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## A study on fullerene incorporated into a porous silicon matrix

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**Abstract.** Samples with low-energy C<sub>60</sub> ions implanted into porous silicon were fabricated with the ionized cluster beam deposition approach for improving the light emission of C<sub>60</sub>. Depth analysis by secondary-ion mass spectroscopy showed that C<sub>60</sub> had been incorporated into porous silicon. The photoluminescence spectrum measured under excitation by an Ar<sup>+</sup> laser (514.4 nm) at room temperature showed a large number of intense and well resolved fine-structure peaks. These features indicated the strong coupling of vibrational progressions with the electron states of C<sub>60</sub>, induced by the interaction between the C<sub>60</sub> molecule and the nanometre-sized silicon particles.

A study on new functional material is one of the most active fields currently. C<sub>60</sub> acts as a new functional molecule that has been widely studied since 1990. With a highest occupied molecular orbit (HOMO)–lowest unoccupied molecular orbital (LUMO) gap of about 1.9 eV in the molecular state [1] (and down to 1.5 eV in the solid state [2, 3]), a C<sub>60</sub> film shows the characteristics of a semiconductor. From the applied point of view, it is very important to study the optical properties of C<sub>60</sub>. As a main feature, the photoluminescence (PL) has been measured in either different morphologies or different matrices by many groups [1, 4–6]. However, different optical spectra have been reported even for the nominally same morphologies. Thus, the microscopic interpretation of the fluorescence spectra, in particular for the solid phase [4–7], has been controversial up to now. Generally the light emission efficiency is very low at room temperature and slightly enhanced at low temperatures. The spectra show a broad profile with some fine structures interpreted as vibrational progression [4, 6]. A special example is the light emission spectra of a single crystal of pristine C<sub>60</sub> consisting of several pair peaks of false origins measured by Guss *et al* [4]. They found that each pair corresponded to C<sub>60</sub> itself or to a defect, an X-trap (oxygen or other chemical impurities), through which the radiative coupling of electron states with vibrational modes  $t_{1g}$  and  $t_g$  were strengthened. They suggested that the light emission was affected seriously by the morphologies of C<sub>60</sub>. Several groups [8–10] have been trying to change the optical properties of C<sub>60</sub> through trapping C<sub>60</sub> in a microporous solid with a channel diameter greater than 1 nm. They found marked enhancement in light emission and a blue shift in

the photon energy relative to those of pristine  $C_{60}$ . The quantum confinement effect (QCE) was considered to be the main reason for the increasing emission efficiency and the energy shift. The QCE or interaction of  $C_{60}$  with morphologies may cause changes in symmetry which induce the forbidden transition to be broken partially.

A different matrix will lead to different optical characteristics for the  $C_{60}$  embedded in it, due to the QCE geometry and host-guest interactions. So the selection of the matrix is important to change the light emission of  $C_{60}$ . Considering the diameter of  $C_{60}$  molecule to be about 1 nm and pores of diameter about 1.5 nm in the sponge-like structure of porous silicon (PS), we think that PS is suitable as a matrix for trapping  $C_{60}$ .  $C_{60}$  may be put into the PS matrix readily and a strong interaction may be expected. Here we report the results of our studies on the PS sample implanted with  $C_{60}$  at room temperature. The PL spectrum features a baseline profile similar to that of PS as well as a large number of fine peaks on the baseline. Depth analysis of the samples embedded with  $C_{60}$  using the secondary-ion mass spectrum approach shows that  $C_{60}$  has been incorporated into PS. The fine structures of the PL spectrum are studied and assigned to the vibrational modes of  $C_{60}$ .

PS was manufactured by anodization of boron-doped-type (100) crystalline silicon wafers of resistivity 5–10  $\Omega\text{ cm}^{-2}$  in HF solution in ethanol (1:1 by weight). The constant etching current density was about 40 mA  $\text{cm}^{-2}$  for 10 min in the dark. This is similar to the preparation of a wafer described in more detail elsewhere [11, 12]. After rinsing with deionized water and drying completely in air, stable bright-orange colour PL from the sample can be observed with the naked eye under UV lamp irradiation. Then low-energy  $C_{60}$  ions of purity 99.5% were deposited on the PS samples in the ionized cluster beam deposition apparatus. In fact,  $C_{60}$  evaporated on the surface of sample is purer since the evaporation temperature of  $C_{60}$  is much lower than those of  $C_{70}$  and other larger fullerenes. By increasing the energy of  $C_{60}$  ions to 400 eV,  $C_{60}$  may be broken up into amorphous carbon on the silicon substrate, which has been studied well in our previous work [13]. To avoid fragmentation of  $C_{60}$  and damage to the structure of PS by the collision of  $C_{60}$  with the surface of PS, the energy should be lower than 200 eV. The thickness of the  $C_{60}$  film is about 200 Å. In order to observe conveniently the changes in the sample implanted with  $C_{60}$  relative to PS, deposition on one part of the PS was prevented. The part deposited with  $C_{60}$  ions of about 60 eV energy emits slightly weaker fluorescence than the undoped part under UV lamp irradiation. The sample deposited at 200 eV energy appears black-grey under sunlight, like amorphous carbon, and shows no fluorescence under irradiation by either a UV lamp or an  $\text{Ar}^+$  laser, indicating that the structures of the  $C_{60}$  molecule and PS must be damaged.

An  $\text{Ar}^+$  laser with an output of 5145 Å was used to excite the samples. The PL was obtained with a multiplier and an HRS2 spectrometer. Although the PL intensity of the implanted sample is weaker slightly due to a thin solid film of  $C_{60}$  on the PS surface, it is strong enough to be observed under weak irradiation with a fluence of about 0.5 W  $\text{cm}^{-2}$ . In figure 1, the solid curve and the broken curve show the PL spectra of the part implanted with  $C_{60}$  of energy about 60 eV and the part with no  $C_{60}$ , respectively, on one PS sample at room temperature. The exciting intensity of the laser on the samples was about 0.5 W  $\text{cm}^{-2}$ . The spectra were taken in the wavelength range from 6000 to 10 000 Å. In contrast with PS, the PL of the sample with  $C_{60}$  exhibits a large number of peaks on a baseline profile similar to the PL profile of PS under the same conditions and a long tail in the long-wavelength direction. The intensities of some peaks are about one third those of the baseline. The positions corresponding to the peaks labelled in the spectrum are given in table 1. The existence of  $C_{60}$  must be responsible for these peaks and the long tail fluorescence. In comparison with the PL spectra of purified  $C_{60}$  that had been obtained previously with

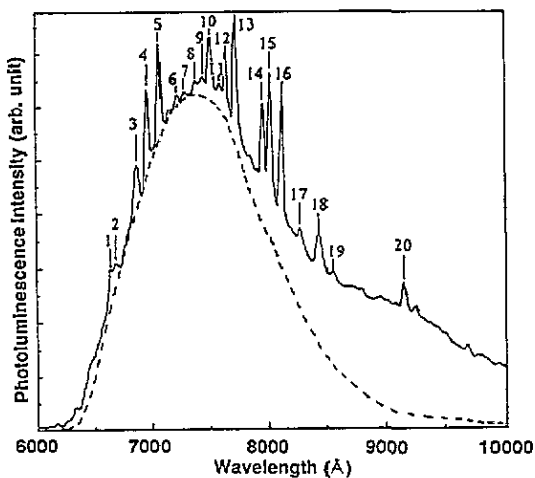


Figure 1. PL spectra of  $C_{60}$  embedded in PS (—) and PS with no  $C_{60}$  (---) at room temperature. The numbers labelling the fine-structure peaks are listed in table 1.

different morphologies, most peaks in this work are very intense and well separated at room temperature. The many intense peaks are likely to be due to the vibrational progression of  $C_{60}$ . In table 1 we also give the results on  $C_{60}$  in the solid state at 10 K observed by Guss *et al* [4] and in toluene at 80 K by Eun-joo Shin *et al* [6]. The positions of some fine peaks are approximately identical with the results obtained by other researchers as referenced, respectively, but the relative intensities are different from theirs and some fine peaks appear only in our PL spectrum. These suggest that the vibrational strengths of the radiative transition of  $C_{60}$  are changed, probably due to the strong interaction between the molecular  $C_{60}$  and the PS matrix.

To check the depth distribution of the  $C_{60}$  molecule along the direction perpendicular to the PS surface, we carried out a depth analysis with a secondary-ion mass spectrometer. The secondary-ion intensities of atomic carbon and silicon versus the depth are shown in figure 2. The intensity of silicon remains almost unchanged and the carbon ion intensity decreases with increasing depth. The inset shows the initial part of the carbon distribution more clearly. The platform at 60 Å corresponds to the  $C_{60}$  film deposited on the surface of PS from the time when the recording of the secondary-ion counts were started. The more rapidly decreasing part labelled with two arrows after the platform gives a depth of about 250 Å. This suggests that the  $C_{60}$  molecules have been put into deep inner pores of PS.

To understand our PL spectrum preliminarily, it is helpful to compare our results to those on  $C_{70}$  obtained by Eun-joo Shin *et al* [6] and Sibley *et al* [15]. The  $C_{70}$  molecule has more carbon atoms and a lower symmetry ( $D_{5h}$ ) and, correspondingly, more active Raman and infrared vibrational modes than  $C_{60}$  has. The electron-phonon coupling is strong, due to mechanical distortion. So the light emission measurements showed higher efficiencies, better resolution, wider wavelength range and richer fine structures than  $C_{60}$  does for the same measurements. The coupling of the two lowest electron states [15] with Raman modes was assigned as the false origins for a broad range of the PL peak distribution, as listed in table 1. In figure 1, the  $2700\text{ cm}^{-1}$  spectral range from approximately  $12\,300$  to  $15\,000\text{ cm}^{-1}$  is too large to represent a vibronic interval that couples with a single electron state. The peaks are too strong to be assigned as the transitions of multiphonon-electron coupling processes. A picture of single-phonon coupling with two separated electron states, as in the

**Table 1.** Positions of fine-structure peaks in the PL spectrum observed for  $C_{60}$  embedded in PS with respect to the wavelength and wavenumber. The results for  $C_{60}$  obtained by Guss *et al* [4], Eun-joo Shin *et al* [6] and for  $C_{70}$  in toluene at 77 K by Sibley *et al* [15] are listed in the table also.

	This work		PL of $C_{70}$ in [15]			
	Wavelength (Å)	Wavenumber ( $cm^{-1}$ )	[4], wavelength (Å)	[6], wavenumber ( $cm^{-1}$ )	Wavenumber ( $cm^{-1}$ )	Assignment
1	6604	15 140				
2	6650	15 040		15 040	15 012	0-0 ( $S_1-S_0$ )
3	6835	14 630	6832( $x_1, t_{1u}$ )	14 610	14 681	
4	6938	14 410	6951( $x_1, h_u$ )	14 330	14 503	
5	7042	14 200	7037( $x_2, t_{1u}$ )		14 284	
6	7192	13 900	7184( $x_2, h_u$ )		13 863	
7	7250	13 790			13 777	
8	7354	13 600	7324( $C_{60}, t_{1u}$ )	13 560		
9	7411	13 490	7465( $x_3, t_{1u}$ )			
10	7481	13 370	7474( $C_{60}, h_u$ )			
11	7562	13 240	7570( $x_4, t_{1u}$ )			
12	7619	13 123				
13	7688	13 010	7735( $x_5, t_{1u}$ )			
14	7919	12 630	7898( $x_5, h_u$ )		12 614	0-0 ( $T_1-S_0$ )
15	7988	12 520				
16	8104	12 340			12 360	0-260
17	8242	12 130		12 080		
18	8404	11 900			12 014	0-571
19	8519	11 740			11 796	0-260-571
					11 699	
					11 252	
					11 224	0-260-2X571
					11 064	0-1568
20	9131	10 950			10 929	

$C_{70}$  molecule, may be reasonable.

Accordingly, we suppose that there is strong interaction between the  $C_{60}$  molecule and the matrix containing it. The  $C_{60}$  molecule appears as a single entity in the matrix since the photon energies of most peaks, like the sharp molecule energy levels of  $C_{60}$  in toluene, are higher than 1.5 eV, the energy gap of solid state  $C_{60}$  (corresponding to the solid-state effect [2, 3]). The strong interaction results in a change in molecular symmetry (into  $D_{5d}$  perhaps [16, 17]). In the isolated state, the first lowest excited states of  $C_{60}$  are in  $D_{5d}$  symmetry and the first transition to the ground state ( $I_h$  symmetry) is dipole forbidden and only weakly allowed via vibrational coupling. In our experiment, the interaction of  $C_{60}$  with PS not only may change the situation of  $C_{60}$  in excited states but also may affect that in ground state. Although it is difficult to know the lowered symmetry clearly, we may expect that it will cause the split and energy shifts of electron states [16, 17] and the electron-phonon coupling will be strengthened. The quantum yields of radiative transition will be enhanced over a broad region and richer fine structures will appear. On the other hand, the interaction of  $C_{60}$  with the matrix makes the hot rotation of the  $C_{60}$  molecule less or causes it to stop completely. From this perspective, the broad emission profile, corresponding to quasi-continuum states for every vibrational mode, will be suppressed drastically. The PL spectrum becomes well resolved. As a result, the luminescence intensity is increased. Considering the similarity of the PL baseline profile of  $C_{60}$  in PS to the PL spectrum of

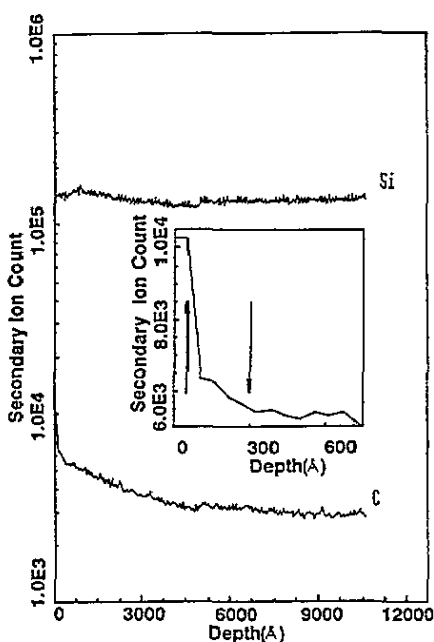


Figure 2. Secondary-ion mass spectra of silicon (upper curve) and carbon (lower curve) versus the depth in a sample implanted with  $C_{60}$  ions of energy about 60 eV. This gives the depth where the  $C_{60}$  ions are embedded as about 250 Å. The inset shows the initial part of the carbon spectrum more clearly. The distance between the two arrows gives the depth of  $C_{60}$  molecules in PS.

PS, another interpretation may be suggested i.e. that the light emission of PS was modified by the vibrational modes of  $C_{60}$ , like the results of Nissen *et al* [18] in which the oxygen molecule PL from crystalline  $C_{60}$  showed the vibrational structure of  $C_{60}$ . The coupling of the oxygen molecule energy level with the vibrational modes of  $C_{60}$  induced a series of resolved PL peaks. However, the PL spectrum of PS shows a broad band, due to the size distribution of the Si crystal particles in PS. The coupling of PS with any mode of  $C_{60}$  will still be a broad band in the PL spectrum with no well resolved peaks as shown in figure 1. This is contrary to our result. So we think that the PL special features of our sample should correspond to the light emission of  $C_{60}$ .

It is difficult to argue this point in more detail because the structure of the PL spectrum is very complicated. Further detailed theoretical information on the electron structure of the  $C_{60}$  molecule in the special symmetry state and more experimental results would be required to fully understand the emission spectrum. This deserves further work. Anyway, we think that it may be a valuable method for embedding clusters in microporous material for improving the optical properties of the clusters studied.

In summary, we have fabricated samples of PS with  $C_{60}$  embedded by the ionized cluster beam deposition for improving the light emission of  $C_{60}$ . We have obtained an intense and well resolved PL spectrum from our samples. The depth analysis by the secondary-ion mass spectroscopy demonstrated that  $C_{60}$  had been implanted into PS. A large number of fine-structure peaks of the PL spectrum are assigned as the vibrational progression coupling with electron states of  $C_{60}$ , induced by the interaction between the  $C_{60}$  molecule and nanometre-sized silicon particle.

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## References

- [1] Wang Y 1991 *J. Phys. Chem.* **96** 764
- [2] Siato S and Oshiyama A 1991 *Phys. Rev. Lett.* **66** 2637
- [3] Ching W Y, Huang M Z, Xu Y N, Harter W G and Chan F T 1991 *Phys. Rev. Lett.* **67** 2045
- [4] Guss W, Feldman J, Göbel E O, Taliani C, Moho H, Müller W, Häussler P and ter Meer H-U 1994 *Phys. Rev. Lett.* **72** 2644
- [5] Feldmann J, Fischer R, Göbel E O and Schmitt-Rink S 1992 *Phys. Status Solidi b* **173** 339
- [6] Eun-joo Shin, Jeunghye Park, Minyung Lee, Dongho Kim, Yung Dong Suh, Sung Ik Yang, Seung Min Jin and Seung Keun Kim 1993 *Chem. Phys. Lett.* **209** 427
- [7] Matus M, Kuzmany H and Sohmen E 1992 *Phys. Rev. Lett.* **68** 2822
- [8] Fabrizia Negri, Kamber I, Schmidt W, Stucky G, Guegel A, Muelken K, Unger K and Schuth F 1993 *Fullerenes, 1st Int. Interdisciplinary Colloq. on the Science and Technology of Fullerenes (Santa Barbara, CA, 1993)* p 161
- [9] Anderson M W, Sci J, Leigh D A, Moody A E, Wade F A, Hamilton B, Rimmer J S, Gardelis S and Carr S W 1993 *Fullerenes, 1st Int. Interdisciplinary Colloq. on the Science and Technology of Fullerenes (Santa Barbara, CA, 1993)* p 155
- [10] Zhu Lei, Li Yufen, Wang Jie and Shen Jun 1995 *J. Appl. Phys.* **77** 2801
- [11] Canham L T 1990 *Appl. Phys. Lett.* **57** 1046
- [12] Liu K F, Zhu L, Wang S Y, Wong W Y and Zhong X F 1994 *Chin. Phys. Lett.* **11** 189
- [13] Ren Z M, Ying Z F, Xiong X X, He M Q, Li Y F, Li F M and Du Y C 1994 *J. Phys. D: Appl. Phys.* **27** 1499
- [14] Cheville R A and Halas N J 1992 *Phys. Rev. B* **45** 4548
- [15] Sibley S P, Argentine S M and Francis A H 1992 *Chem. Phys. Lett.* **188** 187-193
- [16] Ru Rou-li, Fu Rong-tang and Sun Xin 1994 *Phys. Rev. B* **48** 17 615-8
- [17] Wang W Z, Wang C L, Su Z B and Yu L 1994 *Phys. Rev. Lett.* **72** 3550
- [18] Nissen M K, Wilson S M and Thewalt M L W 1992 *Phys. Rev. Lett.* **69** 2423