Diamond & Related Materials 43 (2014) 12–22

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Diamond-like carbon (DLC) films as electrochemical electrodes

Aiping Zeng [a],*, Victor F. Neto [a], Jose J. Gracio [a], Qi Hua Fan [b]

[a] Centre for Mechanical Technology and Automation, Department of Mechanical Engineering, Aveiro Institute of Nanotechnology, University of Aveiro, Aveiro 3810-193, Portugal
[b] Department of Electrical Engineering and Computer Science, South Dakota State University, Brookings, SD 57007, USA

ARTICLE INFO

Article history:
Received 11 October 2013
Received in revised form 26 December 2013
Accepted 4 January 2014
Available online 9 January 2014

Keywords:
Diamond-like carbon films
Electrochemistry
Electrode

ABSTRACT

Amorphous carbon can be any mixture of carbon bonds of sp^3, sp^2, and even sp^1, with the possible presence of hydrogen. The group of mixture, of which there is a high fraction of diamond-like (sp^3) bonds, is named diamond-like carbon (DLC). Unlike the crystalline carbon materials: diamond, graphite, carbon nanotube, fullerene and graphene, DLC can be deposited at room temperature without catalyst or surface pretreatment. Furthermore, its properties can be tuned by changing the sp^3 content, the organization of sp^2 sites and hydrogen content, and also by doping. This paper firstly reviewed the electrochemical properties of DLC films and their applications.

Contents

1. Introduction

Carbon is very versatile and can crystallize in the form of diamond and graphite. Recently, there have been continuous and important advances in the carbon science, such as chemical vapor deposition (CVD) of diamond [1] and the discovery of fullerenes [2], carbon nanotubes [3,4], and single-layer graphene [5]. There have also been major developments in the field of disordered carbons. In general, an amorphous carbon (a-C) can have any mixture of sp^3, sp^2, and even sp^1 sites, with the possible presence of hydrogen. An amorphous carbon with a high fraction of diamond-like (sp^3) bonds is known as diamond-like carbon (DLC). DLC can have some extreme properties similar to diamond, such as high mechanical hardness, chemical inertness, optical transparency,

---

* Corresponding author. Tel.: +351 234370830; fax: +351 234370953.
E-mail address: aiping@gmail.com (A. Zeng).

0925-9635/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.diamond.2014.01.003

and it is a wide band gap semiconductor [6–15]. It is much cheaper to produce than diamond. DLC films have widespread applications as protective coatings in areas such as optical windows, magnetic storage disks, car parts, and biomedical coatings and as micro-electromechanical devices (MEMs).

There has been intense research to apply boron doped CVD diamond, carbon nanotube, fullerenes and graphene into electrochemical applications: energy storage and sensing. Unlike these carbon materials, DLC films can be deposited at room temperature without surface specific treatment or metal catalyst. Therefore they are easily fabricated into micro-devices with conventional semiconductor technology in mass production. The electrical conductivity of DLCs can also be tuned by doping. These characteristics have led to recent efforts in studying the electrochemistry of intrinsic DLCs and doped DLCs with the goal to replace highly boron doped CVD diamond as electrode materials, particularly used for electroanalysis. This paper will review the electrochemistry of DLC films.

2. Structure, deposition, physical properties and doping of DLCs

2.1. Structure, deposition and physical properties of DLC

The term diamond-like carbon (DLC) was originally employed by Aisenberg and Chabot referring to thin amorphous carbon films exhibiting physical and chemical properties similar to diamond [16]. DLC is a metastable allotrope of carbon composed of a mixture of sp^3- and sp^2-hybridized carbon, which is incorporated into an amorphous matrix. Depending upon the chemical composition of DLC, two types of layers can be discriminated: hydrogenated and hydrogen-free DLC. Hydrogenated films are deposited from hydrocarbon sources [17–19], or in the presence of hydrogen gas, and can contain up to 60% hydrogen. In contrast, hydrogen-free films are deposited using solid carbon sources (graphite [16,20–25] or fullerene [26]) sources either in vacuum or in the presence of noble gases. Hydrogen-free DLC typically contains <1% hydrogen. Hydrogenated films generally exhibit lower hardness values, lower wear resistance, and lower thermal stability compared to hydrogen-free DLC. Furthermore, each type of DLC film can be further subdivided into two additional groups based upon the fraction of sp^3-hybridized carbon present in the film. The different compositional arrangements are graphically represented in the form of a ternary phase diagram in Fig. 1, as first used by Jacob and Moller [27].

There are many a-Cs with disordered graphitic ordering, such as soot, chars, glassy carbon, and evaporated a-C. These lie in the lower left hand corner. The two hydrocarbon polymers, polyethylene $(CH_2)_n$ and polyacetylene $(CH)_n$, define the limits of a triangle in the right hand corner beyond which interconnecting C–C networks cannot form, and only molecules form. Deposition methods have been developed to produce a-Cs with increasing degrees of sp^3 bonding. Sputtering can extend from sp^2 bonding some way towards sp^3 bonding. If the fraction of sp^3 bonding reaches a high degree, McKenzie [11] suggested that the a-C is denoted as tetrahedral amorphous carbon (ta-C), to distinguish it from sp^2 a-C. Ta-C films can be deposited by the methods of filtered cathodic vacuum arc (FCVA) (sp^3 C fraction can reach 85% [28]) and pulse laser deposition (PLD) (sp^3 fraction can reach 70% [29]). A range of deposition methods, such as plasma enhanced chemical vapor deposition (PECVD) [9], is able to reach into the interior of the triangle. This produces a-C:H. Although this is diamond-like, it is seen from Fig. 1 that the content of sp^3 bonding is actually not so large, and its hydrogen content is rather large. High plasma density PECVD reactors can produce a high sp^3 bonded material with low hydrogen, which is called hydrogenated tetrahedral amorphous carbon (ta-C:H) by Weiler et al. [30]. Sp^3 C for ta-C:H can reach 70% [30]. A-C and a-C:H films are also able to be synthesized by electrochemical deposition from hydrocarbon solvents [31,32] but there is much less research carried out on the electrochemical depositions compared to the vacuum approaches.

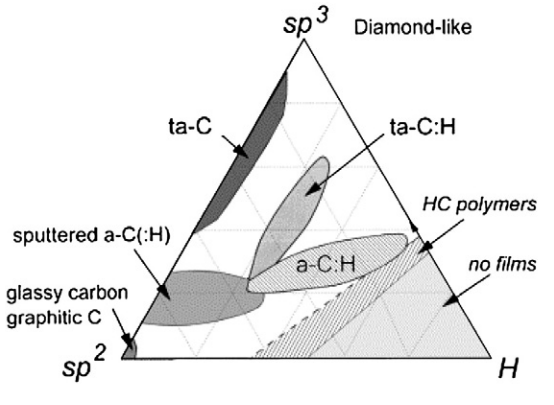

Fig. 1. Ternary phase diagram of bonding in amorphous carbon–hydrogen alloys [27,37].

The sp^3 bonding of DLC determines many beneficial properties of diamond, such as its mechanical hardness, chemical and electrochemical inertness, and wide band gap. Typical properties of the various forms of DLC are compared to diamond and graphite in Table 1 [27,29,30,33–37]. It is possible to produce DLCs by a wide range of vacuum deposition methods [6,20]. The sp^3 bonding of carbon in DLCs is a function of ion energy, and the highest sp^3 fractions are formed by C^+ ions with ion energy around 100 eV [30].

2.2. Doping DLC films

According to ab initio calculations and first principle simulations [43], a-C is naturally slightly p-type due to the presence of defects. Here, the defects are classified into two types: sp^3 or sp^2 dangling bonds and any sp^2 clusters containing an odd number of sp^2 sites [43,44]. The π and π* bands are localized, whereas the σ and σ* bands are delocalized. There have been extensive studies of nitrogen incorporation in all forms of DLC. Nitrogen is an obvious candidate as a donor in ta-C and ta-C:H. It was noted that ta-C and ta-C:H have narrower band gaps than diamond does, so that the levels like N which are deep in diamond can be shallow in ta-C and ta-C:H. The nitrogen can be introduced as a gas into the deposition atmosphere where it becomes ionized by the plasma, or it can be introduced by a separate ion gun [45]. Generally, introducing low levels (~1%) of nitrogen into a ta-C matrix results in a decrease in conductivity, followed by an increase at higher amounts (>2%). Un-doped ta-C is slightly p-type with Fermi level lying just below mid-gap [45,46], and the initial incorporation of nitrogen causes the Fermi level to shift towards mid-gap, thereby decreasing the conductivity. With increased nitrogen incorporation, the Fermi level continuously shifts towards the conduction band resulting in slightly increased conductivity. In addition, at high nitrogen content sp^2-hybridized carbon clustering increases, also contributing to the electrical conductivity observed.

Subsequently, a hydrogenated analogue of ta-C, ta-C:H, deposited from a low pressure plasma beam source has an optical gap of 2.7 eV [47], but again the conductivity activation energy for undoped ta-C:H is much less than a half of the optical gap, suggesting that the Fermi level lies well away from mid-gap [47]. N additions to ta-C:H are also found to give a strong increase in the conductivity, while the optical gap remains unchanged. In this case, it was not possible to observe the initial decrease in conductivity as Fermi level passed through mid-gap [47]. These latter results, therefore, suggest that N does act as a substitutional donor in ta-C and ta-C:H, but its role in a-C:H with low sp^3 C fraction is less clear. N incorporation in the a-C:H films also favors the formation of sp^2 units [47]. Thus, in all the forms of DLC, nitrogen acts as a weak donor in the compensation mode and the N-doped DLC is a weak n-type semiconductor.