Cryogenics 86 (2017) 118–122

Contents lists available at ScienceDirect

Cryogenics

journal homepage: www.elsevier.com/locate/cryogenics

Research paper

Low temperature transport properties of pyrolytic graphite sheet

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ARTICLE INFO

Article history:
Received 11 April 2017
Received in revised form 5 August 2017
Accepted 9 August 2017
Available online 11 August 2017

Keywords:
Graphite
Thermal link
Thermal conductivity
Electrical conductivity
X-ray diffraction
Raman spectroscopy

ABSTRACT

We have made thermal and electrical transport measurements of uncompressed pyrolytic graphite sheet (uPGS), a mass-produced thin graphite sheet with various thicknesses between 10 and 100 μm, at temperatures between 2 and 300 K. Compared to exfoliated graphite sheets like Grafoil, uPGS has much higher conductivities by an order of magnitude because of its high crystallinity confirmed by X-ray diffraction and Raman spectroscopy. This material is advantageous as a thermal link of light weight in a wide temperature range particularly above 60 K where the thermal conductivity is much higher than common thermal conductors such as copper and aluminum alloys. We also found a general relationship between thermal and electrical conductivities in graphite-based materials which have highly anisotropic conductivities. This would be useful to estimate thermal conductance of a cryogenic part made of these materials from its electrical conductance more easily measurable at low temperature.

1. Introduction

Graphite is an allotrope of carbon with layered structure. The structure results in strongly anisotropic thermal and electrical transports [1] along with other unique properties such as self-lubrication [2] and high stability up to 4000 K [3]. With added characteristics of flexibility, graphite sheets are industrial products making use of those properties. Grafoil [4] is one of the best known commercial products based on this material, and is used in a wide variety of applications, e.g., sealing gaskets, thermal insulators, electrodes, and as a chemical reagent [5]. It consists of small natural graphite crystals (≈ 10–20 nm) [6] which are first powdered, then exfoliated at high temperature, and finally rolled under high pressure. It is also widely used as an adsorption substrate for basic research of two dimensional physical and chemical properties of adsorbate thin films [7] because of its atomically flat surface of microcrystallites and large specific surface area. For this purpose, there is another type of exfoliated graphite called ZYX [8], synthesized from HOPG (highly oriented pyrolytic graphite) under rather moderate exfoliation and re-compression conditions, with larger platelet size (≈ 100–200 nm).

Recently, a new flexible graphite sheet, pyrolytic graphite sheet (PGS) [9,10], has been invented. PGS is a thin graphite sheet of 10–100 μm in thickness with a single-crystal-like structure, synthesized by heat decomposition of polymeric films. Because of its extremely high in-plane thermal conductivity (2–5 times higher than that of copper at room temperature) and low density (≈ 80% of aluminum), PGS and its composites are being used for thermal management in electronic devices like smartphones [10]. It is potentially useful for cryogenic applications, especially in space engineering. One recent example is its use in a vibration isolated thermal link for cryocoolers [11]. However, so far only little is known about physical properties of PGS, including thermal transport at cryogenic temperatures.

In this article, we report results of crystal analysis and electrical and thermal transport measurements at 2–300 K for PGS. Here we focused on an uncompressed version of PGS since it has higher crystallinity and thus higher in-plane conductivity than compressed commercial PGS. By measuring both electrical and thermal conductivities, we could deduce a general relationship between them for graphite family materials where the standard Wiedemann-Franz law [12] is not applicable. Other characteristics important for application as an adsorption substrate, such as nitrogen adsorption isotherm and real space imaging of morphology with various microscopes, will be published elsewhere [13].

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http://dx.doi.org/10.1016/j.cryogenics.2017.08.004
0011-2275/

2. Pyrolytic Graphite Sheet (PGS)

Commercial PGS [9] (hereafter, cPGS) is made first by carbonizing a stack of polymer films of a few μm thick at $T \lesssim 1000$ K, then by graphitizing the resultant foamed carbon precursor at $T \approx 3000$ K, and finally by compression (rubbing) which reduces the thickness by 30–50%. Compared to chemical vapor deposition, which is used to synthesize HOPG, this is a convenient mass production method for thin graphite sheets of good crystallinity. Previous transmission electron microscopy (TEM) observations [14] show that the cross-sectional structure of a similar kind of graphite to that used in the present study is laminar of ultra-thin crystalline graphite layers of 6–7 nm thick which corresponds to 16–20 graphenes. The average lateral size of each layer is determined to be 10–100 μm from electron channeling contrast imaging with scanning electron microscope (SEM) [15]. In general, thinner cPGS has higher crystallinity because, in the graphitization process, the liberated gas can escape more easily and the temperature distribution is more uniform.

The final compression procedure makes cPGS flexible (like paper) so as to be more useful in practical applications. However, it may break the lateral crystalline structure on large scales. Therefore, in this work, we mainly studied physical properties of uncompressed PGS (hereafter, uPGS) which is produced by exactly the same method as cPGS except the absence of the final compression. As a trade off, uPGS is mechanically brittle and inflexible. Thus, to shape it precisely, it is recommended to use a punch designed for cutting thin metal films [16].

The nominal thicknesses of uPGS studied here are 10, 17, 25, and 100 μm. We denote them as uPGS-10 μm, for example, in the following. Their actual thicknesses measured by micrometer are 19 ± 2, 29.7 ± 0.6, 56 ± 3, and 145 ± 4 μm, respectively. For comparison we also studied properties of cPGS-10 μm whose measured thickness is 13 ± 2 μm.

3. Crystalline structure and defects

Out-of-plane X-ray diffraction was measured for uPGS-17 μm with a powder X-ray diffractometer [17] using Cu Kα_1 emission. The uPGS sample of 10×10 mm^2 was glued onto a glass holder with GE 7031 varnish. Sharp diffraction peaks from graphite are observed indicating that PGS is made purely of graphite crystals (see Fig. 1). Interplanar spacing d_{002} is determined as 0.33583(7) nm from peaks indexed as (002), (004), and (006) using Nelson-Riley function [18]. From the full width at half maximum (FWHM) of the rocking curve of the (002) peak at $2\theta = 26.346$ deg, the mosaic angle spread is determined as 8.2 ± 0.1 deg as shown in the inset of Fig. 1. This value is consistent with a mosaic angle spread (= 10 ± 3 deg) roughly estimated from real space SEM imaging of a cross section of uPGS-17 μm [13]. In-plane X-ray diffraction was also carried out (the data not shown here). The sample was a stack of 29 uPGS-100 μm sheets (13×5 mm^2 each) fixed with epoxy glue (Stycast 1266) each other. In addition to the peaks from regular spacing between graphene layers such as (002), those from in-plane honeycomb lattice like (110) and peaks indicative of three-dimensional graphite lattice indexed by (101), (102), (103), and (112) are observed. d_{002} is determined as 0.33592(6) nm from the (002), (004), and (006) peaks, and the in-plane lattice parameter a is determined as 0.2463 nm from the (100) and (110) peaks. All these diffraction results agree very well with the previous study for pyrographite films [19].

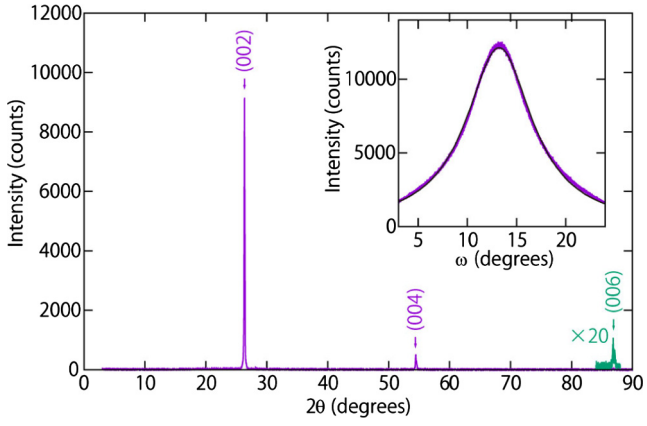

Fig. 1. Out-of-plane X-ray diffraction spectrum for uPGS-17 μm. (Inset) Rocking curve of (002) peak at $2\theta = 26.346$ deg where the FWHM is 8.2 deg.

Raman spectra of cleaved surfaces of uPGS of 17, 25, and 100 μm thick were measured at a wavelength of 532 nm using a laser Raman microscope [20] with a fixed exposure time of 8 s. For comparison, cleaved surfaces of HOPG, Grafoil, and ZYX were also measured. The most intensive features in Raman spectroscopy for graphite are G (≈1580 cm^{-1}) and G′ (≈2710 cm^{-1}) peaks. The relative intensity of G peak to G′ one, I(G)/I(G′) is a good representative of the number n of graphene layers for $n \lesssim 6$ [21]. Measured I(G)/I(G′) values for uPGS are similar to those of other graphites, which confirms that they are thick enough graphites (see Table 1). It is consistent with that all of them have similar FWHM values of G′ band (≈ 60 cm^{-1}: not shown in the table). D band is known to appear if the surface contains edges or defects where the threefold symmetry of honeycomb lattice is broken [22]. The D band signal was not detected in uPGS and HOPG within experimental errors indicating high crystallinity with immeasurably small amounts of domains and defects [23].

4. Electrical resistivity measurement

We made in-plane ($\rho_\parallel$) and out-of-plane ($\rho_\perp$) electrical resistivity measurements for uPGS samples of four different thicknesses, i.e., 10, 17, 25, and 100 μm, in the temperature range between 2 and 300 K. They were carried out by the 4-terminal method using the AC transport and resistance options of Physical Properties Measurement System (PPMS) of Quantum Design, Inc. The typical sample size is 0.5×9 mm^2 for the $\rho_\parallel$ measurement and 3×3 mm^2 for the $\rho_\perp$ one. Gold lead wires of 50 μm in diameter were glued to the samples with rubber-based carbon paste [24] which adheres strongly to graphite.

Results of the $\rho_\parallel$ measurement are shown in Fig. 2. $\rho_\parallel$ values of the uPGS samples are in between those of exfoliated graphites (Grafoil and ZYX) and natural graphite. Importantly, thinner uPGS has lower $\rho_\parallel$ in order of thickness. This is consistent with the fact that thinner uPGS has better crystallinity. Note that the variation of

Table 1
Intensity ratios of I(G)/I(G′) and I(D)/I(G) in Raman spectra for various graphite materials. All the surfaces were cleaved before the measurements.

Material	Nominal thickness	I(G)/I(G′)	I(D)/I(G)
uPGS	100 μm	3.2(1)	$< 10^{-3}$
	25 μm	3.1(1)	$< 10^{-3}$
	17 μm	3.1(1)	$< 10^{-3}$
HOPG	–	3.3(2)	$< 10^{-3}$
ZYX	–	3.2(1)	0.003(2)
Grafoil	130 μm	3.3(1)	0.015(4)
	250 μm	3.3(1)	0.033(4)