



Ambient-temperature fabrication of microporous carbon terminated with graphene walls by sputtering process for hydrogen storage applications

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ABSTRACT

A very thin amorphous carbon film (10–30 nm), has been bombarded with sputtered Cr nanoparticles, resulting in inelastic collision between the nanoparticles and the nuclei of the C-atoms causing atom displacement and re-arrangement into graphene layers. The process occurs at ambient temperature. Fabrication of graphitic microporous carbon terminated with few-to-multilayer graphene walls has been verified by Raman spectroscopy and scanning transmission electron microscopy. High resolution transmission electron micrographs reveal that the formation of graphene layers is highly sensitive to the sputtering parameters. With a gradual increase in the sputtering voltage/current density/time from 3.5 kV/40 mA-cm⁻²/1.0 min to 5.0 kV/70 mA-cm⁻²/3.0 min the graphitic domains are found to transform from semi-graphitized layers to well-defined, highly ordered, larger-area graphene walls within the microporous network. The mechanism of this graphitic microporous carbon formation is assumed to be due to two simultaneous processes: in one hand, 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 on the other hand, the charged metal nanoparticle/ion bombardment under sputtering resulted in the inelastic collision between the nanoparticles/ions and the nuclei of the C atoms followed by atom displacement (and displacement cascade) and re-arrangement into ordered structure to form graphitic domains within the microporous carbon network. H₂ storage experiment of the samples depicts excellent hydrogen storage properties. This simple, cost-effective, complementary-metal-oxide-semiconductor-compatible, single-step process of metal-graphene hybrid nanomaterial formation may find interesting applications in the field of optoelectronics and biotechnology. Additionally, this method can be adopted easily for the incorporation of transition metals into graphene and similar graphitic carbon nanostructures and may enhance the hydrogen storage capacity for energy-related applications.

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1. Introduction

Hydrogen storage is one of the most important applications in the field of clean energy generation because H₂ is considered to be an ideal source of energy for efficient and environmental friendly applications [1]. Because of its tremendous importance, the US Department of Energy (DOE) has set a gravimetric goal of 8–9 wt.% hydrogen storage by 2017, and various groups around the globe are actively engaged in the research of safe and compact storage of hydrogen in solid-state materials to achieve this target. Among various solid sources used for hydrogen storage medium, carbon-based nanomaterials are found to be promising because of the possibility of efficient reversibility, fast kinetics, and high capacity owing to large surface area [2]. Among different carbon-based nanostructures, graphitic micro/mesoporous carbon

and metal-incorporated/corrugated graphene nanostructures are widely explored for improved hydrogen storage [3–5]. Especially, metal-incorporated/decorated graphene is reported to show very high hydrogen uptake capacity due to its hybridization/polarization with metal atoms [2,5,6]. On the other hand, micro/meso-porous carbon, containing partially graphitic structures, also shows enhanced hydrogen uptake capacity because of the high surface area into the porous morphology and favorable hydrogen binding energy (BE) at the graphene walls of the localized graphitic network [3,4,7]. Therefore, metal-incorporated, graphitic micro-/meso-porous carbon, containing few-to-multilayer graphene walls, may potentially enhance the hydrogen BE to the desired range of ~0.2–0.6 eV to fulfill the elusive DOE goal [2,8]. But the main issue in this regard is the lack of proper fabrication techniques to incorporate metal atoms into the porous carbon/graphene network to satisfy the desired H₂ BE, and hence, warrants much attention.

Fabrication of graphene has been realized by various physical and chemical-based techniques [9–12], whereas metal incorporation/decoration is performed by a solution-based process [13]. On the other hand, partially graphitic micro/meso-porous carbon formation as well

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as metal incorporation are performed via template-based or chemical etching techniques followed by elevated temperature annealing for activation/carbonization/graphitization [3,4,7,14–17]. As most of these processes are solution-based and involve high temperature treatments, they are not compatible to modern solid state fabrication techniques and also not suitable for low-cost high-throughput processes. Thus, the adoption of alternative vacuum-based, low/ambient-temperature methods is needed for diverse device applications. And in that respect, partial graphitization of solid carbon sources via ion/electron irradiation technique is found to gain renewed interest for possible controlled graphitization through clean processes [18,19]. Among various solid carbon sources, amorphous carbon (a:C) is found to be a useful source material for this type of irradiation method, because it consists of mostly sp^2 -bonded carbon atoms, and therefore, the derived graphene layers will be extremely pure. Also it is very easy to synthesize under most of the vacuum-based techniques (which are complementary metal-oxide semiconductor {CMOS} compatible) under ambient temperature, and therefore, can easily be integrated with modern solid state device fabrication technologies for future applications. But the formation of stable graphitic nanostructures under ion/electron beam (e-beam) irradiation from a:C is found to be challenging because of the presence of dangling bonds in the unordered structure of a:C, which appears to influence the dissolution of the ordered domain into the unordered species [20] once the irradiation is withdrawn. To overcome this, catalytic graphitization of a:C is performed by incorporating metal particles (Fe, Co Ni etc.) into the a:C layers followed by e-beam irradiation, causing the dissolution of carbon atoms into metal particles to form eutectic followed by the supersaturation and ordered precipitation of graphitic layers at the metal-film interface [21,22]. But e-beam lithography is a highly time-consuming process for large area graphitization of a:C film, and therefore only suitable for short-range graphitic network formation, and impractical for volume production as the longer time exposure to electron irradiation of the sample is reported to cause the re-amorphization of the already created graphitic layers [23].

In this current study, we have shown the graphitization of a:C thin film by irradiation of energetic metal nanoparticles using sputtering process. At an optimum sputtering voltage, current (density) and time, the thin a:C layer transforms into metal-incorporated microporous carbon network embedded with short-range few-to-multilayer graphene walls due to the energy transfer of the bombarded sputtered metal (Cr) nanoparticles/ions into the carbon matrix at ambient temperature. The number of graphene layer formation and the degree of crystallization are found to be highly sensitive to the sputtering parameters. The microporosity formation is facilitated by a dry-etching process caused by the sputtering plasma. Previously, we have reported the preliminary results of the site-specific formation of partially graphitic microporous carbon on some pre-selected areas (using etched mask), via metal sputtering process for potential hydrogen storage applications [24]. In this report we are presenting the detailed study of the effect of sputtering current/voltage and time on the number of graphene layer formation and the degree of ordering of the graphene walls within the microporous network at various sputtering conditions. Since the results suggest that the degree of graphitization and number of graphene layer formation are highly dependent on the sputtering parameters, large area, single-to few-layer graphene can be fabricated by this simple method by a proper optimization of the deposition conditions. Therefore, this ambient temperature, CMOS-compatible process can find interesting applications in device fabrication industry for the large-area synthesis of metal-incorporated graphitic microporous carbon, terminated with highly ordered few-to-multilayer graphene walls, for hydrogen storage and related clean energy applications.

2. Experimental details

Fabrication of graphitic microporous carbon is performed by treating thermally evaporated ultra-thin a:C film under sputtering plasma.

Initially, a:C thin film (thickness ~ 10 – 30 nm) is deposited on commercially available Si wafer (Sigma Aldrich, Korea) and formvar-stabilized 200-mesh Cu-grid (Ted Pella Inc., US) via a thermal evaporation system (JEOL, JEE-400) using standard carbon rod. The thickness of the film is monitored by in-situ quartz crystal monitor. Next, these a:C-coated substrates are introduced into a direct-current (dc) sputtering chamber (Quorum Technologies/Emitech, UK) which consists of a Cr sputter-target as upper electrode with a base pressure of 10^{-3} Pa. The layout of the experimental process and the sputtering parameters is furnished in Fig. 1. The substrate temperature is kept at ambient condition while the sputtering voltage, current (density) and time are varied to observe their effect on the degree of graphitization of the samples. The substrate temperature is measured before and after each sputter-deposition via thermocouple arrangements. Since the samples are placed on a metallic substrate holder, the local heat generated from the waste kinetic energy of the incident particles is rapidly dissipated through it, keeping the substrate at relatively lesser temperature. The details of the experimental process are reported elsewhere [24]. The samples are then characterized under confocal Raman microscope (alpha300#, WITec), at a laser excitation wavelength of 532 nm, to verify the formation of graphitic microporous carbon. To observe the degree of graphitization at different sputtering conditions, microstructural and morphological characterizations are performed by scanning transmission electron microscope (S-TEM, Tecnai G² F20 with 200 and 80 kV e-beam energy). Graphitic microporous carbon, fabricated on the a:C-coated Cu-grid, is directly introduced into the S-TEM unit for high-resolution (HR)-TEM analysis. To verify that the formation of graphitic microporous carbons on two different substrates (Si wafer, Cu-grid) under identical sputtering parameters shows similar features (i.e. negligible substrate effect), Raman characterizations are done on samples prepared on both types of substrates before and after sputtering treatment. Both sets of the samples show similar Raman curves (shown and described later), indicating minimal substrate effect. The only difference is that the Raman peaks for graphitic microporous carbon prepared on Cu-grid via sputter treatment show a very strong background noise due to fluorescence generated by the Raman laser, and mask the signals considerably (shown later). Hence the samples are prepared on Si substrate for proper Raman characterizations. Additionally, the negligible substrate effect is further justified by the fact that the entire fabrication is done at ambient substrate temperature. The necessary activation energy for graphitization of the a:C film is provided by the energetic sputtered nanoparticles/ions by a top-down approach through the film surface (explained later). In our experimental condition, we believe that the substrate effect can only come into play for graphitization, if the activation energy is provided by a bottom-up approach (probably through substrate heating). With the current operating conditions, the local temperature enhancement at the a:C film surface due to sputtering plasma is found to be at most 20 °C, which is much less than the required temperature (>500 °C) for graphitization through thermal treatment [4,7,15].

3. Results and discussion

Fig. 2 represents the TEM micrographs of untreated and sputter-treated samples, indicating the formation of micropores within a:C films. Fig. 2(a) shows the untreated a:C films indicating smooth surface structure, whereas Fig. 2(b) depicts the formation of micropores (pore diameter <2 nm) under sputtering treatment of 3.5 kV/ 40 mA cm^{-2} / 1.0 min of sputtering voltage/current (density)/time, respectively. Fig. 3 represents the HRTEM micrographs of graphitic microporous carbon fabricated on a:C-coated Cu-grid at different sputtering conditions. Fig. 3(a-i) and (a-ii) shows the semi-graphitized wall formation within the microporous carbon network at sputtering voltage/current-density/time ($V/J/T$) of 3.5 kV/ 40 mA- cm^{-2} / 1.0 min and 3.5 kV/ 40 mA- cm^{-2} / 3.0 min, respectively. With increase in the deposition time, the semi-graphitized

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