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Nanostructured tantalum nitride films as buffer-layer for carbon nanotube growth

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ABSTRACT

Tantalum nitride (TaN_x) films are usually used as barriers to the diffusion of copper in the substrate for electronic devices. In the present work, the TaN_x coating plays an extra role in the iron catalyzed chemical vapor deposition production of carbon nanotubes (CNT). The CNTs were grown at 850 °C on TaN_x films prepared by radio frequency magnetron sputtering. The correlation between the CNT morphology and growth rate, and the pristine TaN_x film nature, is investigated by comparing the evolution of the nano-composition, roughness and nano-crystallinity of the TaN_x films both after annealing and CVD at 850 °C.

1. Introduction

Numerous studies have been devoted to the understanding of the carbon nanotube CNT growth by catalytic chemical vapor deposition CCVD. The growth model generally adopted assumes three stages: (i) the decomposition of the hydro-carbon precursor on the catalytic nanoparticles, (ii) the diffusion of C atoms inside this particle, and (iii) the separation phase in which graphene cylinders precipitate at the surface of the catalytic particle [1]. This description takes into account general observations, such as the catalytic particle location inside the CNTs, and the catalyst–substrate reactivity [2,3]. Indeed, the substrate has important consequences on the CNT growth, a process that is widely optimized on oxides (quartz and silica) but remains random on naked silicon, carbon or steel [4–6]. The probably best option nowadays is coating the unfavorable substrate [7–9] before the CCVD process, using either oxides (Al_2O_3, In_2O_3:Sn, SiO_x…) or nitrides (TiN, SiN_x…).

We have recently shown that it was possible to grow aligned carbon multiwall nanotubes by the CCVD process on silicon coated by TaN_x thin films [10]. While using the decomposition of ferrocene diluted in toluene at 850 °C, a strong correlation was found between the nitrogen concentration in TaN_x buffers and the CNT growth rate and morphology. In particular we have shown that their length and diameter decrease when the amount of N increases in the thin films. This reveals a strong interaction between Fe based catalyst nanoparticles and the TaN_x phases.

From the literature it is known that TaN_x compounds exhibit a large range of nanostructure and properties associated to the nitrogen content [11–14]. They present a variable oxidation degree: from the metallic bcc-Ta which is easily covered by a wide gap dielectric oxide like Ta_2O_5 to the stoichiometric cfc-TaN which is oxygen inert. Both tantalum compound families, namely nitrides and oxides, are used as copper diffusion barrier in nanoelectronics [15,16], which is shown to strongly depend on the nitrogen content, acting also on the thermal stability of the films [17]. In this paper, the diffusion at 850 °C of iron in the TaN_x thin films has been studied, in order to gain physical insight about the influence of the initial nano-composition and nanostructure of the films on the phenomenon. We will explore the structure of both pristine and thermal treated TaN_x films. The thermal treatment was done at 850 °C, which is the temperature required for the CNT growth process while using ferrocene, which decomposes at 813 °C. We will focus the study on the interaction between the iron based catalyst and the thin TaN_x films during the CCVD deposition.

2. Experiment

2.1. TaN thin film synthesis and treatment

The TaN_x films (40 and 130 ± 10 nm thick) were sputter deposited from a Ta metallic target on a <100> silicon substrate in reactive Ar/N_2 plasma excited by a 13.56 MHz radio frequency. The Ar flow rate was fixed at 100 sccm while the N_2 flow rate was varied from 0 to 20 sccm ($\tau = N_2/[N_2 + Ar]$). The plasma power and pressure were set at 400 W and 0.5 Pa respectively. The background pressure was better than 10^{-5} Pa.

The TaNx films (130 nm thick) were heated up to 850 °C in a quartz reactor and exposed during 12 min to a continuous flow of aerosol composed of ferrocene diluted in toluene (2.5 wt.%), dragged by Ar (3 l/mn). This as-called assisted aerosol CCVD process [18]

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allows the growth of aligned carbon nanotubes on TaNx thin films [10]: this is illustrated by Fig. 1, including the CNT carpet obtained for $\tau = 1\%$ and $\tau = 9.1\%$. Pristine TaN_x coated Si were annealed at 850 °C during the same time in the reactor under Ar flux (3 l/mn) without aerosol containing the catalyst.

2.2. TaN thin film characterization

Rutherford backscattering spectroscopy (RBS) was used for quantitative determination of the Ta content inside 40 nm thick films. Oxygen and nitrogen contents were determined by nuclear reaction analysis (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. The surface chemical bonding was checked by X-ray photoelectron spectroscopy XPS, (KRATOS AXIS UltraDLD) using Al K_α monochromatized source (1486.6 eV). The core levels (Ta4f, N1s, and O1s) were recorded with a resolution of 0.2 eV, in floating configuration with charge compensation. The energy was calibrated with a gold coating on glass. AFM (DIGITAL Instrument 3100) was used to map the surface and to measure the root mean square roughness R_q from 5 μm^2 area, in the tapping mode to avoid mechanical modifications of the surface. The X-ray diffraction pattern was recorded in glancing incidence (~1°) using a Bruker diffractometer equipped with a Cu source ($\lambda = 0.154$ nm). The nanocrystals size was evaluated by using the width of the diffraction peaks.

3. Results

3.1. Chemical composition

Figs. 2 and 3 show the [N]/[Ta] and [O]/[Ta] atomic ratio, inside and at the surface for the pristine and the annealed films.

The pristine film composition varies from pure Ta to TaN for τ close to 5% and to Ta_3N_5 for $\tau = 13.8\%$. As expected the oxygen content is very small inside the films. During annealing at 850 °C for 12 min, most of nitrogen is going out of the films except in the vicinity of TaN: in that case we have found a stoichiometry close to Ta_2N. After annealing the [O]/[Ta] ratio inside the films increases from 2 to 3.

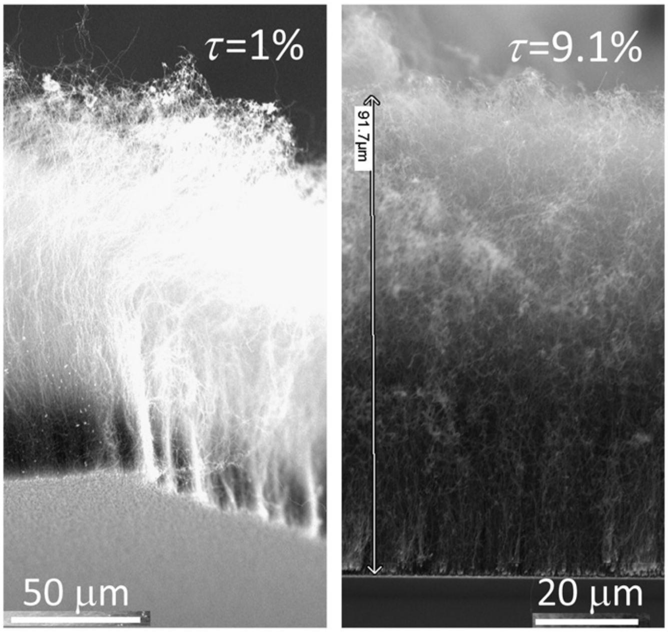

Fig. 1. Typical scanning electron microscopy (SEM) image of aligned carbon nanotubes grown on TaN_x thin films deposited on silicon for $\tau = N_2/[N_2 + Ar]$ taking the values 1% and 9.1%.

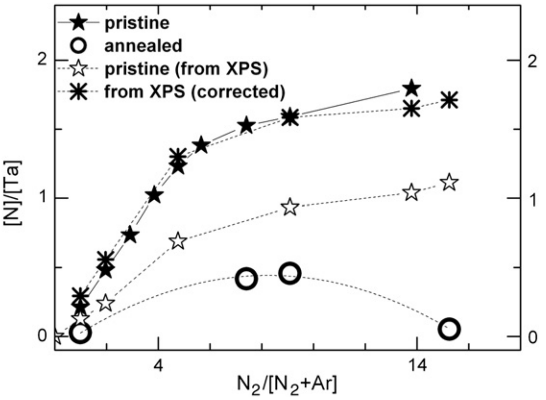

Fig. 2. [N]/[Ta] atomic ratio as a function of $\tau = N_2/[N_2 + Ar]$ in the plasma, in the bulk for pristine (stars) and annealed TaN_x thin films (open circle); Bulk data were recorded by nuclear analysis. The ratio extracted from the N1s and Ta4f core level area for 130 nm films becomes consistent with bulk data (open stars and 8 branches-crosses), oxygen atoms being localized at the extreme surface of the films.

The Ta4f core levels, indicative of the Ta species surrounding at the film's surface are presented in Fig. 4. They may be mostly decomposed in two contributions, each contribution generating a doublet $4f^{7/2}$ and $4f^{5/2}$ separated by 1.9 eV. The core level with the lowest binding energy is asymmetric; its maximum shifts from 21.9 eV (Ta $4f^{7/2}$) for low N content to 23.9 eV for Ta_1N_1. It corresponds to the Ta–N bonding inside the films, which shifts from Ta^0 (21.6 eV) towards high energy (Ta^{2+}) when the nitrogen content increases, due to the electro-negativity of nitrogen. It is interesting to notice that for [N]>[Ta], the charge transfer between N and Ta atoms slightly decreases. The asymmetry of this core level may be reproduced by adding a component (Ta $4f^{7/2}$ located at 285.9 eV), which indicates the progressive formation of TaN phases [19,20].

The highest energy core level is located at 26.7 eV (Ta $4f^{7/2}$) for low N. This value is due to Ta^{5+} states, corresponding to Ta_2O_5 [21,22]. It represents 57% of the signal while the TaN_x films are very clean (Fig. 3): we then assume that Ta–O bindings are localized at the extreme surface. When N increases, the superficial oxygen decreases down to [O] = [Ta], with a Ta $4f^{7/2}$ core level located at 26.1 eV.

The ratio [N]/[Ta] extracted from the Ta 4f total area is underestimated (Fig. 2), because only 33% (low N content) to 63% (high N content) of the Ta 4f signal may be attributed to atoms inside the films: the values obtained after correction of XPS data, are consistent with the values obtained by nuclear analysis.

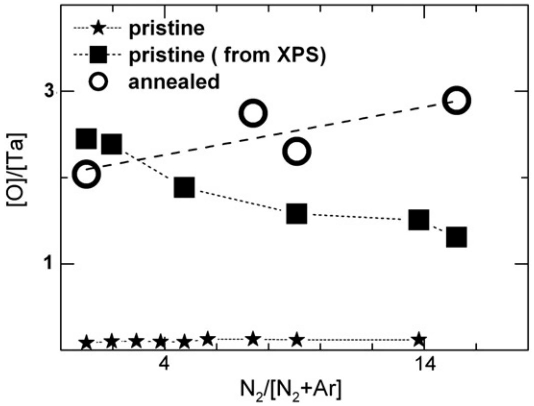

Fig. 3. [O]/[Ta] atomic ratio as a function of $\tau = N_2/[N_2 + Ar]$ in the plasma, for pristine TaN_x thin films in the bulk (stars) and at the surface (square), and for the annealed TaN_x thin films in the bulk (open circle).