Thin Solid Films xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

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

Effect of temperature on the synthesis of nanoporous carbon from copper/carbon thin films to nanoporous carbon for sensing applications

L. Donero [a,b], N. Bouts [a], A.A. El Mel [a], B. Le Borgne [b], E. Gautron [a], L. Le Brizoual [b], F. Le Bihan [b], P.Y. Tessier [a,*]

[a] Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, B.P. 32229, 44322 Nantes Cedex 3, France
[b] Institut d'Electronique et de Télécommunication de Rennes (IETR), Université de Rennes 1, Campus de Beaulieu, 263 Avenue du Général Leclerc CS 7420, 35042 Rennes Cedex, France

ARTICLE INFO

Article history:
Received 23 May 2016
Received in revised form 30 September 2016
Accepted 6 October 2016
Available online xxxx

Keywords:
Nanoporous
Carbon
Copper
Nanocomposite thin films
Sputtering
Etching

ABSTRACT

Over the last few years, a broad panel of carbon materials was proposed for sensing applications. Among these materials, nanoporous carbon (np-C) is of particular interest due to its high specific surface area and low fabrication cost. In this contribution, the synthesis of np-C thin films using an approach combining the growth of copper/carbon nanocomposite thin films by co-sputtering followed by a selective wet etching of copper in nitric acid is studied. By adjusting the deposition conditions (e.g., powers applied to the sputtering targets, deposition temperature) of the nanocomposite thin films, it is shown that the pore size and the structure of the carbon skeleton can be modified. Furthermore, the possibility of integrating such nanoporous materials in field effect transistors for sensing application is also demonstrated.

1. Introduction

Nanoporous carbon (np-C) is an appealing material for a broad range of practical applications in various research fields including catalysis [1], biosensing [2], energy storage (supercapacitors) [3], filtration and purification of gas and liquids [3,4]. The interest toward this class of material arises from their good mechanical stability [3], and high active specific surface area [5]. These properties can be modulated by adjusting the characteristics (e.g., size, shape and density) of the nanopores [6].

Enormous efforts have been dedicated lately to the development of novel techniques allowing synthesizing nanoporous materials with adjustable properties, [7,8] including wet-chemical and electrochemical routes [9], template approaches [10], chemical vapor deposition [5,11], pyrolysis of organic polymer precursors [3] and low-energy cluster beam deposition [11]. Recently, our group has developed a two-step approach to synthesize np-C thin films [6]. The process consists in the deposition of copper/carbon nanocomposite (nc-Cu/C) thin films followed by a selective chemical etching of the copper phase in order to obtain np-C.

Metal/carbon nanocomposites (nc-Me/C) can be described as heterogeneous materials consisting of metal or metal rich nanoparticles embedded in a carbon film matrix. This kind of material has been widely studied during the last two decades, mainly for coating applications [12]. Different systems have been explored, including Ni [13], Fe [14], Cu [15,16], Au and Pt [14]. Our nc-Cu/C thin films were synthesized by co-sputtering of a graphite and a copper target in co-focal configuration at low temperature [6]. We have made clear that it was possible to control the size and density of the obtained nanopores by adjusting the nc-Cu/C sputtering conditions. We also showed that the electrical conductivity of the obtained np-C was dependent on its microstructure and morphology [6]. Nevertheless, our study was limited to the synthesis of nc-Cu/C films deposited at low temperature (i.e. no intentional heating was applied to the substrate during the deposition). The deposition temperature can drastically impact the morphology and the microstructures of such nanocomposite materials. For example, in the case of nc-Ni/C thin films, an increase of the deposition temperature leads to a strong modification in film morphology and structure due to the self-organization of the metal within the carbon matrix during the growth [17].

In case of the nc-Cu/C films, the deposition temperature can also strongly modify the morphology of the obtained nc-Me/C material, and thus the one of the np-C formed after nitric acid etching. The aim of this paper is to evaluate the impact of the deposition temperature on the morphology/structure of nc-Cu/C thin films and the consequence on the formation of the np-C thin films.

2. Experimental section

The nc-Cu/C thin films were synthesized using a co-sputtering process [6]. The film depositions were performed on thermally oxidized

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

http://dx.doi.org/10.1016/j.tsf.2016.10.014
0040-6090/

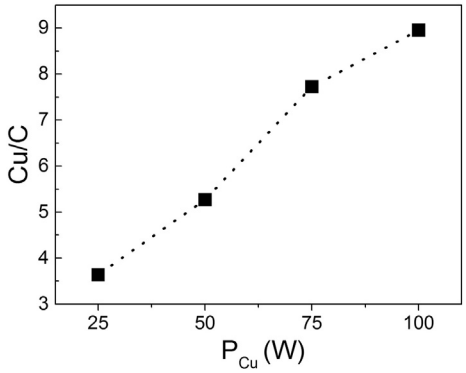

Fig. 1. Evolution of the composition of nc-Cu/C films as a function of the electrical power, P_{Cu}, applied to the copper target.

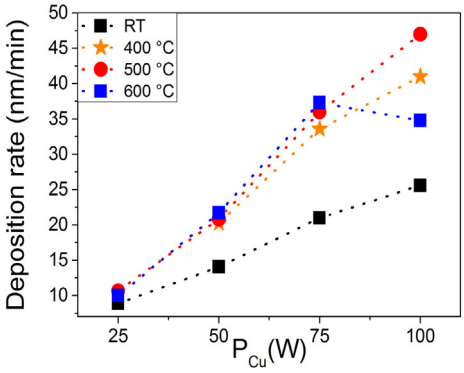

Fig. 3. Evolution of the deposition rate of nc-Cu/C films at different substrate temperatures as a function of the electrical power, P_{Cu}, applied to the copper target.

silicon substrates (500 nm SiO_2). A copper and a graphite target mounted on DC magnetron sources in co-focal configuration were used. The deposition pressure was fixed to 0.5 Pa. The chemical composition of the films was adjusted by tuning the electrical powers applied to the targets. The electrical power applied to the graphite target was fixed to 100 W. In order to change the copper content in the nc-Cu/C thin films, four electrical powers were applied to the copper target: P_{Cu} = 25 W, 50 W, 75 W and 100 W. Four deposition temperatures were also tested: room temperature (RT - no intentional heating), 400, 500 and 600 °C. During the deposition, the substrate rotation speed was 5 rpm. The deposition time at room temperature was adjusted in order to obtain thin films with a mean thickness around 500 nm. The chemical composition of the films was evaluated using energy dispersive X-ray spectroscopy (EDS) with JEOL 5800 operating at 5 kV. The crystalline structure of the films was probed using X-ray diffraction (XRD) with Moxtek D8 in a configuration Bragg-Brentano. The x-ray source is copper anode. The morphology was analyzed using scanning electron microscopy (SEM) with JEOL 7600 F microscope operating at 15 kV. Transmission electron microscopy (TEM) imaging of copper nanoparticles was carried out on a Hitachi H9000-NAR microscope operating at 300 kV equipped with a LaB_6 filament and exhibiting a point-to-point resolution of 0.18 nm. To obtain nanoporous carbon, the nc-Cu/C thin films were exposed to concentrated nitric acid solution for 1 min (70 wt.%, Sigma Aldrich). According to our previous work, to obtain nanoporous carbon using such an approach, the copper nanoparticles must be percolated otherwise the nitric acid cannot propagate within the material and selectively dissolve the copper phase. This can be easily identified by measuring the electrical conductivity of the films [6]. Based on our previous work, we have carefully selected the values of P_{Cu} in such a way that the copper nanoparticles percolate within the carbon matrix. The structure of the carbon phase was probed using Raman spectroscopy carried out on a Renishaw in Via Raman microscope equipped with a 514 nm argon laser. To avoid any possible sample damage, the laser power was limited to 1.5 mW.

3. Results and discussions

3.1. nc-Cu/C: effect of electrical power and substrate temperature

Fig. 1 shows the evolution of the Cu/C atomic ratio as a function of the electrical power applied to the copper target deduced from EDS measurements for thin films deposited at room temperature. The Cu/C ratio varies from 3.6 to 9 by adjusting the power applied to the copper target from 25 to 100 W. Since we ensured the ability of the process to modify the chemical composition of the films, these four conditions were repeated at deposition temperatures of 400, 500 and 600 °C. From the plan-view SEM micrographs (Fig. 2) at RT (Fig. 2 a–d), one can conclude that all the films exhibit a globular morphology which is the typical characteristic of nc-Cu/C films grown by magnetron sputtering [18–20]. No significant evolution of the morphology with P_{Cu} can be seen. In the case of films deposited at 500 °C, we observe a more porous structure when increasing P_{Cu} (Fig. 2 e–h). This evolution is observed for all temperature conditions. The evolution of the deposition rate as a function of P_{Cu} for all temperature conditions (RT, 400 °C, 500 °C and 600 °C) is presented in Fig. 3. The deposition rate is defined as the ratio of the apparent thickness to the deposition time. The apparent thickness is estimated from cross-sectional SEM micrographs. As expected, a linear increase of the deposition rate with P_{Cu} is observed at RT. The most surprising result is the increase of the deposition rate with the deposition temperature for a constant value of P_{Cu}. This effect becomes more pronounced for high values of P_{Cu} which correspond to high content of copper within the films. For example, at P_{Cu} = 100 W,

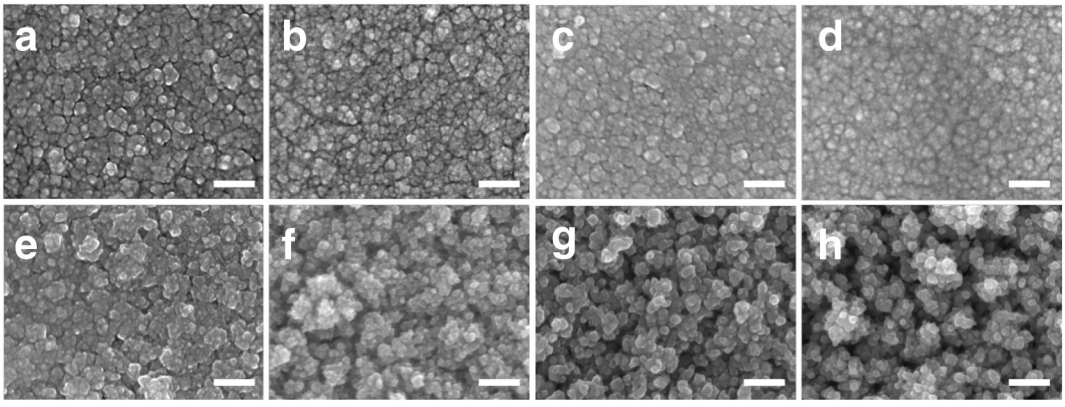

Fig. 2. Top-view SEM micrographs of nc-Cu/C thin film grown at room temperature (a–d) and at 500 °C (e–h) with different values of P_{Cu}: 25 W (a and e), 50 W (b and f), 75 W (c and g) and 100 W (d and h) - (Scale bar 100 nm).

Please cite this article as: L. Donero, et al., Effect of temperature on the synthesis of nanoporous carbon from copper/carbon thin films to nanoporous carbon for sensing applica..., Thin Solid Films (2016), http://dx.doi.org/10.1016/j.tsf.2016.10.014