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Switching dynamics of morphology-structure in chemically deposited carbon films – A new insight

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ABSTRACT

Carbon is one of the most investigated materials and shows chaotic behavior in terms of evolving structure. Synthesizing carbon materials largely depend on the deposition technique, process parameters, condition of substrate surface and ratio of the gaseous chemistry. A variety of techniques have been employed to depositing carbon films from various gaseous mixtures to different substrate materials. In this study, carbon thin and thick films are discussed for different techniques known as hot filament chemical vapor deposition and microwave plasma chemical vapor deposition where their synthesis process has been explained in a new context. Here, we discuss attained dynamics of atoms (or their tiny grains) amalgamating into a particular phase of grain or crystallite and electron-dynamics responsible for binding atoms in the formation of all sorts of tiny grains, grains and crystallites controlling overall morphology-structure of films thickness at few nanometers to several microns. Carbon atoms when in solid state, on amalgamation at flat surface result into bind under uniform electron-dynamics and when the amalgamation is at uneven surface, (even at atomic level) they result into bind under non-uniform electron-dynamics. Where binding of atoms is at uniform electron-dynamics, a graphitic structure evolves following by different modifications into other carbon phases depending on the orientation of electron states with respect to centre of inner part of atom known as nucleus. Substrates under appropriate surface defects or abrasion result into an improved rate of nucleation of tiny grains, hence, their increased rate of growth. This study embarks on unexplored science of carbon films where in addition to localized process parameters nature of substrate also influence dynamics of formation of tiny clusters, grains and crystallites at their initial stage of formation. Our results and discussions enlighten us to revisit the nucleation and growth mechanisms of different sorts of films deposit at any scale and at any substrate surface constituting different composition.

1. Introduction

Recognition of an element is based on atomic number and in the Periodic Table it provides the position depending on the nature of electronic states. Elements where atoms possess filled states should work in a different way to ones with unfilled state (s). The occupancy of only one unfilled state in the case of hydrogen atom leads into different behavior compared to those comprised two broad categories; atoms with filled states and atoms with unfilled state (s). In carbon atom, not all of the outer eight states are filled and having the deficiency of four electrons according to Periodic Table. This attribute of carbon atom allows us to treat it gas as well as solid depending on the orientation of sets of electrons around the inner part of the atom known as nucleus [1]. In this context, the key factor to evolve carbon structure (master) should be the certain orientation of sets of electrons around the nucleus following by their varying placement angles around the nucleus and with respect to centre of nucleus made under certain arrangement of the process, thus, resulting into emerge modified phase of master structure, one at a time depending on the mechanism of certain arrangement.

It has been disclosed that gold atoms amalgamate under attained dynamics following by their binding under electron-dynamics [2]. In such atoms where electrons, on excitation de-excite to restore the positions (states), photons shape-like Gaussian distribution are resulted and is the cause of binding atoms in any sort of structure [3]. A tiny shaped particle has been

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discussed along with elongation and modification into smooth elements [4]. A carbon film, where tiny grains possess two-dimensional structure (graphite structure or master structure) has been discussed along with enhanced field emission characteristics on elongation and modification of tiny grains into smooth elements, known as UNCD/NCD film [5]. The formation mechanism of different tiny particle under varying concentration of gold precursor has been discussed elsewhere [6]. Again, efforts have been made to tap tiny shaped particles of silver, binary composition of gold and silver and gold in pulse-based electronphoton-solution interface process while processing their precursors where it was concluded that nature of precursor is the one, directing conditions for the formation of large size shaped particles [7]. A tiny particle changing shape and size under varying ratio of pulse OFF to ON time has been investigated elsewhere [8]. A diffusion mechanism of atoms and tiny-sized particles starting from the stretching of electron states of atoms has been discussed while developing extended shape particles under unprecedented fast rate of their development [9] where the law of reflection also included the orientation of surface made into smooth elements dealing incident light and reflected light. Atoms of suitable elements belonging to metals and semi-metals group experience electron transitions and they do elongate or deform but not ionize while inert gas atoms split under suitable field of photonic current [10] and revealing the phenomenon of heat energy and photon energy has been discussed elsewhere [11], in which silicon atom was considered to be the intermediate component for regulating the energy. A tiny-sized particle capable to work either as an effective nanomedicine or as a defective nanomedicine has been discussed elsewhere [12].

In most cases, to deposit and synthesize material, it is extracted from the precursor. Different processing approaches have been utilized for the synthesis of various carbon materials under the variation of process conditions, on examining, revealed different characteristics regardless of that atomic nature of the targeted material (carbon) can never be changed in an isolated system due to naturally built-in machine as per fundamental laws; both energy and mass is remained conserved. Again, special emphasis was remained on the morphology-structure change in those materials under varying process parameters. Despite of that, what nature of the source precursor an atom dealt in the course of dissociation or detachment is to be autonomous, the affinity with counterpart either to atoms of the similar nature or different nature is crucial while targeting needed material evolving certain phase of structure; it also invokes fundamental question, “how atoms of carbon evolve structure and switch electron-dynamics resulting into modification of the phase into those known in their exceptional hardness”? It is necessary to address such fundamental questions of materials science while synthesizing carbon-based materials at nanoscale to microns as they set foundation of advanced engineering and then owing to varying properties (characteristics) under the length scale.

A large number of publications have been appeared on the fabrication of microcrystalline diamond films as well as nanocrystalline diamond (NCD) and ultrananocrystalline diamond (UNCD) films under varying conditions and their synthesis mainly involve techniques known as hot filament chemical vapor deposition (HFCVD) and microwave plasma chemical vapor deposition (MPCVD). A vast range of morphological features of such films observed under different process parameters have been published. However, due to greater availability of parameters range and enhanced growth rate, diamond films synthesized *via* HFCVD show more versatility in terms of morphological features. The morphology of the grains/crystallites in various diamond films targets some selective applications. For example, diamond films evolved with large crystallites (very large size grains) are strong candidates for heat sink application and free-standing diamond films for X-ray windows [13,14], a film in average (reasonable) size of grain is considered suitable for application like high frequency loudspeaker diaphragms [13], a film in small grain size is suitable for cutting tools applications [13,15] and a film in ultra-small size of grain is considered to be a strong candidate for field emission or display panel applications [16–18].

Physics and chemistry in processing carbon-based materials under a range of schemes have been explained in quite a number of studies. In HFCVD, growth mechanism of cubo-octahedral diamond is the competing growths of (100) and (110) crystallographic planes [19]. Model study of diamond films only validates the critical role of aromatic condensation and interconversion of carbon phases mediated by atomic hydrogen in gas-activated deposition [20]. In hot-filament reactor, transport of atomic hydrogen to the growing surface is diffusion limited process under commonly employed conditions [21]. Understanding CVD diamond growth is a complex phenomenon which makes modeling of diamond crystallization a challenging task [22]. In HFCVD and under specific conditions of argon gas environment, the transition of microcrystalline diamond film to nanocrystalline diamond film is observed [23]. On reducing the secondary nucleation, diamond coatings show a very high purity in Raman signal, thus, varying the gas pressure that expands the window of depositing films at high/low growth rate [24]. An improved model of growth mechanisms of diamond films grown *via* HFCVD both in $Ar/H_2/CH_4$ and traditional CH_4/H_2 gas mixtures give some useful information regarding carbon atoms and methyl radicals [25]. May and Mankelevich [26] developed a model for diamond crystallite sizes ranging from 10 nm to several millimeters where growth of diamond is a sliding scale between atomic hydrogen and hydrocarbon radical, and different growth conditions only serve to fix the resulting film morphology and growth rate. In HFCVD, growth rate of the diamond films is influenced jointly by substrate temperature and total pressure [27]. Effects of methane concentration on the characteristics of diamond films have been studied in both HFCVD [28] and MPCVD [29].

Mainly, UNCD/NCD films meant specifically for field emission applications were developed under varying process parameters, gas concentrations/dopants and also with composite/hybrid structures [16–18,30–37]. In UNCD/NCD films, the encapsulated basic idea provides effective route to conduct heat while charge is conducted (flow of electrons) through transpolyacetylene layer around the boundaries of tiny grains. However, our recent studies reveal that in the course of attempting scientific goals considering conduction of charge (flow of electrons) is not a viable solution [5,10] and conduction of heat energy along with propagation of photons characteristics current have been discussed elsewhere [11]. Again, a field force influences (forces) atoms from a distance depending on the nature of their electron states [1].

Our previous studies (also referred the work of others in this study) discussed the various aspect of processing thin thick films of diamond (mainly) along with graphite under various process conditions in the course of employing different substrates' materials and seeding treatment of substrate in chemical vapor deposition as referred in the text. However, the heart of underlying science of carbon-based materials remained crucial and peculiar since the birth of carbon; how, an evolving structure switches one phase to another one, in some cases restoring the phase back, and what are the implications of that phase with respect to neighboring ones, what are the binding mechanism of carbon atoms, their primitive cell evolution and last but not least features of thin or thick film deposited on different nature substrate. These are the questions, which intrigued all through the career of a materials scientist, and more than that to those worked/working on carbon-based materials. This study is an attempt to address many of them, in some