

Review Article

A Brief Review on the *In Situ* Synthesis of Boron-Doped Diamond Thin Films

Vadali V. S. S. Srikanth, P. Sampath Kumar, and Vijay Bhooshan Kumar

School of Engineering Sciences and Technology, University of Hyderabad, Hyderabad 500046, India

Correspondence should be addressed to Vadali V. S. S. Srikanth, vvsssse@uohyd.ernet.in

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Diamond thin films are well known for their unsurpassed physical and chemical properties. In the recent past, research interests in the synthesis of conductive diamond thin films, especially the boron-doped diamond (BDD) thin films, have risen up to cater to the requirements of electronic, biosensoric, and electrochemical applications. BDD thin films are obtained by substituting some of the sp^3 hybridized carbon atoms in the diamond lattice with boron atoms. Depending on diamond thin film synthesis conditions, boron doping routes, and further processing steps (if any), different types of BDD diamond thin films with application-specific properties can be obtained. This paper will review several important advances in the synthesis of boron-doped diamond thin films, especially those synthesized via gas phase manipulation.

1. Introduction

Diamond thin films, which are *nowadays* routinely synthesized by employing chemical vapor deposition (CVD) technique, possess unique properties like high thermal conductivity, high carrier mobilities, high break-down field characteristics, chemical inertness, biocompatibility, bio-sensing ability and so forth [1–11]. In the recent past, researchers worldwide have been exploring diamond thin films especially for electronics, biosensing, and electrochemical applications [9–11]. However, to realize these applications, it is necessary that the diamond thin films are electrically conductive in nature (in addition to possessing a combination of the above-mentioned properties) which are otherwise insulating. The conductivity of diamond thin films can be attuned to an application requirement typically by carrying out suitable doping events. Amongst the available conductive (doped, p- and n-type [9–16]) diamond thin films, the p-type semiconducting boron-doped diamond (BDD) thin films [17–35] are the most popular ones and are being studied extensively. BDD thin films are synthesized by substituting some of the sp^3 hybridized carbon atoms in the diamond lattice with boron atoms. BDD thin films are mainly obtained by (i) *in situ* (during diamond thin film synthesis) and (ii)

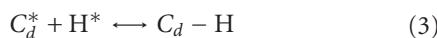
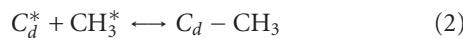
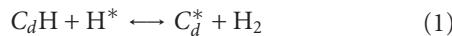
ex situ (after diamond thin film synthesis) doping routes. *In situ* doping involves gas phase manipulation, that is, addition of certain amount of boron containing gas species to the diamond forming gas mixtures during the diamond thin film synthesis. *Ex situ* doping involves boron doping into the already synthesized diamond thin films mainly via ion implantation. Depending on the diamond thin film synthesis conditions and the above-mentioned boron doping routes, and further processing steps (if any), different types of BDD thin films with application-specific properties can be obtained. BDD thin films-based electrochemical sensors, biosensors, water purification electrodes, unipolar devices, ultraviolet light generators, and so forth have already been developed [9–11].

This article will review several advances in the synthesis of BDD thin films (especially those synthesized via gas phase doping) that brought about unique variations in physical and chemical characteristics of the films making them as suitable electrode materials. In the next section, a brief discussion on the typical CVD technique used to synthesize diamond thin films will be made. In the subsequent section, several aspects of BDD thin films including concept of doping, *in situ* boron doping, and electrode applications will be discussed. This

paper will be concluded with several remarks on BDD thin films.

2. CVD of Diamond Thin Films

In CVD of diamond thin films, one carbon atom at a time is added from a carbon containing activated gas phase (maintained at a lower pressure) to an initial template (a pretreated substrate) resulting in a thin film that constitutes sp^3 carbon atom network (the diamond). Typical CVD diamond thin film synthesis protocol involves gas mixture activation, gas-phase reactions, and the subsequent transfer of diamond forming gas species onto the substrate surface; subsequent surface reactions lead to the formation of a diamond thin film. Hydrocarbon (typically methane)/hydrogen gas mixtures are employed and their activation leads to a harsh environment dominated by reactions involving atomic hydrogen. Activation can be done via surface-mediated thermal process (as in hot filament CVD) or via energy transfer from gas-phase collisions with excited free electrons (as in microwave plasma enhanced CVD). Due to the activation, molecular hydrogen (H_2) dissociates into atomic hydrogen. Diamond growth takes place via site-activation by a surface hydrogen abstraction reaction (1), followed by addition reaction (2) of a hydrocarbon radical like CH_3 . C_d represents a surface radical. The competition between surface activation reaction (1) and H-atom recombination reaction with the surface radical site (3) determines the number of active nucleation sites available for a particular set of synthesis conditions.



The stable nanosized crystallites formed during the nucleation stage typically exhibit spherical shapes. With time, nucleation density increases up to a certain value upon which it terminates or ceases to occur at a measurable rate. The isolated crystallites now grow and develop facets due to the relatively high rate of surface carbon diffusion from the surrounding surface sites. Once the crystals grow large enough to coalesce with each other, they form grain boundaries and then continue growing as a continuous diamond film. The morphology of a growing diamond surface depends on the rates at which different diamond planes grow. Under typical growth conditions, the morphology assessment of a diamond film can be made by the growth parameter $\alpha = \sqrt{3}(\nu_{100}/\nu_{111})$ where ν_{100} and ν_{111} are the normal growth velocities of (100) and (111) diamond planes, respectively. The grains exhibiting the fastest growth in the direction perpendicular to the substrate overshadow other slower-growing grains to form a continuous film with a columnar structure. This mode of film growth is known as evolutionary selection principle. Diamond grain growth dependent on facet reactivity and selectivity which is on the contrary to evolutionary selection principle is also possible under certain CVD experimental conditions. Depending on the synthesis conditions like substrate surface pretreatment,

reaction temperature and pressure, and gas composition, epitaxial, oriented, and polycrystalline (with micron- and nano-sized grains) diamond thin films (Figure 1) can be synthesized. Please refer to chapter 2 in reference [11] for more details on aspects of diamond thin film nucleation and growth.

After the advent of low pressure gas phase synthesis (CVD) of diamond thin films [38–40], numerous noteworthy and path breaking advances have successively taken place [1–11, 41–49]; these advances have made the following possible: (i) tremendous increase in diamond thin film growth rates, (ii) substrate selectivity and large area deposition, (iii) low temperature deposition, (iv) single crystalline thin film synthesis, (v) phase mixture diamond nanocomposite thin film deposition, (vi) doped diamond thin film synthesis, and so forth. At present various CVD methods such as hot filament, direct current (DC) plasma, radio frequency (RF) plasma, microwave plasma, electron cyclotron resonance (ECR) microwave plasma CVD, and so forth, and their hybrids are being used to synthesize diamond thin films with highly consistent and desired properties.

3. BDD Films

3.1. Concept of Doping Diamond Thin Films. Diamond is electrically semiconducting (almost insulating) in nature as a consequence of the tetrahedral closed/tight arrangement of carbon atoms that form the diamond lattice; the band structure of diamond constitutes a completely filled valence band and an empty conduction band separated by a wide band gap of 5.5 eV [50–53]. The energy band diagram of boron-doped diamond is shown in Figure 2. Diamond thin films synthesized via the previously mentioned CVD routes (Section 2) are also insulating in nature unless and otherwise they are synthesized in some special and specific conditions. As discussed previously, for many applications the diamond thin films need to be electrically conductive in nature to a desired extent (semiconducting through metallic to even superconducting). There are several ways of achieving this via controlled experiments.

Several nanometers depth of a hydrogen terminated diamond thin film surface can be made p-type semiconductive typically by exposing (via physisorption) it to appropriate adsorbates. These surface adsorbates can be solvated ionic species or neutral species with high electron affinity; in the former case, the species apparently extract electrons from the valence band and react electrochemically and in the later case, the species reduce the ionization potential of the diamond surface and makes its electron affinity apparently negative which in turn leads to an exchange of electrons between the valence band and the species. These processes leave behind holes as the charge carriers. This hole-mediated conduction is explained in terms of a doping famously known as surface transfer doping [54–56]. Diamond thin films can also be made conducting by annealing them under vacuum at high temperatures [57]. Due to annealing, the nondiamond conductive carbon phase formed along the

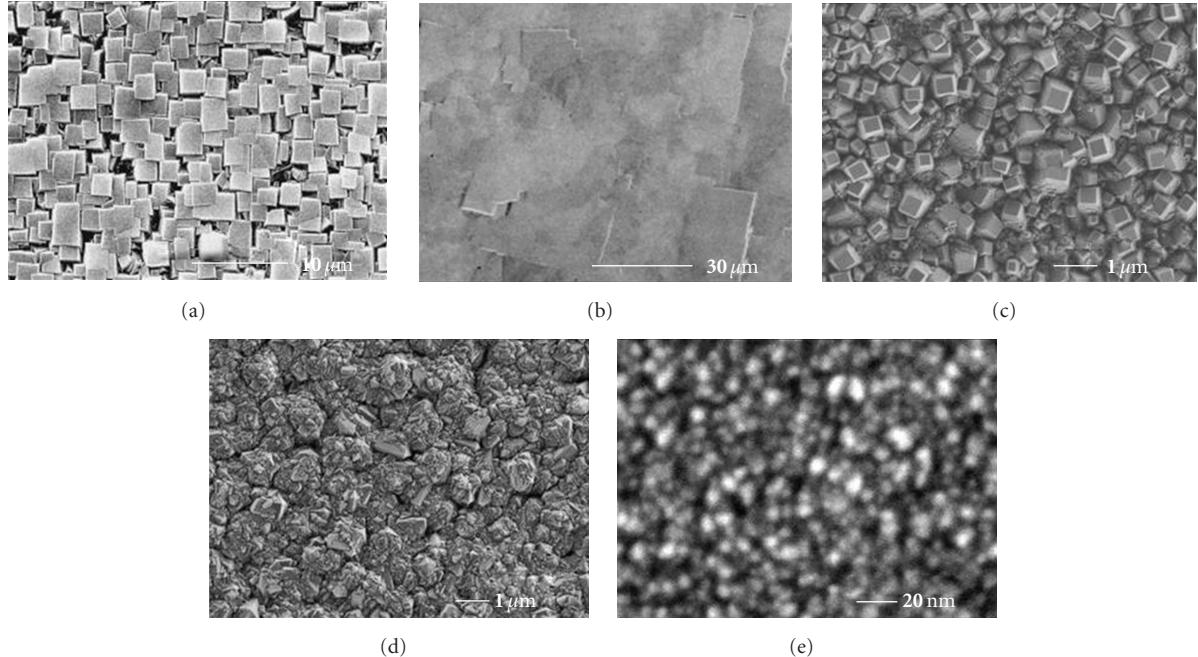


FIGURE 1: Plane view scanning electron micrographs of (a) epitaxial [36], (b) highly oriented (001) [37], (c) (001) oriented, (d) polycrystalline, and (e) nanocrystalline diamond thin films.

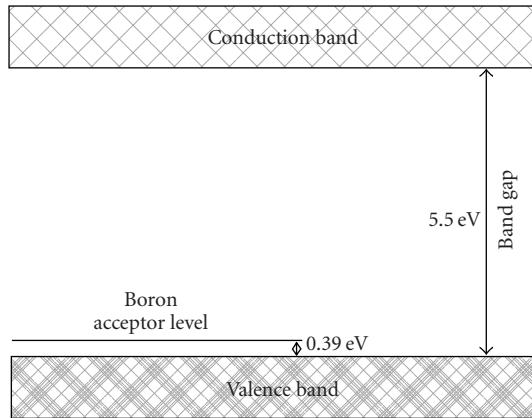


FIGURE 2: Boron acceptor level in the band gap of diamond.

diamond grain boundaries and structural defects formed in the film bulk will result in p-type semiconduction.

As mentioned previously, diamond thin films can also be made conductive by substitutional doping. Here, hetero-atoms (like B, Al, N, P, S, Si, Ni, As, Sb, Cr, Ni, Fe, W, Mo, etc.) with slightly different electronic configurations are made substitutes for some of the sp^3 carbon atoms in the diamond lattice leading to the formation of new energy levels in the band structure that facilitate both p- and n-type conduction depending on the type of dopant. The introduction of a p-type dopant (B, Al, etc.) causes the formation of discrete acceptor levels (Figure 2) above the valence band of diamond. These energy levels are accessible to valence band electrons. When electrons are promoted into

these levels, delocalized holes form in the valence band which facilitates the conductance. A hetero-atom inclusion causes n-type doping (N, P, etc.) by forming a donor level whose electrons can be easily excited into the conduction band.

The closely packed diamond lattice makes substitutional doping, a challenging task. Some of the above-mentioned dopants can be incorporated into the lattice during the synthesis of diamond thin films whilst some can be incorporated via ion implantation [58–60]. Doping via ion-implantation involves forcing the dopant ions into the subsurface regions of diamond thin films rendering them semiconductive. During ion-implantation, since the dopant ion energy is greater than the binding energy of the sp^3 carbon atoms, not only severe damage takes place in the diamond thin films but there is also a possibility of disturbing the stability of the metastable sp^3 bonds leading to the formation of stable sp^2 graphitic bonds upon subsequent high temperature annealing that is carried out to annihilate the damages. However, doping and damage levels can be evaluated prior to the ion-implantation experiments via computer simulations [61], and proper experiments can then be carried out. It has also been pointed out that doping via ion-implantation leads to the formation of resistive diamond thin films, probably due to the compensation (of the desired electrical activity of the dopants) arising from damage-related centers forming in between acceptor and donor energy levels [62]. Other substitutional doping issues that are still difficult to experimentally overcome are (i) high solubility of certain dopants like nitrogen leading to the formation of valueless very deep donor energy levels and (ii) the development of shallow n-type dopants [62].

Amongst the above-mentioned substitutional dopants, the most exploited and successful one is undoubtedly boron. Both geometrically (covalent radius of boron atom is 0.088 nm whilst that of carbon atom is 0.077 nm) and energetically [62] boron atoms are probably the only dopants that can be substitutes for carbon atoms in the diamond lattice. Boron doping into diamond thin films can be done by using any of the following: (i) gas phase manipulations while synthesizing diamond thin films via CVD routes, (ii) ion-implantation, and (iii) high temperature diffusion [25]. In the next section, various aspects of gas phase synthesis (*in situ*) of BDD thin films will be discussed.

3.2. BDD Thin Films via In Situ Doping. Boron containing precursors like diborane, trimethylboron, triethylboron, boron oxide dissolved in acetone/ethanol/methanol, trimethyl borate dissolved in the acetone [35], borane trimethylamine, boron trichloride, boric acid, and other boron-containing unconventional sources (obtained via etching boron, boron oxide, boron nitride, and boron rod) have been introduced into the gas phase during the CVD of diamond thin films to finally obtain BDD thin films [59, 60]. Theoretical thermodynamic studies suggested that the concentrations of BH_3 , BH_2 , and BH radicals in the activated B-C-H gas mixture modify the concentrations of diamond forming radicals (like CH_3 , C_2H_2 , etc.) and atomic hydrogen [63]. The relative efficiencies of boron and carbon incorporation into a growing film from a given B-C-H gas mixture are dependent upon gas phase activation route and other diamond synthesis conditions [64]. During the synthesis of BDD films, the boron species formed in the gas phase give assistance to the surface diffusion of diamond forming species on the already formed diamond surfaces [65]. This leads to the incorporation of boron atoms into both the growing {100} and {111} diamond thin film surfaces. It was found that there is preference (almost 10 times) in the incorporation of boron in {111} growth sectors [28–30]. Boron substitution, diamond crystallinity, and diamond surface morphology are closely related and greatly influence each other during the *in situ* synthesis of BDD thin films [66, 67]. Boron concentration relative to carbon in the gas phase (B/C) has also a strong effect on the growing diamond crystals structure and stability. Low level (<500 ppm B/C) boron addition into the gas-phase not only increases the sizes of growing diamond crystals that will finally constitute the diamond thin film but also enhances the diamond film growth rates. Intermediate level (1000–5000 ppm B/C) boron addition results in p-type BDD thin films with other characteristics similar to the diamond thin films that will be obtained without boron in the gas phase at the same experimental conditions. High level (>4000 ppm B/C) boron addition results in the loss of crystallinity [31, 32]. Still higher level (8000–10000 ppm B/C) disturbs the diamond phase stability. At this level of boron concentration, the much needed (to selectively etch graphite over diamond) atomic hydrogen content in the gas phase gets depleted due to the increase in reactions

between boron species and hydrogen. This in turn results in tremendous decrease in rate at which graphite is etched. Thereby more graphitic content can be found along with diamond in the final BDD thin films [33]. Synthesis of diamond thin films via CVD routes generally takes place in a highly diluted hydrogen gas environment. Thereby hydrogen develops as an impurity within the diamond lattice; but in the case of *in situ* boron doping, hydrogen can form a complex with substituted boron within the lattice and pacify it, which is undesired [68]. It has also been shown that deuterated BDD thin films can be n-type electrical conductors [69]. It has also been shown that single substitutional boron atoms are more stable than boron pairs [62, 70]. If carefully observed, irrespective of the CVD and doping methodologies, an approximately equal ratio of boron to carbon as used in the gas phase constitutes the BDD thin film composition [71].

Substrate selection is very important to synthesize BDD thin films as electrode materials. BDD thin films are often deposited on conductive and self-passivating substrates [72–77]. Natural diamond single crystals, Silicon, graphite, glassy carbon, carbon fiber, titanium, tantalum, tungsten, molybdenum, and niobium are the commonly used substrate materials. Uniform and defect-free BDD thin films can be deposited on silicon substrates. But the brittleness of silicon limits its usage in applications. Also, large area depositions are not possible on silicon. Large area BDD thin film depositions are possible on metal substrates. But to protect the metal substrates from hydrogen embrittlement during CVD process and to improve the adhesion of BDD thin film, an interlayer deposition prior to the BDD deposition is often needed. Thick free-standing BDD thin films can also be obtained. Firstly the thick film is deposited onto typically silicon substrates and in a subsequent step the silicon is removed by chemical etching. Single-crystalline BDD thin films can be obtained by using natural diamond single crystals as the substrates. BDD thin film-based conducting diamond electrodes are the most used ones [73]. In practice, it is required that the substitutional boron in BDD thin films stays in its position during any electrode operation in which the BDD film participates. Theoretically it was shown that the substitutional boron stays in the diamond lattice with a low dynamic distortion [62, 78], and its ionization energy has been predicted as 0.39 eV [62, 79] which matches very closely with the experimental value of 0.37 eV [80]. As the number of doped boron atoms in diamond lattice increases from high to very high values, the acceptor level starts to broaden into a band, and above 3.9×10^{21} boron atoms cm^{-3} in diamond lattice, the broadened band starts to overlap with the valence band resulting in a metal to insulator transition [60, 81]. BDD thin films with typically 10^{19} – 10^{21} boron atoms cm^{-3} in diamond lattice are useful, especially for electrode applications. BDD electrodes have been used to (a) detect very low concentrations of toxic metal ions like lead [82], (b) treat wastewater [83], (c) monitor industrial wastewater by determining chemical oxygen demand [84, 85], (d) synthesize organic and inorganic substances [86], (e) record neurochemical and electrical information in neural prostheses [87], (f) sense several biomolecules [88], and so forth.

4. Conclusions and Future Perspectives

The research field of synthesis of BDD thin films has matured enough and is now delivering thin films with desired and reproducible properties. BDD thin films can now be synthesized routinely on a variety of substrates. However, the elementary general mechanisms of boron substitution into diamond lattice are not completely characterized, understood, and explained. This hinders the control on boron doping and thereby realization of applications that need to be yet explored. With the advent of powerful multiscale modeling and simulation (including quantum level) methodologies, it is now possible to (i) interpret complex experimental data and to establish predictive doping models, (ii) obtain clear-cut ideas on new dopants, and (iii) design and execute novel doping schemes. Compared to the p-type conduction in diamond thin films, n-type conduction has not that matured and demands a greater attention both experimentally and theoretically.

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