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Synthesis of metal-incorporated graphitic microporous carbon terminated with highly-ordered graphene walls—Controlling the number of graphene layers by ambient-temperature metal sputtering

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ABSTRACT

Metal-incorporated, graphitic microporous carbon, containing highly ordered graphene layers, has been converted from highly thin amorphous carbon film by a metal nanoparticle sputtering process at ambient substrate temperature. A standard direct-current magnetron sputtering system is used in this purpose. The process consists of a dual effect of activation and graphitization of amorphous carbon to graphitic microporous carbon. The sputtering plasma, containing energetic ions and sub-atomic particles, act as dry-etchant to activate the a:C film to transform it into microporous carbon. Whereas, the inelastic 'knock-on' collision between metal nanoparticles/ions and the nuclei of C atoms manifests the atom displacement and re-arrangement into ordered structure to form graphitic domains within the microporous carbon network. The average number of graphene layer formation has been controlled by adjusting the sputtering voltage and current, as the carbon atom displacement rate is dependent on the irradiation current density. Raman spectroscopy and scanning transmission electron microscopy confirms the high controllability of the number of graphene layer formation as a function of sputtering parameters. The method is simple, cost-effective and compatible with modern solid-state device fabrication processing, as it comprises vacuum-based physical vapor deposition techniques, and also, can be adopted easily for transitional metal incorporation into graphene and other carbon nanostructures for potential hydrogen storage and related clean energy applications.

1. Introduction

Carbon-based high surface area materials are very promising for hydrogen storage in fuel cell applications because of light atomic mass, which may lead to higher gravimetric properties like larger specific surface area, greater specific pore volume, and better wt% hydrogen storage [1]. Many interesting carbon nanostructures and nanocomposites have been studied for improved hydrogen storage applications which include micro/mesoporous carbon, graphene, carbon nanotube, fullerene, among others [2–6]. Especially, the recent advancements of graphene-based nanomaterials have opened up a new horizon in next generation electronic, optoelectronic and energy-related devices [7–11]. Indeed, metal-incorporated/doped, molecular electron-donor and -acceptor intercalated few-layer graphene have been reported to show very interesting applications in hydrogen storage system, which is very important for clean energy applications [4,6]. Several groups theoretically prescribed that metal incorporated and corrugated graphene nanostructures can significantly improve the molecular and atomic hydrogen uptake capacity due to polarization or hybridization of H_2 with metal atoms to achieve the desired gravimetric goal of 8–9 wt% set by the U.S. Department of Energy (DOE) for 2017 [5,12]. Although the theoretical results seem to be exciting, not much experimental works have been done in this regard due to the lack of proper fabrication techniques to incorporate metal atoms within the graphene network to give required H_2 binding energy [4], and hence, deserve much attention. Also, the recent advancements in the fabrication of partially graphitic micro/mesoporous carbon has shown improved hydrogen uptake capacity due to the high surface area into the porous structure and favorable hydrogen binding energy in the local curvature of graphene sheets in the short-range graphitic structures [1,3,13]. Therefore a metal-incorporated partially graphitic porous carbon network containing few-layer graphene may potentially improve the hydrogen storage capacity to achieve the elusive DOE goal.

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The fabrication techniques of partially graphitic micro/mesoporous carbon include template-based syntheses followed by annealing at elevated temperature for carbonization and graphitization [1–3,13–17], whereas activation of carbon materials by some chemical etchants is also used for the formation of microporous carbon [1,18]. But most of these processes are solution-based, and therefore, not compatible to modern solid state device fabrication techniques, especially, the complementary-metal-oxide-semiconductor integrated-circuit (CMOS IC) fabrication industry, and hence, not commercially viable. Also, the general trend of high temperature treatments for improved graphitization of high surface area carbon nanostructures [2,15–17] may not be suitable, in practice, for low-cost high throughput processes. Several groups attempted ambient-temperature electron or ion irradiation to solid carbon sources to locally graphitize the samples [19–21]. These methods are particularly interesting because of the use of vacuum-based processes and also, do not involve high temperature treatment and therefore, suitable for practical device fabrication. Previously, Zwanger et al. [22] reported the conversion of amorphous carbon (a:C) into carbon onions under high electron flux densities ($\sim 2.0 \times 10^{-6}$ to 2.5×10^{-6} A/cm^2), and observed that these nanostructures are highly unstable and dissolve quickly into the amorphous material after the irradiation is withdrawn. This shows that the formation of stable graphitic nanostructures from a:C is challenging because of the presence of dangling bonds in the unordered structure of a:C, which influences the dissolution of the ordered domain into the unordered species. Catalytic graphitization of a:C has also been done by incorporation of metal particles (Fe, Co Ni etc.) in a:C layers followed by electron beam irradiation [23,24]. Although, all these reports involve the local graphitization of the a:C films, they have opened up new possibilities of large area crystallization of a:C by the adoption of proper energetic irradiation technique. Indeed, e-beam lithography is a time-consuming process for large area scanning. Therefore, large area crystallization under e-beam irradiation requires very long time and hence, not practically viable. Also longer time exposure to electron irradiation of the sample can tend to the re-amorphization of the already created graphitic layers [20,25].

Recently, for the first time, the preliminary results of site-specific deposition of partially graphitic microporous carbon via metal sputtering using etched mask for potential hydrogen storage applications is reported by this group [26]. At a certain sputtering voltage, current and time, conversion of a:C to partially graphitic carbon at preselected areas of the sample is observed owing to the energy transfer of sputtered atoms/ions to the carbon matrix. Also, the a:C layer is observed to be converted into disordered microporous carbon and considered to be due to the presence of sputtering plasma that acts as dry-etchant and provides the necessary activation for morphological conversion. In the present study, ambient-temperature fabrication of larger-area, metal-incorporated graphitic activated carbon nanocomposite, terminated with multilayer graphene walls is reported, which is having the similar synthesis protocol presented previously by this group [26], but with a wide variation in the sputtering parameters to observe its effect on the degree of graphitization. Detailed Raman characterizations depict the signature of few-to-multilayer graphene formation within the microporous carbon network, which is completely different from previously reported results by others on the formation of partially graphitic micro/mesoporous carbon. The novelty and main difference between the current results and the previous reports is that the Raman data and microstructural analyses depict a change in the degree of graphitization as a function of sputtering parameters, indicating the controllability of the current process in terms of the number of graphene-layer formation within the microporous carbon. As the current fabrication method is a combination of simultaneous activation and crystallization of a:C for graphitic microporous carbon formation, the process is novel, yet simple and highly efficient for large area graphitization of carbon nanostructures for various energy-related applications. Also sputtering, being a CMOS-compatible low-cost process and capable of large-area deposition, can easily be scaled for volume production of various vacuum-micro/nanoelectronic devices. Previously, metal-incorporated/functionalized carbon nanostructures were fabricated by solution-based processes followed by high-temperature treatments [27]. In the current case, the in situ graphitization of a:C by metal sputtering constitutes a single-step process of metal-graphitic carbon hybrid nanomaterial formation. Therefore, this process can easily be tuned and optimized for controlling the electronic structure of graphene by external atomic/molecular induction [9], thus allowing a variety of interesting and important applications including hydrogen storage and related clean energy processes.

2. Experimental

2.1. Fabrication

The fabrication technique is a two-step process, which consists of the deposition of a:C thin film on Si substrate by thermal evaporation followed by the bombardment of sputtered metal nanoparticles on the as-deposited a:C films under ambient temperature. The evaporation unit (JEOL JEE-400) consists of a conventional vacuum system, which is evacuated to 3×10^{-6} mbar by standard differential pumping arrangements. Standard carbon rods (diameter ~5 mm) are used as the evaporation source and the evaporation is carried out by means of the heat generated locally at the contact point of two carbon rods by passing a current, which fused and evaporated the carbon by Joule heating. The Si substrates are placed nearly 8 cm away from the evaporation source to deposit a:C films on the substrates. Before placing into the deposition chamber, the Si substrates are cleaned by standard substrate cleaning procedure. Firstly, Si substrates are immersed in 20% HF solution for 5 min for removing the surface oxide layers. Then they are cleaned in deionized water and finally with alcohol in an ultrasonic cleaner. As far as the carbon evaporation is concerned, initially, the carbon contact point is pre-heated to an extent of red heat followed by white heat by increasing the current and then the current is further increased rapidly to 35 A to evaporate the carbon for few seconds and then the shutter is removed for the deposition of the carbon film on the substrate. The film thickness is maintained at 10 nm and controlled by the in situ standard quartz crystal monitor.

After the a:C thin film deposition, the as-synthesized samples (a:C-coated Si substrates) are introduced to a dual-head, turbo-pumped, direct-current (dc) vertical sputter-coater system (Model # K675XD, Quorum Technologies/Emitech, UK) for local crystallization of the a:C film by metal nanoparticle sputtering. Standard Cr target (57 mm diameter × 0.3 mm thick, Product # TK8845, Quorum Tech. Ltd., UK) is used as the upper electrode for metal sputtering and the samples are kept at the lower electrode (anode). The sample-to-target distance is kept at 3.0 cm with a base pressure of 10^{-5} mbar. The summary of the metal sputtering parameters is furnished in Table 1. Before sputtering, the target is cleaned in Ar atmosphere with 150 mA/cm^2 current density and 1×10^{-2} mbar of Ar pressure for 30 s, and then the shutter is opened to expose the sample in the sputtering plasma. The sputtering times are kept to very small values to create a small shower of energetic atomic clusters to hit the a:C films under the applied sputtering voltages, which transfer the necessary energy to the a:C layer to locally crystallize it into short-range graphene layers. Higher deposition time is not adopted because it generally leads to the deposition of a continuous