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Wet-chemical catalyst deposition for scalable synthesis of vertical aligned carbon nanotubes on metal substrates

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ABSTRACT

A scalable process for carbon nanotube (CNT) growth on metallic substrates has been developed including dip-coating steps for the wet-chemical catalyst and co-catalyst layer deposition and a subsequent chemical vapor deposition step.

Organic metal salt/2-propanol solutions were applied as precursors for alumina co-catalyst thin films and the actual Fe (Co, Mo) catalyst layer. Vertical aligned carbon nanotube forests were obtained on catalyst-coated nickel foil in a thermal CVD process at atmospheric pressure and 730 °C using ethene as carbon source. The influence of the catalyst composition on growth rate, density and structure of resulting CNT films was investigated.

1. Introduction

The efficient synthesis of vertical aligned carbon nanotube (VA-CNT) films via CVD growth was discovered in 2004 by Hata et al. [1,2] and has been intensively studied since then. Most promising applications are field emission displays [3–5], lithium ion cells, optical polarizers [2,6], gas sensors [7], heat conductors and electrochemical double layer capacitors [2]. For the scalable production of such devices atmospheric pressure deposition techniques and direct synthesis on conductive substrates need to be developed.

For the CVD growth, substrates are typically covered by a buffer layer with the actual catalyst layer on top. Most frequently used are low pressure physical vapor techniques for the deposition of Al_2O_3 buffer layers and Fe thin films as catalyst [1,8–11]. An alternative route is the wet-chemical catalyst deposition using metal nitrates, chlorides and acetates in polar organic solvents like ethanol and methanol [12–16] deposited mostly for low-pressure CVD processes. Precursor solutions can be applied via dip-coating which is essential for the development of scalable processes. However, for the direct deposition on metal substrates, challenges like poor wetability and sufficient homogeneity need to be overcome.

In this Letter, wet chemical methods based on metal complex solutions were developed to deposit the buffer as well as the catalyst layer on nickel foils. The catalyst compositions were tested to achieve an optimum in the CNT APCVD process using ethene as precursor. Growth rates and resulting CNT properties were investigated.

2. Experimental

2.1. Aluminum-complex for Al_2O_3 deposition

The stable aluminum(2,4-pentadionate)$_x$(iso-propoxide)$_x$ Al(AcAc)$_x$(iPrO)$_3$ complex in 2-propanol is prepared by hydrolysis of aluminum isopropoxide (Al(iPrO)$_3$) (Merck) [17]. Al(iPrO)$_3$ is added to a 2 mol·l^{-1} solution of acetylacetone (AcAcH, VWR) in 2-propanol with a molar ratio of 0.5 according to AcAcH. The precursor solution is stirred for 2 h followed by water hydrolysis of the aluminum complex with a molar ratio of 0.85:1 H_2O:Al(iPrO)$_3$. Afterwards, the concentration of Al(iPrO)$_3$ is adjusted to 60 g·l^{-1} with 2-propanol and the resulting complex is agitated for further 3 h. Finally, concentrated nitric acid (65%, Acros) is slowly added to the solution forming a clear, slightly yellow aluminum complex. Before dip coating, 0.05 wt.% (regarding the aluminum complex) cetyltrimethylammonium bromide (CTAB, Acros Organics) as surfactant is added to enhance the substrate wet-ability.

2.2. Synthesis of carboxylate solutions

2.2.1. M^x(2-ethylhexanoate)$_x$-complexes

Fe(2-ethylhexanoate)$_3$ (Alfa Aesar, 50% in mineral spirits) and Co(2-ethyhexanoate)$_2$ (Sigma Aldrich, 65% in mineral spirits) are

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dissolved in 2-propanol (Berkel). For optimizing the Fe:Co ratio and the growth kinetics an entire catalyst concentration of 0.22 mol·l^{-1} in iPrOH/mineral spirit is used. For controlling the carbon nanotube diameter the concentration is varied starting with 0.022 mol·l^{-1} and ending with 0.22 mol·l^{-1}. Experiments with Mo addition are done with Mo(2-ethylhexanoate)$_4$ (Strem Chemicals).

For the deposition procedure on the metallic substrates rough nickel foil (R_a = 25 nm) (Alfa Aesar, 99% Ni) are cut into pieces of 3.5 × 3.5 cm^2 and primarily coated with Al_2O_3 and than with the respective Fe/Co/Mo combination.

2.2.2. M(Oleate)$_x$ synthesis

Different metal oleates are synthesized by a simple phase-transfer reaction similar to that described by Park et al. [18]. For the preparation of a 0.28 mol·l^{-1} metal oleate solution in toluene (VWR) 20 mmol of the correspondent metal salt are dissolved in a mixture of distilled water and ethanol. Following metal salts are applied: $FeCl_3·6H_2O$ (Grüssing), $Cr(NO_3)_3·9H_2O$ (Grüssing), $MnCl_2·2H_2O$ (Grüssing), $Ni(NO_3)_2·6H_2O$ (Sigma Aldrich) and $CoCl_2·6H_2O$ (ABCR). An appropriate amount of sodium oleate (>82%, Riedel de Haën) is suspended in toluene. The volume ratio between water, ethanol and toluene is 0.43:0.57:1. After combining the solutions the mixture is heated to 70 °C for 4 h under agitation. The resulting colored upper organic layer is washed three times with 15 ml distilled water using a separatory funnel.

2.3. Dip coat procedure

The substrates are coated using a dip coater type LTB 300 VA (Walter Lemmen). Before coating, the substrates are cleaned with ethanol and annealed at 300 °C. The aluminum oxide layer is deposited via 1.0 mm·s^{-1} lifting speed; the resulting film is annealed 5 min at room temperature and 5 min at 300 °C. Subsequently, the catalytic coating is obtained by moving the Al_2O_3 coated substrate out of the metal carboxylate solution with a speed of 2.0 mm·s^{-1} and a subsequent thermal treatment at room temperature (5 min) and 350 °C (5 min). A dip-coated layer with 0.22 mol/l catalyst concentration has a thickness of approximately 45 nm on 30–40 nm Al_2O_3.

2.4. CVD process

CNT growth by APCVD is performed with a quartz tube (40 mm diameter) positioned in a split tube furnace (HTM Reetz). The substrate is moved into the quartz tube and annealed (65 K/min) to the process temperature (730 °C). 1.0 slm (standard liter per minute) argon (5.0, Linde AG) as carrier gas, 0.17 slm ethene (3.5, Linde AG) as carbon precursor, 0.67 slm hydrogen (5.0, Linde AG) as in situ reductive for the oxidized catalyst layer are used for the CNT deposition. A small water amount (85 ppm) as soft oxidant for in situ emerging amorphous carbon plays an important role for the catalyst activity enhancement [1,19]. Water is transported in the entire gas flow by a stainless steel bubbler with argon as carrier gas.

The optimal water vapor concentration in the entire gas flow has been investigated by a laser diode spectrometer (Fraunhofer IWS) containing a laser with a small frequency band width in the near infra-red. For this investigation polished silicon with catalyst/buffer layer deposited by pulsed laser technique was used as an 'ideal' substrate. An optimum of 85 ppm water vapor could be observed resulting in the highest CNT film thicknesses.

20 min growth time is applied for the investigation of the optimal catalyst composition and the experiments regarding the different CNT diameters. CNT lengths are controlled by variation of the growth time from 5 to 40 min.

2.5. Characterization methods

The CNT morphology is characterized by a scanning electron microscope (SEM) (Zeiss type DSM 982 GEMINI) with a heat-able field emission tungsten cathode. All samples are tilted by 45° so that CNT lengths appear shortened in the SEM images. For the investigation of the CNT film homogeneity substrates with 2.6 cm maximum length could be analyzed by SEM due to the size limitation of the substrate holder.

For transmission electron microscopy (TEM) samples are crushed under ethanol and deposited Cu grids covered by carbon supporting films. TEM data are acquired with a MORGAGNI 268D TEM (100 kV; W filament, top-entry; line-resolution = 0.3 nm).

The CNT structure is investigated by a Raman spectrometer Renishaw type Renishaw 3000. The Ramanshift on each sample is measured three times at two different locations using laser beam wave lengths of 785 and 514 nm. The software GRAMS/32 Version 4.1 averages over three measured spectra.

Nitrogen adsorption is carried out with a surface area and pore size analyzer Quantachrome Quadrasorb SI. The specific surface area (SSA) is calculated by using the values between 0.05 and 0.1 p/p_0.

3. Results and discussion

The applied process chain includes the catalyst (oxidized iron, cobalt and molybdenum) and buffer (Al_2O_3) coating procedure and the subsequent CVD process by using ethene as carbon precursor.

3.1. Aluminum oxide films

An Al_2O_3 supporting layer is found to be crucial for the growth of at least 5 μm high VA-CNT via CVD. This layer acts both as co-catalyst for the hydrocarbon decomposition [20] and as diffusion barrier for the metal particles [11]. In this work, the aluminum oxide film is deposited by a sol–gel synthesis developed by Yang et al. [17] and a dip-coating process. The Al_2O_3 precursor is an aqueous/alcoholic alumina sol synthesized by hydrolysis of $Al(iPrO)_3$ with acetylacetonate (AcAc) as chelating agent to avoid the precipitation of aluminum hydroxide.

Figure 1 shows infrared transmission spectra of the as synthesized aluminum complex, $Al(iPrO)_3$ and aluminum triacetylacetonate $Al(AcAc)_3$. The spectrum of the synthesized complex represents peaks both of the spectrum of $Al(AcAc)_3$ and of $Al(iPrO)_3$. Nass et al. [21] reported a resulting mixed chelate complex using aluminum-sec-butoxide, 2-propanol and AcAcH as educts.

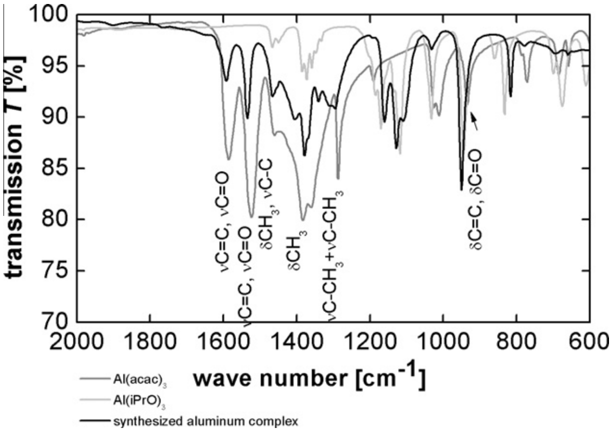

Figure 1. Infrared transmission spectra of the synthesized aluminum complex, Al $(AcAc)_3$ and $Al(iPrO)_3$.