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Sacco, Leandro Nicolas; van Ginkel, Hendrik Joost ; Vollebregt, Sten

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Synthesis of Carbon nanofibers (CNFs) by PECVD using Ni catalyst printed by spark ablation

Leandro Nicolas Sacco
*Department of
Microelectronics,
Delft University of Technology*
2628 CD, Delft, The
Netherlands
l.n.sacco@tudelft.nl

Hendrik Joost van Ginkel
*Department of
Microelectronics,
Delft University of Technology*
2628 CD, Delft, The
Netherlands
h.j.vanGinkel@tudelft.nl

Sten Vollebregt
*Department of
Microelectronics,
Delft University of Technology*
2628 CD, Delft, The
Netherlands
s.vollebregt@tudelft.nl

Abstract—The precise control of patterned arrays of carbon nanofibers (CNFs) is an issue of interest in a wide range of applications. In the present work, we report the synthesis of CNFs grown by plasma-enhanced CVD (PECVD) from a Ni catalyst patterned *via* aerosol printing of nanoparticles (NPs) by a spark ablation technique. The printing speeds were adjusted to vary the catalyst density and characterize the CNFs distribution in the pre-patterned lines. Depending on the printing speed, different CNFs distributions are obtained, ranging from dense vertically-aligned CNFs (VACNFs) to sparse individual CNFs.

Keywords—Carbon nanofibers, printing catalyst, spark ablation, vertically-aligned CNFs.

I. INTRODUCTION

The accurate area-selective control of carbon-based nano-objects, such as carbon nanotubes (CNTs) and CNFs, is vital for the development of many applications, like sensors and electrodes [1]. Typically, chemical vapor deposition (CVD) techniques and their derivatives, Hot-Filament CVD, microwave CVD, and PE-CVD [2], are the most implemented methods for CNTs/CNFs production. These methodologies are straightforward, easy to scale up and have relatively low-cost setups. In terms of CNTs quality, the CVD technique can produce large yields with high crystallinity [3].

In the catalyst-supported CVD techniques, typically, the catalyst is deposited onto a substrate. Many strategies were deployed to deposit the catalyst on the substrate [4]–[8]. The most predominant approach relies on a thin film deposition followed by a heat treatment step to obtain a nanostructured catalyst [7]. To pattern the catalyst, typically photolithography and e-beam lithography are adopted. Both approaches are characterized by high reproducibility and precision. But expensive techniques are involved in these production processes [9]. Focus Ion beams (FIB) technique was also used to pattern a Ni catalytic thin film. High precision can be achieved through this methodology. However, it is a local

technique, and radiation defects and partial doping of the catalyst by ions of the source can be induced [10].

Alternatively, different processes have been developed to circumvent the complex and/or time-consuming catalyst patterning [11], yet, many efforts are still required regarding the optimization of the patterning parameters. For instance, micro-contact printing allows a simple one-step approach to pattern catalyst lines with high homogeneity [12], but the patterned stamps are obtained by lithography. Controllable patterning also has been achieved by dip-pen nanolithography (DPN) [13], in this case, the tip of an atomic force microscope (AFM) is dipped in catalyst NPs suspended in a liquid that acts as ink. This is a mask-free technique and allows control of the patterning through an intended software, reflecting the flexibility of this approach. Besides, the throughput of DPN can be substantially increased using specially fabricated arrays of cantilevers [14]. However, there are still some critical issues to overcome, mainly related to reproducibility [13]. Direct printing of the catalysts using ink-jet printing (IJP) has attracted much attention to grow pre-defined patterns of CNFs on a variety of substrates. The IJP is a flexible technique because the ink can be simply patterned on a variety of substrates. Furthermore, the catalyst ink can be adjusted to grow high-quality vertically aligned arrays of single- and few-walled CNTs [11] or multi-walled CNTs [15]. Though some problems were detected during the droplet formation that can lead to non-uniform catalyst printing [15] because the shape of the precursor droplets on substrates can have a huge influence on the synthesized carbon nanostructures [16].

Herein, we present a new approach to pattern Ni catalyst onto a SiO₂/Si substrate using a spark ablation NP generator (VSParticle G1) coupled with an aerosol impaction printer equipped with an x-y-z stage developed by VSParticle B.V. The system allows having a spatial resolution in the range of a few tens of microns. By adjusting the distance between the nozzle and the printing speed, different catalyst densities can be obtained. In the present work, 6 different print speeds were considered to subsequently grow CNFs by a PECVD method. The variation in the catalyst density has a large impact on the

CNFs growth [17]. Then, depending on the Ni NP density different CNFs distribution types were detected, ranging from VA-CNFs up to low dense sparse CNFs.

The introduced methodology can be defined as chemical-free since the entire process is free from any chemical contamination of a wet-type solution approach. Furthermore, can be considered as a flexible, and relatively straightforward approach to pattern catalyst for the growth of CNFs, which can serve as a first building block in many applications.

II. EXPERIMENTAL SECTION

A. Catalyst printing

A spark ablation generator (G1, VSParticle B.V.) was used to generate a Ni nanoparticle aerosol from 99.99% Ni electrodes. The electrodes were placed opposite from each other and a repeating spark was generated in the gap between them at 1 kV and limited to 6 mA. The ablated material is carried away using 1.5 l/min. N₂ gas (99.999% purity, 1 bar) towards an impaction printer (Proto 0, VSParticle B.V.) operated at 0.48 mbar. The pressure difference over a 0.1 l/min. nozzle accelerates the gas to supersonic speeds towards the sample placed 1 mm below the nozzle exit [18]. The inertia of the nanoparticles impacts them on the substrate. The residual gas flow was diverted to the exhaust.

The nickel catalyst was printed in lines of 12 mm long using XY-motion of the nozzle. To achieve variation in NP surface coverage and film thickness, the printing speed was varied at 1, 5, 10, 25, 50, and 100 mm/min.

B. CNFs growth

The CNFs were grown by PECVD, using the nickel catalyst deposited on a 300 nm thick thermally oxidized silicon wafer. The samples were loaded in an AIXTRON BlackMagic Pro reactor with a cold wall heating system configuration. During the heating stage, the pressure was set to 9 mbar, with 700 sccm of H₂ flow, and the temperature is ramped up to 650 °C. Next, 20 sccm acetylene (C₂H₂) was used as a carbon feedstock for the CNFs synthesis.

Regarding the plasma parameters, a 100 W power pulsed-DC plasma was used. The electric discharge was kept for 15 minutes, then, the sample was cool down inside the reactor in a N₂ atmosphere.

C. Material characterization

The topography of the Ni catalyst was inspected with a NT-MDT NTEGRA AURA (NT-MDT, Moscow, Russia) atomic force microscope (AFM). The measurements were performed in semi-contact mode at a rate of 0.60 Hz with a scanning area of 25 μm², acquiring 256 lines per map. The R_a value was calculated from the AFM images. The used tips were PointProbe® Plus (PPP) (purchased at Nanosensors) with a tip radius of curvature < 10 nm. A Scanning Electronic Microscope (SEM) Hitachi Regulus 8230 was also used to inspect the Ni NP structure and the grown CNFs. The CNFs density was extracted using the open-source “ImageJ” software [19], as described in a previous report [20]. Raman spectroscopy was carried out to accessing the quality of the synthesized carbon nanostructures. Raman measurements were performed with a Renishaw inVia Reflex spectrometer coupled with a 532-nm laser source and a 50× objective. All the characterization techniques were performed close to the centre zone of the printed lines. At least three scans or Raman spectra were taken in each sample.

III. RESULTS AND DISCUSSIONS

The present work aims to establish if the catalyst printing by the spark ablation technique meets the criteria to grow CNFs by a PECVD method. The Ni NP catalyst density was varied by adjusting the printing speeds. The dependence between the Ni coverage on the substrate and the CNFs growth was studied. Fig. 1. summarizes the Ni catalyst distribution printed at different speeds. For each printing speed, both the R_a value was calculated from the AFM images, and the level of Ni catalyst coverage was extracted from the SEM micrographs. The R_a value also decreases as the Ni NPs become sparser. The studied printing speeds enable us to vary the NP distribution, from full coverage of Ni catalyst NPs up to approximately 10 Ni

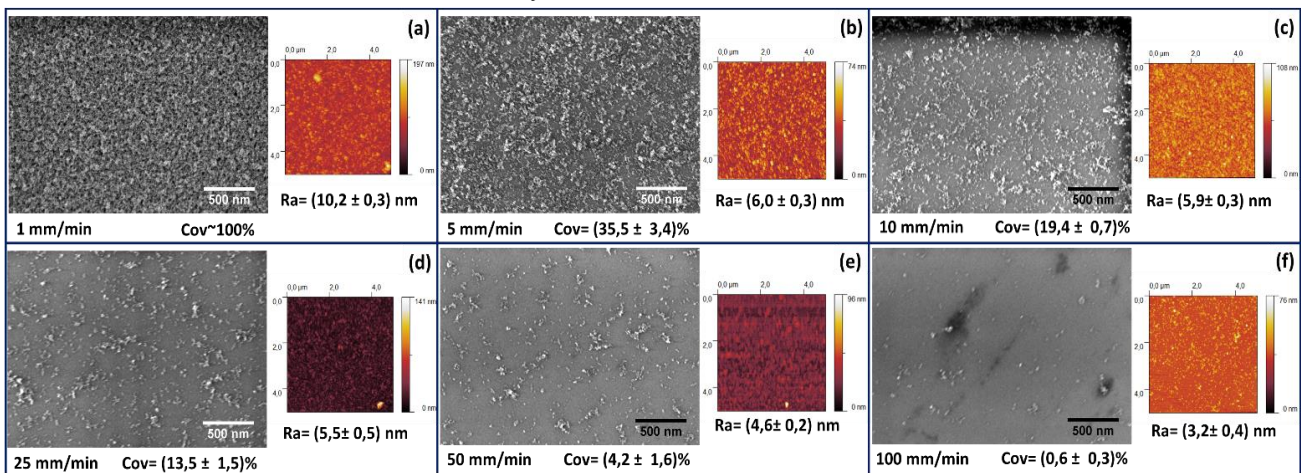


Fig. 1. Fig. 1. SEM and AFM images of Ni catalyst printed by spark ablation technique at different print speeds: (a) 1 mm/min, (b) 5 mm/min, (c) 10 mm/min, (d) 25 mm/min, (e) 50 mm/min and (f) 100 mm/min. For each print speed the Ni catalyst coverage (Cov) and the Ra values are indicated.

NPs per μm^2 . As expected, for the highest printing speed the lowest catalyst density is obtained.

Fig. 2. shows the dependence between the printing speed and the level of coverage. Interestingly, two regimes are detected depending on the printing speeds. The rate of coverage sharply decreases for print speeds ranging from 1 mm/min up to 10 mm/min, resulting in an approximately 80% reduction of the surface coverage by the Ni catalyst. Instead, in the range from 25 mm/min up to 100 mm/min, the level of coverage monotonically decreases from 13% down to approximately 0.5%.

The synthesis of CNFs was performed on the 6 different printed lines with their associated Ni catalyst distribution. Fig. 3 shows the SEM top-view images of the CNFs distribution. For the fully covered line with Ni catalyst, the CNFs have grown vertically aligned perpendicular to the substrate, as indicated by Fig. 3.a. This result is expected since during the PECVD process the electric field aligns the nanotubes during growth [21]. Furthermore, the presence of the Ni catalyst at the top surface of the VA-CNFs surface clearly indicates that a tip-growth mode took place during the nanofiber formation. In Fig 3.b, where the Ni catalyst coverage is approximately 35%, just some of the CNFs were grown keeping the preferential direction imposed by the electric field. As the Ni catalyst coverage decreases, the CNFs alignment is completely lost as shown by Fig. 3.c-f. This phenomenon was previously reported in a work carried out in our group but then was caused by a change in C_2H_2 feedstock [22]. In this case, the alignment was affected by the carbon feedstock supply at fixed catalyst thickness. The bending of the CNFs grown by PECVD can be explained by fluctuations in the carbon precipitation step that may lead to non-uniform stresses at the NP/CNF interface [22].

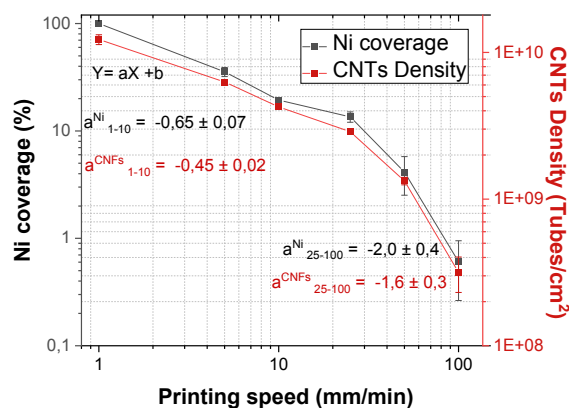


Fig. 2. Log-Log graph of the Ni catalyst coverage (left y-axis) and CNFs density (right y-axis) as a function of the printing speed. From linear fits, the slope of the Ni coverage as a function of printing speeds in both ranges 1-10 mm/min and 25-100 mm/min were calculated, a_{Ni}^{1-10} and a_{Ni}^{25-100} respectively. Identically, the slope of the CNF density as a function of printing speeds in both ranges were calculated, a_{CNFS}^{1-10} and a_{CNFS}^{25-100} .

In Fig. 2. the same trend regarding the Ni catalyst coverage and the density of CNFs is observed, indicating

that as the printing speed increases, also the amount of CNTs decreases. The slopes in a log-log scale were calculate in both ranges of printing speeds (1-10 mm/min and 25-100 mm-min). In the range of slower printing speeds, there is a difference of 30% between the slope values for the Ni coverage and the CNFs density, but, for printing speeds higher than 25 mm/min, the slope values overlap within the standard error. This can be attributed to the fact that for high catalyst coverage, the Ni NPs are clustered, but, for low levels of Ni catalyst, the NPs are more sparse, and can be considered that there are deposited as individual Ni NPs. Then, this result suggests that depending on the catalyst distribution, a different fraction of Ni NPs are catalytically active for the CNF synthesis.

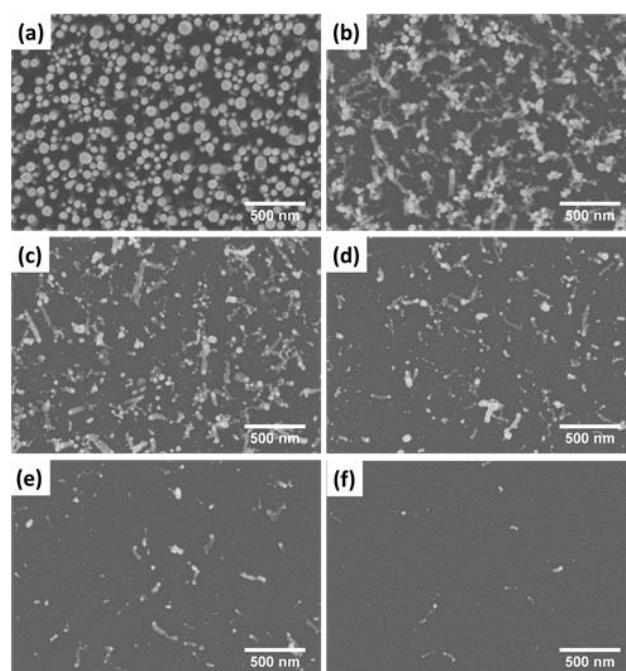


Fig. 3. SEM images of the CNFs grown on the Ni catalyst printed with 6 different print speeds: (a) 1 mm/min, (b) 5 mm/min, (c) 10 mm/min, (d) 25 mm/min, (e) 50 mm/min and (f) 100 mm/min.

Raman spectroscopy was performed on the synthesized CNFs grown with different Ni catalyst densities. Fig. 4 shows the Raman spectrum of the carbon nanostructures. The D-peak located at $\sim 1350 \text{ cm}^{-1}$ is sensitive to the defects in the hexagonal graphite structure, while the G-peak at $\sim 1570 \text{ cm}^{-1}$ arises due to the tangential stretching mode of the graphite plane. The 2D-peak is an overtone of the D-band and it is characteristic of graphitic structures. Only, the sample with VA-CNFs displays the three characteristic peaks of CNFs. The D/G ratio intensity for this sample is higher than 1 reflecting the high amounts of defects on the crystal lattice, which is common for plasma-grown CNF. As the printing speed increase, the 2D peak seems to be masked with a background signal. This can be attributed to an excess of carbon feedstock during the PECVD that is nucleated at the substrate leading to the formation of an amorphous carbon layer. Also, it is necessary to consider that if CNFs sidewalls are more exposed to the electric field during the PECVD process, i.e. the field lines are not parallel to the

sidewalls, more damage on the CNFs walls is expected due to the possible bombardment by radicals, dramatically affecting the CNFs quality and quantity. To complete the characterization, further TEM observations are required to fully define the type of synthesized carbon nanostructure.

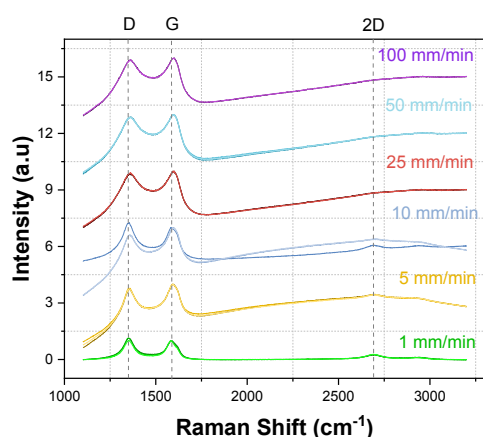


Fig. 4. Raman spectra of the grown CNFs by PECVD on the Ni catalyst printed at different speeds.

IV. CONCLUSIONS

A novel methodology to pattern Ni catalyst based on the spark ablation technique was introduced in the present work, which was used for the growth of CNFs by PECVD. The presented approach can be defined as versatile since no lithography steps or chemicals are required, and the catalyst area and density can be pre-defined by the printing settings.

The CNFs distributions were correlated with the level of coverage obtained by the adjustment of the printing speed. VA-CNFs were grown when the Ni catalyst fully covered the substrate. Both the alignment and crystallinity of the tubes decreases as the Ni catalyst coverage decrease.

Further studies are required to assess the printing resolution of the pattern. Besides, TEM analysis is required to study the grown carbon nanostructure in detail in order to determine if the defects are linked to plasma damage resulting from the reduction in density.

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