

GeTe Encapsulated within Single-Walled Carbon Nanotubes

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ABSTRACT

Due to an impressive portfolio of unusual properties arising as a result of their reduced dimensionality, carbon nanotubes are expected to provide a viable solution to down scaling challenges triggered by the aggressive miniaturisation of conventional electronic components. Carbon nanotube-based devices make use of their semiconductor behaviour whereas their metallic behaviour is needed to serve as interconnects. Due to their unique dimensions and geometry, nanometer diameter-sized carbon nanotubes also provide an exceptional opportunity of engineering novel one-dimensional structures within their hollow inner cores. Filling the inner cores of carbon nanotubes with foreign materials opens new possibilities of obtaining one-dimensional structures with sometimes novel structures and modified crystal chemistries compared to their bulk counterparts.

One can envisage the use of phase change materials to be encapsulated within carbon nanotubes, as these materials are currently some of the most promising materials for data-storage applications and offer great potential as an emerging non-volatile electronic memory. As well as creating one-dimensional structures in architectures not known before, the encapsulation method offers the opportunity to study the properties and phase change behaviour of these materials at their smallest conceivable scale.

We show that the binary chalcogenide compound GeTe, one of the most studied phase change materials, can be effectively encapsulated within single-walled carbon nanotubes and report on a scanning tunnelling microscopy study, coupled with structural investigations by aberration corrected high resolution transmission electron microscopy. As well as resolving the structure of encapsulates at the atomic level, we determine that the filling species arrange themselves into continuous nanowires with lengths of up to a few hundred nm. Based on scanning tunnelling spectroscopy data, information on the electronic structure of encapsulated nanowires has been extracted with the aid of the predicted density of states for the particular nanotubes. Aspects related to charge transfer between the host nanotube and the encased material, as well as information on the occupied band structure of these systems have been examined using ultraviolet photoelectron spectroscopy experiments and the work function of the hybrid systems determined.

Key words: GeTe, carbon nanotubes

1. INTRODUCTION

Recent years have witnessed an increased demand for more powerful computers and continuous miniaturisation of electronics. As the drive towards miniaturisation continues, the utilization of the low-dimensional electronic properties would facilitate very fast and functional devices. In particular, the exceptional electronic properties not found in other materials of the one-dimensional carbon allotrope, carbon nanotubes (CNTs) makes them ideal candidates for future solid-state nanoelectronic devices. Indeed, designs of a carbon nanotube-based electromechanical universal memory [1], as well as a non-volatile random access memory (RAM) using carbon nanotubes for molecular computing have been proposed [2], showing that these devices present competitive capabilities to existing memory technologies.

Single-walled carbon nanotubes (SWNTs) are one atom thick structures with carbon atoms arranged in hexagons, resembling a sheet of chicken wire, wrapped up to form tubes 10000 times thinner than a human hair. The

manner in which the carbon hexagons are arranged along the tube axis determines whether the nanotube has metallic or semiconducting character.

In addition to remarkable physical and chemical properties, due to unique dimensions and geometry, the central cavity of SWNTs has been shown to serve as a template for the controlled growth of one dimensional crystals, providing an unparalleled opportunity of engineering structures with sometimes entirely novel co-ordinations and stereochemistry [3]. For example, studies on HgTe-filled SWNTs using restored high resolution transmission microscopy (HRTEM) along with density functional theory calculations found that when confined into the inner cores of SWNTs, HgTe adopts a unique structure, with new coordination geometries not observed in the bulk, that becomes a semiconductor with a band gap of 1.2 eV, in contrast to its semimetallic bulk counter part.

A wide range of organic, as well as inorganic materials have been shown to fill the inner cores of SWNTs [4,5], however no reports of phase change materials encapsulated within SWNTs exist. HRTEM and restored HRTEM show that the filling species can arrange themselves into clusters or can form continuous chains inside the nanotubes, depending on their initial size and on the van der Waals forces exerted by the CNTs walls. They mainly respect the bulk structural chemistry of the starting material but new structures have occasionally been obtained [3].

Motivated by the increased interest in phase change materials as potential replacement of silicon-based flash-type memory and substantiated by the efforts of leading semiconductor companies in the field of solid-state non-volatile electric memories, one can envisage the encapsulation of phase change materials within SWNTs with the view to using the newly formed composite systems as active elements in such storage devices.

Numerous phase changing materials have been developed, a few examples include GeTe [6], SbTe [7], SnSe [8], $\text{Ge}_1\text{Se}_1\text{Te}_2$ [9], GeInSbTe [10] and compositional variants of AgInSbTe [10], etc, and their properties investigated to assess their suitability as memory switching components.

The dimensionality of these systems ranges from thin films to nanowires and to nanoparticles. In particular, GeSb and GeSbTe thin films deposited in the amorphous form show higher crystallization temperatures compared to thicker films and bulk material as the thickness is reduced below 20 nm [11], requiring higher power for switching the memory state.

Phase change nanoparticles have also been fabricated by various methods such as laser ablation, self-assembly and solution-based methods [12]. Most of nanoparticles with diameters between 20 nm and 80 nm show similar crystallization temperatures as their thin film counterparts, except for GeSbTe [13]. In this case, GeSbTe nanoparticles tend to exhibit only the fcc phase for the 20 nm particles, whereas thin films of GeSbTe form only the hexagonal phase.

Phase change nanowires grown via a catalyst-assisted vapour-liquid-solid (VLS) process seem to provide a viable alternative in terms of switching speed, endurance and data retention time and seem promising as building blocks for non-volatile scalable memory [14]. In particular, for GeTe nanowires it was found that the melting point is significantly reduced (390 °C) compared to that of the bulk material (725 °C), therefore advantageous for the reduction in the programming energy required for phase switching. This aspect, evidenced also for In_2Se_3 nanowires, suggests that further reduction in the nanowire diameter may possibly result in even lower melting point which would consequently lead to a further reduction in the thermal energy for the phase transition.

Diameters of the phase change nanowires previously synthesized range between 200 nm and 20 nm and depend on the size of the catalyst particle. Therefore, using carbon nanotubes with diameters as low as 1 nm, as templates for creating thinner nanowires may represent the ultimate size limit in exploring the behaviour of these materials at their smallest conceivable scale that no other existing synthesis method is currently able to afford. We report here that GeTe, one of the most studied phase change materials, can efficiently be encapsulated within SWNTs. We also present information on the structure of the encapsulated nanowires as extracted from high resolution transmission electron microscopy, in addition to electronic structure information from photoemission experiments and scanning tunneling microscopy.

2. EXPERIMENTS

Arc-discharge SWNTs with a narrow diameter distribution centered around 1.4 nm were used in this study after air thermal annealing at 450 °C, employed to remove amorphous carbon and –COOH groups present on the surface of nanotubes after acid purification.

The filling procedure employed in this study exploits the capillary properties of carbon nanotubes and it is based on the ability of the molten filling material to wet the surface of the nanotube [15]. SWNTs were heated in a

quartz tube sealed under vacuum with the molten filling material to 100 °C above the melting point of GeTe and allowed to cool down slowly to room temperature. Transmission electron microscopy (TEM) and scanning TEM (STEM) were used to validate the presence of the filling material within SWNTs and assess the filling yield of the sample.

Ultraviolet photoelectron spectroscopy (UPS) measurements were carried out using He I radiation (21.22 eV) from an Omicron HIS13 windowless He lamp, on an Omicron Multiscan UHV system equipped with an EA125 hemispherical photoelectron energy analyser. All spectra were recorded at room temperature, with an overall resolution better than 190 meV, determined from the Fermi edge of a clean Au film. An electron pass energy of 5 eV and an analysis area of 2 mm diameter determined by the entrance slit of the photoelectron analyzer has been used. For UPS measurements, films were prepared by drop casting the nanotube material directly onto the supporting sample plate, after sonication in acetone and subsequent ultracentrifugation in order to remove excess GeTe material left after the filling process.

For STM experiments, a suspension of filled carbon nanotubes was prepared by drop-casting on Au substrates. The instrument used for the STM studies is a commercial Omicron VT Multiscan STM. STM tips were electrochemically etched W wire prepared immediately before introducing them into the UHV chamber. All measurements were carried out at room temperature in constant current mode. Typical scanning conditions used with this sample were 0.1 nA for the tunnelling current and a positive sample bias of 0.1 V. Scanning tunnelling spectroscopy (STS) measurements were performed by interrupting the scanning and the feedback at preset locations and recording the tunnelling current variations during the sample bias ramp (usually between - 2 V and + 2 V). STM images were processed using WSxM software [16].

3. RESULTS & DISCUSSION

The filled material was examined using HRTEM and representative images indicating that GeTe have been effectively incorporated within SWNTs is presented in Figure 1a. Additionally, energy dispersive X-ray spectroscopy (EDX) analysis confirming the identity of the filling elements within the sample is presented in Figure 1b. Based on a statistical analysis of the TEM data, a filling yield in excess of 80 % has been estimated.

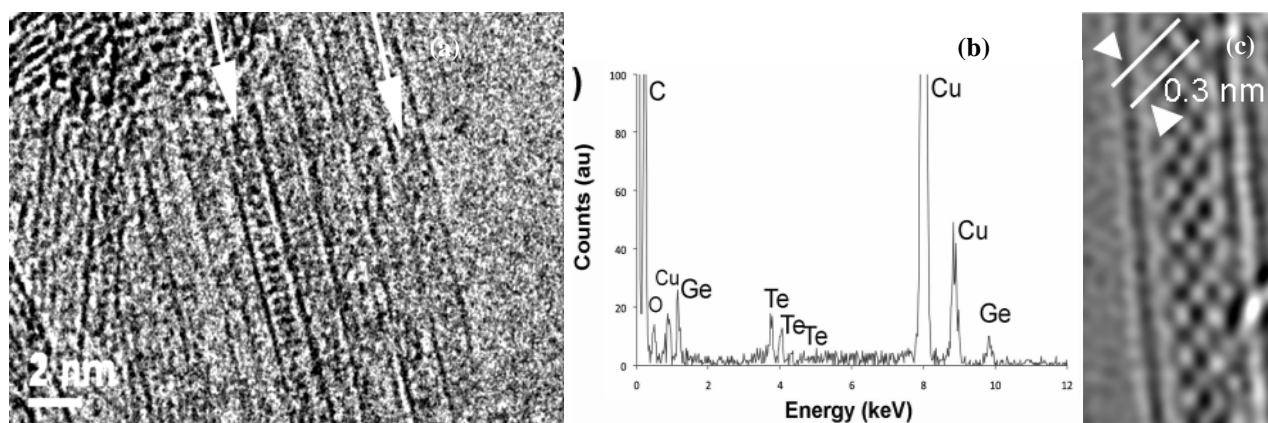


Figure 1. HRTEM image of a bundle of SWNTs containing amorphous (right arrow) and crystalline (left arrow) GeTe filling (a). (b) Energy dispersive X-ray spectroscopy (EDX) spectra obtained from the same region as the image in (a) indicating the presence of Ge and Te as filling elements. (c) Aberration-corrected TEM image of an individual SWNT indicating crystalline filling. The filling material appears as black dots within the SWNTs and continuously fills the nanotube's inner cavity.

Continuous nanowires with lengths up to a few hundred nm and diameters in the range of 0.9 nm to 1.2 nm are found to form within the inner cores of nanotubes. Whereas for thin films crystallization has been shown to no longer occur for thickness below 2 nm [11], variable crystallisation is found within SWNTs, with both amorphous and crystalline filling observed within the same sample, possibly correlated with the nanotube diameter. A lattice spacing

of 0.3 nm is found for the GeTe filling, as determined based on aberration-corrected TEM data (Figure 1c). The 0.3 nm value is not consistent with bulk GeTe, however previous studies on encapsulated materials within SWNTs have shown that the confinement can induce the formation of novel structures, not previously found in bulk form, giving rise to modified physical and chemical properties.

Ultraviolet photoelectron spectroscopy has been utilised to extract information on the electronic band structure of the filled nanotubes. The electronic structure is depicted in Figure 2a, where the valence band spectra of both the filled and pristine nanotubes, taken at excitation energy of 21.22 eV (He I) are shown.

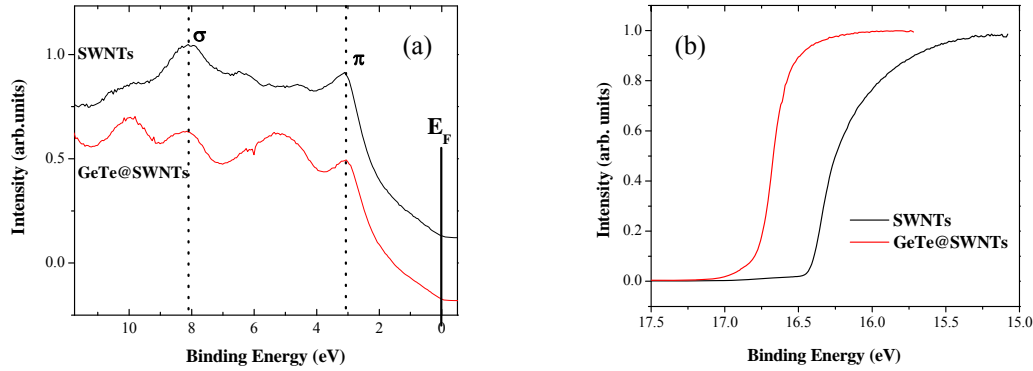


Figure 2. (a) UPS spectra of pristine and filled SWNTs. Energies are defined with respect to the Fermi energy E_F and spectra are shifted vertically for clarity. Dotted vertical lines indicate the maximum position of the π and σ bands of SWNTs. (b) Secondary electron cut-off for the work function determination.

In order to enable a quantitative comparison, the spectra have been normalised to the secondary electron peak and the Shirley background subtracted. The spectrum measured on the pristine nanotubes shows the well-known features characteristic to the three-fold coordination of C atoms: the σ -bands corresponding to the strong in-plane bonding situated at ~ 8.1 eV and the π -bands at ~ 3.1 eV, representative of the weak bonding perpendicular to the graphene plane.

The valence band structure of GeTe-filled SWNTs displays some features that could be attributed to the filling material. Previous UPS measurements of bulk GeTe indicate a subband from 0 to 6 eV, in the Ge 4p region, that contains some fine structures at around 1.8 eV, 3.5 eV and 4.9 eV, respectively [17]. The 4.9 eV feature of the subband is visible in our photoemission spectrum, however we do not observe the feature at 1.8 eV, possibly due to a different local structure of the GeTe confined within the nanotubes with respect to the bulk material, that could modify the electronic structure and give a different photoemission response. The feature at 3.5 eV is obscured by the presence of the π states of the SWNTs, as is the lower Ge 4s subband at around 8 eV, by the σ states of the SWNTs existing in the same region.

No energy shift of the π bands of the filled sample with respect to the pristine SWNTs is observed, suggesting the absence of charge transfer between the tubes and the filling. According to a rigid band shift model, electron transfer from the nanotubes to the filling material would lead to a shift of the Fermi level towards the valence band [18]. Changes in the work function of the filled nanotubes with respect to the pristine ones are revealed by the secondary electron threshold of the photoemission spectra (Figure 2b). The work function is given by the secondary electron cut-off, since the electrons responsible for the secondary edge have just sufficient energy to overcome the workfunction of the material. Upon filling with GeTe, the work function is reduced by 0.4 eV, which can be attributed to the presence of an electric dipole at the interface between the nanotube and the filling, which changes the energy an electron needs to leave the sample.

To further investigate the electronic properties of these systems, scanning tunneling microscopy has been applied to GeTe-filled carbon nanotubes and the results depicted in Figure 3, showing atomically resolved images of an individual filled SWNT in comparison with the case of a pristine, unfilled SWNT. Atomically resolved images of SWNTs allow for the determination of the chiral angle, θ , which gives the orientation of carbon hexagons with respect to the nanotube axis, and of the diameter, d , of the tube, which are linked to the structural indices (n , m) of the nanotube.

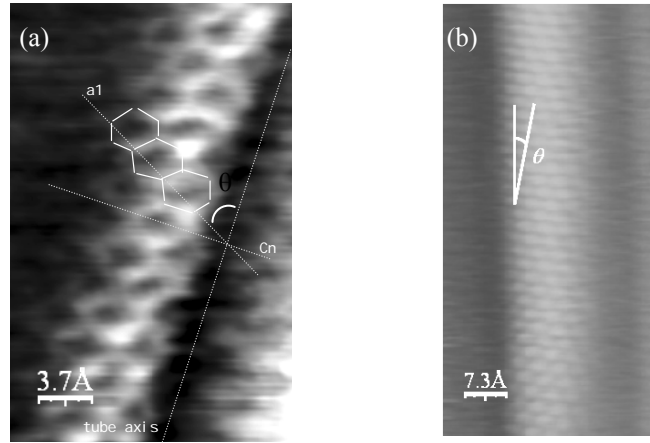


Figure 3 Atomically resolved STM images of pristine SWNT showing the honeycomb structure (a) and GeTe-filled SWNT (b).

The pair (n, m) determines whether a SWNT will be a metal or a semiconductor and their dependency on the chiral angle and diameter is given by:

$$n = \frac{\pi d}{a} \frac{2}{\sqrt{3}} \sin\left(\frac{\pi}{3} - \theta\right) \quad m = \frac{\pi d}{a} \frac{2}{\sqrt{3}} \sin \theta \quad [19]$$

More precisely, a SWNTs is metallic if $(n-m)/3$ is an integer, and otherwise semiconducting, according to band structure calculations.

The best description for the pristine tube shown in Figure 3a is given by the chiral indices $(9, 8)$, calculated using (1.15 ± 0.10) nm for the diameter and $(28 \pm 1)^\circ$ for the chiral angle. An $(9, 8)$ tube is expected to be semiconducting, as the ratio $(9-8)/3$ is not an integer. For the GeTe - filled nanotube shown in Figure 3b, a chiral index $(15, 5)$ is obtained based on a diameter of (1.4 ± 0.10) nm and a value $(14 \pm 1)^\circ$ for the chiral angle.

The electronic properties of carbon nanotubes have been shown to be sensitively dependent on their atomic structure and this is furthermore reflected by the tunneling spectra recorded simultaneously with the STM images using scanning tunnelling spectroscopy (STS). In STS experiments, the current is recorded as a function of the bias applied to the sample and the obtained normalised differential conductance, $(V/I) \cdot (dI/dV)$, is proportional to the electronic local density of states (LDOS) of the examined nanotube.

As indicated in Figure 4a, for the pristine nanotube, the normalised differential conductance contains sharp peaks, representing the theoretically predicted van Hove singularities (vHs), a clear signature of the LDOS spectra of a 1-D system.

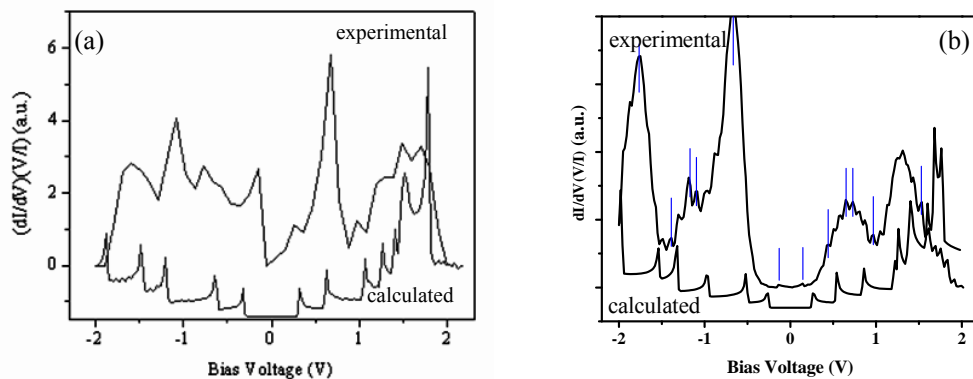


Figure 4 Experimental and calculated DOS for pristine (a) and GeTe-filled SWNT (b). Blue lines in (b) highlight the presence of van Hove singularities associated with the GeTe inner filling.

The calculated DOS for a tube having chiral indices (9, 8) is included in the graph in Figure 4a for comparison with the experimental DOS. Each peak in the experimental spectrum has a correspondent in the calculated one, furthermore substantiating the assignment of (9, 8) chiral indices based on the atomically resolved STM image.

For the GeTe-filled nanotube, a detailed analysis of the experimental tunnelling spectra reveals the peaks corresponding to the theoretically predicted van Hove singularities of a (15, 5) tube, but some extra peaks can be identified and they are indicated by the blue lines in Fig. 4 (b). A possible explanation for the existence of these extra peaks could be that they are due to the GeTe inner filling, which is also one-dimensional in nature, thus expected to display the van-Hove singularities in the electronic structure. Furthermore, a band gap of 0.3 eV for the GeTe inner filling could be assigned based on the first van Hove singularities at the onset of the valence and conduction band in the tunneling spectrum.

4. CONCLUSION

We report on the encapsulation of GeTe within the inner cores of SWNTs and show that continuous GeTe nanowires of uniform morphology are formed, in contrast to catalyst-assisted vapour-liquid-solid synthesis methods which result in various mixed morphologies (straight, helical, etc. nanowires). The catalyst-grown structures often contain other impurities and always exhibit an oxide layer on the surface of the nanowire, whereas encapsulation within carbon nanotubes offers a protective shell to prevent oxidation of the encased nanowire and maintain its chemical composition.

Photoemission spectroscopy shows no charge transfer between the encased nanowires and the nanotubes, suggesting that their electronic properties are not affected by each other's presence. Owing to the reduced dimensionality of the encapsulated nanostructure a lower melting point is expected compared to that of the bulk material (725 °C), therefore advantageous for the reduction in the programming energy required for phase switching. Scanning tunnelling microscopy and spectroscopy reveals the presence of van Hove singularities associated with the inner GeTe nanowire and gives information on the electronic features characteristic of the filling.

Due to the small integrated structure, GeTe-filled nanotubes open up interesting possibilities for high density and more compact data storage devices where the encasing nanotubes could act as the interconnects to provide the means for effectively controlling the encapsulated nanowires so as to store data and to access the stored data. For this to become reality, future work should assess whether the encapsulated nanowires possess all the required attributes of a phase-change non-volatile electric memory.

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Biographies

Cristina E. Giusca studied physics at the University of Bucharest, Romania where she received her BSc and MSc degree, after which she worked for two years as a research assistant in the National Institute for Physics of Materials, Romania. While there, the work focused mainly on structural and electronic properties investigations of C₆₀-polymer composites. She completed her PhD at the University of Surrey, U.K and the work leading to her doctoral thesis concentrated on probing the electronic structure of carbon – based materials using scanning probe microscopy tools. She is a research fellow at the Advanced Technology Institute (ATI), University of Surrey, UK since 2007. Current research work focuses on applying ultrahigh vacuum scanning tunnelling microscopy and photoelectron spectroscopy methods to explore the structural and electronic behaviour of various nanostructures for the development of practical devices.