Thin Solid Films xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Growth control of carbon nanotubes using nanocomposite nickel/carbon thin films

N. Bouts [a], M. Gaillard [b], L. Donero [a], A.A. El Mel [a], E. Gautron [a], B. Angleraud [a], C. Boulmer-Leborgne [b], P.Y. Tessier [a,*]

[a] Institut des Matériaux Jean Rouxel (IMN), UMR 6502, Université de Nantes, CNRS, 2 rue de la Houssinière, B.P. 32229, 44322 Nantes Cedex 3, France
[b] Groupe de Recherches sur l'Energétique des Milieux Ionisés (GREMI), UMR 7344, Université d'Orléans, CNRS, 14 rue d'Issoudun, B.P. 6744, 45067 Orléans Cedex 2, France

ARTICLE INFO

Article history:
Received 23 May 2016
Received in revised form 10 October 2016
Accepted 10 October 2016
Available online xxxx

Keywords:
Carbon
Nanotubes
Nickel
Plasma
Nanocomposites

ABSTRACT

Recent papers have demonstrated that the growth of carbon nanotubes (CNTs) by plasma enhanced chemical vapor deposition (PECVD) was possible using nanocomposite nickel/carbon (nc-Ni/C) thin films as catalysts. In this study, the growth of CNTs by PECVD in H_2/C_2H_4 atmosphere was achieved using nc-Ni/C thin films deposited by a hybrid plasma process combining the sputtering of a nickel target and the deposition of hydrocarbon by PECVD using Ar/CH_4 atmosphere. In order to identify the most favorable conditions to obtain dense CNTs arrays using nc-Ni/C thin films, the Ni content in the catalyst as well as the growth conditions of the CNTs were varied. Films containing 40, 55 and 65 at.% of Ni were selected for this study. The growth temperature of the CNTs was varied between 500 and 700 °C whereas the electrical power applied to the PECVD source was tuned from 30 to 50 W. Scanning electron microscopy and Raman spectroscopy were employed to probe the morphology and the structure of the CNT's. Depending on the chemical composition of the nc-Ni/C thin films, different trends were observed. No CNTs were obtained neither for the highest nickel content (i.e. %Ni = 65 at.%) nor for the lowest growth temperature (i.e. 500 °C). On the other hand, for temperatures exceeding 500 °C, while a high power on the PECVD source (i.e. 50 W) was found to be necessary to obtain CNTs in the case of films with a moderate Ni content (i.e. %Ni = 55 at.%), a lower power (i.e. 30 W) was sufficient for the film with the lowest Ni content (i.e. %Ni = 40 at.%). This difference in behavior was attributed to the differences in microstructure of nc-Ni/C thin films which is directly related to their chemical composition.

1. Introduction

Since their discovery carbon nanotubes (CNTs) have revealed their impressive properties making them ideal candidates for a broad range of applications in many research areas including microelectronic [1–3], energy storage [4,5], and smart coatings [6]. Despite the huge number of publications dealing with CNTs, such as references [1–22] are representative, most of the growth approaches reported so far require high temperatures which is incompatible with microelectronic standards. For this reason, the race toward the development of low temperature growth approaches is still running. In general, the growth of CNTs requires using metal nanoparticles dispersed over a substrate surface as a catalyst. These nanoparticles are heated up in the presence of a hydrocarbon precursor (typically acetylene) and a reductive gas such as hydrogen or ammonia. In appropriate experimental conditions (e.g. pressure, temperature, gas flows and ratios, etc.…), carbon atoms start segregating at the catalyst surface leading to the formation of CNTs. The final characteristics of the obtained CNTs (i.e. diameter, density, etc.…) are in general strongly dependent on the ones of the catalysts. The metal nanoparticles can be prepared simply by dewetting. Such approach consists in depositing a thin film of the metal catalyst followed by thermal annealing at a relatively high temperature to form metal nanospheres. To control the size distribution and density of these nanoparticles, one must carefully adjust the thickness of the metal film, the annealing temperature and time. This approach has already shown its ability to obtain well adapted catalyst nanoparticles for the growth of CNTs. Nevertheless the high temperatures required in such an approach can be a limiting factor for some applications.

Nanocomposite metal/carbon (nc-Me/C) thin films consisting in metal or metal-rich nanoparticles embedded in an amorphous carbon matrix have been widely studied during the three last decades [23–38]. The methods used to synthesize this kind of material are based on cold plasma technology. Such processes allow adjusting the

* Corresponding author.
E-mail address: pierre-yves.tessier@cnrs-imn.fr (P.Y. Tessier).

http://dx.doi.org/10.1016/j.tsf.2016.10.025
0040-6090/

size, the distribution and the shape of the metal nanoparticles by simply tuning the deposition parameters without the need of applying any intentional external heating to the substrate during deposition. Since the nature of the metal inserted in the amorphous carbon matrix can be simply controlled by using different targets, many systems have been considered, including nc-Ti/C [27–31,39,40], nc-Co/C [41–44], nc-Pt/C [45–47], nc-Ni/C [25,33,35–37,47–62] and nc-Cu/C [23,38,47,63–77]. Among the studied systems, nc-Ni/C thin films appeared to be very promising candidates for the growth of CNTs [78–80]. Nevertheless, the impact of the nc-Ni/C composition and morphology on the growth of CNTs was not explored in detail.

In this paper, we report on the growth of CNTs using nc-Ni/C catalysts thin films presenting three different chemical compositions: % Ni = 40, 55 and 65 at.%. The films were deposited using a hybrid plasma process combining the sputtering of a nickel target and the deposition of hydrocarbon by plasma enhanced chemical vapor deposition (PECVD) using methane as precursor. The CNTs were grown by PECVD with various temperatures and electrical powers applied to the plasma source. All the samples were characterized using scanning electron microscopy (SEM) and Raman spectroscopy.

2. Experimental details

2.1. nc-Ni/C catalysts deposition

The nc-Ni/C thin films were deposited using a hybrid plasma process combining the sputtering of a nickel target and the deposition of hydrocarbon by PECVD using Ar/CH_4 atmosphere as a precursor. This process has already been described elsewhere [25,81]. Briefly, a nickel target of 50 mm in diameter and 99.99% in purity was fixed to a magnetron source connected to a radiofrequency (RF) generator via a matching box. The RF power applied to the magnetron was fixed to 150 W. The target was located at 80 mm from the substrate holder. A coil was inserted at an equal distance between the target and the substrate holder, and was connected to another RF generator via a matching box. The RF power applied to the coil was 150 W. The coil is employed to create an additional plasma between the target and the substrate surface. A gas mixture composed of argon and methane was introduced in the chamber for all the depositions. In order to modify the chemical composition of the films, the methane fraction was varied between 14 and 38%, leading to thin films presenting three different Ni contents ranging between ~65 and ~40 at.% as evaluated by X-ray photoelectron spectroscopy (XPS). The XPS analysis procedure is described in Section 2.3. The deposition pressure was kept constant at 0.67 Pa, and the deposition time was fixed to 30 min. In these conditions, the film thickness ranges from 500 to 800 nm depending on the methane ratio injected in the deposition chamber. The nc-Ni/C thin films deposition conditions are summarized in Table 1.

2.2. CNTs growth

The growth of CNTs was carried out using a RF PECVD process. The growth conditions are summarized in Table 2. The nc-Ni/C thin films were first annealed until reaching the required temperature for the growth of CNTs. Three different temperatures were explored: 500, 600 and 700 °C. After 15 min of annealing, a mixture of H_2 and C_2H_4 was injected into the chamber and a RF discharge was generated. According to previous studies [20], the fraction of C_2H_4 was fixed to 33% and the power applied to the source was varied between 30 and 50 W. This process typically allows the growth of CNTs from standard Ni catalysts at a temperature over 600 °C.

Table 1
nc-Ni/C deposition conditions. P_{Target} corresponds to the power applied to the target and P_{Coil} corresponds to the power applied to the coil.

Name	P_{Target} (W)	P_{Coil} (W)	Pressure (Pa)	CH_4 ratio (%)	Ni content (at.%)
nc-NiC 1	150	150	0.67	14	65
nc-NiC 2	150	150	0.67	25	55
nc-NiC 3	150	150	0.67	38	40

Table 2
CNTs growth conditions. P_{Source} corresponds to the power applied to the PECVD source.

Name	Annealing time (min)	Growth time (min)	H_2 flow (sccm)	C_2H_4 flow (sccm)	Pressure (Pa)	P_{Source} (W)	$T_{annealing}$ (°C)
CNT 1	15	30	40	20	1.1	30	700
CNT 2	15	30	40	20	1.1	30	600
CNT 3	15	30	40	20	1.1	50	600
CNT 4	15	30	40	20	1.1	50	500

2.3. Material characterization

The chemical composition of the films was determined by XPS using a Kratos Nova spectrometer. The X-ray source is a monochromatic Al Kα. A pass energy of 20 eV was employed for high-resolution spectrum. Before each analysis, an argon sputter cleaning procedure (argon ion energy of 500 eV, current density of 1 $\mu A \cdot cm^{-2}$) was applied during 120 s to remove the surface contamination resulting from the exposure of the samples to the ambient atmosphere during the transfer from the deposition chamber to the XPS tool. SEM micrographs were recorded using a Jeol 7600 F microscope operating at 5 kV. For the Raman spectroscopy analyses, a Renishaw inVia Raman spectrometer was used with an incident wavelength of 514 nm. All the Raman spectra were fitted appropriately to extract: i) the position of the D, Pos (D), and G peaks Pos (G); ii) the full width at half maximum of the D peak, FWHM (D), and the one of the G peak, FWHM (G), iii) the ratio between peak intensities I_D/I_G. TEM observations were recorded using a Hitachi H-9000 NAR microscope (LaB_6 Filament, Scherzer Resolution: 0.18 nm) operating at 300 kV.

3. Results and discussion

3.1. nc-Ni/C 1 - % Ni = 65 at.%

Fig. 1 presents the SEM micrographs obtained for nc-Ni/C thin film initially containing 65 at.% of Ni after the growth of CNTs in different conditions. The CNT-4 condition resulting in the complete delamination of the film is not presented here.

Based on the SEM observations, one can conclude that there is a lack of CNTs on the metal grains. Moreover, it can be remarked that decreasing the temperature from 700 °C (Fig. 1a–c) to 600 °C (Fig. 1d–f) while fixing the electrical power on the source to 30 W (CNT 1, 2) leads to an increase in size of the observed grains on the surface. On the other hand, when fixing the growth temperature to 600 °C (CNT 2, 3), increasing the power applied to the source from 30 (Fig. 1d–f) to 50 W (Fig. 1g–i) does not impact significantly the global morphology of the films. Raman spectra were recorded from the samples between 900 and 1900 cm^{-1} using an incident wavelength of 514 nm (Fig. 2). The parameters extracted from the fit of the D and the G peaks are summarized in Table 3. The Raman study shows that whatever the conditions, the growth process leads to an enhancement of the global order of the amorphous carbon phase within the material: globally, the FWHM of the G peak decreases, whereas the I_D/I_G ratio increases.

3.2. nc-Ni/C 2 - % Ni = 55 at.%

Fig. 3 presents the SEM micrographs recorded from nc-Ni/C thin film initially containing 55 at.% of Ni after the growth of CNTs with different

Please cite this article as: N. Bouts, et al., Growth control of carbon nanotubes using nanocomposite nickel/carbon thin films, Thin Solid Films (2016), http://dx.doi.org/10.1016/j.tsf.2016.10.025