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Thermal conductivity of Kapton-derived carbon

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ABSTRACT

Heat treatment of translucent Kapton®HN polyimide films conducted in inert atmosphere yields black residues. Micro-Raman spectroscopy revealed that the residues obtained between 600°C and 1200 °C are mainly constituted of disordered carbon. Aside its standard application in the structural identification of carbon, the Raman technique has also been used as a means of evaluating the thermal conductivity of Kapton-derived carbon. The aim of this study is to know whether such a tool can also be appropriate for disordered carbon with coherent diameters lower than 2 nm and with variable quantities of heteroatoms (H, O, N). To achieve this aim, a comparative study was undertaken using two other conventional techniques, namely laser flash analysis and photothermal radiometry. It has been found that thermal conductivity increases linearly with the heat-treatment temperature of Kapton and reaches 1.905 $Wm^{-1}K^{-1}$ for the film heat-treated at 1200 °C. The comparison of the experimental results shows that the Raman thermometry is particularly sensitive for sp^2 carbon and predicts quite well the general trend of thermal conductivity of materials. However, the precision is rarely better than 20%.

1. Introduction

Kapton®HN Polyimides form a class of high performance polymers with certain outstanding characteristics, such as high thermal stability (up to 450 °C), chemical inertness, low dielectric constants, and strong adhesion to most semiconductors [1]. These polymers form an integral part of modern micro and nanoscale electronic devices as flexible substrates or packaging elements. Above 600 °C, Kapton-Polyimide is converted into a carbonaceous material, essentially composed of sp^2 carbon [2]. The graphitization process, under the effect of temperature alone, involves heat-treatment of the polymer at around 3000 °C [3]. Kapton-derived carbons are promising candidates for numerous other applications, as electrically conducting materials [4], Microelectromechanical systems (MEMS) [5], and gas permeation membranes [6]. One of our recent studies indicated that the Kapton films annealed below 900 °C were found to be effective absorbers in the terahertz domain [2]. That absorption property can be harnessed for other potential applications, for example in thermal transducers, such as microbolometers specifically devoted to terahertz frequencies. However, for this type of device, other properties such as specific heat capacity and thermal conductivity of the material are the primary concerns [7].

In the extant literature [8], it has been found that the thermal conductivity of carbon-based materials spreads over a broad range 0.01–3000 Wm^{-1} K^{-1} due to its diverse allotropic forms and microstructure [8]. The highly oriented graphitic films issued from Kapton has an in-plane thermal conductivity of the order of 1700 $Wm^{-1}K^{-1}$ [9]. To the best of our knowledge, the thermal properties of Kapton-derived materials not yet completely graphitized (low temperatures < 1200 °C) have not been thoroughly investigated.

There are a number of experimental methods for evaluating thermal conductivity, using either steady state or transient state conditions [10]. These methods can employ different heat sources (electrical, optical, steam) and also different heat detection techniques (contact or contactless) [11]. Each method has its own advantages and drawbacks in terms of the speed, ease of use, and

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preparation of the sample for measurement. The classical steady-state method suffers from parasitic thermal losses [12], whereas electrical heating methods such as the 3 Ω technique require numerous lithographic steps to fabricate heater and thermometer [13]. Such a preparation is difficult to apply to fragile samples. Moreover, an intermediate, electrically isolating layer is needed for electrically conductive materials [14] as those issued from heat-treated Kapton films. For photothermal techniques such as laser flash analysis and photothermal radiometry, sample preparation is minimal [11]. However, depending on the instrument used, greater accuracy is achieved if a relatively flat 1 cm^2 surface of the sample is available [15]. These techniques present another advantage that is non-contact temperature measurement [11].

Raman spectroscopy can also be used for the evaluation of thermal conductivity over a wide range [16–18]. In sp^2 carbon-based materials, the in-plane bond stretching of the carbon atoms results in the symmetry-allowed peak at 1600 cm^{-1}, the so-called Graphitic (G) peak. This G-peak acts like a contactless thermometer while the laser beam accounts for heat source [19]. Evaluation of highly thermally conductive graphene requires an isolating medium (air or a vacuum). Indeed, Balandin et al. [18] suspended single-layer graphene across two isolating legs to estimate the thermal conductivity. But the materials having low thermal conductivity can be measured in their bulk form without any preparation [17]. In general, the thermal conductivity κ_s of a material can be deduced from the linear relation 1 [17].

$$\kappa_s = \frac{2P}{\pi a \Delta T} \quad (1)$$

where P is the absorbed power in μW, a is the heat source (focused laser spot) diameter in μm, and ΔT is the temperature difference between the heat-source and the heat-sink. The relation 1 was originally derived by Nonnenmacher et al. [20], based on the following assumptions: (i) the sample must be at least one order thicker than the heat-source diameter a. (ii) the convection and radiation losses in the air are negligible.

Recent advances in micro-Raman optics and the development of intense monochromatic laser sources provide good sensitivity; a high spatial and spectral resolution, whereby local temperature variation in the material can be easily investigated [21]. However, no experimental verification or comparison by other conventional techniques was found in the literature, more specifically for disordered carbon-based materials.

Therefore, the objective of this study is to evaluate the efficacy of Raman thermometry in ascertaining the thermal conductivity of disordered carbon-based materials issued from the thermal conversion of Kapton film within the temperature interval 600°C-1200 °C.

2. Experimental

As-received yellowish-orange Kapton®HN polyimide films of thickness 125 μm, (Du Pont de Nemours, France) were diced into small rectangles, sonicated, rinsed with pure ethanol and thoroughly dried. Heat-treatments were performed in an alumina tubular furnace at various temperatures with a heating rate of 10 °C/min and a dwell time of 15 min in a flowing inert atmosphere (Argon, 99.999% purity). To avoid mechanical deformation of the films during heating step, the polymers were sandwiched between two alumina plates.

Two well-known techniques, Laser flash analysis and photothermal radiometry, that allow also the determination of thermal conductivity, have been used and the results were compared with those obtained by Raman thermometry. Briefly, in Laser flash analysis (LFA) [15], the thermal conductivity was calculated using the relation $\kappa_s = \rho C_p \alpha_s$, where C_p is the specific heat capacity determined with the differential scanning calorimetry (DSC204 F1 Phoenix®, Netzsch), and ρ is the density measured using buoyancy flotation method. Thermal diffusivity α_s ofthe samples was measured at least five times at 25 °C using LFA467 HyperFlash® (Netzsch). The front side of the sample is heated by a Xenon flash lamp while an infrared detector (InSb) is positioned at the rear side of the sample to record the variation in temperature. For the translucent samples, a thin layer of graphite was sputtered on both sides to make the samples opaque and, hence to improve their absorption and emission properties.

For photothermal radiometry (PTR), thermal conductivity κ_s is deduced from thermal diffusivity and effusivity according to the relation $\kappa_s = e_s \alpha_s$ [22]. The constructed optical workbench consists of a green laser source (Laser Quantum, Ventus HP532, wavelength = 532 nm) that was capable of modulating its output intensity. The laser beam was directed towards the sample where it is mounted horizontally on a holder. Two parabolic mirrors were arranged, so that the infrared radiation emitted by the sample were collected and focused towards a liquid N_2-cooled HgCdTe infrared detector (Judson Technologies). The detector signal was converted to voltage, pre-amplified using PA300, and then amplified using a Lock-in amplifier (Ametek, Signal Recovery7260). The resulting spectrum is a complex voltage that corresponds to the induced periodic heat waves or the temperature modulation of the sample surface as a function of laser modulation frequency. As the samples were (125 ± 5) μm thick, appropriate modulation frequency range 1–100 Hz was chosen. For the translucent samples, a water-based black ink coating was applied on the front side to make the sample opaque and absorptive to the laser radiation. The thermal diffusivity α_s and effusivity e_s of the samples were extracted by fitting the complex voltage to the one-dimensional heat flow model as explained in our published article [22].

In Raman thermometry, a confocal micro-Raman spectrometer (Horiba-Jobin Yvon, LabRam®HR) was used to acquire Raman spectra of the samples. The excitation source is a diode pumped solid state laser (Cobalt Blues®) having a wavelength of 473 nm with a capability to deliver a maximum output power of 25 mW. A 100 × objective lens having numerical aperture 0.9 allowed to excite the sample and also to acquire the spectra in backscattering configuration. The scattered light was spectrally dispersed by a grating (1800 lines/mm) before being detected by a position sensitive CCD. For a selected spot, the recorded spectrum was an average of at least 5 accumulations for the optimized exposure time. To avoid unintentional defocusing or drifting of the laser spot, the Raman intensity and the spot position were checked before and after acquisition.

The thermal conductivity is deduced from relation 1, for which the absorbed power, $P = P_o \times (\%A/100)$ where P_o is the incident power of the laser and A is absorbance (%). The output power P_o of the laser radiation delivered at the focal length of the objective lens was measured using a calibrated power-meter. The absorbance of Kapton-derived carbon was extracted from transmittance and reflectance of the samples using UV–Visible Spectrophotometer (Agilent Cary 5000). The samples were fixed on a holder having an aperture of diameter 1.5 cm. An integrated sphere was used to collect diffusive reflectance in addition to the specular reflectance. A Spectralon© reference standard was employed to calibrate the reflectance.

ΔT is obtained by measuring the Raman shift of the G-peak position (ω_G) recorded at two different incident laser powers P_1 and P_2 (Equation (2)). Usually, P_1 is chosen as a minimum power, so that the laser-induced heating is negligible. Hence, the sample remains in thermal equilibrium at room temperature and is thus considered