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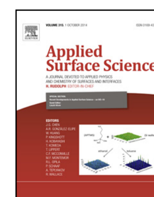

Interface study between nanostructured tantalum nitride films and carbon nanotubes grown by chemical vapour deposition☆

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ABSTRACT

We present the role of nitrogen content in tantalum nitride ultra-thin buffers, on the carbon nanotubes (CNTs) growth by chemical vapour deposition at 850 °C, assisted by ferrocene as catalyst source. Tantalum nitride (TaN_x) films with a very large range of concentration $x = [0, 1.8]$ and various nanostructures, from amorphous Ta(N) to Ta_3N_5, were deposited by Highly Pulsed Plasma Magnetron Sputtering. The buffer films are characterized after heat treatment at 850 °C, and after the CNT growth, by wide angle X-ray scattering in grazing incidence and scanning electron microscopy. The CNT diameter explored by transition electron microscopy shows an all-out value for under stoichiometric thin films (Ta_1-$N_{1-\delta}$, Ta_3-$N_{5-\delta}$) and a minimum value just above the stoichiometric phases (Ta_1-$N_{1+\delta}$, Ta_3-$N_{5+\delta}$). Firstly one shows that the buffer films under the heat treatment present surface modification highly dependent on their initial state, which influences the catalyst particles diffusion. Secondly at the stoichiometric TaN phase we show that a specific ternary phase $FeTa_2O_6$ is formed at the interface CNT/buffer, not present in the other cases, leading to a special CNT growth condition.

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1. Introduction

In the latest years important scientific and technical advances have taken place in the properties, fabrication and functionalization of Vertically Aligned Carbon Nanotubes (or Nano-fibres) (VACNTs) [1–4]. One determining challenge is to control the nucleation-growth of the VACNTs on specific substrate such as carbon fibres, conductive materials such as copper or naked silicon, and to assure the adhesion between the VACNT and the substrate. Our purpose is to study the VACNT growth parameters, by the means of a tunable synthesis technique for the elaboration of Ta-N_x(O) buffers with various composition, nanostructure, and reactivity at the temperature used for the iron assisted catalyst chemical vapour deposition CCVD [5]. Hitherto, this work is based on CCVD operating at medium range temperature, with a continuous feeding of an aerosol providing both the catalyst and the carbon [6]; this technique is the most appropriate for the production of millimetre-size VACNTs on a given substrate [7–9]. While this continuous CCVD process is based on an aerosol composed on toluene and ferrocene, the inter-diffusion of C and Fe atoms occurs above 800 °C, into the catalytic molten nanoparticles, before the formation of the graphitized multi-walls throughout a phase separation: the substrate nature and its interaction with iron have then great consequences on the CNT growth parameters.

If the CNT growth is widely optimized on oxides, it remains unsystematic on metal (Si, Cu, steel) or carbon fibres [10–13]. The today option is then coating the substrate with a thin buffer using a selected nitride or oxide [14–18]. The aim of this paper is to study the evolution of the TaN_x ultra-thin films [$x = 0.1, 1.8$] used as buffer layer of Si substrate during the CNT growth by iron assisted CVD at 850 °C. TaN_x thin films were used for copper diffusion barrier [19–22]: this latter is shown to strongly depend on the nitrogen content, which also act on the thermal stability of the film. Previous similar experiences were performed using compact TaN_x [$x = 0.2, 1.4$] thin films (≈120 nm) deposited by conventional magnetron sputtering; it was shown that an oxidation of the interface CNT-buffers occurs during the CCVD process, and that the oxides compounds and their nano-structuration depend on the initial TaN_x composition [23]. This is explained by an exchange between N, C and oxygen during the CCVD process, which cannot be observed for the VACNT growth on initial oxide buffers. The growth parameters are also completely different for the growth on pure Ta in vacuum, where the lack of oxygen and nitrogen atoms may lead to the formation of the carbide TaC in place of VACNT [24]. Moreover several investigations have been performed on VACNT replacing

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copper for nano-electronic applications, grown with pre-deposited catalyst nanoparticles on pure Ta [25,26]: but the pre-alloying process between the Ta (or TaN) buffer and the catalyst particles on one side, and the continuous injection method we use on the other side, lead to different metallurgic conditions. For that study, TaN_x ultrathin films (≈50 nm) were synthesized by high power pulsed magnetron sputtering HIPPIMS: the ionized species rate is larger by HIPPIMS than by conventional magnetron sputtering; it then allows a larger incorporation of nitrogen in the thin films and usually leads to denser layers [27].

The pristine samples were either submitted to the CCVD process using ferrocene diluted in toluene at 850 °C or just heated up to 850 °C and quenched down to the room temperature under Ar gas flow. The chemical composition of the pristine films was measured by elementary analysis. The nanostructure and the morphology of the ultra-thin films were checked before any treatment and after each process. We present here a detailed study of the evolution of the interface between the CNTs and the TaN_x films in term of atomic diffusion, nano-composition and nano-crystallinity, explored by microscopy (SEM) and grazing incident wide angle X-ray scattering (GIWAXS).

2. Material and methods

2.1. Pristine TaN ultra-thin films synthesis and characterization

Pristine TaN_x thin films were deposited by highly pulsed power magnetron sputtering (HIPPIMS). The films around 60 nm thick were deposited on naked silicon substrate from a Ta target, 99.9999% purity. The deposition chamber (Alcatel SCM650) background pressure was 10^{-5} Pa. The pulse duration was 10 μs or 5 μs with a frequency of 1 kHz, for an average power of 80 W/cm^2. The ultrathin films composition was controlled by the gaseous ratio $R = [N_2]/[Ar + N_2]$ feeding the reactor, ranging from 0 to 21%; it was measured after air exposure by Rutherford Backscattering Spectroscopy (RBS) and nuclear reaction analysis (NRA); oxygen and nitrogen contents were determined by NRA using $^{16}O\,(d,p_0)^{17}O$ at 830 keV and $\theta_{lab} = 90°$ and $^{14}N(d,\alpha)^{12}C$ at 1450 keV and $\theta_{lab} = 150°$ nuclear reactions, respectively. This step is referenced as story A in Fig. 1.

2.2. TaN_x ultra-thin films thermal treatment

The same furnace was used for the thermal treatment and the CVD process: the samples were placed under Ar gas flow at room pressure without removing residual air. For the heat treatment, a fragment of each pristine sample was heated up to 850 °C at 50 °C/min, and then quenched down to the room temperature in a few minutes. This step is referenced as story B in Fig. 1.

2.3. Assisted catalyst CVD

The CNTs were grown under Ar gas flow by chemical vapour deposition of an aerosol composed on toluene as carbon source and 5 wt% ferrocene as iron catalyst source on the pristine ultra-thin films [28]. The temperature of the furnace was maintained at 850 °C for 15 min and then naturally cooled for several hours, at about 5°/min. This step is referenced as story C.

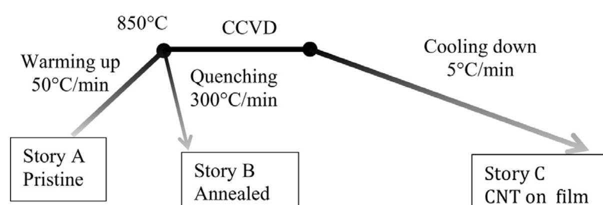

Fig. 1. Scheme of the experimental process performed on the set of TaN ultra-thin films.

2.4. Characterization by glancing incidence wide angle X-ray scattering

Wide angle X-ray scattering was performed in glancing incidence at 0.5° using a home-made apparatus composed on a Mo X-ray source (0.0709 nm) and an image plate detector. The surface of the sample was placed in the incidence plane by measuring the maximum of the tantalum fluorescence at the L edge, using a Si-Li solid detector. The image Plate 2D spectra were integrated after calibration for a 1D projection as a function the wave vector Q ($4\pi/\lambda \sin(\theta)$). The nanocrystals size was evaluated as usual by using the mid-height width of the diffracted symmetric peaks.

2.5. Imaging by electron microscopy

The imaging of the sample has been made using a scanning electron microscope equipped with a field emission gun SEM-Feg for a better resolution (Leo Gemini1525, or SEM Jeol JSM 6060 LV), for the stories B and C. An additional CNT sampling on grids was made for the analysis of the CNTs morphology by transmission electron microscopy (TEM) (Philips CM 12).

3. Results

3.1. Concentration in as-deposited TaN thin films (story A)

A summary of the principal characteristic of the films in the stories A and B is done in Table 1. The evolution of the atomic ratio [N]/[Ta] and [O]/[Ta] into the films at the story A are presented in Fig. 2 as a function of R in the plasma. They both show a logarithmic growth with R in the reactive high power pulsed plasma. The stoichiometry 1:1 inside the films is reached for R around 1%, to be compared to 4% [23] or 15% [29] for continuous reactive magnetron sputtering. The stoichiometry Ta_3N_5 is reached for R close to 9%. The oxygen content increases with nitrogen content and remains 6 times smaller. TaN_x films may be synthesized in various stoichiometric nanostructures, such as a solid solution of metallic α-Ta(N) or β-Ta(N), fcc-TaN to the rock-saltTa_3N_5.

3.2. Structural characteristic of as-deposited TaN thin films

The evolution of the medium range order organization inside the films is illustrated in Fig. 3 in which are presented the X-ray scattering spectra for R smaller than 1%, between 1.2 and 3.6%, at 4% and between 7% and 11%. Below R = 1.2%, the pristine films

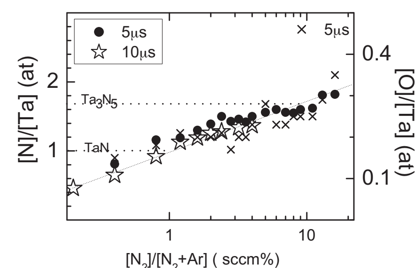

Fig. 2. Evolution of the ratio [N]/[Ta] and [O]/[Ta] for the set of ultra-thin TaN thin films as a function of $R = [N_2]/[N_2 + Ar]$ in the high power pulsed magnetron sputtering experience (story A). The results are presented for the two pulse durations used in the experience (5 μs, 10 μs).

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