Local growth of vertical aligned carbon nanotubes by laser-induced surface modification of coated silicon substrates

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Abstract. The stimulation of carbon nanotubes (CNT) growth in a thermal CVD process using an acetylene/nitrogen gas mixture by KrF-excimer laser exposure of iron nitrate coated silicon is described. At moderate laser fluences of ~1 J/cm² the growth of nanotube bundles up to 100 μm consisting of vertical aligned multi-walled carbon nanotubes (VA-MWCNT) is observed. AFM measurements show the formation of nanoparticles in the laser-exposed areas. At these catalytic sites the nanotubes grow and sustain one another and forming the well-defined bundles. Via the laser exposure the control of the catalytic sites formation and consequently the nanotube growth and properties can be achieved.

1. Introduction

During the last years nanostructured material and surfaces have attracted a lot of scientific and industrial interest due to the extraordinary properties of the material and the new applications that can be achieved. Since the discovery of carbon nanotubes (CNT) in 1991 [1] much work was done to study their growth from DC discharge, pulsed laser ablation, and thermal or plasma assisted vapor deposition processes using specific deposition conditions to obtain defined physical properties, e.g., single-walled or multi-walled carbon nanotubes (SWCNT, MWCNT) [2]. Especially the selective positioning and the growth of aligned carbon nanotubes is essential for some applications, e.g., as field emitters in vacuum microelectronic or flat panel devices [3], as electrode materials for electrochemical sensors [4], or for C-MEMS to realize the connection of the nanostructures with mesoscopic interconnection structures that currently are used in micron technologies.

To achieve the local deposition of CNTs regularly the catalytic surface that consists usually of active particles is patterned by means of photolithography, micro contact printing, or masked metal deposition [3, 5, 6]. For instance, the growth of well-aligned CNTs with a height of ~10 μm using photolithographic patterning of metallic films (Fe) deposited by PLD onto silicon substrates has been demonstrated [3]. The length and the size of nanotubes can be influenced by the properties, e.g., the size and the composition, of the catalytic particles used for the growth [7, 8]. Consequently, the control of the nanoparticle (NP) properties allows the manipulation of the nanotube (NT) growth. The limitation of the growth length is associated with the gas phase decomposition dynamics and the catalyst poisoning [9]. The NT length can be reduced by laser ablation to write 2D and 3D microstructures into already deposited vertically aligned (VA) CNTs [10].

The growth of aligned nanotubes was observed after laser ablation of thin metallic films [11]. Here the cobalt nanoparticles are formed by melting of the film or by the re-deposition of the ablated metal. However, the nanotube bundles that are aligned parallel to the surface do not feature a defined border due to the random distribution of the re-deposited debris. Pulsed laser deposition (PLD) is regularly
used for the deposition of thin films but often accompanied by droplets or particulates that have been exploited for the growth of nanotubes. Recently the local growth of vertically aligned multi-walled carbon nanotubes (VA-MWCNT) has been demonstrated by means of CVD with an acetylene/nitrogen gas mixture using a structured Fe catalytic film [12].

The formation and the properties of the catalytic (metal) particles are very important in CNT growth. This catalytic sites influence the properties of the nanotubes to a great extend. Here the local surface modification of substrates by means of laser exposure of a thin catalyst compound film is proposed and demonstrated.

2. Experimental

Silicon (100) substrates were cleaned and subsequently treated with an oxygen plasma (30 s) to remove surface contaminations. Afterwards iron (III) nitride-ethanol-solutions of different molarities (0.07, 0.14, 0.28, 0.5 M [mol/l]) were spun on to achieve thin iron(III)nitride (Fe(NO₃)₃) films. Interference microscope and AFM measurements reveal the homogeneous covering of the surface with the film. Excimer laser radiation (λ = 248 nm, 30 ns, 10 Hz) was used to expose the iron nitrate coated substrates in air using an x15 Schwarzschild-objective to project a square aperture with a size of 70 x 70 and 100 x 100 μm² onto the substrate surface, respectively. After the laser irradiation the growth of the carbon nanotubes was performed in a normal pressure CVD tube reactor providing a temperature up to 1100 °C and using a gas mixture of 15 sccm acetylene and 1500 sccm nitrogen. The growth temperature that was measured in situ with a thermocouple near the sample was varied between 700 to 800 °C. The samples were moved into the hot zone of the reactor for 3 to 7 min and removed after grow by means of a manipulator. Afterwards the samples were allowed to cool down in a pure nitrogen stream into the reactor. The laser modified as well as the overgrowth samples were investigated by optical microscopy, SEM, AFM, and micro-Raman spectroscopy.

3. Results

Figure 1. SEM pictures of nanotube bundles grown locally at the laser modified sites. (a) Array of CNT bundles grown at different laser fluences (0.4 to 2 J/cm² from right to left) as well as the pulse numbers (1 to 10 from bottom to top). The arrows refer to the view direction of the enlarged pictures. (b) Single CNT bundle (exposure: 1.1 J/cm², 5 pulses) and enlarged view of the bundle sidewall.

Figure 1a shows an array of CNT bundles grown onto laser-exposed areas of an iron nitrate coated silicon substrate. The CNT bundles grow preferentially perpendicular to the surface only at specific laser exposure conditions. The base area of the bundles corresponds with the size of the used projection mask. Hence, laser irradiation causes specific surface modification to stimulate the local growth of the CNTs. To study the influence of the processing conditions the laser fluence as well as the pulse number have been varied in the range of 0.2 to 2.5 J/cm² and 1 to 25 pulses, respectively. As figure 1 documents the laser fluence is more important to achieve local CNT-growth than the pulse number. Applying medium laser fluences (0.8 to 1.4 J/cm²) a reproducible substrate modification for local CNT growth is achieved. At low laser fluences no alterations in the growth to non-exposed areas
of the substrate are observable, i.e., the laser-induced surface modification is not sufficient for stimulating the growth of CNTs. At high laser fluences (>1.5 J/cm²) also no growth of nanotubes is observed within the laser-irradiated areas probably due to laser ablation but in an annular region outside the mask area the growth is activated. The height of the grown CNT bundles is not proportional to the laser exposure parameters; the CNTs grow as soon as the threshold laser fluence is reached. After exceeding the laser threshold the height of the CNT bundles changes less with laser fluence, pulse number, and growth time. Hence, once a sufficient surface modification is achieved the growth is less but significant influenced by the applied laser processing conditions.

The decomposition temperature of iron nitrate of about 125 °C is reached at laser fluences of less than 0.1 J/cm² but these fluences are not sufficient to modify the film/surface for the enhanced CNT growth. Consequently not only the decomposition of the nitrate is necessary but also the formation of active nanoparticles must be achieved. Laser fluences of more than 0.3 J/cm² meet the requirements of particles formation at the surface. As figure 1a shows at sufficient high laser fluences the modification for CNT growth is completed already with one laser pulse. Consequently, within the first pulse the thin iron nitride film is converted into particles of an iron oxide modification with melting points of 1370 °C and 1565 °C for FeO and Fe₂O₃, respectively, that cannot be removed during the consecutively laser pulses. The single CNT bundle and the enlarged section of the bundle sidewall shown in figure 1b reveals the square cross section according to the used mask size, the sharp edges of the bundle, and the aligned structure of the nanotubes. The individual nanotubes have a certain chirality and touch and probably stick together due to van der Waals forces between adjacent MWCNTs [13]. Hence, the individual nanotubes supporting each other are forming a CNT network that stabilizes the long nanotubes of the CNT bundles and allows the growth of bundles with a height up to 100 μm.

**Figure 2.** a) AFM picture of laser modified iron nitrate surface (1 x 1 μm²; zmax = 15 nm) at a laser fluence of 1.1 J/cm². b) Raman spectrum of VA-MWCNTs taken at the side-wall of a bundle. The G-band peak is fitted with peaks centred at 1582 cm⁻¹ and 1627 cm⁻¹.

Since at the same growth conditions in the not exposed areas only isolated CNT growth occurs laser irradiation forces the formation of highly active iron particles stimulating the growth of CNTs. The initially smooth surface of the iron nitride covered silicon substrate is converted to a rough surface at the same laser exposure conditions that enhance the CNT growth as REM and AFM investigations show. The AFM picture depicted in figure 2a shows dense particles formed into the laser exposed area that have nearly the same height and diameter (2 nm and 25 nm), respectively. The high temperatures during laser irradiation that are higher than the growth temperatures can be the reason for the enhanced catalytic site formation. After exceeding the threshold fluence below that no alterations were observed the size and the height of the particles increase with increasing the laser fluence and the pulse number as a result of the higher temperatures at laser impact. At laser fluences of more than 1.5 J/cm² the laser induced transient temperatures cause phase transitions and ablation of the substrates (Si: T_melt = 1685 K). Thus the iron modifications - either film or particles - are removed in any case by substrate
etching and no CNT growth at the exposed areas is enabled. The annulus-like areas, shown in the inset of figure 1a, around the exposed square sites of modified and overgrown substrates ascertained in the SEM are caused probably by the laser ablation process that results in thermal modification of the surrounding areas, the formation of a laser-induced plasma that modifies the film, and debris deposition. Both can account for the enhanced CNT growth around the exposed areas that are ablated but the thermal or particle bombardment induced modification by the laser plasma is more probable.

The Raman spectrum depicted in figure 2b was taken from the side-wall of a grown CNT bundle showing the typical peak structure of MWCNTs with the main peaks centred around 1350 and 1580 cm\(^{-1}\) known from graphite modifications as D- and G-band that are identified for disorder-induced and the graphite-like structure of carbon, respectively. However, the G-band shows substructures that are intrinsic peaks for the MWCNTs (1355, 1576, 1584, and 1624 cm\(^{-1}\) [14]) can attributed to different kinds of CNT (diameters and chiralities) or defects of MWCNT [15].

4. Conclusion
The local growth of well-defined MWCNT bundles perpendicular to the surface at laser modified substrate sites is demonstrated. The well-defined, sharp edges and steep side-walls are characteristics of the grown nanotube bundles that are caused by the interdigitated nanotubes grown simultaneously. The stimulation of the growth compared to the unexposed areas and the increasing height of the nanotube bundles prove the stimulating effect of laser exposure that leads to the formation of nanometer sized particles known for their catalytic effect to the CNT growth. Hence, an additional parameter allows both the optimisation of the VA-MWNT growth and the growth of different high nanotube bundles at the same nanotube growth conditions.

5. Acknowledgements
The authors are grateful to D. Baumann and E. Salamatin for the help in the experimental work, D. Hirsch for his skilled AFM investigations and U. Täschner (University Leipzig) for the Raman measurements. This work was financially supported in parts by the European Union and the Sächsische Aufbaubank under the contract 6698/1041.

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