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Kapton-derived carbon as efficient terahertz absorbers

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ABSTRACT

The focus of this study is the preparation of carbon-based materials that satisfy the requirements of developing quasi-optic controllable absorbers for terahertz technology. These materials have been obtained from a commercially available organic polymer, Kapton® HN polyimide, through a pyrolysis process conducted in an inert atmosphere at different temperatures. The pyrolysis of Kapton film up to 1200 °C left a black residue principally composed of graphitic-carbon with a yield of about 55%. The D.C. conductivity of materials measured at 295 K increases with increasing pyrolysis temperature. The starting organic polymer is turned from an insulator to conductor material when heat-treated at over 700 °C. Moreover, in the frequency range 220–500 GHz, the pyrolyzed materials show distinct optical properties, which have variant degrees of terahertz absorption. Kapton® HN polyimide that is thermally converted into carbon-based materials may be used for the realization of calibrated terahertz absorbers, particularly for thermal transducers.

1. Introduction

The terahertz (THz) range, usually defined as the 0.3–30 THz region, of the electromagnetic spectrum is a low energy probe (1.24–124 meV, one million times weaker than X-rays) that opens up the possibility of overcoming limitations faced by other techniques. For example, in molecular spectroscopy, rotational and vibrational states of molecules, the Van der waals intermolecular interactions, and hydrogen bonds are best identified in the THz region [1].

In the diagnosis of cancers, THz imaging is a non-ionizing and non-destructive tool that easily distinguishes cancer cells from their normal counterparts. The method is simply based on cell-variations in water content that give the contrast on the THz imaging produced [2]. In telecommunication systems, the increased frequency from the microwaves to the sub-millimeter domain could allow the transmission of uncompressed high resolution and high-definition wireless data. Data transfer rates of about 11 Gbit/s at 0.2 THz [3] and 1.5 Gbit/s at 0.6 THz with 10 nW signal [4] have been achieved.

Although coherent THz source and efficient detector technologies are improving progressively, other components such as absorbers, filters, polarizers, and modulators are seldom available, as opposed to their technological counterparts i.e., in the microwave (electronic) and infrared (photonic) domains. Absorbers are the basic and essential component of integrated THz systems that have found several applications, such as thermal detectors, electromagnetic interference shielding, calibrating loads, and radar systems. The most important criterion required of a typical absorber is near-total absorption of the incident radiation over a broadband range.

Many interesting concepts and materials have been used to fabricate absorbers for the THz region [5–7]. Among functional materials, carbon-based materials have great potential with regards their broad structural-dependent properties, their abundance, and the low cost of application [8]. Lehman et al. [9] showed that an array of carbon nanotubes can be directly attached to the thermopile and that specular reflectance is controlled by the length of the nanotubes. A value of approximately 1% of reflectance was obtained for the longest tubes (1.5 mm) at 0.76 THz. Deng et al. [10] compared the specular reflectance of various materials such as bulk graphite, graphite paste, SiC, 3M-Velvet (carbon and silica) coating, and also their mixed compositions over the frequency range 0.1–3 THz. It was found that where SiC is mixed with 3M-velvet coating at a volumetric ratio of 1:5, a reflectance of less than 0.3% in frequency bands 0.2–0.5 THz and 0.1% in 0.5–2.0 THz can be obtained. Recently, Liu et al. [11] summarized the electromagnetic shielding properties of various carbon nanomaterials. Among them, a single atomic layer thick graphene is the most interesting material due to its intriguing properties. The shielding effectiveness, at

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1.2 THz, of single layer graphene deposited on quartz substrate is −3.7 dB, calculated from the percentage of transmitted power i.e., the ratio of received to incident power, T/T_o ~42% when substituted into the relation 10 × $\log_{10}(T/T_o)$. The shielding effectiveness of graphene-based devices was further improved to −16 dB (T/To ~2.5%) by stacking five graphene layers with insulating layers in between them [12]. However, these values are lower than the shielding effectiveness reported for composites i.e., 35.7wt % of graphite powder embedded in a PMMA matrix shields −50 dB below 0.5 THz [13], whereas 20wt % of graphite and ferrite powder containing silicone rubber shields up to −80 dB at 0.5 THz and −140 dB between 1 and 3 THz [14]. In radar systems, the absorbers are used as beam dumps in quasi-optical systems, as black body calibration sources, and to reduce radar cross-section of military aircraft. Jussi et al. [15] investigated several polymer-based commercial absorbers, namely FIRAM-500™ (Umass Lowell, USA), TKRAM™ (Thomas Keating Inc, UK), TERASORB-500™ (Umass Lowell, USA) and ECCOSORB® (Laird N.V. Belgium), and their transmission coefficients at 0.4 THz were found to be −40, −45, −60, and <−70 dB, respectively. These materials are quite thick, 2–4 mm, and thus are not suitable for waveguide configuration, particularly for attenuator fabrication.

The current interest of this study is to ascertain efficient, reliable and isotropic absorber materials with tunable properties. Our simple and highly reproducible method involves the heat treatment of an organic polymer precursor to yield a carbon residue. Among organic polymers, Kapton® HN Polyimide is the starting material of choice because it is known to produce highly structured graphite besides its high thermal stability and low-k dielectric properties [16]. According to Cunningham et al. [17], the orange-yellow Kapton is not a pertinent choice for optical windows or lenses in the broadband THz region due to its high absorption coefficient at inherent molecular vibration frequencies 4.9, 6.1 and 7.8 THz. However, we demonstrate that heat-treated Kapton opens up the possibility for further potential applications. Several researchers have extensively studied the thermal decomposition and thermo-kinetics [18] of Kapton in addition to the structural, physical and chemical properties of the Kapton-derived carbon films [16]. Raman spectroscopy and X-ray diffraction studies revealed that a heat treatment at 1000 °C leads to the formation of turbostratic carbon [19], composed of aromatic sheets which are randomly oriented to one another. Such structures, termed Basic Structural Units (BSU), were found in almost all carbon materials obtained by carbonization of organic substances. Mory et al. [20] have studied the dielectric response and the conduction mechanism up to 10 GHz, but their response in 0.2–0.5 THz frequencies have not yet been studied. This is explored experimentally and supported theoretically in this study.

2. Experimental

The starting material was a commercially available polyimide known under the trade name Kapton® HN (produced by DuPont de Nemours). The Kapton, in a foil with a thickness of 25–125 (±2) μm, was cut into 20 mm × 20 mm squares and then subjected to heating up to 1200 °C with a dwell time of 15 min in a flowing inert atmosphere (Argon: 99.999% purity). To simulate the behavior of films during the annealing process and to determine the evolved gaseous species, thermogravimetric analysis (Netzsch STA449 F1 apparatus) coupled with quadrupole mass spectrometry (Netzsch QMS403D Aeolos, 70 eV, and electron impact) was employed. The analysis was performed in a dynamic atmosphere of 80 cm^3/min with a heating rate of 10 °C/min.

A confocal micro-Raman spectrometer (Horiba-Jobin Yvon, LabRam HR) was used to acquire Raman spectra of the samples with a 473 nm excitation laser (Cobalt Blues®, DPSS, 25 mW). The scattered radiation was spectrally dispersed by a grating (1800 lines/mm) before being detected by a position sensitive CCD. A 100x objective is used to acquire spectra from various areas to ensure accurate sampling. The spectral resolution is 0.5 cm^{-1}.

The sheet resistance ($r_{d.c}$) measurements were conducted at room temperature using a Bio-Rad HL5500 setup in four-probe configuration. A minimum D.C. current is chosen to avoid parasitic heating of the samples. The ohmic behavior and symmetry factor were verified before each measurement.

Free-space continuous wave THz transmittance and reflectance data were obtained from the scattering (S) parameters of a vector network analyzer (Rohde and Schwarz ZVA24). Two frequency extension modules (FEM) in the J-band (WR3.4, 220–325 GHz) and Y-band (WR2.2, 325–500 GHz) provide the source and detector of THz radiation. The average output power of the THz radiation is *ca* 10 μW. The horn antennae were fixed at Port1 and Port2 to couple the wave propagation from the waveguide to the free-space. The TRM (Through-Reflect-Match) calibration procedure was applied to the output plane of the rectangular waveguides. Using two polymer lenses (30 mm focal length, 25 mm diameter), a collimated beam is formed in the middle of the free-space, where the sample will be mounted on a holder as shown in the schematic diagram (Fig. 1).

The aperture size of the incident wave is set to 6 mm via a tunable iris surrounded by an absorber foam. The parameters S_{11} and S_{21} correspond to the reflection and transmission losses of the incident radiation to the sample. As a reference for reflectance (R), the maximum $|S_{11}|$ of a flat silver mirror is recorded by adjusting the tilt angle of the sample holder to ensure that the beam is perpendicular to the plane of the sample. However, unwanted reflections from the essential components of the workbench such as the horn antenna itself and the lens will be present and cannot be avoided.

For this reason, very low levels of reflectance are very difficult to measure in these quasi-optical experiments. To improve precision and limit the effects of cavities, the measurements were carried out at various positions along the optical axis in steps of 100 μm over a distance of 3 mm and the magnitude of S_{11} values were averaged. This averaging will eliminate the standing waves that occur between the sample and horn antenna due to multiple unavoidable reflections (the Fabry–Perot effect). Even after this averaging, the lowest value of $|S_{11}|$ achieved for the commercial absorber slab TKRAM™ is limited to − 13 dB. This value is far higher than the value (−50 dB) reported by the supplier, where the measurements were carried out at a 45° angle of incidence. However, this is not a restraining factor in this first characterization of carbon-based materials, as the main purpose was to compare the relative behavior of different samples with references (mirror or perfect absorber). For transmittance (T) reference, the maximum $|S_{21}|$ of air was recorded using an empty sample holder. Both transmittance and reflectance spectra of TKRAM are equivalent to the noise floor of the instrumental measurement range.

3. Results and discussion

3.1. Heat treatment

Fig. 2 shows thermogravimetry coupled with mass spectrometry analysis of 125 μm thick Kapton® HN pyrolyzed in inert atmosphere. The polymer remains stable up to 425 °C even though traces of water (M/z = 18, 17) are detected at 100 °C. Further heating results in two types of mass loss phenomena similar to that previously reported in the literature [21]. The major and rapid mass loss of 30% occurs between 500 and 625 °C, followed by a gradual mass loss of about 12% up to 900 °C. In the first phase, the evolved