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Net-shaped pyramidal carbon-based ceramic materials designed for terahertz absorbers

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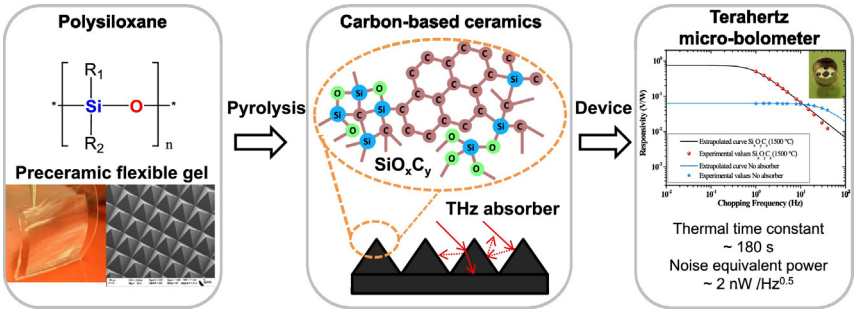
HIGHLIGHTS

- For the first time, the refractive index and absorption coefficient were reported for polymer-derived ceramics at THz domain
- The textured carbosiloxane ceramics exhibit lower reflectivity when compared to the planar surfaces
- The performance of the designed micro-bolometer is in fair competition with the commercially available terahertz power meters

GRAPHICAL ABSTRACT



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ABSTRACT

This study on polymer-derived ceramic (PDC) materials is devoted to the fabrication of 3D structures with vertically aligned pyramids and their optical properties at terahertz frequencies. The materials have been prepared by thermal conversion of a crosslinked polydimethylsiloxane precursor. Pyrolysis of starting polymer in an inert atmosphere yields a ceramic nanocomposite constituted of excess carbon embedded into a Silicon oxycarbide matrix. The excess carbon, essentially composed of small stacked graphene layers, is beneficial to absorption of terahertz radiation. In the frequency domain 500–750 GHz, a gradual variation in refractive index and absorption coefficient was obtained by the progressive thermal transition of the polymer. For samples heat-treated at 1500 °C, a reflectivity of – 3 dB was obtained for planar surfaces, whereas pyramidal surfaces exhibited a much lower value of – 22 dB when measured at oblique incidence and receiving angle of 60°.
For the first time, the proof-of-concept for PDC as the absorber element in microbolometers, specifically dedicated to the terahertz domain has been demonstrated. The microbolometer with 3D absorber element exhibited a responsivity of 0.76 V/W at bias current of 1 mA, time constant of 180 ms, and noise equivalent power of 2 nW/$\sqrt{\text{Hz}}$.

1. Introduction

Terahertz (THz) radiation covers a region spanning from 300 GHz of high frequency microwaves to 10 THz of far-infrared radiation in the electromagnetic spectrum [1]. Nowadays THz is used in a growing number of areas such as cancer diagnostics [2], large-area security

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surveillance, astronomy, chemistry [3] and telecommunication [4]. In most integrated systems, passive components such as attenuators, filters, and absorber elements in thermal transducers, rely on the efficient absorption of the incident radiation by the material.

Most of the devices classically employed in two border frequency regions become either incompatible or inefficient in the THz domain. For instance, microbolometers (thermal detectors) designed for infrared wavelengths (8–12 μm) are not sensitive enough for THz but sensitivity can be improved if the incident radiation is efficiently absorbed and converted into heat. For such a purpose, a few nanometres thick metal layer has been demonstrated to offer a promising solution [5]. The critical parameter in the determination of absorption characteristics is electrical sheet resistance, which is in turn inversely proportional to both the electrical conductivity and the thickness of a metal. This implies that the choices available to obtain efficient metal-based absorbers are limited. Recently, Simoens et al. [6] demonstrated the high absorption of a bolometer using particular geometry of antennas suitable for collecting the THz flux of any polarization. However, such technologies are adapted only to narrow band absorption, whereas the most important criterion for an absorber is near-total and broadband absorption. Therefore, developing an efficient absorber becomes of paramount importance.

Unlike in microwave or infrared domains, absorption mechanisms are very peculiar at THz frequencies. Surprisingly, the absorption process is not only due to excitation of charge carriers but also sensitive to phonons [7]. Among the functional materials, carbon-based materials have received extensive attention due to their diverse properties and also to the wide palette of carbon allotropes available [8,9]. For example in the THz domain, diamond (C sp^3) is transparent whereas graphite (C sp^2) is a strongly absorbent and highly reflective allotrope: in the frequency range 0.1–3 THz, the absorption coefficient and refractive index vary between (1–3.8) × 10^3 cm^{-1} and 16–4, respectively [10]. Usually, graphite is not preferred in its bulk form for absorbers due to its high reflectivity. Several attempts have been made to disperse either graphite powders or other carbon-based nanostructures in organic polymer matrix [11,12]. Although tuneable properties can be achieved, the organic matrices are unsuitable either for long use or at high temperatures in oxidizing environments. By contrast, a matrix-like fused silica (SiO_2) that is transparent and has a refractive index of 1.95 and absorption coefficient of <8 cm^{-1} at 0.1–2 THz [13] seems more appropriate.

The most commonly used technique for the incorporation of carbon as a second phase into a matrix is the powder metallurgy technique [14], which consists of mixing the matrix and carbon phases mechanically. However, there are critical issues associated with the mixing process, including dispersion of the second phase, inhomogeneity, cracks, and pores. All these manufacturing defects can severely affect the optical and mechanical properties of the materials.

To overcome these drawbacks, an alternative approach is to exploit the reactivity and melting phases at high temperatures [15]. However, the difficulties encountered are related to undesirable but inevitable reactions between phases at high temperatures leading to a loss of carbon due to the escape of CO. Therefore, such an approach prevents high carbon content in the material. Carbon solubility did not exceed 3 wt% at high temperatures. The research effort has been directed toward other manufacturing methods such as thermal chemical vapor decomposition [16], reactive sputtering [17], and the chemistry route via organosilicone polymers [18,19]. This last method has provided a significant advancement in the synthesis of a new class of materials and the combination of multiple chemical elements. Thus, carbon-rich silicon oxycarbide materials have been prepared. The process involves two-steps: synthesis of polymeric precursors via sol-gel technique and subsequent pyrolysis at temperatures above 1200 °C. This chemistry route has some advantages, in particular, the possibility to incorporate appreciable amounts of carbon into the oxycarbide network based on Si—C and Si—O bonds.

In this study, polydimethylsiloxane (PDMS), the commercially available Sylgard®184 elastomer, has been used as precursor. Its molecular structure contains two methyl groups attached to the siloxane backbone. The presence of a methyl group attached to silicon (Si-CH_3) promotes formation of free carbon at high temperatures. Another potential source of carbon is obtained using a crosslinker containing Si-vinyl. PDMS elastomer offers an easy processibility for the fabrication of complex channels in micro or nano fluidic devices [20], 3D structures for metamaterials, or photonic applications. It is important to note here that no results on the terahertz optical properties of pyrolyzed commercial Sylgard®184 PDMS have appeared in the literature so far. Although Duan et al. [21] summarized microwave absorption properties of $Si_xO_yC_z$ issued from pyrolysis of silicon-based polymers but their properties in frequencies higher than 300 GHz are not available.

Clearly, there is a need for more detailed studies on polymeric precursors, their resulting pyrolyzed materials, and their potential applications in the terahertz domain. Therefore, the objective of this work is to determine the absorption properties of polysiloxane-derived ceramics and to deepen understanding of the relationships between polymeric structures, the free carbon phase issued from pyrolysis of hydrocarbon groups initially present in the precursor, and the properties thereof.

2. Fabrication

2.1. Pyramidal structures

The basic procedure for the fabrication of pyramidal ceramic microstructures is outlined in Fig. 1. It involves three major steps: fabrication

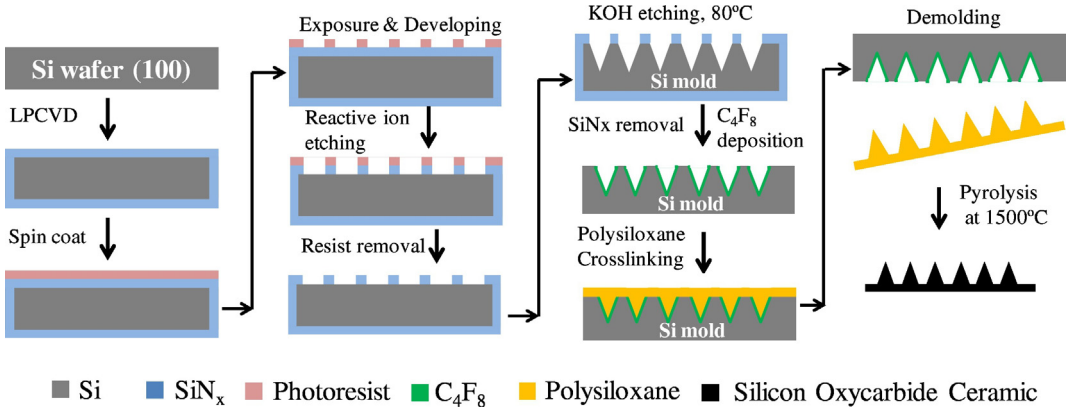

Fig. 1. Schematic diagram showing methodology involved in fabrication of pyramidal ceramics.