Journal of the European Ceramic Society 36 (2016) 3073–3081

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Prominent local transport in silicon carbide composites containing in-situ synthesized three-dimensional graphene networks

Pilar Miranzo[a,*], Laura López-Mir[b], Benito Román-Manso[a], Manuel Belmonte[a], M.Isabel Osendi[a], Carmen Ocal[b,*]

[a] Instituto de Cerámica y Vidrio (ICV-CSIC), Kelsen 5, 28049 Madrid, Spain
[b] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Barcelona, Spain

ARTICLE INFO

Article history:
Received 2 March 2016
Accepted 21 April 2016
Available online 29 April 2016

ABSTRACT

In-situ grown graphene/SiC composites developed by spark plasma sintering have emerged as a very interesting family of materials with expected high performance for advanced applications. In this work, the local functional properties of graphene/SiC ceramics are elucidated for distinct α- and β- SiC polytypes combining scanning probe microscopies. We unambiguously identify all composite constituents and demonstrate the formation of a three-dimensional graphene conductive network inside the composite. The investigated composites exhibit grains with different doping level depending on growth rate during sintering so that conduction paths associated to graphene and matrix networks may compete. The relevance of nanoscale characterization on functional graphene/semiconductor materials is proved as it evidences the type of doping and carrier concentration of the semiconductor and the critical role played by the graphene constituent in the formation of ohmic contacts. Both issues are of crucial importance for understanding the macroscale behavior of these materials and determine their applications.

1. Introduction

For years, silicon carbide (SiC) has raised constant attention because of its multiple applications due to attractive mechanical, thermal and electric properties [1,2]. The interest expands from uses as structural polycrystalline material taking advantage of its thermal, mechanical and tribological properties for friction and wear components, in aerospace applications and for thermal management systems, to functions as a semiconductor single-crystal material in electronics, where its high thermal conductivity, electrical field breakdown strength, and maximum current density make it a promising candidate for high-powered devices at elevated temperatures. As semiconductor element in electronic devices, the capability of changing the dielectric properties of SiC through doping is a very important consideration. In fact, it can be n-type doped by nitrogen or phosphorus and p-type doped by aluminum, boron, gallium or beryllium. Moreover, SiC exists in a large number of polytypes or crystalline forms with diverse characteristics. The most common in commercial uses is the alpha silicon carbide (α-SiC) that refers to hexagonal (nH-SiC) and rhombohedral polytypes (nR-SiC). The cubic 3C-SiC or beta modification (β-SiC) is formed at lower temperatures and has a zinc blende crystal structure (similar to diamond). The electronic characteristics (bandgaps, mobility) of the different polytypes depend on the type and level of doping.

The addition of nanometer sized carbon allotropes (carbon nanotubes and, in particular, graphene) is being nowadays the focus of attention of diverse investigations devoted to improve and modulate the mechanical and electrical performances of these materials for micro-electromechanical devices (MEMs). Similarly, the role of epitaxial graphene on SiC in the characteristics of the solid electrolyte interphase surface [3] and, more recently, the relevance of surface graphitization to activate the electrochemical performances of nanostructured SiC [4] have demonstrated its potential as anode material in lithium storage batteries. On the one hand, epitaxial graphene (EG) grown on single-crystal SiC substrates by different approaches (CVD, elevated heating...) under ultrahigh vacuum (UHV) conditions has been extensively studied [5–7]. In fact, most investigations on thickness controlled graphene creation through elevated heating of SiC have

* Corresponding authors.
E-mail addresses: pmiranzo@icv.csic.es (P. Miranzo), cocal@icmab.es (C. Ocal).

http://dx.doi.org/10.1016/j.jeurceramsoc.2016.04.035
0955-2219/

Table 1
Current measured by CSFM at V_{tip} = +1 V for each composite on the graphene flakes (IG) and on top of the SiC grains (ISiC), electrical conductivity measured at a macroscopic level (σ_e) and TO- and LO-band positions (P) and ILO/ITO ratio for averaged Raman spectra of the different graphene/SiC composites: α-SiC (G/α-SiC), β-SiC (G/β-SiC) and nanosized β-SiC (G/nβ-SiC).

Material	IG (A)	ISiC (A)	σ_e (S·m^{-1})	PLO (cm^{-1})	PTO (cm^{-1})	ILO/ITO
G/nβ-SiC	$1-5\times10^{-6}$	3×10^{-9}	1.0×10^{2}	- - -	804	- - -
G/β-SiC	3×10^{-6}	4×10^{-10}	5.5×10^{0}	981	801	0.08
G/α-SiC	3×10^{-10}	$<10^{-11}$	6.4×10^{-4}	977	796	0.34

relied on such clean UHV conditions. On the contrary, exploitation of graphene synthesis under non-UHV and, in particular, under the extreme conditions of the spark plasma sintering (SPS) is very scarce. In a previous work [8], we demonstrated that EG formed during densification of SiC powders by SPS method on the surface of the SiC grains due to the low oxygen partial pressure and the high temperature in the SPS chamber aided by the current flowing along the SiC specimens. This interesting phenomenon occurred for different SiC materials including α-(mainly containing 6H and traces of 4H and 15R polytypes) and β-(3C polytype) SiC, but the kind of SiC polytype and original powder size had a strong influence over the in-situ formed graphene characteristics (flake size and graphene quality, with a larger amount of disordered stacking in the nano-size powder) and on the electrical conductivity of these graphene/SiC composites. For instance, the amount of defects in the formed graphene depended on the original SiC grain size, whereas the electrical conductivity of the composites depended on both the polytype and the SiC grain size, varying from 8.3×10^{-5} S m^{-1} for the α-SiC material to 1.02×10^{2} S m^{-1} for the nanosized β-SiC (see Table 1 where the properties and characteristics of these composites are collected). More recently, results on the contact-mechanical properties at pre-creep temperatures (850 °C) for these composites have demonstrated quantitative differences associated to the microstructure [9]. In order to further explore the capabilities of the SPS method to design and fabricate SiC materials with tunable conductivity for high performance electromechanical micro-devices, we explore here the local properties of such graphene based nanocomposites evidencing the key roles of polymorphism and initial size of the SiC ceramic powders, and their doping on the microscale conducting behavior. This new understanding is of paramount importance to straightly link the nanoscale behavior to the macroscale performance of these materials in different applications either for friction purposes or for electronic devices and batteries.

The intrinsically nanometric dimensions of the graphene related materials make the use of nano-scale scanning probes particularly worthy for their characterization. A combination of Scanning Force Microscopies (SFM) has been employed for differentiating primary and secondary phases in SiC ceramics, distinguishing the graphene component and determining its spatial distribution, as well as elucidating the electrical and frictional responses of each composite constituent. The capabilities of this combined strategy have been successfully employed for the study of laterally heterogeneous surfaces exhibiting coexistence of surface regions with clearly differentiated electrical properties [10,11]. SFM in its lateral force mode (also known as Friction Force Microscopy, FFM) has been used to identify the diverse constituents via their different mechanical responses. Other SFM variants using conductive probes, namely conducting SFM (CSFM) and Kelvin probe force microscopy (KPFM), have been employed to obtain the local electric current and surface potential (or contact potential difference, CPD) without changing surface location and, therefore, allowing unambiguous correlation of all these magnitudes for each constituent. The electrical response of the in-situ graphene flakes in these composites indicates that they are connected and form a conducting three-dimensional (3D) network, whereas the SiC matrix shows a semiconductor character with n-type or p-type doping depending on the particular composite.

2. Materials and methods

SiC materials were prepared from three different starting powders: α-SiC (S-2022, CERAC, d_{50} = 0.78 μm, polytype 6H), β-SiC (BF-17A, HC-Starck, d_{50} = 0.5 μm, polytype 3C), and nano-β-SiC (NanoArmor, d_{50} = 45–55 nm, polytype 3C), using 5 wt.% of Y_2O_3 (Grade C, H.C. Starck GmbH & Co., Germany) and 2 wt.% of Al_2O_3 (SM8, Baikowski Chimie, France) as sintering additives. The SiC and additive powders were mixed by attrition milling in ethanol for 2 h using Si_3N_4 grinding media. Solvent was evaporated from the suspensions in a rotary-evaporator at 90 °C and the resultant mixture was oven dried at 120 °C and then sieved through a 63 μm mesh. The mixtures were spark plasma sintered (SPS-510CE, SPS Syntex Inc., Japan) into discs of 20 mm in diameter and 3 mm thickness using a heating rate of 133 °C·min^{-1}, an uniaxial pressure of 50 MPa and a holding time of 5 min, under 4 Pa of vacuum atmosphere, at temperatures ranging from 1800 and 1850 °C. The sintered specimens were cut into slabs and polished using silicon carbide paper and successive diamond compounds as the standard procedure to get mirror finished surfaces.

Micro-Raman maps were recorded on cross sections of the different specimens by confocal Raman-atomic force microscopy (model Alpha300AR, WITec GmbH, Germany), using the 532 nm laser wavelength excitation, and an acquisition up to 3000 cm^{-1}. The microstructure of the specimens was observed by field emission scanning electron microscopy (FESEM, S-4700, Hitachi, Japan) on polished and plasma etched surfaces.

Scanning force microscopy (SFM) measurements were performed under low humidity conditions (<5% RH, obtained by a continuous N_2 gas flux) using a commercial head and software from Nanotec [12]. Boron-doped diamond coated Si probes were used for all SFM measurements presented here. These tips exhibit a good electrical conductivity and resistance to wear, making them appropriate for hard samples analysis. On the other hand, their contact resistance (about 10 kΩ on metallic surfaces) is adequate for experiments on resistive samples. An intermediate cantilever spring constant (k = 3.0 N m^{-1}) was chosen as a compromise to have the same probe for contact SFM operation (FFM and CSFM) and dynamic imaging during KPFM. In this work, FFM [13] has been used to assess the chemical differentiation between composite constituents during contact mode measurements. CSFM [14] was used to obtain direct tip-surface conducting response whereas KPFM [15,16] in the lift mode was used to accurately determine local variations in surface contact potential difference (ΔSP). For each sample, distinct nanoscale characterizations were made on exactly the same locations to correlate local properties for the different constituents. Tip-sample conditions were systematically checked by force versus distances curves. The same tip was used in all the experiments of at least one series. Experimental details of these measuring modes and the particular set-up employed are given in the Supplementary Data and can be found elsewhere [17–20].