Fullerene-silicon polymerization evidence

Di Liscia EJ1,2*, Huck-Iriart C2,3, Halac EB1,2, Reinoso M1,2,3 and Huck H1,2

1Gerencia de Física, GlyA, Comisión Nacional de Energía Atómica, Avda. General Paz 1499, (1650) Gral. San Martín, Pcia. Buenos Aires, Argentina
2Escuela de Ciencia y Tecnología, Universidad Nacional de San Martín, Martín de Irigoyen 3100 (1650) Gral. San Martín, Pcia. Buenos Aires, Argentina
3CONICET, Rivadavia 1917, (1033) Buenos Aires, Argentina

Abstract

We report experimental results for C60-Si deposition by simultaneous thermal vaporization of fullerene source and chemical vapor deposition from silane source. The samples were characterized by Scanning Electron Microscopy, Energy-dispersive X-ray spectroscopy, Micro-Raman spectroscopy, Wide-angle X-ray scattering, X-ray photoelectron spectroscopy and its thermal stability was studied, discussed and compared with pure C60 deposited by the same method. A crystalline material was obtained and results suggest that a polymerization of fullerenes bridged by silicon atoms was achieved.

Introduction

Many works have been published about fullerenes and in particular about C60 or buckminsterfullerene, the most stable of fullerenes. Its properties are of great value in a diversity of applications like organic solar cells, hydrogen gas storage, metals strengthening/hardening, optical limiters, solid sensors, drug carriers, etc [1-8]. The fabrication of novel nanostructured materials from fullerenes is promising for several of these applications. However weak van der Waals bond between fullerenes is a serious limitation for some applications and polymerization has been a vastly studied solution. A variety of fulleren polymers were reported, using photopolymerization, pressure-induced polymerization, charge-transfer polymerization mediated by metals, electron beam-induced and plasma-induced polymerization as some strategies to prepare the so-called all-carbon polyfullerenes [9-15]. In particular, using Group IV elements in order to bind fullerene molecules has been investigated and both theoretical and experimental works about fullerenes molecules bonded by silicon bridges have been published by Masenelli et al. and Fujiwara et al. [16-19], which motivates the possibility to construct a polymerized fullerene-silicon material. We report experimental results for deposition of C60-Si material by simultaneous thermal vaporization of fullerene source and chemical vapor deposition from silane source. The materials produced were characterized by Scanning Electron Microscopy, (SEM), Energy-dispersive X-ray spectroscopy (EDS), Micro-Raman spectroscopy, Wide-angle X-ray scattering (WAXS), X-ray photoelectron spectroscopy (XPS) and their thermal stability was also studied.

Experimental

Fullerene and Si were deposited on Ge (100) and Si (100) wafers in a vacuum chamber. Fullerene source was pristine C60 powder (99.9% C60) evaporated at 550°C and silane (SiH4) was introduced in the chamber. The substrate was polarized at -30 V during the process. Substrates were cleaned by an acetone ultrasonic bath. For the sake of comparison, pure fullerene and pure silicon were separately deposited in the same conditions and by the methods used for the mixed samples. Also, in some samples pure fullerene and C60-Si were simultaneously deposited in different zones of the substrate, in order to compare the thermal stability of each material under the same conditions.

Both pure fullerene and fullerene-silicon samples were analyzed by Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS), Micro-Raman spectroscopy, Wide-angle X-ray scattering (WAXS) and X-ray photoelectron spectroscopy (XPS). Microscopy was carried on by a SEM Carl Zeiss NTS SUPRA 40. Raman spectra were recorded using a LabRAM HR Raman system (Horiba Jobin Yvon), equipped with a confocal microscope and a charge coupled device detector (CCD). A 100X objective lens was used, generating a 1.5 μm spot. An 1800 g/mm grating and 100 μm hole results in a 2 cm−1 spectral resolution. The 514 nm line of an Ar+ laser was used as excitation source. The laser power density over the sample was between 0.4 W.mm−2 and 4 W.mm−2. WAXS experiments were performed at INIFTA facilities using a XEUSS 1.0 equipment from XENOCS with a Kα-Cu radiation micro-source. A PILATUS-100K detector was used with 13 cm sample detector distance. One-dimensional curves were obtained by integration of the 2D data using the Foxtrot program. The scattering intensity distributions as a function of the scattering angle (2θ) were obtained in the 2θ range between 3° and 39°. The samples were placed in a motorized sample holder suitable for grazing incidence measurements at room temperature. XPS experiments were made using a Multitécnicos Specs equipped with a dual Ag/Al monochromatic X-ray source and a PHOIBOS 150 hemispheric analyzer in fixed analyzer transmission mode (FAT). The spectra were obtained with 30 eV energy and an Al monochromatic X-ray source.

Correspondence to: Di Liscia EJ, Gerencia de Física, GlyA, Comisión Nacional de Energía Atómica, Avda. General Paz 1499, (1650) Gral. San Martín, Pcia. Buenos Aires, Argentina, E-mail: diliscia@tandar.cnea.gov.ar

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anode at 300 W. The measurements were made on a 2 mm² area over
the sample and at different depths, removing material by sputtering.
For the data analysis, the spectra were fitted by Gaussian/Lorentzian
convolution functions with a previous optimization of the background
parameters. The background was modeled by a Shirley background
function.

Some deposited samples were annealed in vacuum (5.10⁻⁷ mbar) at
600° C after deposition in order to study the material thermal stability.

Results

SEM images for pure fullerene and C₆₀-Si samples are shown in
Figure 1. In the later, hexagonal structures of a few μm are clearly
observed, a major morphologic difference with pure C₆₀ samples.
EDS measurements over several points at different crystals on C₆₀-Si
samples grown on Ge (100) substrates, mainly detected both C and Si
presence at an atomic ratio less than 2% Si respect to C. Also, a weak
signal of oxygen was measured, which could have been absorbed after
deposition when exposed to air. Germanium corresponding to the
substrate was also observed.

Raman spectra from pristine, deposited fullerene and from C₆₀-Si
samples are shown in Figure 2. If a power density above 4 W/
mm² is used a clear change in the spectra is observed. The spectra
show no significant differences between the samples. The breathing
frequencies of pristine fullerene were observed in both deposited C₆₀
and C₆₀-Si samples, indicating that fullerenes were not broken during
deposition. Si-Si signal was not observed, suggesting that there was
not Si segregation. The spectra for pure silicon samples show the
characteristic bands of amorphous silicon [20].

WAXS results are shown in Figure 3. Peaks corresponding to cubic
and hexagonal (marked by arrows) fullerene structures are observed in
both deposited C₆₀ and C₆₀-Si samples [21]. Broader peaks than in the
case of pristine fullerene (our source material) could indicate smaller
grain sizes. Peak positions for the cubic symmetry are the same for all
samples and this implies that silicon atoms among fullerenes are not
significantly changing the lattice parameters nor the distance between
fullerenes. WAXS pattern’s peaks after 600° C in vacuum annealing
become a little thinner, but both cubic and hexagonal phases are still
present.

As cubic phase was the predominant one, numerical calculations
were made using the semiempirical many-body Tersoff potentials,
which had been used and achieved a good description of carbon
fullerenes, including several polymeric phases [14,22]. A zincblende
C₆₀-Si structure was found to be stable.

Results for XPS measurements for annealed C₆₀-Si samples are
shown in Figure 4. The peaks can be assigned to Si₂p, Si₂s, C₁s, and O₁s.

Figure 1. SEM images for pure deposited C₆₀ (a) and deposited C₆₀-Si (b).

Figure 2. Raman spectra for pure C₆₀ (a) and C₆₀-Si (b) deposited samples.

Figure 3. WAXS patterns from pristine C₆₀, deposited C₆₀ and C₆₀-Si on Si(100) wafer
and C₆₀-Si samples deposited on Si(100) and Ge(100) wafers and annealed to 600° C after
deposition.

The peaks position and width shown in Fig 4. lightly change at different
depths. An atom proportion of 53.4% carbon, 27.2% silicon and 19.4%
oxygen was found (after 60 seconds of argon sputtering at 1000 V),
which ensures an enough quantity of silicon in order to form a
zincblende structure as proposed in the simulation results.

In Figure 4 (b) and (c) the analysis for Si₂p and O₁s XPS signals is
shown. The envelop of each Si₂p contribution was the result of 2p 3/2
C\textsubscript{60} samples are completely wiped out when annealed in vacuum at 600º C, leaving the substrate totally clean, C\textsubscript{60}-Si samples morphology alterations after an annealing at 600º C, a temperature at which pure C\textsubscript{60} was completely removed while the mixed silicon are simultaneously deposited by the described method. This suggests that covalent bonds were formed between fullerenes when C\textsubscript{60} deposition is carried simultaneously with silicon deposition. Moreover, calculations employing the semiempirical many-body Tersoff potential found a zincblende structure to be stable and such configuration is in concordance with most of our experimental results.

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