Materials Science Forum
ISSN: 1662-9752, Vol. 881, pp 471-474
doi:10.4028/www.scientific.net/MSF.881.471

Submitted: 2016-08-16
Accepted: 2016-08-16
Online: 2016-11-30

Production and Characterization of Carbon Thin Films by the Magnetron Sputtering Technique

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*In memoriam

Keywords: carbon thin films, magnetron sputtering, nanographite,

Abstract. Carbon thin films were produced by the magnetron sputtering technique. The deposition of the carbon films was performed on Co buffer-layers previously deposited on c-plane (0001) sapphire substrates. The samples were thermally treated under vacuum conditions and characterized by Raman spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD). The XRD peak related to the carbon film was observed and the Raman spectroscopy indicated a good degree of crystallinity of the carbon film.

Introduction

The unusual properties and structure of carbon films have been attracting the scientific interest recently. Their density, toughness and chemical resistance are better than those observed for any other hydrocarbon [1]. The growth of crystalline carbon films, such as graphite and graphene, cannot be described by a universal mechanism with specific routes and conditions. A variety of synthesis strategies and growth modes have been reported [2]. The best-known tool is the use of metal catalysts as buffer-layers through which free carbon radicals are formed, carbon is dissolved in the catalyst, and finally precipitates at the surface [3]. The role of the catalyst, the carbon solubility and diffusion in or on transition metal films, and the influence of temperature are very important issues in the growth of high-quality crystalline carbon films [4]. It has been reported [4] that amorphous carbon films are dissolved by Fe, Co, or Ni buffer-layers at temperatures above 600 °C. The nucleation and growth of crystalline carbon films occur by diffusion of carbon atoms through the buffer-layers [4].

Carbon films have been largely characterized by Raman spectroscopy technique [5 – 9]. The Raman spectra obtained from carbon films can be described in 5 stages of growing crystallization [10]. The first stage refers to the disordered carbon atoms, whereas the second one indicates a higher degree of crystallinity; single-crystalline graphite is associated to the third one, the double layer graphene to the fourth one, and finally the fifth one to monolayer graphene [10]. So when the G band intensity becomes equal to the 2D band intensity, and the D band disappears, double-layer graphene is formed. For double layer graphene, the 2D band is much higher than the G band. It is important to notice that the D band is also almost absent when graphite and graphene are formed indicating that the carbon film has crystallized [10]. Another interpretation for Raman spectra of carbon films has been reported [11] where the ratio I_D/I_G and the G band position define an amorphization/ordering trajectory of the films. When transiting from monocrystalline graphite to graphite nanocrystals and then to amorphous carbon and finally to the tetragonal amorphous carbon, the sp^2 groups become smaller, then topologically disordered, and the structures finally change from rings to chains, with the increase of sp^3 bonding [11]. The Raman spectra of amorphous and nanocrystalline carbon films have been studied [12] and the spectra of comercial graphite films, nanocrystalline diamond films and high temperature annealed nano graphite films have shown crucial differences in the D and G bands. While comercial graphite films have well difined D and G bands, the nanocrystalline diamond films has a broad peak at around 1150 cm^{-1} but the D and G bands are not well defined. The high temperature annealed nano graphite films show only the D and G bands with no other additional peaks [12].

In this work, the deposition of thin carbon films by magnetron sputtering on Co buffer-layers previously deposited on heated sapphire substrates was performed aiming to evaluate the degree of crystallinity of the carbon films, by using Raman spectroscopy and X-ray diffraction analyses.

Materials and methods

Deposition and heat treatment

The depositions of carbon/cobalt were performed using ATC 2000 Sputtering System (Aja International equipment) by DC magnetron sputtering technique. Kurt J. Lesker graphite target (99.999% pure) and an Alfa Aesar cobalt target (99.95 % pure) were used. C-plane (0001) sapphire with the dimension of 1x1 cm were used keeping the substrate/target distance at 15 cm. The substrate-holder was kept at 600°C by thermal radiation from internal incandescent lamp bulbs during the cobalt deposition process. The Co deposition was carried out in a mixture of Ar and 5% of H_2 during 16 min. The DC power supply was set to 100 W, the base pressure was 2 x 10^{-7} Torr, the working pressure was 5 mTorr, and the gas flow was set to 20 sccm. The C deposition was carried out during 60 min, the DC power was set to 150 W, the working pressure was 15 mTorr, the gas flow was 40 sccm, and the substrate temperature was kept to 18 °C. After the carbon deposition the samples were heat treated in a tubular furnace under the pressure of 2.85 x 10^{-5} Torr according to the following steps: 1) firstly the sample was heated (7°C/min) to 750°C; 2) the sample remained at the annealing temperature for 12 minutes and at this point it is expected that carbon dissolve into the cobalt film; 3) finally the sample was cooled down to room temperature.

Characterization

A Jeol table top scanning electron microscope (SEM) was used for the morphological characterization of the samples. A Raman spectrometer HORIBA JOBIN–YVON model LabRAM HR 800, operating with laser He–Ne 632.81 nm and a Rigaku Miniflex II X-ray diffractometer in theta-2theta configuration were used to study the crystallinity of the carbon films.

Results and discussion

Morphological observations

Scanning electron micrographs were obtained aiming to observe the surface morphology of the samples. Fig. 1 shows the surface of the carbon/cobalt film deposited on a heated sapphire substrate as previously described. Various cobalt particles of size varying between 76 and 150 nm can be seen in Fig. 1.

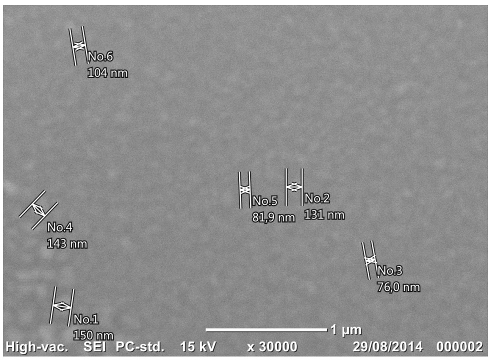

Fig. 1 – Surface morphology of the cobalt buffer-layer deposited on c-plane (0001) sapphire substrate, heated at 600 °C. The image was obtained by SEM.

Crystallinity of the films

The crystallinity of the carbon film was investigated by x-ray diffraction (XRD) and Raman spectroscopy. Fig. 2 shows the XRD pattern of the sample after the heat treatment. It can be seen a peak at ~ 2θ = 26.5° that can be associated to crystalline carbon (ICSD 01-089-8487). There is also a peak related to the sapphire substrate (Al_2O_3) at 2θ = 20.5° (ICSD 01-073-1199), and a peak at 2θ = 37° related to Co_3O_4 (ICSD 03-065-2902).

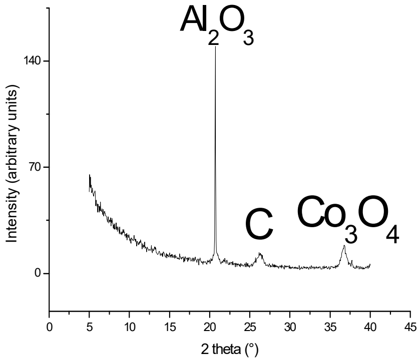

Fig. 2 – XRD pattern of the sample showing peaks related to the carbon film, the sapphire substrate, and the cobalt oxide.

Fig. 3a and 3b show the Raman spectrum before and after the heat treatment (750ºC, 12 min) of the samples, respectively. In Fig. 3a the Raman spectrum shows the D and G bands not well defined, and the $I_D/I_G = 0.90$, indicating that the sample has a high concentration of sp^2 bondings of carbon atoms, and that the carbon film cannot be be considered totally amorphous. It can be seen in the Raman spectrum showed in Fig. 3b, that the D and G bands are better defined, the 2D band is present and the $I_D/I_G = 0.87$. The decrease in the I_D/I_G ratio and the change in position of the G band, when compared to the data found in the literature [11], suggest an improvement in the crystallinity of the carbon film after the heat treatment. Comparing both spectra with those reported in the literature [12], the spectrum shown in Fig. 3a corresponds to high temperature annealed nano graphite. The spectrum shown in Fig. 3b is commonly observed in commercial graphite.

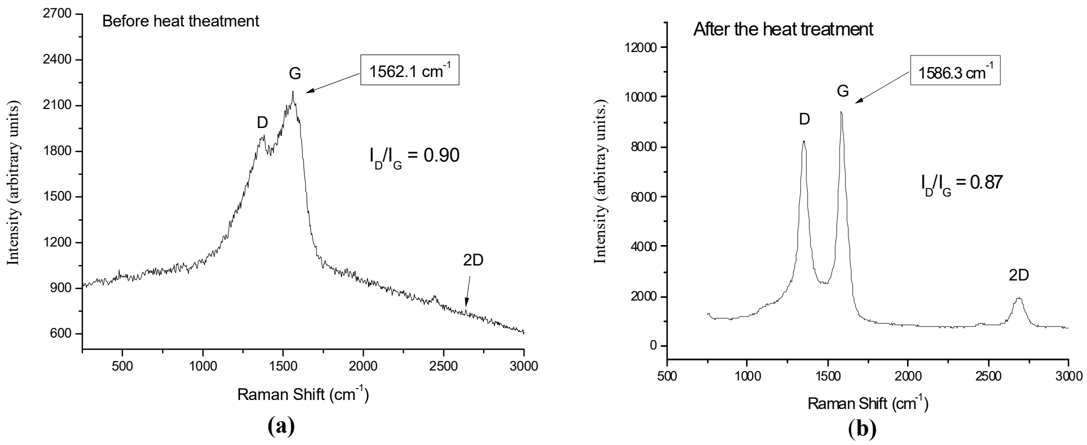

Fig. 3 – Raman spectra of the carbon films: (a) before the heat treatment and (b) after the heat treatment.

Conclusions

The magnetron sputtering technique was used for the deposition of both carbon and Co buffer-layer on c-plane (0001) sapphire substrates. The degree of crystallinity of the carbon thin films was evaluated. After the carbon depositon at 18ºC the film presented a good degree of crystallinity with Raman ratio of $I_D/I_G < 1$. The Raman spectrum of the heat treated film showed the separaton of D and G bands, and the presence of the 2D band that indicate an improved in the crystallinity resulting from the heat treatment procedure. The XRD analysis confirmed the existence of crystalline carbon structures. Based on these results, there is a strong motivation for future research aiming to improve the degree of crystallinity of the carbon thin films to obtain graphene using the magnetron sputtering technique.

Acknowledgements

This work was supported by the National Institute of Photonics (INCT de Fotônica) project granted by the Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq. The authors thank CNEN for the master´s scholarship.

References

[1] H.A. Amorim: Caracterização de Filmes Finos de Carbono Depositados por PECVD Mestrado (Dissertação). Campinas, 1995. Universidade Estadual de Campinas (UNICAMP/FEM). (SP)
[2] K.S. Subrahmanyam, S.R.C. Vivekchand, A. Govindaraj and C.N.R. Rao:J. Mater. Chem. Vol. 18 (2008), p. 1517.
[3] A. Barreiro, F. Börrnert, S.M. Avdoshenko, B. Rellinghaus, G. Cuniberti, M.H. Rümmeli, M.K. Vandersypen: Sci. Reports Vol. 3 (2013), p. 1115.
[4] J.A. Rodríguez-Manzo, C. Pham-Huu, F. Banhart: ACS Nano. Vol. 5 (2) (2011), p. 1529.
[5] Y. Wang, D.C. Alsmeyer, L.R. McCreery: Chem. Mater. Vol. 2 (5) (1990), p. 557.
[6] J.R. Soares, L.G. Cançado, N.P.S. Falcão, E.H. Martins Ferreira, C.A. Achete and A. Jorio: J. Ram. Spec. Vol. 44 (2) (2013), p. 283.
[7] M.S. Dresselhaus, A. Jorio and R. Saito: Annu. Rev. Condens. Matter Phys. Vol. 1 (2010), p. 89.
[8] S. Reich and C. Thomsen: Phil. Trans. R. Soc. Lond. A 362 (2004) 2271–2288.
[9] N. Shimodaira and A. Masui: J. Appl. Phys. Vol. 92 (2002), p. 902.
[10] A.N Yurkov, N.N. Melnik, V.V. Sychev, V.V. Savrans, D.V. Vlasov, and V.I. Konov: Bul. of the Lebedev Phys Inst. Vol. 9 (2011), p. 263.
[11] A.C. Ferrari, J. Robertson: Phil. Trans. A. Vol. 373 (2004), p. 2477.
[12] P.K. Chu, L. Li: Mat. Chem. & Pys. Vol. 96 (2006), p. 253.
[13] J.K. McDonough, Y. Gogotsi: Nature Vol. 23 (2014), p. 61.
[14] M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund. *Science of Fullerenes and Carbon Nanotubes.* (Academic Press, 1996).