



Controlled synthesis of nanocrystalline glass-like carbon thin films with tuneable electrical and optical properties

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HIGHLIGHTS

- Controlled synthesis of nanometer-thin glass-like carbon films by atmospheric CVD.
- The optical and electrical properties are defined by the thickness of these films.
- High transparency (86%) and moderate conductivity (7.8 kΩ/□) are achieved.
- Anisotropy in the through-thickness direction have been demonstrated for first time.

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ABSTRACT

Graphene is an emerging electronic material but expensive and difficult to produce in pure, large-area thin films. Organic electronic applications such as flexible devices and energy applications would benefit from low-cost alternatives to graphene. The controlled synthesis of nanometer-thin carbon films by atmospheric pressure chemical vapor deposition on copper foils is presented. These nanostructured carbon thin films (5–237 nm of thickness) are composed of curved graphene fullerene-like fragments of *ca.* 3 nm average size, which replicate the structure of widely used glass-like carbons. The optical and electrical properties of these nanostructured carbon thin films are defined by the thickness of these films; high transparency (86%) and moderate high electrical conductivity (7.8 kΩ/□) are achieved for the thinnest samples (5 nm). Although these values are in the range of other thin films prepared with graphene, these films are fundamentally different since they are composed entirely of graphene flakes joined by a carbon matrix, which presents a high density of defects; thus they are also interesting candidates for flexible and transparent electronics, especially when biocompatibility, friction, high temperature, UV radiation, and corrosion resistance are also needed.

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1. Introduction

Carbon is a very versatile element, and is able to form a great variety of crystalline structures such as graphene, nanotubes, nanofibers and fullerenes [1–4], and disordered structures such as diamond-like carbon, glass-like carbon, carbon black, and amorphous carbon [5–7]. Since the in-depth characterization of graphene properties in 2004 [8], there has been renewed interest in carbon nanomaterials as thin films for a wide variety of applications, such as energy production/storage, biocompatible scaffolds, and electronics, among others [9–12]. Despite the potential of graphene for so many applications, the large-scale production of

atomically thin and monocrystalline graphene film has not yet been achieved [13–17]. Alongside the ongoing work on graphene, the synthesis and use of other carbon nanomaterials with lower degrees of crystallinity might relax the requirements of production and manipulation processes such as highly controlled atmospheres, substrate preconditioning, sample transfer, etc. Such materials should still have great potential and applicability for flexible electronics because of their high transparency and electrical conductivity, among other interesting properties, and may complement the existing current portfolio of carbon nanomaterials.

Glass-like forms of carbon are a good example of disordered sp²-hybridized carbon materials. The structure of these glass-like carbon materials consists of nearly 100% sp²-hybridized carbon atoms, which forms randomly oriented fullerene-like fragments

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of different sizes, depending on the intensity of the heat treatment used for their production [18–23]. The name of this form of carbon comes from its glass-like appearance, but is now also used for materials with similar structures [24–26]. Glass-like forms of carbon combine interesting properties such as high temperature stability, extreme resistance to chemical corrosion, high hardness, low density, and high impermeability to both gases and liquids [20,23,27] and are already used as electrode materials and crucibles. Interestingly, glass-like forms of carbon can also be produced in thin films that are as transparent as graphene films of similar thickness, by pyrolyzing a photoresist resin [28]. In this way, interesting functional materials such as flexible neuroelectronic implants for dopamine sensing were recently obtained [29]. Carbon materials with a similar disordered structure of single-layered curved and defective graphene sheets, can also have an exceptional specific surface area due to their high density of edge defects, which are of great interest for energy storage applications [12,30]. This embedded nanocrystallites within an amorphous carbon matrix can induce strong paramagnetism [31–34], which is ascribed to the presence of a spin magnetic moment at the graphene layer edges. In summary, the presence of nanoscale crystals and defects in carbon materials may induce interesting properties through the development of nanoporosity or crystal defects, which have advantages for advanced applications over the more crystalline forms of carbon such as graphene or nanotubes.

Here, we study the controlled synthesis of nanocrystalline glass-like carbon thin films (area *ca.* 10 cm²) directly on copper foils by atmospheric chemical vapor deposition. We follow a similar process to that used in production of graphene films [35], but using a wide range of gas concentrations to enable easy film thickness control. We obtain transparent and conductive glass-like carbon thin films formed by randomly oriented and curved graphitic nanocrystallites within an amorphous carbon matrix. Finally, we study the optical and electrical parameters of our thin glass-like carbon films, showing the ability to tune both optical and electrical parameters by controlling the film thickness.

2. Experimental

2.1. Materials

A commercial copper foil was used as catalyst for the chemical vapor deposition of the carbon films (100- μ m-thick copper foil, 99.8% purity, Sigma Aldrich). The copper foil was cut into rectangles of 22 \times 50 mm². The copper samples were dipped in pure ethanol and cleaned by ultrasonication for 10 min. No additional pretreatment of the copper foils was carried out.

2.2. Chemical vapor deposition of carbon films

We used a custom-made chemical vapor deposition reactor [37], which consisted of a longitudinal mobile tubular furnace, to perform the fast heat approach [38]. All the gas lines (Ar, H₂, and C₂H₄) connected to the 22-mm diameter quartz tube were flushed for 10 min, followed by an additional 10 min of Ar to displace trapped air and other gases from the system. The furnace was then ramped to the synthesis temperature (850 °C) with 1000/20 sccm of Ar/H₂ flowing, while keeping the sample outside the heating zone. Once the temperature stabilized, the furnace was rapidly moved (*ca.* 3 s) to locate the center of the heating zone of the furnace around the copper foil. Prior to the last synthesis step, 10 min of annealing with 1000/20 sccm of Ar/H₂ flow was used. Several synthesis conditions were tested to study the effect of the total gas flow ($Q = \text{Ar} + \text{H}_2 + \text{C}_2\text{H}_4$) and the ethylene concentration

[C₂H₄] = C₂H₄/(Ar + H₂ + C₂H₄). The total flow varied from 40 to 540 sccm and the ethylene concentration from 0.04 to 0.5. The synthesis time was fixed at 5 min. After the synthesis, the furnace was moved away from the sample to allow rapid cool down under Ar flow. Details of the process can be found in the [Supplementary Information \(Fig. S1\)](#) and elsewhere [37].

2.3. Carbon film thickness

As-synthesized samples were dipped in FeCl₃-HCl copper etching solution (Sigma Aldrich, 667528) to dissolve the copper foil. Once the glass-like carbon film was detached in the form of flakes, they were cleaned by replacing the etchant with deionized water and washing several times. The carbon flakes were transferred into a thermal oxide wafer (300 nm SiO₂ on Si). Atomic force microscopy characterization (non-contact mode, Park XE150) was carried out.

2.4. Carbon film microstructure

Carbon flakes from three thin carbon films (thickness < 15 nm) were transferred onto a copper grid for analysis under a transmission electron microscope (JEOL JEM 3000F). Raman spectra of all the samples were collected from on top of silicon wafers (Jasco, NRS-5100). At least three measurements per synthesis condition were taken, using a Nd:YAG green laser (532 nm, aperture: 4000 μ m, grating: 1800 l/mm, slit: 200 \times 1000 μ m, resolution: 7.42 cm⁻¹), with two accumulations of 20 s exposure over a range of 1000–3250 cm⁻¹. The effective laser power was about 5.3 mW. We compared the Raman spectra of our carbon films with those of a glass-like carbon rod (Gomensoro, N°61248040) and graphene sheet on a silicon wafer (Graphenea). We also analyzed the spectra of all the carbon films synthesized within this work.

We carried out an additional Raman experiment to ascertain if the layer that is in contact with the copper foil, (“bottom carbon”), has a different Raman spectra than that of the carbon on the top (“top carbon”). ([Supplementary Information, Fig. S4](#)). The analysis of the Raman spectra of the carbon films was carried out by fitting the corresponding band of highly disordered carbons as proposed in several articles [36,39,40].

2.5. Electrical characterization

The thinner carbon films (<20 nm) were spin-coated with poly (methylmethacrylate) (PMMA; 495PMMA A Resists, Microchem). Copper was etched away (using Sigma Aldrich 667528), and finally the carbon thin film/PMMA was electrically characterized. In a standard probe station the needles pierced the thinner samples so, to avoid sample destruction, the sheet resistance of the samples was measured by using contactless conductivity equipment LEI88 (Leighton Electronics Inc.). Each measurement was performed at least 20 times, hence the uncertainty interval for each sample.

2.6. Optical characterization

Transmission measurements were performed on the carbon thin film (<20 nm thick)/PMMA samples by using spectroscopic reflectometry-transmission equipment on a Canon microscope (Sentech FTP). Measurements were obtained by using a \times 10 microscope objective that provided a spot with a diameter of around 20 μ m.

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