Influence of the structure and composition of titanium nitride based substrate on the carbon nanotubes grown by CVD

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Abstract

We present a study of the influence of the substrate nano-structure and composition on the morphological properties of the carbon nanotubes (CNTs) by sequentially growing in situ $TiN_x:O_y$ film, dispersed nickel catalyst particles, and CNTs obtained by CVD. The results show that the stoichiometry and the nanostructures of the substrate intervene in the growing process. Particular attention is pay to the influence of oxygen on the CNT growths. The results show that O prevents the coarsening of the catalyst nickel particles, avoiding the surface diffusion mobility of the precursor atoms involved in the nanotubes growth (Ostwald ripening)[1]. The dependence of the size and density of the CNTs on the amount of O present in the substrate are reported and discussed. The experimental findings show that, besides acting as diffusion barrier between the catalyst particles and the silicon, the substrate also influences the kinetics of growth of carbon nanotubes.

Key words: Structured TiNx:Oy, Carbon nanotubes, Barrier (buffer) layer

Experimental
The non-stoichiometric $TiN_x:O_y$ films were grown on crystalline silicon by Ti ion beam sputtering at 500°C followed by nickel nano-particles deposition at 750°C.The CNTs are grown immediately after the catalyst deposition by feeding acetylene gas and maintaining the substrate at 700°C. *In situ* X-ray photoelectron spectroscopy (XPS) system allows compositional and structural analysis of the samples. The phases of the $TiN_x:O_y$ were analyzed by X-ray diffraction. The quite aligned CNTs were studied by scanning and transmission electron microscopy techniques showing different population density, morphology and diameter as a function of the O substrate content.

Results and discussion
The XPS technique probe up to ~50 Å depth[2]. As the influence of the buffer layer on CNTs grows depend on surface phenomena the probed region is giving a valuable information for our purposes. The XPS spectra of the studied samples showed the bands associated to electrons in Ti2p, N1s and O1s bonds. From the XPS spectra (not shown) were identified the bands associated to electrons in Ti2p$_{3/2}$-N (Ti2p$_{1/2}$-N) bonds, located at ~455 eV[3] (~461,2 eV). The band corresponding to electrons associated to titanium oxide for Ti2p$_{3/2}$-O (Ti2p$_{1/2}$-O) is located at ~457 eV[4] (~463,6 eV). The bands associated to N electrons are located in Ti-N (~397 eV) [3,5] and N-O-Ti (~400 eV) [6]. Finally, the band associated to O electrons are located at O1s-N-Ti (~532 eV)[5] and O1s-Ti (~530 eV)[5,7].

One of the main purposes of the work is studying the possible influence on the CNTs growing of the

buffer layer composition and structure. Therefore, the relative atomic composition of the $TiN_x:O_y$ buffer layers were obtained from the XPS spectra. Figure 1 shows the concentration of oxygen present in the thin films as a function of the ratio of gas $[H_2]/[N_2+Ar]$ used during the films deposition. This concentration shows the reduction effect of hydrogen during the films deposition. This result was important controlling the oxygen content in the buffer layer.
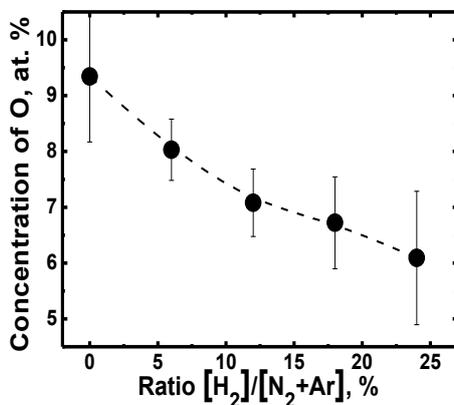

Figure 1. Concentration of O as function of the gaseous mixture $[H_2]/[N_2+Ar]$ used during the films growing.

The X-ray difractograms of the studied samples are shown in Figure 2. The crystalline evolution of the compound is revealed by the dependence of the microstructure of the buffer layer on the material composition. The difractograms show the main reflections associated to the (111) and (200) crystalline orientations of TiN of the studied samples. Also, an ill-defined reflection associated to the (220) TiN orientation is barley observed[8]. The reflection from the (300) crystalline orientation in the Ti_2O_3 compound is clearly displayed in the difractogram[9]. These plots show that the crystalline orientations associated with reflections (111) and (200) of TiN do not strongly depend on oxygen. Meanwhile, the reflection associated with the (300) crystalline orientations in Ti_2O_3 clearly depend on oxygen content, i.e., increasing hydrogen during the deposition process reduce the presence of oxygen in the film.

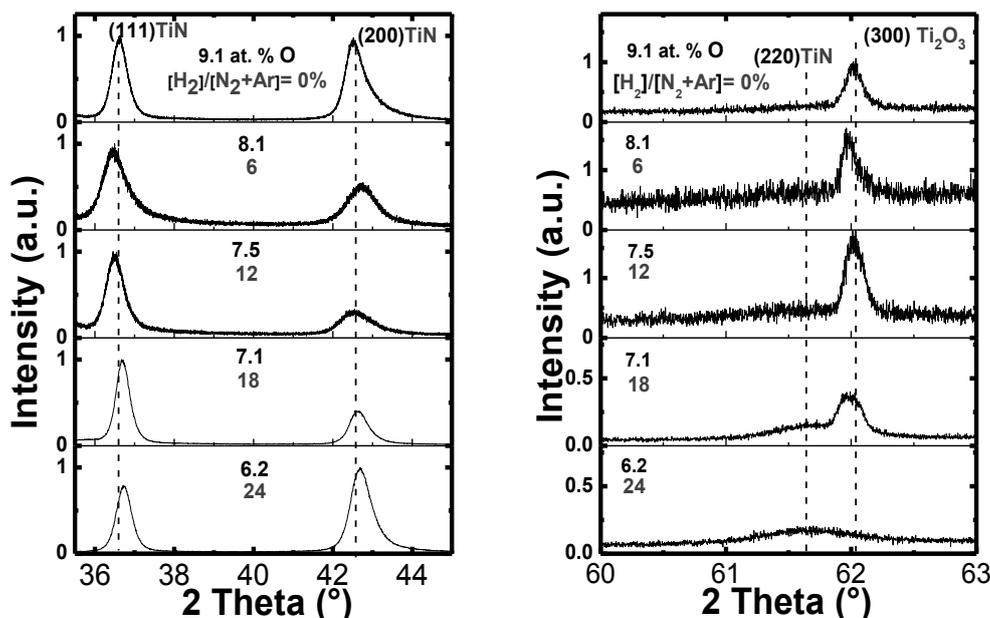Figure 2. X-ray difractograms of the studied $TiN_x:O_y$ films. The relative O concentrations as well as the gaseous mixture used in the deposition of the samples are indicated. For the sake of clarity, in the right panel, the difractograms corresponding to oxygen concentration is expanded.

A set of micrographs for the CNTs grew on the different prepared buffer layers were obtained. Figure 3a. shows a typical "carpet" of carbon nanotubes grown on one of the studied buffer layer, manifesting homogeneity in all film. We remark that in the scale of this micrograph all the samples look similar.

Figures 3b, c, d, e and f show a blow up of the CNTs deposited on different buffers layers. By a systematic counting on these set of micrograph were estimated the density and diameter distribution of the CNTs obtained in each studied substrate. Figure 4a shows the number of nanotubes per unit of area as a function of the concentration of oxygen. This plot shows that increasing O in the buffer layers leads to a higher density of CNTs in almost a factor five.
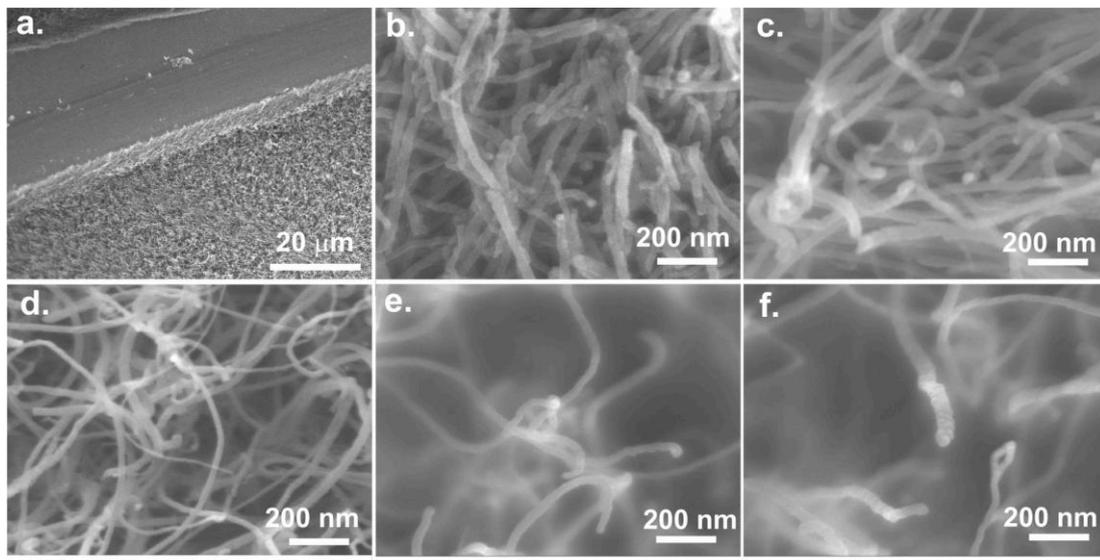

Figure 3. a) SEM top view images of CNTs a) carpet of CNTs; b, c, d, e and f) CNTs grown on different substrates different stoichiometry containing 9.1, 8.1, 7.5, 7.2, 6.2 oxygen at. %, respectively.
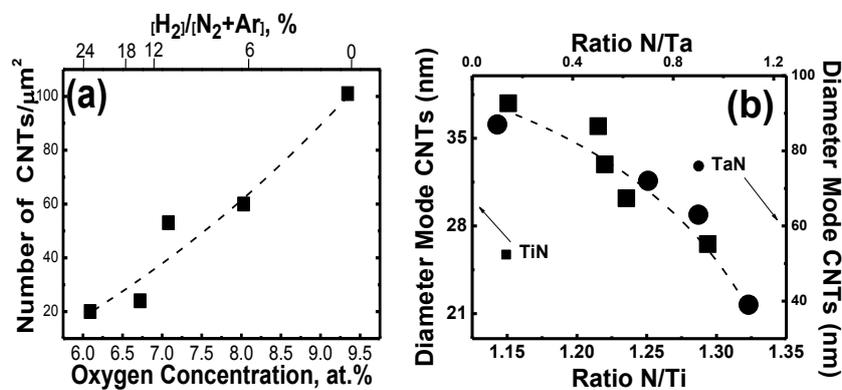

Figure 4 a) Density of CNTs as a function of oxygen concentration (bottom axis) and gaseous mixture (top axis); b) diameter mode of the CNTs grown on the studied substrates as a function s N/Ti (black). With comparison purposes, the experimental data obtained in previous work realized on tantalum nitride substrate[10] are also indicated (filled circles).

The dependence of the CNTs density on oxygen could be explained as a consequence of the inhibition phenomenon known as Ostwald ripening[1,11]. Roughly speaking, this effect consists in the growing of bigger particles at expenses of smaller ones (ripening) by surface migration of the catalyst particles. Our results suggest that the presence of Ti_2O_3 diminishes the catalyst particles surface mobility preventing Ni particles coalescence, i.e., the original number of catalyst particles remains constant. An interesting work regarding with the interaction nickel-titanium oxides films was reported by Dumesic and coworkers[12]. In an experiment realized at equivalent temperatures to the one used in our experiments (750 ^{0}C), these authors showed that, in the *presence of hydrogen*,

the Ni particles reduces the titania film and migrate, coalescing after meeting other catalyst particle. Therefore, we can assume that reducing the Ti_2O_3 phase in the buffer layers will favor the catalyst particles mobility and coalescence, i.e., the number of seeds will diminishes.

Consequently, a smaller CNTs density is expected, as it is experimentally found. Finally, in order to compare with previous results obtained in samples grown on TaN reported by Bouchet, et al.[10] we have plotted the mode of the diameter CNTs as a function of the ratio N/Ti and N/Ta (Figure 4b). As noted, the same trend is obtained in both cases suggesting that the behavior of the metal nitrides of compounds belonging to the p-block metal of the periodic table behaves similarly.

Conclusions

Different concentrations of oxygen were study in order to identify structural changes in the $TiN_x:O_y$ substrates and its influence on the CNTs growth. The Ti_2O_3 phase present in the films is controlled by the presence of hydrogen in the gaseous mixture used during growth. This phase affects the catalyst particle surface diffusion mobility, preventing nickel coalescence. As the nanotubes growing depend on the density of nickel seeds, the density of CNTs is also dependent on the presence of the Ti_2O_3 phase, i.e., by reducing this phase the CNTs density diminishes. The diameter mode as a function of the N/Ti ratio shows a similar trend that the one observed in experiment performed on tantalum nitride buffer layers, suggesting that metal compound from the p-block of the periodic table behave similarly regarding with the CNTs growing process.   Finally, this work shows the importance of the substrate structure and composition on the CNTs growth, showing that it is acting not only as diffusion barrier preventing silicide formation but also intervening on the kinetic of the process.

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