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Research paper

Graphene-laminated architectures obtained by chemical vapor deposition: From graphene to graphite

Hiroki Kitayama, Kengo Shimizu, Tomonori Ohba *

Graduate School of Science, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522, Japan

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ABSTRACT

Graphene and graphite are of great interest in materials science. Using chemical vapor deposition at various CH_4:H_2 ratios, we synthesized materials with graphene-laminated architectures, ranging from graphene to graphite. A lower proportion of CH_4 and lower synthesis temperature produced fewer graphene layers. The transparent properties changed from transparent to semi-transparent, black, and silver as the number of graphene layers was increased. The sheet electrical resistivity ranged from 10^6 to 0.2 $\Omega\,\square^{-1}$, and the smaller resistivity was nearly equaled as the values of highly orientated pyrolytic graphite and glassy carbon. The graphene-laminated materials featured a wide range of transmittance, reflectance, and electrical conductance properties.

Carbon has many isotopes and allotropes, including graphite, diamond, graphene, carbon nanotubes, and fullerenes. Molecular carbons or nanocarbons are mainly sp^2 carbon allotropes, consisting of fullerene and graphene units [1,2]. Graphitized and non-graphitized carbons are formed by stacking and connection of graphene units. Graphene has high transparency at 550 nm and its transmittance decreases monotonically as the number of layers increases [3]. Graphite, which is formed by stacking of graphene, is not optically transparent and appears as black or silver, depending on the extent of the conjugated π-electron system. The appearance of graphite typically changes based on the stacking and orientation of the graphene sheets. The transmittance of graphene decreases by 2.6% with the addition of a single graphene layer (the theoretical value of a single layer is 2.3%), which is useful for determining the graphene layer number [3]. Light reflection can also be used to determine the number of layers and has the advantage of being applicable to any type of substrate [4].

Graphene was first prepared by mechanical cleavage of highly orientated pyrolytic graphite (HOPG), i.e., a top-down process [2]. Chemical vapor deposition can also be used for bottom-up synthesis of graphene and graphene layers [5]. Crystalline graphite has been prepared by heat treatment of pyrolytic carbon and chemical vapor deposition at temperatures above 2500 K; HOPG is generally prepared by hot-press synthesis above 3000 K. We synthesized materials with graphene-laminated architectures, ranging from graphene to orientated graphite at 1200–1300 K, with the use of a bottom-up process by chemical vapor deposition of CH_4. We investigated the transmission and reflection properties associated with these structures.

Graphene-laminated architectures was obtained by chemical vapor deposition of CH_4 on quartz plates at 1200, 1250, and 1300 K for 5 h. A Cu sheet was set next to the quartz plate to act as a catalyst. We used H_2 as the reducing gas. The total combined flow rate was fixed at 200 mL min^{-1}; however, the ratio of CH_4 to H_2 was varied such that the proportion of CH_4 content was in the range of 20–100 vol%. The synthesized graphene was characterized by Raman spectroscopy with the use of a Nd:YAG laser at a power of 0.1 mW (NRS-3000; JASCO, Tokyo, Japan) and X-ray diffraction (XRD) with Cu Kα radiation at 40 kV and 30 mA (SmartLab; Rigaku, Tokyo, Japan). The transmittances and reflectances of the graphene-laminated materials were measured by ultraviolet/visible spectroscopy (V-670 and MSV-370; JASCO, Tokyo, Japan). The electrical conductivity of the graphene was evaluated based on four-probe resistance measurements. HOPG (Crystal Base Inc., Osaka, Japan) and glassy carbon plates (BAS Inc., Tokyo, Japan) were used for comparison.

Photographs of the graphene-laminated materials synthesized on quartz at 1250 K are shown in Fig. 1. The materials synthesized with the use of 20% and 40% CH_4 were transparent, whereas those synthesized with 60% and 80% CH_4 were semi-transparent. The graphene-laminated material synthesized with the use of 80% CH_4 was darker than that synthesized with 60% CH_4. The material synthesized with the use of 80% CH_4 had reflective and semi-transparent properties, as shown by placing the graphene-laminated material in front of a patterned sheet (Fig. 1d, right). Glassy graphene fabricated by Dai and co-workers was black and reflective [6], similar to the graphene-laminated material

* Corresponding author.
E-mail address: ohba@chiba-u.jp (T. Ohba).

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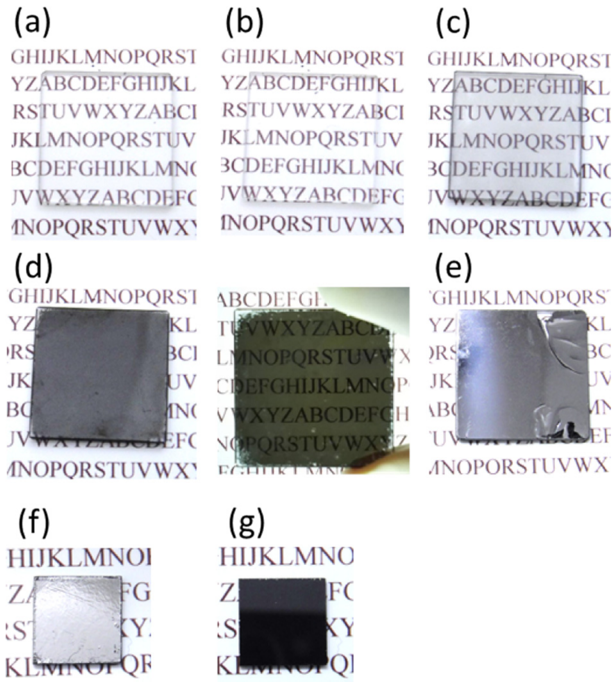

Fig. 1. Photographs of graphene-laminated materials synthesized at 1250 K using CH_4 percentages of 20% (a), 40% (b), 60% (c), 80% (d), and 100% (e). HOPG (f) and glassy carbon (g) are shown for comparison.

synthesized with the use of 80% CH_4. The graphene-laminated material synthesized with the use of 100% CH_4 was metallic and mirror-like, indicating highly orientated graphite, which resembled that formed through HOPG processes (Fig. 1f) rather than glassy carbon (Fig. 1g). However, the graphene surface of the material synthesized with the use of 100% CH_4 was rough because of the difference between the thermal expansion coefficients of graphene and quartz during cooling after synthesis. Obraztsov and co-workers reported that nanometer-level thin graphite films synthesized by chemical vapor deposition have micrometer-sized domains [7]. The domains of the graphene-laminated material synthesized with the use of 100% CH_4 were much larger and thicker than those of thin graphite films, as shown below. Mirror-like graphene-laminated materials were also synthesized with the use of 100% CH_4 at 1200 K and 60%–100% CH_4 at 1300 K (Fig. S1).

Fig. 2a shows Raman spectra of the graphene-laminated materials and a typical graphite. All the graphene-laminated materials showed a D band at approximately 1350 cm^{-1}. The graphene-laminated materials synthesized with more than 20% CH_4 had a G band at approximately 1600 cm^{-1} and a 2 D band at 2700 cm^{-1}. The Raman spectra of the graphene-laminated materials synthesized at 1200 and 1300 K (Fig. S2) resembled those of the materials synthesized with low and high CH_4 percentages, respectively, at 1250 K, based on the photographs. These graphene-laminated materials featured defective sp^2 structures. The G/D ratios suggested that the graphene-laminated materials synthesized with the use of 40% CH_4 were similar to glassy carbon and those synthesized with more than 40% CH_4 had more crystalline sp^2 structures than glassy carbon. However, HOPG had a much higher G/D ratio, i.e., 970 (Fig. 2b). A higher proportion of CH_4 produced amorphous carbon on the surface, which features a relatively small G/D ratio. The 2D bands shifted from 2690 to 2697 cm^{-1} as the proportion of CH_4 was increased; the HOPG and glassy carbon bands appeared at 2714 and 2690 cm^{-1}, respectively. The shift of the 2 D band to higher wavenumber can be attributed to the greater number of graphene layers [8]. The 2D/G ratio is also an indicator of the number of graphene layers [9]. The 2D/G ratios indicated that the graphene-laminated materials synthesized with the use of 40% had approximately one or two layers, and those synthesized with 60% CH_4 had a few layers. For processes with 80%, and 100% CH_4, multilayers were formed. The 2D/G ratios for HOPG and glassy carbon were similar to those of the graphene-laminated material synthesized with 60% CH_4 (see Fig. 2b).

The XRD patterns in Fig. 3 feature (0 0 2) peaks at 25.7°, corresponding to the distance between graphene layers, for the materials synthesized with the use of 60%–100% CH_4. The broad peak at 20° is assigned to quartz. The average distance between the graphene layers was 0.346 nm, which is intermediate between the interplanar distances of glassy carbon (0.351 nm) and HOPG (0.335 nm). The graphene-laminated materials synthesized with the use of 100% CH_4, HOPG, and glassy carbon had (0 0 4) peaks at 55°. The (10) peak was only observed for glassy carbon. Fig. S3 shows the XRD patterns for the graphene-laminated material synthesized with the use of 100% CH_4 and pieces removed from quartz substrate. The pieces featured the (10) peak at 45°, indicat-

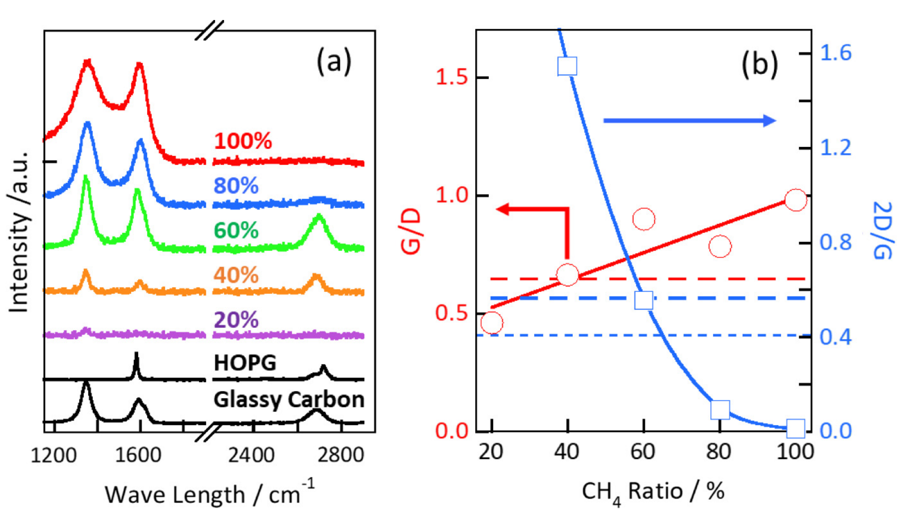

Fig. 2. (a) Raman spectra of graphene-laminated materials and graphite. (b) G/D and 2D/G ratios for graphene-laminated materials and graphite. Symbols: graphene-laminated material; dotted line: HOPG; and dashed line: glassy carbon.