Raman scattering of C$_{60}$ molecules embedded in porous silicon

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Received 18 September 1996; accepted for publication 29 October 1996
Communicated by L.J. Sham

Abstract

Raman spectra of C$_{60}$ molecules embedded in porous silicon (PS) through both physical deposition and chemical coupling were examined in the wavenumber ranges 400–550 and 1400–1500 cm$^{-1}$. Some new vibrational modes relevant to C$_{60}$ molecular environments and disorder effects inside solid C$_{60}$ were obtained with large intensities. Particularly, a downshift of the pinch A$_g$ mode which is sensitive to charge on the C$_{60}$ was observed of more than 12 cm$^{-1}$, indicating a charge transfer of at least 2 electrons per C$_{60}$ molecule in our samples. The experimental result is consistent with our previous analysis that the enhanced photoluminescence of the C$_{60}$ molecules embedded in PS arises from the radiative recombination of carriers which form in PS and then transfer to C$_{60}$ molecules.

PACS: 78.30.-j; 68.35.Ja; 82.65.-i

Porous silicon (PS) as a kind of new nanometer material with intense red–green emission has been investigated widely in theories and experiments over the past five years. However, its instability in structure and light-emission has regrettably limited its applications. In recent years, much attention has been paid to other Si-based light-emitting materials due to their great potentials in optoelectronics and the great demand of full-color displays. Many Si-based materials have been developed and their photoluminescence (PL) properties have also been explored [1–6]. On the other hand, it is well known that fullerene (C$_{60}$), with a highly symmetrical structure and various unusual physical properties [7,8], can only emit weak PL at room temperature [9,10] but its properties can change with environments. Hamilton and co-workers [11] reported the white PL of the C$_{60}$ molecules confined in cages of zeolite at room temperature. This experiment indicates that if C$_{60}$ molecules are placed in certain environments, we can expect to observe an improved PL at room temperature related to C$_{60}$ molecules. In a previous work [12], we embedded C$_{60}$ molecules in the pores of PS by both physical deposition and chemical coupling and then examined the PL spectra. The obtained results show that the embedded C$_{60}$
molecules can emit PL at room temperature as intense as that of ordinary PS and the C\textsubscript{60} molecules in different states may show different PL spectra. Further analysis of the PL excitation spectra indicates that the excitation process in the embedded C\textsubscript{60} molecules is completely similar to that in PS. The enhanced PL mainly arises from the radiative recombination of carriers which form in PS and then transfer to C\textsubscript{60} molecules.

From the beginning Raman spectroscopy proved to be a very useful tool to watch the doping process [13–17]. Especially, a strictly linear relation between charge on the C\textsubscript{60} and the position of the Raman line for the pinch mode was clearly stated and a quasilinear shift of the As pinch mode of about 6 cm\textsuperscript{-1} per elementary charge on the C\textsubscript{60} molecules was observed [18]. In view of these theoretical and experimental results, in this Letter we extend our original work [12] by examining the Raman spectroscopy of the embedded C\textsubscript{60} molecules in the frequency range of the A\textsubscript{g} pinch mode. Our aim is to present its microstructure and to find evidence for the carrier transfer from PS to the embedded C\textsubscript{60} molecules by means of Raman scattering. The obtained results are in agreement with our previous conclusion. The frequency of the A\textsubscript{g} mode shifts down by more than 12 cm\textsuperscript{-1}, indicating a charge transfer of at least 2 electrons per C\textsubscript{60} molecule in the major portion of our samples.

The starting PS samples were made from ⟨100⟩ oriented p-type silicon substrates of 1–3 \Omega cm resistivity, with a thickness of 400 \mu m. PS layers of thickness \sim 20 \mu m were formed by anodization in an electrolyte of ratio 2 to 1 of HF: C\textsubscript{2}H\textsubscript{5}OH with a current density of \textit{J} = 15 mA/cm\textsuperscript{2}. Two kinds of PS samples with embedded C\textsubscript{60} molecules were prepared, one by physical deposition (sample A) and the other by chemical coupling (sample B) as described before [12]. For the sample A, a 4 \times 10\textsuperscript{-4} M C\textsubscript{60}/toluene solution was directly dropped uniformly onto the starting PS, and about 1 mg/cm\textsuperscript{2} C\textsubscript{60} molecules survived in the pores after the toluene volatilized. The sample was then washed by toluene to remove the major free C\textsubscript{60} molecules existing in the pores. After the treatment described above, these surviving C\textsubscript{60} molecules exist in different states, some of them adjacent to the Si atoms of the highly absorbent pore wall; others in the pores are of free and perfect or oxygen-free C\textsubscript{60} molecular structure [19]. For the sample B, the C\textsubscript{60} molecules contained in 4 \times 10\textsuperscript{-4} M C\textsubscript{60}/toluene were covalently tethered to the pore wall of the starting PS by the silane coupling agent [CH\textsubscript{3}(C\textsubscript{2}H\textsubscript{5}O)\textsubscript{2}Si(CH\textsubscript{2}-NHCH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{2})] [20]. The experiment was as follows: First, the coupling agent/ethanol (1 \times 10\textsuperscript{-2} M) was dropped onto the surface of PS, so the coupling agent molecules were combined with PS through Si–O–Si bonds [21]; Second, the remaining uncombined coupling was washed away by toluene and a 4 \times 10\textsuperscript{-4} M C\textsubscript{60}/toluene solution was dropped on the treated PS wafers. In this process, some carbon–carbon double bonds in the C\textsubscript{60} molecules were broken and combined with the amine groups of the silane coupling agent [21]. The surplus C\textsubscript{60} molecules then accumulated in the pores in the polycrystalline form. Finally, the free uncombined C\textsubscript{60} molecules in the pores were washed away by toluene again.

Raman spectroscopic measurements were carried out on a SPEX 1403 Raman spectrometer with a double monochromator system. A cooled RCA 3103A photo-multiplier tube and photon counting electronics interfaced to a microcomputer were used to collect and analyze the data. In order to weaken high PL background, the 496.5 nm line of an Ar\textsuperscript{+} laser was employed as excitation beam. To avoid changes in the structures of C\textsubscript{60} molecules and PS caused by laser irradiation, a low laser power of 15 mW focused at an area of about \pi \times 0.8^2 \text{ mm}^2 was selected to illuminate the samples. A good signal to noise ratio could be obtained with reasonable integration times even though the scattering background from the PL increased with vibrational mode frequency. All experiments were performed in air and in unpolarized backscattering geometry. The spectral resolution of the instrument was 2 cm\textsuperscript{-1} and the scanning accuracy 1 cm\textsuperscript{-1}.

Figs. 1a and 1b show the Raman spectra of sample A with physical deposition, measured in the two frequency ranges 400–550 and 1400–1500 cm\textsuperscript{-1}. The figure displays the high PL scattering background and intense Raman peak of ordinary PS structure with asymmetric broad lineshape. In addition, eight vibrational modes related to the embedded C\textsubscript{60} molecules can be observed with large intensities. Their frequencies are given in Table 1. For comparison, the Raman modes of perfect C\textsubscript{60} molecules are
also listed in Table 1. It can be seen from Table 1
that the embedded $C_{60}$ molecules show more Raman
vibrational modes. The corresponding Raman spectra
of sample B with chemical coupling are shown in
Figs. 2a and 2b. In addition to the Raman peak of
ordinary PS structure, the figure also clearly displays
seven Raman vibrational modes whose frequencies
are different from those obtained from the sample A.
The frequencies of these modes are also listed in
Table 1. However, the figure is noteworthy in two
aspects: First, the mode at $504 \text{ cm}^{-1}$ appears as a
wing of the PS phonon mode. In our previous work
[25], the mode was attributed to the contribution of
both longitudinal and transverse optical phonons at
phonon wavevector $q \neq 0$. To identify its origin, we
examined the irradiation time dependence of its fre-

tency. The obtained result indicates that its inten-
sity and frequency hardly changed during irradiation
for more than 60 min. Therefore, the $504 \text{ cm}^{-1}$
mode is not related to ordinary PS structure but
depends on the embedded $C_{60}$ molecules; Second,
the two modes at $466$ and $492 \text{ cm}^{-1}$ clearly display
broad lineshapes consisting of two small peaks. These
results above indicate that the $C_{60}$ molecules under
different environments have different vibrational
properties.

In the 174 vibrational modes of perfect $C_{60}$
molecules, only two $A_{g}$ and eight $H_{g}$ modes are
Raman active and four $F_{1u}$ modes are infrared ac-
tive. These Raman active modes appear as intense
lines in the Raman spectrum of solid $C_{60}$ at room
temperature. When perfect $C_{60}$ molecules situate in
the crystalline environments, some of the degenera-
cies of the vibrational modes are lifted and their
splitting can be observed due to the crystal field. In
addition, the disorder effects in solid $C_{60}$ will also
cause the appearance of some additional peaks. From
Table 1, we can see that the number of the vibra-
tional modes in the embedded $C_{60}$ molecules is
obviously larger than that in the perfect $C_{60}$
molecules. Also, certain modes such as those ob-
erved at $526$ (sample A) and $504 \text{ cm}^{-1}$ (sample B)
are suggested by theory to have $F_{1u}$ symmetry [24]
and thus should not be Raman active, but now they

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<td>The partial Raman vibrational frequencies (cm$^{-1}$) of perfect $C_{60}$ molecules (Refs. [22–24]) and the embedded $C_{60}$ molecules in the frequency ranges 400–550 and 1400–1500 cm$^{-1}$</td>
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Fig. 1. Raman spectra of sample A with physical deposition in the wavenumber ranges (a) 400–550 cm$^{-1}$ and (b) 1400–1500 cm$^{-1}$. Eight vibrational modes related to the embedded $C_{60}$ molecules can be observed.
Raman Shift (cm$^{-1}$).

Fig. 2. Raman spectra of sample B with chemical coupling in the wavenumber ranges (a) 400–550 cm$^{-1}$ and (b) 1400–1500 cm$^{-1}$.

Seven vibrational modes related to the embedded C$_{60}$ molecules can be observed and the two modes at 466 and 492 cm$^{-1}$ clearly show broad lineshapes consisting of two small peaks.

become Raman active. These results indicate that some additional features in the obtained spectra are mainly connected with the C$_{60}$ environments and disorder effects within solid C$_{60}$ that remove the pure icosohedral molecular symmetry. For the sample B with chemical coupling, according to the self-assembly property [20] and scanning tunneling microscopy observation [26], we can infer that the C$_{60}$ molecules in the pores can form multilayer structures with hexagonal and simple cubic arrays, and therefore have more complicated couplings with PS. This is confirmed by more splitting features of the Raman modes shown in Fig. 2.

The most characteristic Raman mode related to the carrier transfer in the PL spectra is the A$_g$(2) pentagonal pinch mode at the frequency of 1464 cm$^{-1}$ [18]. The mode will shift to the low frequency region when there exists a charge transfer to C$_{60}$ molecules. For our experimental results, many reasons may cause the downshift of the A$_g$(2) mode: charge transfer, molecular distortions, covalency effects, etc. However, our previous study [12] on the PL spectra has verified that the enhanced PL of the embedded C$_{60}$ molecules mainly arises from carrier transfer from PS to C$_{60}$ molecules. Therefore, the downshift of the A$_g$(2) mode is also mainly connected with the charge transfer. In the obtained Raman spectra, modes at 1449 and 1473 cm$^{-1}$ (in sample A) as well as 1445, 1466 and 1484 cm$^{-1}$ (in sample B) are observed, instead of the A$_g$(2) mode at 1464 cm$^{-1}$. This raises the question: which mode is really related to the A$_g$(2) mode? According to the previous results on Raman scattering of C$_{60}$ molecules [13–18], it the modes at 1449 and 1445 cm$^{-1}$ cannot be observed in the Raman spectra of perfect C$_{60}$ molecules. Their appearances are the result of the downshift of the A$_g$(2) mode resulting from the charge transfer to C$_{60}$ molecules. Thus, it can be inferred that for our results there exists a charge transfer of at least 2 electrons from PS per C$_{60}$ molecule in the major portion of the samples under consideration. For the sample B with chemical coupling, the A$_g$(2) mode is shifted to lower frequency than for the sample A with physical deposition, indicative of stronger bonding and, therefore, greater electron transfer to the C$_{60}$. However, the origins of these modes at 1473, 1466 and 1484 cm$^{-1}$ must be addressed. Similar to the situation for the C$_{60}$ molecules on silver and Si surfaces [26–28], their origins can be explained according to the coverage dependence of C$_{60}$ molecules on material surfaces. At lowest coverage, the A$_g$(2) mode appears as a single peak at about 1430 cm$^{-1}$. As the coverage increases, it splits into a doublet, corresponding to the 1449 and 1473 cm$^{-1}$ modes in our sample A as shown in Fig. 1. At the highest coverage, three peaks can be observed, corresponding to the 1445, 1466 and 1484 cm$^{-1}$ modes in our sample B as shown in Fig. 2. The A$_g$(1) mode at 492 cm$^{-1}$ also splits into an obvious doublet. These results are completely consistent with our observation. This coverage effect can only be the result of the interaction of the C$_{60}$ molecules with the PS surface which leads to the charge transfer. In addition, they may also be slightly affected by the oxygen occupation in
the interstitial positions of the C$_{60}$ molecules in the pores [19].

In conclusion, we have investigated Raman scattering of the C$_{60}$ molecules embedded in PS through both physical deposition and chemical coupling. A charge transfer of at least 2 electrons per C$_{60}$ molecule is determined according to the frequency shift of the pinch A$_2$ mode. This result is consistent with our previous analysis that the enhanced PL from the embedded C$_{60}$ molecules arises from the carrier transfer from PS to C$_{60}$ molecules.

One of the authors (X.L. Wu) would like to thank Dr. Y. Jin for his help in the experimental measurements. The work was supported by the Croucher Foundation of Hong Kong and the Ke-li Fellowship of Nanjing University.

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