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Electrical behavior of nickel/carbon nanocomposite thin films

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ABSTRACT

The relationship between the microstructure and the electrical behavior of nickel/carbon nanocomposite (nc-Ni/C) thin films is reported. A particular attention was accorded to the role of the chemical composition and the nature of the amorphous carbon matrix on the electrical behavior of the material. The nc-Ni/C thin films were synthesized using two different cold plasma processes both allowing to finely control the chemical composition, structure and morphology of the films. The first process combines magnetron sputtering of a nickel target and the deposition of hydrogenated carbon by plasma enhanced chemical vapor deposition using methane as a precursor. The second process consists in the co-sputtering of a nickel and a graphite target in pure argon plasma. For the two deposition processes, a similar increase in the electrical conductivity with the Ni content was observed and attributed to the percolation of the Ni nanograins through the carbon matrix. The percolation threshold was evaluated around 41 at.% of Ni for the two deposition processes. For lower Ni concentrations, the microstructural study indicated that the electrical conductivity is governed by the nature of the amorphous carbon phase which is found to be dependent on the deposition process as revealed by μ-Raman spectroscopy.

1. Introduction

Consisting in metal-rich nanoparticles embedded in a carbon matrix, metal/carbon nanocomposite (nc-Me/C) thin films have been intensively studied during the three last decades. Their main interest concerns their various tunable properties which directly depend on the nature and the proportion of the metal inserted in the carbon matrix. The morphology of nc-Me/C was also reported to be strongly dependent on the nature as well as the proportion of the metal inserted in the material [1–6]. Several processes have been developed allowing to finely control the proportion of metal within the films such as non reactive [4,7–13] and reactive [14–17] sputtering, hybrid Physical Vapor Deposition (PVD)/Plasma Enhanced Chemical Vapor Deposition (PECVD) processes [14,18–21], ion or electron beam deposition [2,5,22–26], arc discharge [12,27], pulsed laser deposition [28] and electrodeposition [29]. The micro-organization of the host carbon matrix was generally reported to be dependent on the deposition process itself [12]. The obtained properties being strongly related to both the structure of the metal nanograins and the micro-organization of the amorphous carbon matrix, these characteristic have to be considered with the same care. In the particular case of nc-Ni/C thin films, very interesting piezoresistive behaviors have been reported, associating high gauge factors (GFs) and low temperature coefficients of resistance [17,30–34]. In Ref. [33], Petersen et al. studied the impact of the deposition process on the piezoresistive properties of nc-Ni/C thin films deposited by direct current (DC) and radiofrequency (RF) sputtering; while DC sputtered thin films present GFs lower than 4, GFs higher than 15 were reported for RF sputtered thin films. This observation is confirmed by other studies for which high GFs are obtained only for nc-Ni/C thin films deposited by R.F. reactive sputtering in C_2H_2 atmosphere [17,30–35]. Hence, it is clear that according to the employed process, some physical properties of the material will not be the same.

In this study, we aimed to compare the electrical behavior of nc-Ni/C thin films having a wide range of chemical compositions deposited by two different plasma processes. The relationships between the structure and the electrical behavior of such nc-Ni/C thin films are investigated. The first process is a hybrid process which combines PVD and PECVD using CH_4 as a carbon precursor; it

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allows growing nc-Ni/C thin films with a hydrogenated amorphous carbon matrix. The second approach is a co-sputtering process, consisting in the simultaneous sputtering of nickel and carbon targets using a pure argon plasma; it allows synthesizing hydrogen-free nanocomposite films. By comparing these two deposition processes, we expect to highlight the role of hydrogen in the amorphous carbon matrix on the electrical transport of the nanocomposite films. The chemical composition of the thin films was determined using X-ray photoelectron spectroscopy (XPS). The hydrogen content was measured using elastic recoil detection analyses (ERDA). The micro-organization of the amorphous carbon matrix was studied using multi-wavelength Raman spectroscopy. The four probes method was used to access to the electrical conductivity of the films.

2. Experimental setup

2.1. Thin films deposition

2.1.1. Hybrid process

The nc-Ni/C:H films were deposited using a hybrid plasma process combining the sputtering of a nickel target and the deposition of carbon by PECVD using methane as a precursor. This process is described in detail elsewhere [3]. Briefly, a nickel target of 50 mm in diameter and 99.99% in purity was fixed to a magnetron source connected to a 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 role of the coil was to create an additional plasma between the magnetron and the substrate surface to enhance the methane decomposition [3]. A gas mixture composed of argon and methane was introduced to the chamber. The methane ratio is defined by:

$$\%CH_4 = \frac{\varphi_{CH_4}}{\varphi_{Ar} + \varphi_{CH_4}} \times 100 \tag{1}$$

where φ_{CH_4} and φ_{Ar} are the methane and argon flows, respectively.

In order to modify the chemical composition of the films, the methane ratio was varied between 0 and 72% by varying the gas flows injected in the reactor and keeping the total flow constant at 10 sccm. 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 was between 500 and 800 nm depending on the methane ratio injected in the deposition chamber. In pure argon plasma, only Ni atoms were sputtered from the target and pure Ni thin film was formed. When using a mixture of methane and argon, the plasma generated by the coil led to the dissociation of methane into hydrocarbon species. Therefore, simultaneously to the deposition of the sputtered nickel atoms, these hydrocarbons species are deposited onto the substrate, leading to the formation of nc-Ni/C:H films. All the film depositions were performed at floating potential.

2.1.2. Co-sputtering

The second process used to grow non-hydrogenated nickel/carbon nanocomposite (nc-Ni/C) thin films was a co-focal sputtering process. Two magnetrons sources in a co-focal geometry and located at 130 mm from the rotating substrate holder were used to simultaneously sputter a nickel and a graphite target. The two cathodes were equipped with two different targets: graphite (50 mm, 99.99 at.% in purity), and nickel (50 mm, 99,99 at.% in purity). The angle between the normal to the substrate surface and the normal to the targets surfaces was 30°. For this process and since the carbon precursor is solid, only argon was used as a sputtering gas. The deposition pressure was fixed to 0.5 Pa. The DC power applied to the graphite target was kept constant at 100 W, whereas the power applied to the nickel target was varied between 0 and 180 W. The simultaneous sputtering of nickel and carbon targets led to the growth of hydrogen-free nc-Ni/C thin films. Depending on the ratio between the power applied to the nickel target and the one applied to the graphite target (P_{Ni}/P_{Gr}), the deposition time was adjusted to obtain thicknesses around 500 nm on single crystal (100) silicon substrate. For electrical measurements, silica substrates were used to guaranty the electrical insulation of the films from the substrate. All the depositions were performed with substrates at floating potential.

2.2. Material characterization

The surface composition of the films was evaluated by XPS using a Kratos Nova spectrometer equipped with monochromatic Al Kα Radiation (1486.6 eV). Before each analysis, an argon erosion stage was carried out to eliminate the surface contamination. The argon ion energy was fixed to 500 eV, allowing to softly clean and remove the surface contamination layer while avoiding any possible drastic structural modifications of the material as well as preferential erosion. The erosion stage was performed during 120 s. The hydrogen content in the films was determined using ERDA on a Cockcroft-Walton tandem accelerator using a He^+ beam (2 MeV, 75° incidence angle with respect to the surface normal). The spectra were acquired by using silicon surface barrier detectors with scattering angle of 30°. A 13 μm thick Mylar foil was placed in front of the detector on the forward scattering angle to filter the H recoils from the He scattered particles. Previous calibration spectra were made for all the samples to evaluate the possible damages induced by successive exposure to the probing beam. The quantification of the ERDA data was obtained by using the cross section for the 1H(a,p)4He process given by Quillet et al. [36]. SEM micrographs were recorded with a Jeol 7600 F microscope operating at 5 kV. TEM observations were performed with a Hitachi H-9000 NAR microscope operating at 300 kV equipped with a LaB_6 filament. Near-UV micro Raman analyses were performed on a Horiba Jobin Yvon HR 800 UV spectrometer, using a He-Cd laser (λ = 325 nm corresponding to 3.81 eV). For the other wavelengths (λ = 458, 515, 633 and 788 nm, respectively corresponding to 2.71, 2.41, 1.96 and 1.57 eV) a Renishaw inVia Raman spectrometer was used. In films deposited by the hybrid process, a previous study [3] has revealed the presence of fcc nickel crystallites at low carbon content and a nickel carbide crystalline phase at a relatively high carbon content. For films deposited by co-sputtering, the XRD results are very similar to the one obtained in case of the hybrid process (Fig. S2 – Section 2 – Supporting information). To measure the electrical conductivity of the thin films, a four probes system was employed.

3. Experimental results

3.1. Chemical composition

For all the samples, only nickel, oxygen and carbon were detected with XPS. These elements were quantified using respectively the Ni 2p, O 1s, and C 1s core level peaks. The evolutions of the chemical composition as a function of the various deposition parameters for the two processes are presented in Fig. 1. The composition was also checked by energy dispersive X-ray spectroscopy (EDS). The evolution of composition given by EDS was found to be consistent with the one obtained by XPS (Fig. S1 – Section 1 - Supporting information). The hybrid plasma process