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SiC bonding in $(C_{60})_nSi_m$ clusters

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Abstract. This paper deals with a new type of SiC bonding where silicon atom seems to bridge C_{60} molecules. We have studied films obtained by deposition of $(C_{60})_nSi_m$ clusters prepared in a laser vaporization source. Prior deposition, free ionized clusters were studied in a time-of-flight mass spectrometer. Mixed clusters $(C_{60})_nSi_m$ were clearly observed. Abundance and photofragmentation mass spectroscopies revealed the relatively high stability of the $(C_{60})_nSi_n^+$, $(C_{60})_nSi_{n-1}^+$ and $(C_{60})_nSi_{n-2}^+$ species. This observation is in favor of the arrangement of these complexes as polymers where the C_{60} cages may be bridged by a silicon atom. Free neutral clusters are then deposited onto substrate making up a nanogranular thin film ($\simeq$ 100 nm). The film is probed by Auger and X-ray photoemission spectroscopies, but above all by surface enhanced Raman scattering. The results suggest an unusual chemical bonding between silicon and carbon and the environment of the silicon atom is expected to be totally different from the sp^3 lattice: ten or twelve carbon neighbors might surround silicon atom. The bonding is discussed to the light of the so-called fullerene polymerization as observed for pure fullerite upon laser irradiation. This opens a new route for bridging C_{60} molecules together with an appreciable energy bonding, since the usual van der Waals bonding in fullerite could be replaced by an ionocovalent bond. Such an assumption must be checked in the future by XAS and EXAFS experiments.

PACS. 78.30.Na Fullerenes and related materials – 36.40.-c Atomic and molecular clusters

1 Introduction

Silicon carbide has attracted much interest as hard material and semiconductor with wide band-gap. In both crystalline, despite the existence of numerous polytypes, and amorphous phases, SiC bonding has been described in terms of covalent tetrahedrally sp^3 lattices with more or less chemical ordering following the state of disorder. A new SiC bonding has been still recognized in heterofullerenes [1] where one or several atoms take the place of carbon atoms in fullerene-like cluster. In this case, the SiC bonding is quite different from those observed in common lattices. Besides, since C_{60} fullerenes can be produced in macroscopic amounts and with high purity, the synthesis and study of derived materials have stimulated numerous experimental and theoretical works. Although metallic compounds of C_{60} have been extensively studied, only a few experiments involving group IV elements have been reported so far [2,3]. The pronounced covalent character of their bonding in the bulk phase could offer the possibility of forming strong and localized connections between the carbon cages so as to give rise to a new family of doped fullerides.

In this paper, we report the results of our study of a C_{60}+Si film obtained by deposition of $(C_{60})_nSi_m$ clusters produced in a laser vaporization source. The thin film was then studied by X-ray photoemission and Auger electron spectroscopies, but above all by surface enhanced Raman scattering. Comparing the Raman spectra of the C_{60}+Si film with those of a reference C_{60} film, we were brought to consider an unusual SiC bonding where silicon atoms may bridge two or more C_{60} molecules.

2 Experiment

A schematic view of the experiment is given in Fig. 1. Silicon-C_{60} clusters are produced in a double-target laser vaporization source, one of which consists of a monocrystalline silicon rod (GoodFellow Inc.) and the other is a flat disk (1.5 cm in diameter) obtained by pressing C_{60} powder (MER Inc.). Both targets are independently vaporized by two Nd:YAG pulsed laser beams (532 nm, 10 Hz, 15 ns width) perpendicular to each other and to the axis of the nucleation chamber. Both targets are set tangentially to this chamber in such a way that they face two aperture holes for the lasers impacts (inset in Fig. 1). In the same time, they undergo rotation and translation motions

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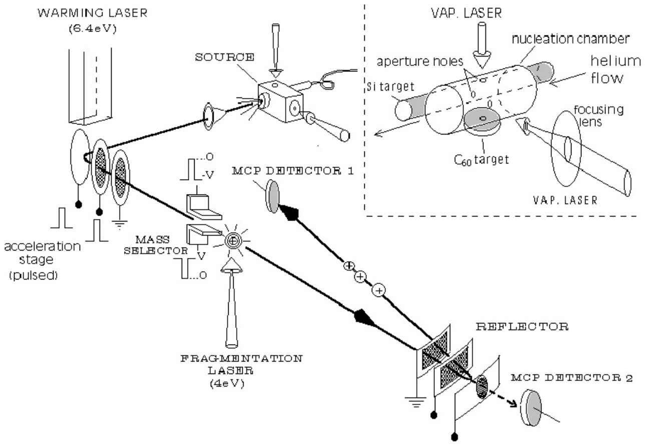

Fig. 1. Scheme of the experimental setup.

to make their abrasion more uniform. The quenching of the resultant plasma by a pulsed high pressure helium burst (4 to 6 bars) ensures the clusters growth in the source chamber, until the clusters-carrier gas mixture is expanded through a conical nozzle (2.5 mm in diameter). Nascent ionized clusters can then be deviated in a reflectron time-of-flight mass spectrometer to characterize the abundance mass distribution. Two additional lasers (ArF excimer laser, 6.4 eV and XeCl excimer laser, 4 eV) can also be used to carry out photofragmentation studies.

Thin films ($\simeq 100$ nm) are obtained by cluster deposition on the substrate in the ultrahigh vacuum (UHV) deposition chamber, charged clusters being deflected by an electric field. Silver-coated silicon wafers are used as substrate for X-ray photoemission spectroscopy (XPS) and Auger electron spectroscopy measurements, whereas LiF is used for Raman scattering. In this case, the sample is then protected by a silver coverage using a Knudsen cell, while XPS and Auger measurements, being carried out in a UHV analysis chamber, do not require any protection of the sample. Silver coverage also allows a surface enhancement of the Raman spectra.

3 Results and discussion

3.1 Gas phase study

The complete gas phase study already led to an article by Pellarin *et al.* [4], so we will briefly report here the main results. The naturally ionized $(C_{60})_n Si_m^+$ were analyzed by abundance (Fig. 2) and photofragmentation time-of-flight mass spectroscopy. The most abundant and stable clusters were found to be for $m = n$, $n-1$ or $n-2$, for which structures with a silicon atom linking two or more C_{60} molecules can be imagined. Additionally, $(C_{60})Si_m^+$ and $(C_{60})_n Si_m^+$ with $m \gg n$ were also observed. Photofragmentation studies showed that these clusters dissociate upon irradiation, losing Si_m^+ products or C_{60}^+, depending on the value of m. This is in favor of silicon clusters weakly bound to C_{60} molecules.

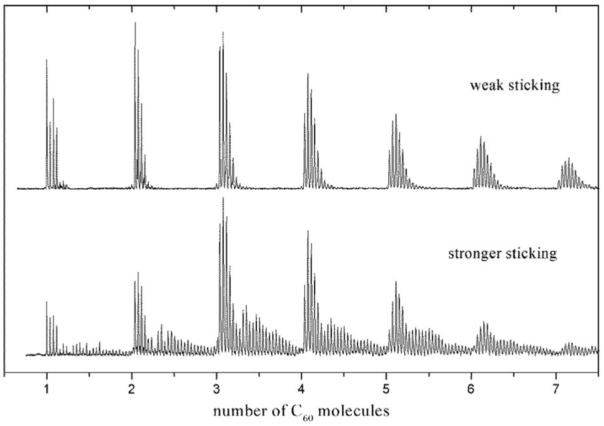

Fig. 2. Experimental mass spectra of $(C_{60})_n Si_m^+$ charged clusters obtained a two different degrees of silicon attachment, corresponding to two different source operation conditions.

3.2 XPS and Auger electron spectroscopy

XPS and Auger electron spectroscopy measurements were carried out *in situ* just after the cluster deposition. In a first time, XPS was used to determine the relative proportion of silicon and carbon in the film. Using the C_{1s} and the Si_{2p} core levels, we found that the stoichiometry was about one silicon atom per C_{60} molecule. Moreover, the XPS study revealed that the silicon does not segregate in the film: the Si_{2p} line does not correspond to Si with silicon neighbors, neither crystallized nor amorphous silicon.

In a second time, Auger electron spectroscopy permitted to check that there was no oxygen in the film. Besides, the Si_{LVV} and C_{KLL} lines were measured. They confirmed that the silicon atoms had not gathered together, for the Si_{LVV} line does not correspond neither to silicon diamond, nor to amorphous silicon. Furthermore, the Si_{LVV} line shape was found to be unusual, reflecting an unusual valence band because the shape of an Auger line is related to the electronic structure [5].

3.3 Raman scattering

As it was said before (Sect. 2), the silver coating protects the sample against oxidation, but it also allows surface enhanced Raman scattering to occur. Experiments were carried out with a Dilor micro-Raman spectrometer, using a green argon laser (514.5 nm) on the C_{60}+Si film and on a reference C_{60} film obtained in the same conditions, by laser vaporization of a C_{60} target and cluster deposition.

Concerning the C_{60} film, we can identify nine of the ten Raman active vibrational modes of the C_{60} molecule (Fig. 3). Let us remind that the C_{60} molecule possesses $3 \times 60 - 6 = 174$ vibrational modes, corresponding to 46 different frequencies, 10 of which are Raman active (Table 1). Because of the weak van der Waals interactions between the C_{60} molecules, the peaks observed in the Raman spectrum of the film are almost those of a single

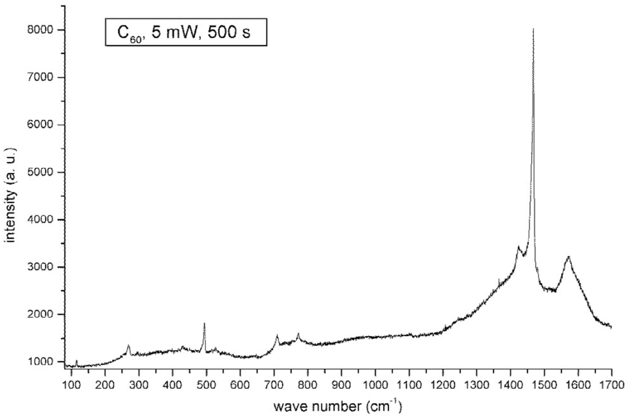

Fig. 3. Raman spectrum of the reference C_{60} film.

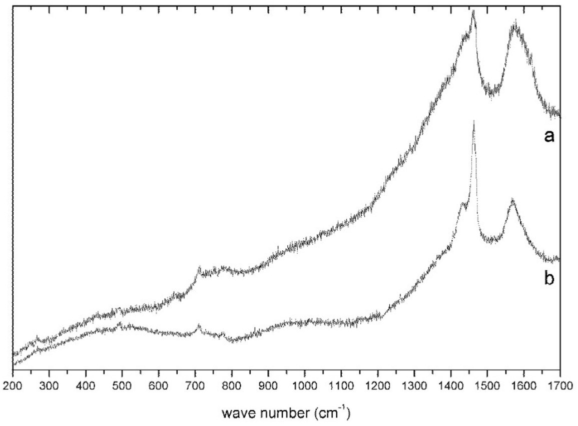

Fig. 4. Raman spectra of the C_{60}+Si film recorded with a three months interval. (b) was recorded just after the deposition while (a) was recorded three months later.

Table 1. Vibrational modes observed in Raman scattering.

Exp.^{a}	Exp.^{b}	Exp.^{c}	Mode	Calc.^{d}
255.5				
269	270	273	$H_g(1)$	269
296				
430	430	432.5	$H_g(2)$	439
488.5				
494	494	497.5	$A_g(1)$	492
527.5	526		$F_{1u}(1)^*$	505
709.5	710	711	$H_g(3)$	708
772	770	775	$H_g(4)$	788
		1101	$H_g(5)$	1102
1243	1252	1251	$H_g(6)$	1217
1424	1426	1426.5	$H_g(7)$	1401
1467.5$^\sharp$	1468	1470	$A_g(2)$	1468
1572	1572	1577.5	$H_g(8)$	1575

^{a}Frequencies (in cm^{-1}) observed in this work.

^{b}Frequencies (in cm^{-1}) observed by Shi *et al.* [6].

^{c}Frequencies (in cm^{-1}) observed by Dong *et al.* [7].

^{d}Frequencies (in cm^{-1}) calculated by Jishi *et al.* [8].

*inactive Raman mode.

$^\sharp$Peak made of several peaks in fact (see text).

molecule. Some modes correspond in fact to several peaks: the $H_g(1)$ mode has split in three peaks at 255.5, 269 and 296 cm^{-1}, the $A_g(1)$ mode corresponds to two lines at 488.5 and 494 cm^{-1}, and the $A_g(2)$ breathing mode (pentagonal pinch) peak, situated around 1467.5 cm^{-1}, is made of three different peaks. These peaks, not observed in pure C_{60} spectra, are attributed to phototransformed C_{60}. Indeed, the film undergoes a transformation upon laser irradiation. This phototransformation has already been studied [9–12] and is usually referred to as a polymerization, following a 2+2 cycloaddition mechanism [13]. The $A_g(2)$ peak corresponding to single C_{60} molecules is the highest of the three peaks, situated at 1468 cm^{-1}. The other peaks could be assigned to different $(C_{60})_n$ polymers. A kinetic study showed that even for a quite low laser power the film phototransforms. This transformation is evidenced by the relative decrease of the intensity of the peaks corresponding to single C_{60} molecules (269 cm^{-1}, 494 cm^{-1} and 1468 cm^{-1}), but it must be noticed that the peaks attributed to C_{60} polymers do not grow in exchange. It also seems that some amount of polymerized C_{60} is initially present.

Looking to the C_{60}+Si spectra (Fig. 4), we still can discern the vibrational modes of C_{60} and peaks that were attributed to phototransformed C_{60}. The spectra are yet quite different from the one of the C_{60} film: every peak is less intense, namely the lone C_{60} $A_g(2)$ mode. There is also a striking change in the spectrum during three months, mainly for the $A_g(2)$ peak, whereas there is no evolution for the C_{60} film, although both samples were prepared in UHV and protected by a silver coating. Besides, kinetic studies showed that there was no more evolution of the spectrum upon laser irradiation.

Let us now compare the Raman spectra of pure C_{60} powder, the C_{60} film, the phototransformed C_{60} film, the C_{60}+Si film freshly prepared and three months later. We can see (Fig. 5) that the phototransformed C_{60} film spectrum is very close to the C_{60}+Si film one, the more recent spectrum being even closer. The single C_{60} $A_g(2)$ mode situated at 1468 cm^{-1} has almost disappeared in both spectra. They are also very similar in the small wave number region. These results can be analyzed in term of polymerization. Indeed, it is commonly admitted that the phototransformation of C_{60} is a polymerization, thus if we consider that when we put silicon atoms into the film they bridge C_{60} molecules together, it is not surprising that the C_{60}+Si film and the phototransformed C_{60} film have almost the same Raman spectrum. This assumption can also explain the fact that there is no more evolution of the C_{60}+Si film spectrum upon laser irradiation, because if silicon atoms are linked to C_{60} molecules and

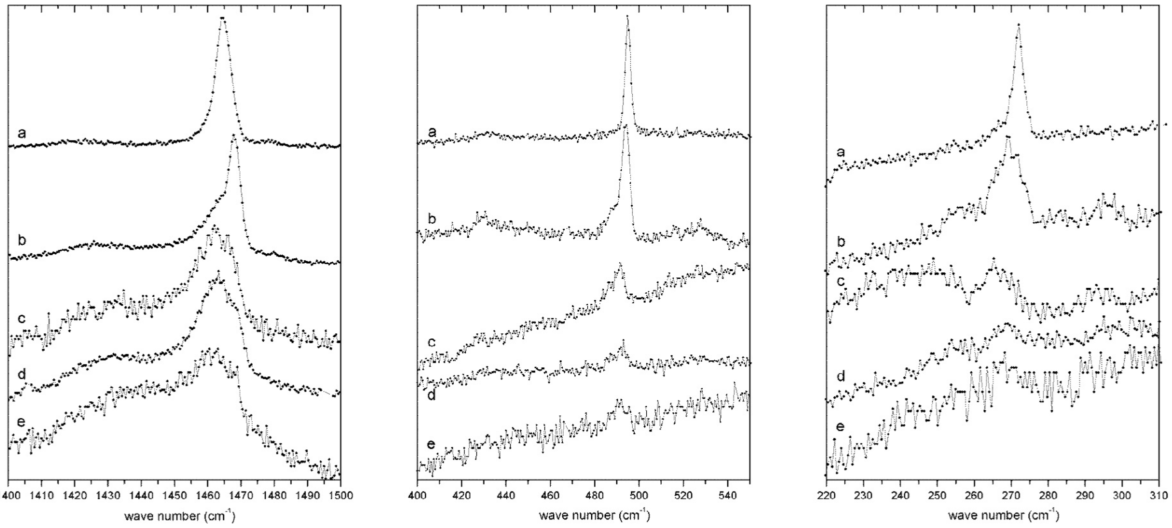

Fig. 5. Comparison between different Raman spectra of pure C_{60} powder (a), the C_{60} film (b), the phototransformed C_{60} film (c), the C_{60}+Si film freshly prepared (d) and three months later (e). The spectra are arbitrarily scaled.

form polymers, photopolymerization of C_{60} can no more occur. However, according to the time evolution of the Raman spectrum, this Si-assisted polymerization must be a slow phenomenon. Initially there are some C_{60}+Si polymers and/or C_{60} polymers in the C_{60}+Si film (peaks not present in the pure C_{60} powder), but it remains single C_{60} molecules and silicon atoms not bound to C_{60} molecules. We have then to answer the question: where were initially these silicon atoms? It would be consistent with the gas phase results to have C_{60} clusters, Si clusters and C_{60}+Si polymers initially present in the film, but we can not clearly identify Si-rich regions neither with XPS nor with Raman scattering. Another question we have to think about is: why does the intensity of each peak decrease? In our Raman spectra, the polymerization is evidenced by the decrease of the intensity of single C_{60} peaks, but the peaks attributed to polymers do not grow. Let us remind that it is very difficult to do quantitative measurements with Raman scattering because we do not know the polarizabilities, that is to say the ratio between the intensity of a peak and the population. Thus, a decrease of the Raman signal can also be due to a decrease of the polarizability, and surface enhanced Raman scattering could complicate the situation. In the case of the phototransformation of the C_{60} film, we have also to envisage that some C_{60} could be destroyed by the laser radiation.

4 Conclusion

We have studied the interaction between silicon and C_{60}, both in the free $(C_{60})_n\mathrm{Si}_m^+$ clusters and in C_{60}+Si films obtained by cluster deposition. We find that in the gas phase, silicon may link two or more C_{60} molecules, to form stable polymers. We then compare the Raman spectra of a reference C_{60} film with the one of the C_{60}+Si film. The latter is very close to the spectrum of phototransformed C_{60}, that is to say polymerized C_{60}. We can therefore consider that silicon atoms are bridging C_{60} molecules. It would mean that we are in presence of a completely new kind of SiC bonding, because we can not consider the usual sp^3 covalent bonding. We have to envisage a Si atom surrounded by maybe ten or twelve carbon atoms. This assumption have to be confirmed by other experiments, like EXAFS which could allow us to determine the local environment of silicon atoms.

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