Vacuum 112 (2015) 17–24

Contents lists available at ScienceDirect

Vacuum

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

Raman and thermal desorption spectroscopy analyses of amorphous graphite-like carbon films with incorporated xenon

G.A. Viana*, F.C. Marques

Universidade Estadual de Campinas, Unicamp, Instituto de Física "Gleb Wataghin", 13083-859 Campinas, SP, Brazil

A R T I C L E I N F O

Article history:
Received 30 July 2014
Received in revised form
21 October 2014
Accepted 24 October 2014
Available online 11 November 2014

Keywords:
Raman
Carbon
Sputtering
Xenon
TDS
Amorphous graphite-like carbon

A B S T R A C T

Structural and thermodynamic properties of xenon incorporated in amorphous carbon films deposited by means of a sputtering system free of vacuum pumping during the deposition were investigated by visible Raman (Vis–Raman) scattering and thermal desorption spectroscopy (TDS), respectively. Vis–Raman measurements, carried out before and after the xenon desorption, revealed a polycrystalline material rich in C-sp^2 sites that form randomly dispersed nanosized graphite clusters (nanocrystals) of approximately 1 nm. After xenon desorption, a compensating mechanism, activated by the thermal heating, promotes a more ordered C-sp^2 network as revealed by the linewidths of both D and G bands, as well as by the I_D/I_G ratio evolution. The TDS thermograms show that the xenon onset effusing temperature is approximately 120 °C. Besides, they also revealed two different regimes, at low and at high temperatures, associated with desorption of xenon atoms trapped either in an interconnecting void network or within the graphite nanocrystals. From the latter regime, the xenon diffusion free energy (activation energy) was determined to be 1.2 eV (115.7 kJ/mol) on the basis of the diffusion-limited desorption standard model.

1. Introduction

In the last decades, amorphous carbon (a-C) films have been extensively investigated by physicists, chemists, engineers and related researchers, attracted by the possibility of developing stable alloys with a distinct C-sp^2 to C-sp^3 ratio. This ratio would give desirable mechanical, optical and electromagnetic properties such as high hardness [1,2], chemical inertness and infrared transparence [3,4], a low friction coefficient [5] and high field emission [6–8]. Additionally, some studies have reported important biological features such as bio-, hemo- and neuro-compatibility [9–13], listing this type of material in a large number of biological applications. Recently, Gonçalves et al. [14] have proposed xenon-implanted amorphous carbon (Xe@a-C) as a potential material for anticancer treatment, generally named brachytherapy [15–17], based on the ^{124}Xe into ^{125}I transmutation promoted by thermal neutron bombardment. However, to carry out any type of *in vivo* experiment with Xe@a-C, or even with any type of a-C acting as a specific element driver (almost the same role as a drug delivery medium [18]), it is essential to investigate the thermal stability of a-C with the intended elements to be implanted, or incorporated, within its matrix. Moreover, despite the fact that some authors have reported on thermal desorption spectroscopy (TDS) results of post-applied Xe on carbon allotrope surfaces [19,20], such as highly oriented pyrolytic graphite (HOPG) and single-walled carbon nanotubes (SWCNT), no results have been reported on Xe incorporated in amorphous (graphite-like) carbon. In addition, all reported results are concerned with the incorporation of Xe after the deposition process of the film (conventional implantation) and not during the film deposition, as realized here.

Xe, because of its transmutation ability into iodine [14], was incorporated on graphite-like (a category of a-C) carbon thin films (Xe@a-GLC) by DC-sputtering that was free of vacuum pumping during the deposition process. The results of Vis–Raman and TDS measurements carried out on Xe@a-GLC are reported. By means of TDS, it was possible to investigate the host matrix thermostability through the Xe desorption behavior and to determine its thermodynamic parameters, such as the diffusion coefficient and the diffusion free energy (or activation energy). Structural changes in the carbon matrix, promoted by the thermal desorption process, were examined by Vis–Raman spectroscopy.

---

* Corresponding author. Tel./fax: +55 19 35215376.
E-mail address: gviana@gmail.com (G.A. Viana).

http://dx.doi.org/10.1016/j.vacuum.2014.10.019

2. Experimental details

2.1. Deposition details

The Xe@a-GLC films were deposited onto grounded corning glass (7059) and c-Si <111> substrates by DC-sputtering. The film deposited onto corning glass substrate was used to the optical transmission spectroscopy, while the one deposited onto c-Si substrate was used to the remained characterizations realized in this work. Previously to the depositions, the substrates were rinsed in thermal and ultrasonic bath of distilled water, ethanol, and acetone. The reactor chamber was evacuated prior to deposition to 10^{-8} Torr (~10^{-6} Pa). Concurrently, the walls of the chamber were heated up to 120 °C for 12 h to degas the trapped gases, mostly water vapor. Then, a gate valve connecting the chamber to the vacuum pumps (oil free) was closed, which ceased the pumping on the sputtering chamber. This procedure is desirable due to the use of expensive gases, such as ^{124}Xe. Depending on the deposition setup, the film deposition without vacuum pumping can save a very large quantity of gas, as reported elsewhere [21]. A controlled Xe flow was injected into the chamber until the pressure reached 4×10^{-2} Torr (~5 Pa). A 99.99% pure graphite target of 2 in × ¼ in, placed on a negatively biased electrode (cathode), was bombarded by Xe ions with a −4.8 kV DC bias voltage. The distance between the target and the substrates was of 2 in. A film thickness of 380 nm was measured with a Veeco Dektak-150 Surface Profiler. The deposition rate was of approximately 1.3 nm/min. A diagram of the deposition system is presented in Fig. 1.

2.2. Optical transmission spectroscopy

Visible and near-infrared optical transmission spectroscopy in the range of 350–2450 nm was carried out using a Perkin Elmer λ9 photospectrometer. The optical constants, refractive index and extinction coefficient were recovered from the transmittance data using the Pointwise Unconstrained Minimization Approach (PUMA) package [22–24].

2.3. Rutherford backscattering spectroscopy

Rutherford backscattering spectroscopy (RBS), used to determine the presence of Xe in the a-GLC matrix and to confirm the non-presence of spurious elements, was carried out using the following parameters: a He^{+} (α-particle) beam energy of $E = 2.2$ MeV, a charge of $Q = 40$ μC, a current of $I = 60$ nA and a detection angle of $\theta = 170°$. The RBS spectra were analyzed through the SIMNRA (Version 6.0) package [25–28].

2.4. Vis–Raman

Vis–Raman scattering spectroscopy was performed at room temperature using a confocal NT/MDT micro-Raman spectrometer with a He–Ne laser energy (wavelength) of 1.96 eV (633 nm) in a backscattering geometry as the excitation source. A beam of 35 mW was focused onto a spot with a diameter of 1 μm. The acquisition × accumulation time was 5 × 2 s. No sample damage promoted by the laser heating was observed after carrying out these measurements.

2.5. TDS

TDS measurements were carried out in a quartz tube that was evacuated to 10^{-8} Torr (~10^{-6} Pa) and heated up by a programmable furnace to approximately 1000 °C. The effused Xe was monitored by a Hiden (Model Halo 201) quadrupole mass spectrometer. A very low and accurately controlled flow of He was used as a system parameter of control during the TDS measurements.

2.6. Intrinsic stress

The intrinsic stress (σ) was calculated through the Stoney's equation [29,30] after determining the curvature radii of the substrate before and after the film deposition. The curvature radii were optically determined as described in Ref. [31].

2.7. Energy dispersive X-ray spectrometry

Energy dispersive x-ray spectrometry (EDS) was carried out in a high resolution scanning electron microscope FEI, model Inspect F50, equipped with an Oxford 80 mm^2 Silicon Drift Detector (SDD) operated at 8 kV.

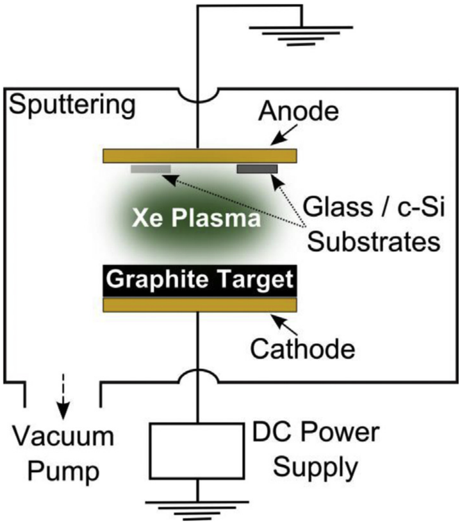

Fig. 1. Diagram of the DC-sputtering deposition system employed in this work.

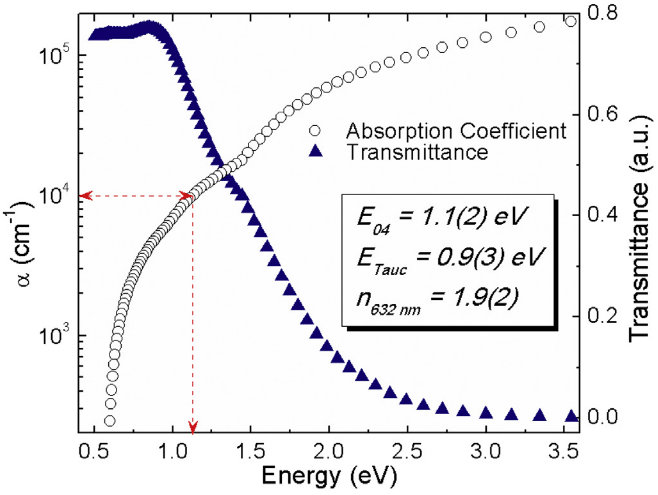

Fig. 2. Absorption coefficient (open circles) calculated from the transmittance (blue filled triangles) measured by visible and near-infrared transmission spectroscopy. The figure also presents the optical band gap and refractive index values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)