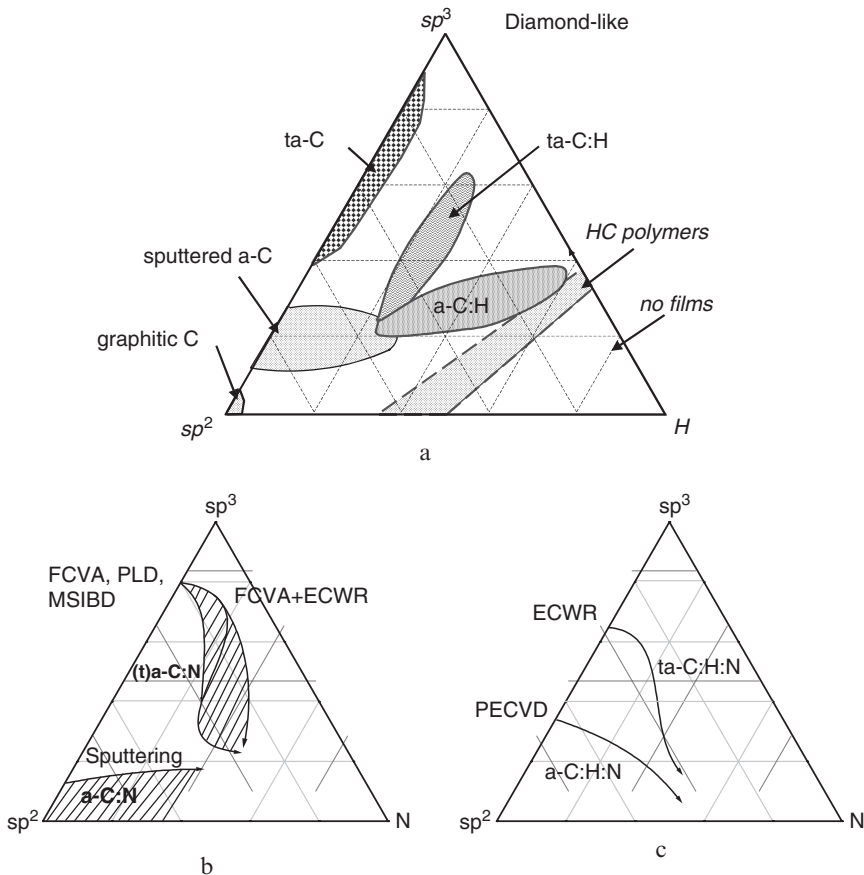

Fig. 1 (a) Ternary phase diagram of amorphous carbons. The three corners correspond to diamond, graphite and hydrocarbons respectively. (b,c) Ternary phase diagrams of amorphous carbon nitride alloys, without hydrogen (b) or with hydrogen (c), showing sp^2 C, sp^3 C and N

The key parameters are: (1) the sp^3 content; (2) the clustering of the sp^2 phase; (3) the orientation of the sp^2 phase; (4) the cross-sectional nanostructure; 5) the H or N content.

Tetrahedral amorphous carbon (ta-C) is the diamond-like carbon (DLC) with the maximum C–C sp^3 content. This material can be grown with deposition techniques involving energetic ions such as filtered cathodic vacuum arc (FCVA), mass selected ion beam deposition (MSIBD), and pulsed laser deposition [1–7]. The sp^3 content alone mainly controls the elastic constants [8], but films with the same sp^3 and H content but different sp^2 clustering, sp^2 orientation, or cross-sectional nanostructure can have different optical and electronic properties [9]. As we move from ordered graphite to nanocrystalline graphite, to amorphous carbon, and finally to sp^3-bonded ta-C, the sp^2 groups first become smaller, then disordered, and finally change from ring to chain configurations [9–11]. The evolution of the sp^2 phase clustering can be represented by the *amorphisation* trajectory [9–11] (Fig. 2) consisting of three stages from graphite to ta-C: (1) graphite→nanocrystalline graphite (nc-G); (2) nanocrystalline graphite→ sp^2 a-C; (3) a-C→ta-C. Note how the sp^2 clustering evolution and the sp^3 content evolution follow two distinct paths (Fig. 2b).

We classify hydrogenated amorphous carbons into four types [12]:

1. a-C:H films with the highest H content (40–60 at. %). These films can have up to 70% sp^3. However, most of the sp^3 bonds are hydrogen terminated and this material is soft and has low density. We call these films polymer-like a-C:H (PLCH). Their band gap ranges from 2 to 4 eV. They are usually deposited by plasma-enhanced chemical vapour deposition (PECVD) at low bias voltage [13–15].
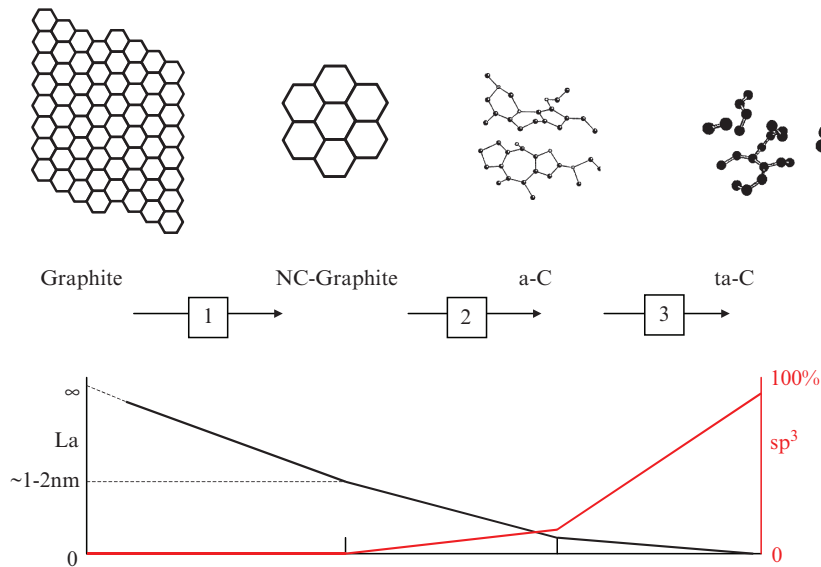

Fig. 2 (a) Variation of the sp^2 configuration along the three amorphization stages. (b) Schematic comparison of the evolution of the sp^2 cluster size (L_a) and sp^3 content. Note that in stages 1–2 to a strong sp^2 cluster size decrease corresponds a relatively small sp^3 increase, whilst the opposite is seen in stage 3

2. a-C:H films with intermediate H content (20–40 at. %). Even if these films have lower overall sp^3 content, they have more C–C sp^3 bonds than PLCH. Thus, they have better mechanical properties. Their optical gap is between 1 and 2 eV. We call them diamond-like a-C:H (DLCH). They are usually deposited by PECVD [12–14], or electron cyclotron resonance (ECR), or reactive sputtering at moderate bias voltage [12,14–18].

3. Hydrogenated tetrahedral amorphous carbon films (ta-C:H). ta-C:H films are a class of DLCH in which the CC sp^3 content can be increased whilst keeping a fixed H content, as in Fig. 1a. Many films defined in literature as ta-C:H are just DLCHs. However, due to the highest sp^3 content (~70%) and 25–30 at. % H, ta-C:Hs are really a different category as indicated by their Raman spectra, their higher density (up to 2.4 g/cm^3) and Young's modulus (up to 300 GPa) [1,8,19]. Their optical gap can reach 2.4 eV [20]. These films are deposited by high-density plasma sources such as electron cyclotron wave resonance (ECWR) [20,21] and plasma beams (PBS) [22,23].

4. a-C:H with low H content (less than 20 at. %). They have a high sp^2 content and sp^2 clustering. The gap is under 1 eV. We call them graphite-like a-C:H (GLCH). They are usually deposited by PECVD at high bias [13,14] or by magnetron sputtering [18].

Carbon nitrides are another important class of carbons often used for tribological applications. As for hydrogenated amorphous carbons, it is possible to classify the bonding in carbon nitrides into four types, based on the bonding in the corresponding N-free film [24]. The changes in the properties of carbon nitrides N content is increased should be compared with the corresponding N-free films. Thus, the variation of mechanical and electronic properties when N is added to a sp^2-bonded carbon differs from when N is added to a high sp^3 film. This is true whether H is present or not. There are four basic types of carbon nitrides, derived from sp^2 a-C, tetrahedral amorphous carbon (ta-C), a-C:H (from polymeric to diamond-like) and ta-C:H. Figure 1b and c shows the ternary phase diagrams which summarise the compositions of carbon nitrides with increasing N content [24]:

1. a-C:N. Here N is introduced in amorphous carbons with a high fraction of sp^2 bonds. An unusual aspect of these films is that a-C:N deposited above 200°C can become nanostructured, with a strong cross-linking between graphitic planes, which gives an increase in mechanical hardness and large elastic recovery [25–28]. However, this does not require an increase of the sp^3 fraction (see Fig. 1b,c) but can rather be seen as an increase in disorder [26–28]. This beneficial effect is exploited in carbon nitrides used in magnetic storage, since the deposition of the carbon layer on the disk is performed at ~200°C, the process temperature resulting from the magnetic layer deposition.

2. ta-C:N. This group includes films deposited by MSIBD [29], PLD [30], or FCVA [31–34], either under N$_2$ atmospheres or by nitrogen-assisted beams. Low pressure deposition and high ionisation ensure that film growth is controlled by ions. Resistivity and optical gap decrease when compared to the pure ta-C films

[24]. Generally, the sp^3 content of ta-C remains high at 80–90% up to about 10% N, and then the sp^3 content and density fall rapidly [24]. This sharp decrease is due to the high deposition pressure [35]. The sp^2 sites begin to clustering at low N contents (1%), before the sp^3 to sp^2 transition and this decreases the band gap [24]. Note that, although a general decrease of sp^3 content with N is observed, the trends are different according to the deposition systems [24]. This implies that the evolution of the sp^3 fraction and the degree of clustering of the sp^2 phase can be different for films of the same N/C ratio [24].

3. a-C:H:N. These are usually grown by PECVD [36–38]. a-C:H:N films have been deposited using a mixture of an hydrocarbon gas, such as methane, acetylene, benzene, and N_2 or NH_3. N incorporation is hindered if a high fraction of N_2 or a high substrate temperature is used. The best conditions for nitrogen incorporation correspond to the lowest H content in the gas phase. In contrast to a-C:N, the hardness in a-C:H:N decreases with N, due to the formation of more terminating groups, such as NH_2 and nitrile [24]. Higher substrate temperatures and bias decrease the overall N and H content, giving a more graphite-like material. In principle each a-C:H:N can be further classified as DLCHN, PLCHN. GLCHN, by considering the properties of the pristine a-C:Hs and their classifications, as described above.

4. ta-C:H:N. These are prepared by high-density plasma sources, such as electron cyclotron wave resonance (ECWR) [39,40], ECR [41,42], or helicon sources [43]. Introducing nitrogen into ta-C:H induces clustering of the sp^2 phase, without an appreciable sp^3 to sp^2 conversion, up to ~20% at N, with a corresponding increase in conductivity and decrease of optical gap. Higher N contents cause a transition to a lower sp^3 fraction and give softer films similar to PLCHN [24].

There are then many other carbon films studied in literature, which evolve from the pattern presented so far. Here we will not deal with them in detail. The discussed characterisation techniques can be extended to their case. For instance, their Raman spectra can be easily understood by considering the effect on the sp^2 clustering of the heteroatoms and using the rules for the interpretation of the spectra we will present in Section 5. Clearly, if carbides are formed, they will also show their Raman signature.

It is worth mentioning: (1) fluorinated DLCs, which can be used as low dielectric constant insulators to improve the switching performances of circuits (see, e.g. Ref. [44]). (2) Amorphous carbon–silicon alloys (a-C_{1-x}:Si_x:H_y) and hydrogenated carbon–silicon alloys (a-C_{1-x}:Si_x:H_y). They are studied both in the Si-rich and C-rich composition range [45]. The Si-rich alloys have a wider band gap than a-Si:H and are widely used as p-type window layers in a-Si:H-based solar cells [46]. The C-rich alloys are of interest as luminescent materials and as mechanical coating materials. The addition of Si to a-C:H has the beneficial effect of reducing the grown-in compressive stress, improving the thermal stability, and maintaining the low friction coefficient of a-C:H to a higher relative humidity [45,47,48]. (3) Metal incorporated films to reduce stress, wear and lower friction (see, e.g. [49]). (4) Nanostructured sp^2 carbons [50]. These are interesting in their own right. They