

# THE IMPACTS OF Ti-N FILM PROPERTIES ON THE SYNTHESIS OF VERTICALLY ALIGNED CARBON NANOFIBERS

Farzan A. Ghavanini, Maria L. Damian, Damon Rafieian and Per Lundgren

Department of Microtechnology and Nanoscience (MC2), Chalmers University of Technology, Göteborg, Sweden

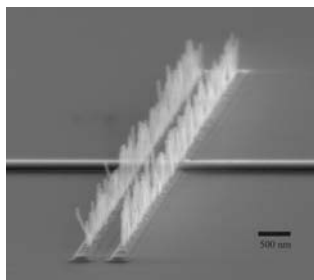
## Introduction

The synthesis of vertically aligned carbon nanofibers (VACNFs) using catalytic plasma enhanced chemical vapor deposition (c-PECVD) in which position, diameter, length, and alignment of the nanofibers are accurately determined has offered an unprecedented opportunity to realize a new bottom-up-engineered material with excellent mechanical and electrical properties [1]. The achievements during the last few years in reproducible synthesis of high quality VACNFs have led to the adoption of the new material for nanoelectromechanical systems (NEMS). Good examples of such systems include the nanoelectromechanical switches [2] and the nanoscale memory cell [3]. Currently, the authors are pursuing the realization of a nanoelectromechanical variable capacitor (varactor) device based on VACNFs (see Fig. 1). The performance of such a device is crucially dependent on the electrical properties of the underlying electrodes. However, excellent candidates for the electrodes material such as copper and gold are not known to yield successful VACNF synthesis. A possible solution to incorporate these materials is to deposit a thin buffer layer between them and the catalyst seeds. Being known as an effective diffusion barrier [4], titanium nitride has been nominated for this purpose because of its VACNF synthesis compatibility [5] as well as its CMOS compatibility [6] which is an important parameter for future NEMS integration.

In this work we investigate the impacts of Ti-N film properties on the subsequent growth of VACNFs.

## Experimental

The Ti-N thin films were deposited on top of thermally oxidized silicon with an oxide thickness of 400 nm in a

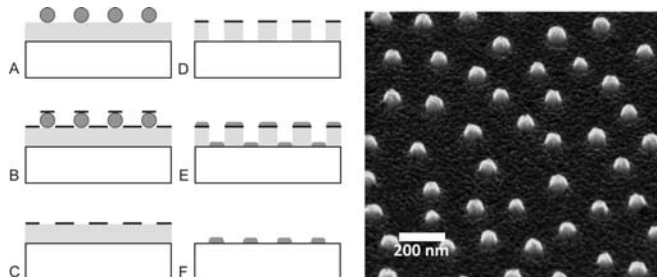


**Fig. 1** A SEM micrograph of a VACNF based nano-electromechanical varactor taken at sample tilt of 30°. The electrodes are 10  $\mu\text{m}$  long. The VACNFs are about 80 nm wide and a micrometer long.

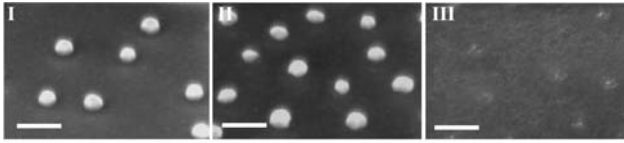
commercial (NORDIKO 2000) dc magnetron sputtering chamber with a base pressure of less than  $3 \times 10^{-6}$  mbar. The process pressure was kept at 2.5 mTorr for all depositions while the nitrogen to argon flow ratio was changed to modify the film stoichiometry and microstructure. The applied plasma current was set to 800 mA. The sheet resistance of the deposited film was measured in a four-point-probe setup within 2 minutes after the chips were exposed to the atmosphere in order to control the level of the film oxidation. The film resistivity was then calculated using the measured thickness of the deposited film.

We adopted hole-mask colloidal lithography [7] to conveniently produce Ni catalyst seeds in a diameter range of 40 to 100 nm on top of the Ti-N films. For this purpose a sacrificial polymethyl methacrylate (PMMA) film was spin-coated onto the Ti-N film which was followed by a 5 s oxygen plasma treatment to improve its hydrophilicity. Water suspended, charged polyelectrolyte was pipetted onto the polymer surface to produce a thin adhesive layer. A colloidal solution containing polystyrene (PS) spheres was deposited on the surface followed by nitrogen blow dry (Fig 2.A). 10 nm of gold was then deposited on top of the stack in an electron-beam evaporation equipment (Fig 2.B). The PS spheres were stripped away using an adhesive tape leaving nano-scale holes in the thin gold film (Fig 2.C). Reactive oxygen plasma etching was used to remove the PMMA underneath the openings in the gold mask (Fig 2.D). Finally, 50 nm of Ni was deposited in the same electron-beam evaporation chamber and the colloidal pattern was transferred to the Ti-N substrate in a lift-off process (Fig 2.E-F). The SEM micrograph of Fig. 2 shows the Ni seeds on top of the Ti-N film patterned by the colloidal lithography.

The annealing of the catalyst seeds and the VACNF synthesis were performed in an AIXTRON Black Magic PECVD reactor. The formation of catalyst nanoparticles from the catalyst seeds was studied by annealing the samples at different temperatures in an ammonia atmosphere at 3 mbar. The synthesis of the VACNFs was performed on separate chips starting with an annealing step followed by a short ammonia plasma treatment and then growth in a  $\text{C}_2\text{H}_2/\text{NH}_3$  PECVD process. The interaction of the substrate and catalyst



**Fig. 2** The left panel shows the schematic illustration of the hole-mask colloidal lithography. The right panel is a SEM micrograph of Ni seeds patterned on top of Ti-N substrate using this method.

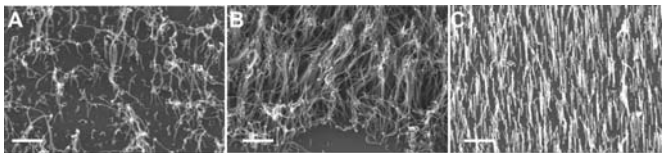


**Fig. 3** SEM micrographs of the Ni seeds on top of the Ti-N substrate after annealing at I) 500 °C, II) 600 °C, and III) 700 °C. Sample tilt is 45° and the scale bar shows 200 nm.

seeds was studied by scanning electron microscopy (SEM) and the chemical composition of the Ti-N films was investigated using X-ray photoelectron spectroscopy (XPS) technique.

### Results and Discussion

Fig. 3 shows the effect of the annealing process at 100 °C per minute for three different final temperatures on the Ni catalyst seeds. While annealing at 500 °C has negligible effect on the seeds, the same process at 600 °C has reduced both the thickness and the diameter of the seeds. Annealing at 700°C has led to complete disappearance of the seeds. These results can be explained by diffusion of the Ni seeds into the Ti-N substrate. Although the diffusion of Ni into titanium nitride substrates has been quantified previously [4], our observations suggest for a much faster diffusion rate which implies high level of porosity in the substrate. The microstructure including the grain size and the grain boundaries of the Ti-N film together with its stoichiometry are the main factors determining its porosity. In order to reduce the film porosity and therefore prohibit the Ni diffusion we increased the nitrogen to argon gas flow ratio while keeping the other deposition conditions constant. Table 1 gives the stoichiometry of three deposited films as obtained by XPS measurements. As expected, the resistivity of the Ti-N films (see Table 1) decreases as the nitrogen content in the film approaches to 50%. This is explained by the changes in the film microstructure which results in an increased density of voids that occurs with deviations from the stoichiometry [8]. This is indeed in agreement with our observations as shown in Fig. 4. The highest Ni diffusion is observed in film A which has the highest resistivity and the lowest nitrogen content in the film. Consequently, film A has resulted in very sparse VACNF growth (see Fig. 4 A). The VACNF density has increased in film B which has a lower resistivity and has reached a maximum in film C with the lowest resistivity (see Fig. 4 B-C).



**Fig.4** SEM micrographs after VACNF synthesis on top of three different Ti-N films as given in Table 1. Sample tilt is 45° and the scale bar shows 1 µm.

**Table 1. Deposited Ti-N substrates properties**

Film	A	B	C
Stoichiometry	Ti <sub>0.68</sub> N <sub>0.32</sub>	Ti <sub>0.52</sub> N <sub>0.48</sub>	Ti <sub>0.50</sub> N <sub>0.50</sub>
Resistivity	226 µΩcm	175 µΩcm	146 µΩcm
Growth mode	Base growth	Base growth	Tip growth

Another important observation is the transition from curly unaligned nanofibers grown on top of samples A and B to well-aligned VACNFs on top of sample C. SEM observations showed that this is due to a transition in the nanofibers growth mode from base growth to tip growth. We explain this phenomenon through the increased substrate porosity in film A and B which favors a base growth mode. It has been explained previously that vertical alignment is achieved in a tip growth mode while a base growth mode would lead to unaligned nanofibers [9].

### Conclusions

We showed that the properties of the Ti-N films play an important role in the subsequent growth of VACNFs. Their impact could be as considerable as changing the growth mode from tip to base where the vertical alignment of the fibers disappears. This emphasizes the importance of the substrate film properties especially when VACNF-based device fabrication is in mind.

### References

- [1] Melechko, A.V., et al.; Vertically aligned carbon nanofibers and related structures: Controlled synthesis and directed assembly. *Journal of Applied Physics*, **2005**. 97(4): p. 39.
- [2] Jang, J.E., et al.; Nanoelectromechanical switches with vertically aligned carbon nanotubes. *Applied Physics Letters*, **2005**. 87(16): p. 163114-1.
- [3] Jang, J.E., et al.; Nanoscale memory cell based on a nanoelectromechanical switched capacitor. *Nature Nanotechnology*, **2008**. 3(1): p. 26-30.
- [4] Garcia-Cespedes, J., et al.; Optimal deposition conditions of TiN barrier layers for the growth of vertically aligned carbon nanotubes onto metallic substrates. *Journal of Physics D-Applied Physics*, **2009**. 42(10).
- [5] Teo, K.B.K., et al.; Field emission from dense, sparse, and patterned arrays of carbon nanofibers. *Applied Physics Letters*, **2002**. 80(11): p. 2011-2013.
- [6] Wittmer, M. and H. Melchior; Applications of TiN thin-films in silicon device technology. *Thin Solid Films*, **1982**. 93(3-4): p. 397-405.
- [7] Fredriksson, H., et al.; Hole-mask colloidal lithography. *Advanced Materials*, **2007**. 19(23): p. 4297.
- [8] Sundgren, J.E.; Structure and properties of TiN coatings. *Thin Solid Films*, **1985**. 128(1-2): p. 21-44.
- [9] Merkulov, V.I., et al.; Alignment mechanism of carbon nanofibers produced by plasma-enhanced chemical-vapor deposition. *Applied Physics Letters*, **2001**. 79(18): p. 2970-2972.