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Tantalum-oxide catalysed chemical vapour deposition of single- and multi-walled carbon nanotubes

Bernhard C. Bayer[1,*], Carla Castellarin-Cudia[2,3], Raoul Blume[4],
Stephen A. Steiner III[5], Caterina Ducati[6], Daping Chu[1], Andrea Goldoni[3],
Axel Knop-Gericke[7], Robert Schlögl[7], Cinzia Cepek[2],
John Robertson[1], Stephan Hofmann[1]

[1]Department of Engineering, University of Cambridge, Cambridge, CB3 0FA, UK
[2]Istituto Officina dei Materiali-CNR, Laboratorio TASC, I-34149 Trieste, Italy
[3]Sincrotrone Trieste SCpA, I-34149 Trieste, Italy
[4]Helmholtz-Zentrum Berlin für Materialien und Energie, D-12489 Berlin, Germany
[5]Department of Aeronautics and Astronautics, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[6]Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, CB2 3QZ, UK
[7]Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin-Dahlem, Germany

[*] *Corresponding Author: bcb25@cam.ac.uk, Tel.: +44/(0)1223/748291, Fax: +44/(0)1223/748348*

Experimental Methods (full)

1. Sample preparation and atmospheric pressure nanotube growth

P-type doped Si(1 0 0) wafers covered with 200 nm thermally grown SiO_2 (Si/SiO_2(200 nm), Si-Mat, Germany) and n-doped Si(1 0 0) samples with ~2 nm native oxide (Si(1 0 0), Compart Technology, UK) were cleaved by hand to samples of approximately 5 mm x 5 mm.
Alumina (Al_2O_3) was deposited onto some Si/SiO_2(200 nm) samples in a rf-magnetron sputter deposition system (CCR, Germany) from a stoichiometric Al_2O_3 target (99.995%, PI-KEM, UK). Base pressure of the system was ~$5x10^{-6}$ mbar, the sputtering gas used was Ar (99.9995%, BOC GASES, UK) at 30 sccm (leading to ~$2.5x10^{-4}$ mbar during deposition), an applied power of 120W and an applied DC-bias of ~300 V. The thickness of the Al_2O_3 films was determined by spectroscopic ellipsometry (Woollam, USA) to (10±3) nm.
Tantalum (Ta) was sputter deposited onto Si/SiO_2(200 nm), Si/SiO_2(200 nm) Al_2O_3 10 nm and Si(1 0 0) samples as well as onto perforated SiO_x TEM membranes (200 µm window, 50 nm oxide thickness, SPI supplies, USA) in a custom built DC-magnetron sputtering system from a metallic Ta target (99.95%, PI-KEM, UK). The base pressure of the system was ~$8x10^{-6}$ mbar, the sputtering gas used was Ar (99.9995%, BOC GASES, UK) at 25 sccm (leading to ~$2x10^{-3}$ mbar during deposition), an applied power of 30W and an applied bias of ~300 V. Samples were then left to oxidise in ambient air for a minimum of 24 h.
Ta-oxide films of nominal thicknesses of 0.1 nm, 0.2 nm, 0.5 nm, 0.7 nm, 1.0 nm, 2.0 nm and 5.0 nm were thus prepared (measured by spectroscopic ellipsometry (Woollam, USA) with an estimated uncertainty in film thickness of ±30%).

Chemical Vapour Deposition (CVD) of Carbon Nanotubes (CNTs) was conducted at atmospheric pressure in a custom-built 2 inch diameter quartz tube furnace (i.e. hot-wall system, Carbolite, UK) after transferring the pre-prepared samples in air to the furnace. Prior to the growth of CNTs the process gases Ar (99.9995%, BOC GASES, UK), H_2 (99.9995%, BOC GASES, UK) and CH_4 (99.9995%, BOC GASES, UK) or C_2H_2 (99.6%, Air Products, UK) were flushed for several minutes at room temperature through the system. Then the system was heated to the desired temperature at 20ºC/min in an Ar flow of ~1000 sccm. In the CH_4 recipe, H_2 was then flushed for 10 min (200 sccm), followed by 15 min of 500 sccm CH_4 plus H_2 of 100 sccm. In the C_2H_2 recipe, after reaching growth temperature, Ar was flushed for 5 min (4000 sccm). Then H_2 (500 sccm) plus Ar (200 sccm) were introduced for 3 min pre-treatment, after which 10 sccm C_2H_2 were added for 30 min to the H_2/Ar mixture. After growth, the system was flushed with 4000 sccm Ar for 5 min, then the heater turned off and the system left to cool in an Ar flow of ~400 sccm. The system was re-opened and samples were taken out when the system had cooled down to ~30ºC. Temperatures tested included 650°C, 750°C, 850ºC, 900ºC and 950ºC. The system was cleaned by heating it in air to 950ºC after each run to remove carbon deposits in the tube.

The morphology of the samples was studied using a Scanning Electron Microscope (SEM, FEI Philips XL30 sFEG) in plan view with electron acceleration voltages of 1 to 5 kV. Transmission Electron Microscopy (TEM, Tecnai F20, 200 kV acceleration voltage) was employed for samples either directly grown on the perforated SiO_x TEM membranes or after scratching tubes from the wafers onto standard Cu TEM grids. Atomic Force Microscopy (AFM) measurements were done on a Veeco Dimension in tapping mode. Raman spectroscopy of nanotubes without transfer from substrates was done with a Renishaw Ramascope-1000 Raman spectrometer (633 nm).

2. X-ray photoelectron spectroscopy (XPS) details

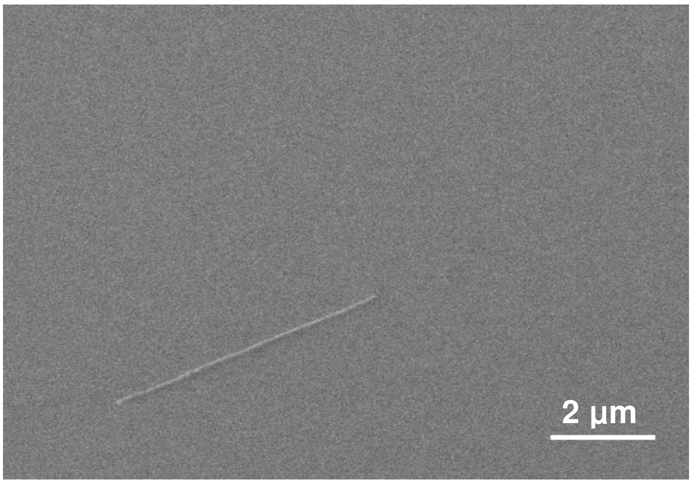
The *in-situ* and *ex-situ* XPS experiments shown in Figures 3 and 5, have been performed in normal emission geometry using a conventional Mg X-ray lab source (hν = 1253.6 eV) and a 120° spherical sector electron energy analyser, with an overall energy resolution of 1.2 eV (VG Escalab MKII). All the measurements and all sample treatments have been done in high vacuum condition at a base pressure of ~10^{-9} mbar (up to ~$2x10^{-8}$ mbar during sample annealing at 850°C). The photoelectron binding energy has been referenced by fixing the Si2p XPS binding energy (BE) at 99.6eV and the spectra have been normalized to the incident photon flux. The data was analysed by performing a non-linear mean square fit following the Levenberg-Marquardt algorithm. We have used a Shirley background, and we have reproduced the photoemission intensity by using Doniach-Sunjic.

The *in-situ* XPS experiments during H_2 and hydrocarbon exposure, shown in Figure 4, were performed at the ISISS beamline of the FHI/MPG located at the BESSY II synchrotron facility in Berlin, Germany. The high pressure XPS setup consists of a reaction cell attached to a set of differentially pumped electrostatic lenses and a differentially pumped analyzer (Phoibos 150, SPECS GmbH), as described elsewhere.[S1] The spectra were collected in normal emission in vacuum and gas with a probe size of ~ 100 µm x 1 mm. The samples were heated from the back using an external IR-laser (cw, 808 nm). The temperature was controlled via a K-type thermocouple in direct contact with the sample surface. Gases were introduced in the reaction cell using calibrated mass flow controllers (Bronkhorst).

Contamination was excluded by survey spectra of the samples at the beginning of each experiment. The Ta4f photoelectron spectra were taken at a photon energy of 330eV with a spectral resolution of 0.3 eV. The kinetic energy of the electrons correspond to an electron mean free path of ≈ 8 Å. The total XPS information depth is ≈ 2 nm, that is, 95% of all detected electrons originate from 3λ.[S2] For XPS analysis, the photoelectron binding energy (BE) is referenced to the Fermi edge, and the spectra are normalized to the incident photon flux. Background correction was performed by using a Shirley background.[S3] The spectra were fitted following the Levenberg-Marquardt algorithm to minimize the χ^2. Peak shapes were modeled by using asymmetric Doniach-Sunjic functions convoluted with Gaussian profiles.[S4] The accuracy of the fitted peak positions is ≈ 0.05 eV.

Note that due to the higher resolution and different charge correction methodology for the synchrotron-based XPS, the obtained binding energies between Figures 3 & 5 (lab-source-based XPS) and Figure 4 (synchrotron-based XPS) vary slightly.

CNT growth on Al_2O_3



Supplementary Figure 1: SEM image showing the typical sparse and short nanotube growth from Ta-oxide on Al_2O_3 supports (Ta-oxide 0.5 nm film on Al_2O_3, CH_4-based CVD at 950°C).

Supplementary References

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