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Multi-scale electrical response of silicon nitride/multi-walled carbon nanotubes composites

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ABSTRACT

Dense silicon nitride (Si_3N_4) composites with various amounts (0–8.6 vol%) of multi-walled carbon nanotubes (MWCNTs) are electrically characterised by combining macroscopic dc–ac and nanoscale conductive scanning force microscopy (C-SFM) measurements. In this way, a coherent picture of the dominant charge transport mechanisms in Si_3N_4/MWCNTs composites is presented. A raise of more than 10 orders of magnitude in the electrical dc conductivity compared to the blank specimen is measured for MWCNTs contents above 0.9 vol%. Semiconductor and metallic-like behaviours are observed depending on both the temperature and the MWCNTs content. Macroscopic measurements are further supported at the nanoscale by means of C-SFM. The metallic-type conduction is associated to charge transporting along the nanotube shells, whereas the semiconductor behaviour is linked to hopping conduction across nanotube–nanotube contacts and across intrinsic defect clusters within the nanotubes.

1. Introduction

Silicon nitride (Si_3N_4) based materials are well known for their extraordinary strength and hardness at high temperatures that make them suitable for applications under wear conditions, like cutting tools or ball bearings [1]. The full potentiality of these materials is only partially achieved by the difficulty inherent to their machining. Recent works [2,3] have shown the possibility of the efficient electric discharge machining (EDM) for Si_3N_4 materials when adding an electric conductive second phase, such as TiN [2] or $MoSi_2$ [3]. The amount of such second phases required to get a reasonable reduction in resistivity was around 30 vol%. Besides, it has been pointed out that problems caused by static electricity in Si_3N_4 bearings could be avoided by the addition of highly conducting carbon nanotubes (CNTs) [4]. Therefore, the change from highly electric insulator to conductor in Si_3N_4 materials without degrading other properties would have great technological interest.

The step raise in electrical conductivity is the common trend observed in ceramic/CNTs composites once percolation of the CNTs network is achieved [4–11]. Due to their high aspect ratio, quite low percolation thresholds, between 0.64 and 3.0 vol%, have been reported for ceramic/CNTs composites [7–10]. Conductivity values after percolation seem to depend much on the CNT type and purity as well as on the composite processing procedure, which may damage the nanotubes. For single-walled carbon nanotubes (SWCNTs) containing alumina composites, electrical conductivities (σ) of 10^3 S m^{-1} have been reported [5], whereas in composites containing multi-walled carbon nanotubes (MWCNTs) much lower values, in the order of 10 S m^{-1}, have been attained [4,6–9]. For $MgAl_2O_4$/SWCNTs composites processed by in situ catalytic chemical vapour deposition (CVD) [10], σ was well fitted by the scaling law of the percolation theory as $\sigma = k(p - p_c)^t$, giving a percolation threshold, p_c, of 0.64 vol% and an exponent, t, of 1.73. In Si_3N_4/MWCNTs composites, electrical conductivity values about 10 S m^{-1} for nanotube contents between 1 and 5 wt% have been reported [4,6], but values for p_c have not been given yet.

In the present work, we describe the electrical properties of Si_3N_4 with various contents of MWCNTs in dc and ac conditions for a wide temperature range, highlighting the effect of nanotube content and their connection within the network. The local electrical response of the composites is also analyzed and correlated with their nanostructure by means of conductive scanning force microscopy (C-SFM).

2. Experimental procedure

Si_3N_4 materials containing MWCNTs, in concentrations ranging from 0.9 to 8.6 vol%, were prepared as described elsewhere [12]. In short, CVD synthesized MWCNTs of 30 nm diameter and 1–5 μm

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length, according to the supplier (Nanolab Inc., USA), were thoroughly mixed with Si_3N_4 (SN-E10, UBE Industries, Japan) plus liquid forming sintering additives, 2 wt% of Al_2O_3 (SM8, Baikowski Chimie, France) and 5 wt% of Y_2O_3 (Grade C, H.C. Starck GmbH & Co., Germany). Compositions were spark plasma sintered (Dr. Sinter, SPS-510CE, Japan) at 1585 °C for 5 min in vacuum (6 Pa), applying a pressure of 50 MPa. Specimens were discs of 20 mm diameter and about 3 mm thick. A blank sample without nanotubes was equally processed for comparison. All specimens had densities above 99% of the theoretical, good nanotube dispersion and no evidence of degradation, as previously reported [12]. Microstructures on both polished and plasma etched (CF_4/5 vol% O_2 at 100 W for 40 s) and fracture specimens containing MWCNTs were observed using a field emission scanning electron microscope (FESEM, Hitachi S-4700, Japan). Besides, samples were also prepared for observation in the transmission electron microscope (TEM, 200 kV JEOL JEM 2000 FX) following usual cutting, dimpling and ion thinning procedures.

Micro-Raman spectra of the original MWCNTs and the composites were taken using the 540 nm laser wavelength excitation (in via, Renishaw equipment, UK).

For the macroscopic electrical characterisation, either two or four probe method was used depending on the electrical conductivity level initially measured. Resistivity under dc conditions was calculated from the current density versus electric field curves measured in a Keithley Sourcemeter 2410 model. For the ac characterisation an Agilent 4294A Precision Impedance analyzer was employed scanning the frequency range 10–10^7 Hz. Measurements at different temperatures, from 273 to 573 K in 50 K steps and at 2 K min^{-1} heating rate, were carried out in a home-made furnace that can be fitted to each probe configuration.

Scanning force microscopy (SFM) measurements were performed under low humidity conditions (2% RH, obtained in a N_2 atmosphere) using a commercial head and software from Nanotec. [13]. Commercial silicon Cr/Pt coated probes and boron-doped diamond probes with force constants k = 0.2 and 3.0 N m^{-1} were used for both morphological and conductive SFM measurements. To check tip–sample conditions, the adhesion force was systematically determined from force versus distance curves prior to and after each conductivity experiment. The conducting tip was placed in direct contact with the sample, under controlled load, i.e. by using a normal force feedback, and the current was measured between tip and sample. The sample was always grounded and the voltage was applied to the tip (V_{tip}). Direct electric contact to ground was established through a metallic clamp attached at the sample border. We note that the ability to control the applied load permits avoiding any undesirable tip-induced effect, separating and controlling the mechanical response of the system under study. The conducting response of the sample surface was obtained by following different strategies [14]: (i) simultaneously acquiring topographic images $z(x, y)$ and current maps $I(x, y)$ over a given region at a given voltage, and (ii) acquiring I–V characteristics curves at selected (x, y) locations on the surface. I–V curves were performed at least on five different regions for each sample and, within each region; 30–40 I–V curves were recorded.

3. Results and discussion

According to previous results of present authors [12], the processing route used for these Si_3N_4/MWCNTs composites produces reasonably good dispersion of the MWCNTs within the Si_3N_4 matrix, as FESEM observations of fractured surfaces revealed [12]. Besides, the spark plasma sintering conditions allow high relative densities, $\geqslant$99.0%, while avoid nanotubes degradation, as micro-Raman spectroscopy data confirmed by showing similar intensity ratios for the characteristics bands of MWCNTs, i.e. D/G and G′/G [12], in both the composites and original nanotubes.

TEM observations indicate that MWCNTs are bent and twisted at Si_3N_4 grain boundaries (Fig. 1). Then, we can expect that the bulk electrical transport behaviour of the Si_3N_4/MWCNTs composites could be controlled by the nanotubes network but not by the non-conductive Si_3N_4 matrix.

Fig. 2 shows the dc electrical conductivity as a function of the MWCNTs content. The value in the plot for the blank Si_3N_4 corresponds to the detection limit of our experimental set-up, 10^{-13} S m^{-1}; therefore, the real conductivity must be even lower. For the 0.9 vol% MWCNTs specimen, a sharp conductivity increase of more than 10 orders of magnitude (4×10^{-2} S m^{-1}) is registered as compared to the reference Si_3N_4 specimen, which infers a

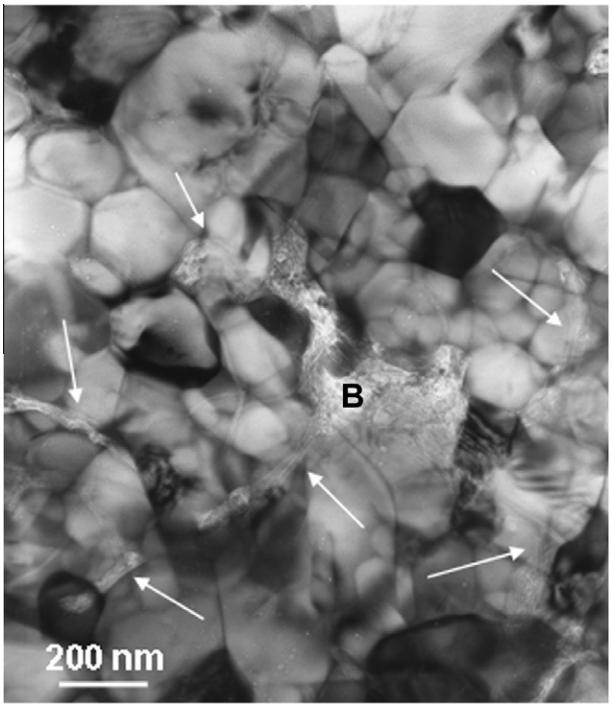

Fig. 1. TEM micrograph for the composite containing 5.3 vol% of MWCNTs. The nanotubes are pointed out by arrows. A MWCNTs bundle is shown marked with a "B".

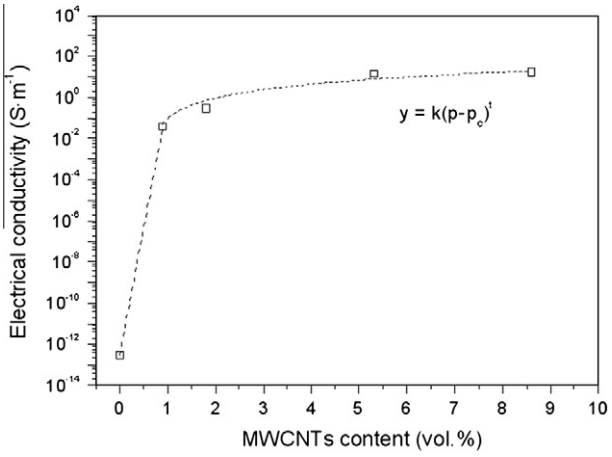

Fig. 2. Measured dc conductivity as a function of MWCNTs content. Electrical conductivity values represent an average of at least three measurements with a standard deviation of ~5%.