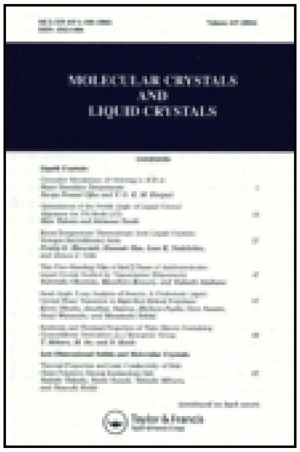

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006

To cite this article: W. P. Piryatinskii, N. I. Klyui, A. G. Rozhin & V. A. Semenovich (1998): Electron Processes in Low-Dimension Porous Si-Fulleren System: Photoluminescence Study, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 324:1, 13-18

To link to this article: http://dx.doi.org/10.1080/10587259808047127

Mol. Cryst. Liq. Cryst., Vol. 324, pp. 13–18
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Electron Processes in Low-Dimension Porous Si-Fulleren System: Photoluminescence Study

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We have investigated the electron properties of porous Si-fulleren system using the time resolved photoluminescence (PL). The investigation of PL spectra shows that as a result of absorption of C_{60} molecules on the surface of Si wires the donor-acceptor centers are formed. It plays the role of sensibylisators of fulleren PL. The effects observed are connected with photoinduced carrier transfer from porous Si to C_{60} molecules, those are the radiative recombination centers.

Keywords: fulleren, porous Si, photoluminescence

INTRODUCTION

Over the last years the fullerence (C_{60})molecules have attracted great interest for their outstanding physical, mechanical and chemical properties[1]. High stability and possibility to dope C_{60} molecules by different kinds of impurities can give oportunity to use them as protective and modificative coatings. Porous Si (por-Si) is one of the most perspective matereals for Si-based optoelectronics[2]., The publications, which demonstrate unique PL properties of por-Si-C_{60} systems have appeared recently[3,4]. In this case, an increasing of PL intensity was observed for C_{60} embeded into por-Si. The significant modification of por-Si PL spectrum for such system also took place. In view of this, the investigation of por-Si + C_{60} system properties by time resolved PL method, which allows one to get new information about por-Si attracts considerable attention.

EXPEREMENTAL DETAILS

Porous Si layers were fabricated by anodizing 10 Ω cm p-type Si (100) substrates with aluminum back contact. The electrolyte was 49%HF:C_2H_5OH=1:1, the current density was 50 mA/cm^2 and time 5 min. The fulleren molecules (C_{60}) were embedded in the porous Si by two methods. In the first stage (the same for the two methods) the microcrystalls of C_{60} were desolved in toluene. In the first method, porous Si layers were exposed into C_{60}/toluene solution for a long time. After that layers were treated in the pure toluene and dried. Porous Si layers were dipped into C_{60}/toulene solution in the second method. The solution were evaporated during a few days. The PL spectra were excited by using nitrogen laser (λ_e=337.1 nm, τ=10 ns, P=5 kW). For detecting of time resolved PL we used the stroboscopic registration system. All measurements were carried out at 77 K.

RESULTS AND DISCUSSION

Integral PL of por-Si is characterized by presence of a broad intensive band at 690 nm and a weak shoulder near 450-550 nm. The latter is usually attributed to luminescence of oxidation products on the por-Si surface [5]. The intensive luminescence at 600-700 nm is interpreted to be due to quantum size effect in por-Si quantum wires [6]. In time resolved PL spectrum of por-Si the downshift of PL band from 450 nm to 700 nm is observed when the time resolution is changed from nano- to microseconds.

The por-Si PL spectrum measured with ns time resolution at T=77 K is presented in Fig. 1, curve 1. A distinct band at 550 nm is observed in the spectrum mentioned. Curve 2, Fig. 1 represents the PL spectrum of C_{60} crystals being in suspended state in oversaturated toluene solution and cooled to 77 K. The PL spectrum of fullerite deposited on quartz cell walls after toluene evaporation was the same. The integral PL spectrum and the PL spectrum measured with ns time resolution were practically identical for C_{60}. The PL lifetime at 77 K was about 1.7 ns. In C_{60} PL spectrum an intensive band at 750 nm with less intensive vibronic replica at 820 nm are observed (curve 2, Fig. 1). At the present time there are few explanations of PL of C_{60} in condensed state. The PL is supposed to be originated from defects on grain boundary surface which lead to local distortion of C_{60} molecule symmetry and increasing of radiative t_{1u} - h_u transition probability. It should be noted that this transition is forbidden in dipole approximation [7]. On the other hand, the PL can be connected with localization of electron excitation (molecular excitons) on quasi two-dimension spherical C_{60} surface [8]. The possibility of such localization can be provided by existence of rather weak π -bonds which take part in double bonds formation in C_{60} molecules. When measuring C_{60} PL spectrum at intensive laser excitation (laser beam was focused onto the sample in a spot of diameter 100 mcm) a PL band at 700 nm and a shoulder at 680 nm appear in addition to the above mentioned PL bands (curve 2, Fig. 1). The relative intensity of the bands at 700 and 680 nm was increased with increasing time delay to 5 ns. PL in the spectral region near 680 nm is explained by existence of free S-excitons. Curve 3, Fig. 1 shows the spectrum of ns PL for the por-Si+C_{60} structure prepared by the first method. At low concentration of C_{60} molecules in pores the PL spectrum of por-Si (curve 1) is modified and the PL maximum is shifted to 600 nm. Besides, a shoulder at 700 nm is also observed (curve 3, Fig. 1). The PL band at 600 nm may be attributed to emission from C_{60} ionic forms [3] and is a result of creation of donor-acceptor pairs on the por-Si surface. The shoulder at 700 nm in PL spectrum is caused by crystallization of C_{60} in the pores. For the por-Si+C_{60} structures prepared by the second method (with high concentration of C_{60} molecules in the pores) the creation of C_{60} nanoclusters in the pores takes place. As a result, in the PL spectrum of the por-Si+C_{60} structure two distinct PL peaks at 630 and 750 nm are observed (curve 4, Fig. 1). As was mentioned above the PL band at 630 nm is stipulated by creation of donor-acceptor pairs on the por-Si surface. At the same time, the PL band at 750 nm is caused by emission from C_{60} nanoclusters incorporated into pores. It should be pointed out that the PL intensity of C_{60} nanoclusters embedded into por-Si is much higher than that for C_{60} dissolved in toluene and being in suspended state before freezing (curve 2 and 4 in Fig.1, correspondingly). The PL excitation conditions were the same for the both mentioned cases.

The presented results may be interpreted in the framework of a model that takes into account transfer of exciton energy or charge from por-Si to absorbed C_{60} molecules. The most preferable mechanism is photoinjection of free carriers in the por-Si and their recombination on C_{60} molecules. It was proposed in [3] that the C_{60} sencibilization process is mainly connected with charge transfer. Our results show that this process is most effective near C_{60} nanocrystal or small diameter wire surfaces. Carriers separation in por-Si and carriers transfer into C_{60} will be effective in case that the levels of electrons and holes localization in C_{60} are lower and higher than conductive E_c and valence E_v bands, correspondingly (see fig. 2). Quasi two-dimensional por-Si is direct bandgap material [9] in contrast to familiar silicon. The recombination process of carriers is more effective near the surface of small diameter wires

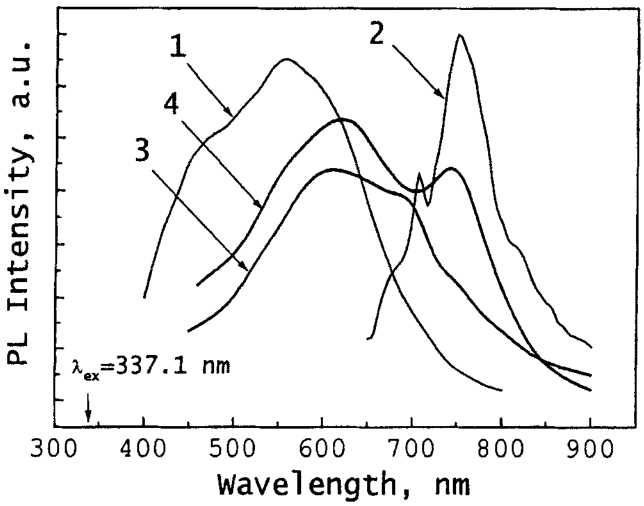

FIGURE 1. PL spectra of por-Si (1), C_{60} (2), por-Si-C_{60} system (3,4) registrated with nanoseconds time resolution. T=77 K. For convinience the intensity of spectrum 2 is incresed 4 times.

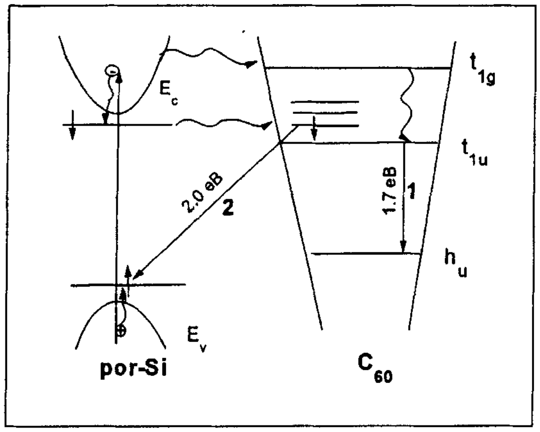

FIGURE 2. Diagram of electronic prosesses in por-Si-C_{60} system.

characterized by wider bandgap than the large ones. In this case the condition that the levels of electrons and holes localization in C_{60} are brought into por-Si forbidden gap asserts better. High efficiency of electron capture by C_{60} molecule is also determined by the fact that C_{60} is an effective oxidator (acceptor). It is not improbable as well that in addition to C_{60} molecular emission (Fig. 2, transition 1) the recombination process can takes place under C_{60} physical absorption (Fig.2 , transition 2). Then, as in the case with donor-acceptor complexes, electrons and holes are localized on C_{60} molecules and surface states of por-Si, respectively. These states may appear due to availability of the oxidation products on Si-wires.

It was concluded that PL properties of por-Si were substantially changed under physical and chemical absorption of C_{60} molecules on Si-wires. Effect of drastic enhancement of PL intensity for C_{60} embedded into por-Si was observed. The mechanisms of the effects mentioned abovewere proposed.

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