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Research paper

Effects of catalyst configurations and process conditions on the formation of catalyst nanoparticles and growth of single-walled carbon nanotubes

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ABSTRACT

The synthesis of well-aligned and type-enriched semiconducting single-walled carbon nanotubes (sc-SWCNTs) with high quality by means of catalytic chemical vapour deposition (CCVD) on wafer-level are essential prerequisites for the implementation of nanodevices for sensor and electronic applications. In particular, the Co-Mo bilayer catalyst system is promising due to its ability to grow semiconducting enriched SWCNTs by CCVD. However, there is still a gap in understanding how to adjust catalyst properties aiming further improvements in SWCNTs film composition and morphology. In particular, surface morphological evolution during catalyst conditioning as well as its impact on SWCNT growth are not clearly understood. Here we present a systematic investigation on effects of catalyst support layer, catalyst preparation conditions, catalyst type and composition as well as gas composition for catalyst treatments on the size of catalyst nanoparticles (NPs) and the properties of CCVD grown SWCNTs. We show that H_2 treatment favors the formation of small catalyst NPs with narrow size distribution in the case of Al_2O_3 support layer. Moreover, we correlate the growth rates, quality of SWCNTs structures and sc-SWCNTs content with the Co-Mo catalyst morphological evolution.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) represent a class of one dimensional nanoscale materials that consist of carbon atoms forming a tube like structure [1]. Due to their unique structure and bonding conditions, they show remarkable mechanical, electrical and thermal properties making them attractive in different application areas ranging from electronics to medicine [2–4]. To exploit the unique intrinsic properties of SWCNTs in wafer-based electronic and sensor applications, the integration technology should fulfill the following essential prerequisites: well-aligned dense SWCNT arrays with controlled orientation, type-enriched semiconducting or metallic SWCNTs, high quality SWCNTs as well as compatibility with typical wafer-level device fabrication processes [5–10]. From the zoo of different integration methods, catalytic chemical vapour deposition (CCVD) is considered as a promising method for SWCNT growth directly on the substrate in particular from the vantage point of low cost and scalability to wafer level. In addition, the CCVD process is attractive because of its ability to tune both the catalysts and operating conditions to develop a process that offers high SWCNTs yield, quality and electronic type selectivity [11]. Nevertheless, CCVD grown SWCNTs are not yet pure and selective enough for direct use in devices due to contaminations like multi-walled CNTs, amorphous carbon and metallic SWCNTs that strongly affect device performance. These challenges are addressed by optimization of CCVD process with respect to the catalyst (type, size and composition) and CCVD process parameters (temperature, process time, pressure, gas compositions and carbon source) [12,13]. As a result, extensive research work has been done to develop a controlled synthesis of SWCNTs. Although a large number of works reported in the field of controlled growth of SWCNTs by CCVD, the effect of catalyst and synthesis parameters on the resulting grown SWCNTs are not fully understood yet [14,15]. It is accepted that controlling the catalyst nanoparticle properties is the most straightforward approach to influence the characteristics of resulting CCVD grown SWCNTs. For instance, size of catalyst nanoparticles directly correlates with SWCNT diameters [16]. Equally, appropriate catalyst composition is one of the crucial parameters for SWCNT growth [17]. Apart from monometallic transition metal catalysts (i.e., Fe, Ni, and Co), multicomponent catalysts have been considered useful for CCVD synthesis of SWCNTs. Different studies in the past decade have reported about the potential of bimetallic or trimetallic catalysts towards chirality selection, diameter control and quality enhancement of grown SWCNTs [18–22]. As an example, Molybdenum (Mo) added to Cobalt (Co) or Iron (Fe) bimetallic catalyst system has been attracting attention for CCVD growth of SWCNTs due to its high growth efficiency of SWCNTs and their potential towards electronic type-enrichment of

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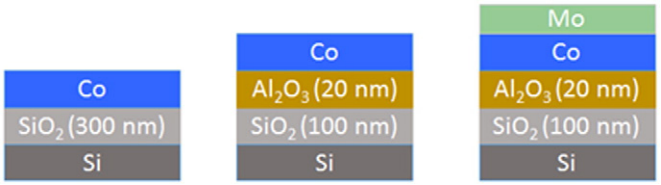

Fig. 1. Schematic of different sample configurations.

grown SWCNTs. It is assumed that pure Mo does not participate in the CNT nucleation as it converts to Mo carbide (Mo_2C) during the CCVD process. Nevertheless, Mo added as a co-catalyst to Co can enhance the catalyst-assisted reactions of feedstock gases by forming alloy catalysts with Co [23]. On the other hand, in order to synthesize vertically aligned SWCNTs on a Si substrate using CCVD, a support layer is required between the substrate and catalyst layer due to its important role in preventing silicide formation and retarding surface diffusion of catalytic nanoparticles (NPs). Among different suitable support layers [24], Al_2O_3 has been widely used because of its ability to promote CNT growth. Although the size of catalyst NPs can be controlled by adjusting deposition thickness of the catalyst layer and annealing temperature, Al_2O_3 support layer with suitable thickness and surface morphology is especially effective in hindering the agglomeration of catalyst NPs formed on the Al_2O_3 layer. This enables the formation of small size NPs with high density that is essential for growth of small diameter SWCNTs with vertical alignment [25–29].

Here, we present an extended study on the effect of main factors such as gas composition, support layer and catalyst configurations on the NP formation as well as CCVD grown SWCNTs. The sample configurations as well as catalyst preparation conditions were correlated with the height, quality as well as SWCNT type composition of CCVD grown vertically aligned SWCNTs by applying different characterization methods such as atomic force microscopy (AFM), scanning electron microscopy (SEM) and Raman spectroscopy.

2. Experimental

For direct growth of SWCNTs on substrates by the CCVD method, preparation of catalyst nanoparticles is a crucial step. In order to investigate the effect of support layers as well as different catalyst configurations on the formation of the catalyst NP and SWCNT growth, three sets of substrates were prepared as schematically shown in Fig. 1:

SiO_2-Co: On Si (100) wafers with 300 nm thermally grown SiO_2 layer, two different cobalt (Co) catalyst layer thicknesses (0.5 nm, 1 nm) were deposited by means of physical vapour deposition (PVD). These samples served as a reference for NP and CCVD studies.

Al_2O_3-Co: In order to investigate the effect of Al_2O_3 support layer on the NP formation and CCVD growth of SWCNTs, a second set of samples was prepared having an additional sputtered 20 nm thick Al_2O_3 interface layer between SiO_2 and the catalyst. For studying the effect of different Co layer thicknesses, samples with 0.5 nm, 1 nm and 0.7 nm Co were prepared.

Al_2O_3-Co-Mo: Finally, different bilayer of Co-Mo catalyst thicknesses were investigated for the CCVD growth of SWCNTs. Co-Mo bilayer catalysts were prepared by ion beam sputtering deposition (IBSD) having various thickness. Thereby, first Co layer and then Mo layer were deposited on 20 nm thick Al_2O_3 using two different deposition rates.

Growth of SWCNTs was performed in a vertical cold-wall CCVD reactor with a showerhead gas distribution system (Fig. 2-a) for homogenous coating of wafer substrates. Briefly, substrates with catalyst loaded into the CVD chamber and the chamber was heated to the target temperature (840 °C) with a ramp rate of 20 °C/min in presence of H_2 and/or N_2 at 20 kPa chamber pressure. Then the substrate was kept at target temperature for 5 min. This procedure referred as catalyst pretreatment, intends to reduce oxidized catalyst and convert the catalyst layer into nanoparticles. After studying the effect of gas environment on catalyst NP formation, the pure H_2 environment with 100 sccm flow rate was selected to proceed with growth studies. Thus, after the NP formation, SWCNTs growth was initiated by adding C_2H_4 (purity > 99.9995%) to the H_2 gas flow (70 sccm) into the chamber with a certain flow rate that was always fixed for duration of 10 min. After 10 min growth time, the C_2H_4 supply was terminated and the chamber was cooled down to room temperature under H_2 and N_2 atmosphere. Four main process steps for CCVD growth of SWCNTs as well as the corresponding parameters in each step are summarized in Fig. 2-b.

The morphological evolution of the substrate and metal surface as well as the resulting catalyst nanoparticle size were characterized ex-situ by use of atomic force microscopy (Agilent AFM) in tapping mode having a super sharp AFM tip with a tip radius of curvature <2 nm (Nanosensors TM, SSSNCHR). As-grown SWCNTs were characterized ex-situ by using Raman spectroscopy (Renishaw) with five different wavelengths (488 nm, 514 nm, 532 nm, 633 nm and 785 nm) and 12 points measurement where all spectra were averaged finally to a single spectrum for each sample. Equally, the height and morphology of as-

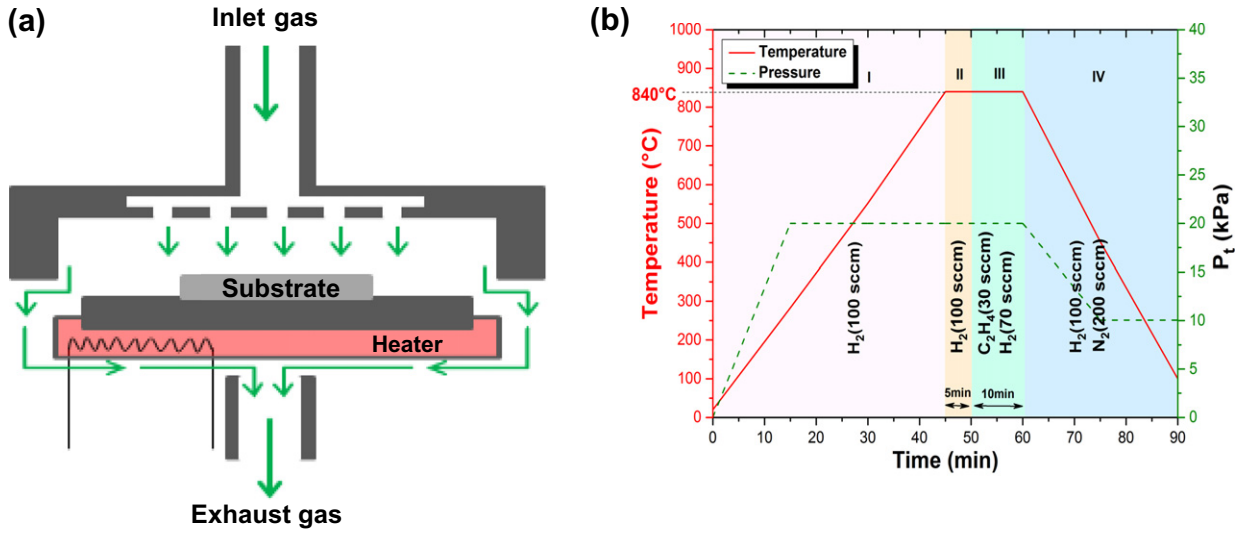

Fig. 2. Schematic of CCVD set-up (a) and exemplary CCVD process sequence for growth of SWCNTs (b).