Excitation transfer from porous silicon to polymer

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Abstract

The optical properties of porous silicon (PS) and poly[2-methoxy-5(2′-ethylhexyloxy-p-phenylenevinylene)] (MEH-PPV) polymer composites were investigated. The experiment results showed that the luminescence intensity of the composites was enhanced and the PL peak position was found red shift. The pore structure of PS decreased the collision and increased conjugation of MEH-PPV molecules, which caused the enhanced luminescence of the composites. Also, the reaction between the surface states of PS and MEH-PPV molecules provided a route of non-radiation recombination that then transferred a part of excitation energy of PS to MEH-PPV. And the excitation transfer caused the enhanced luminescence and red shift.

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1. Introduction

As a candidate of silicon-based light emission materials, PS has been investigated extensively since Canham discovered the visible luminescence of PS [1–5]. However, the instability of PS, for example, due to the oxidation [2,3] which led to the formation of non-radiative recombination centers as well as low emission efficiency, impeded the application of PS. Therefore, passivation of the PS surface by organic molecules [6–9], inorganic nano-particles [10,11] and oxidation of PS [12] was used to improve the instability and emission efficiency. In all the passivation materials, the electroluminescent organic materials working with PS were considered as the potential application for light-emitting diodes (LEDs). Furthermore, those organic–PS composite systems may possess properties of both the components to adapt the requirements of specific functions.

Among the organic–inorganic composite systems, poly(p-phenylene vinylene) (PPV) was an important one because of its good electroluminescent property [13,14]. After mixing of PS and PPV polymer, it was found that the PS grains decreased the turn-on voltage of the LED while the luminescence property of PPV was not influenced [15,16]. Recently, Nguyen and his co-workers used a sulfanyl route precursor to fill into the pores of PS and then converted the precursor into PPV by heating in vacuum [17]. After the precursor converted into PPV, the PPV was infiltrated into the pores of PS and an energy transfer mechanism between the PS and PPV was found [18]. However, the composite materials presented a broad emission band, which did not show evidently the combined properties of both the components.

In this work, a ramification of PPV and MEH-PPV was used to fill into the pores of PS by means of spin-coating technique. MEH-PPV is easy to dissolve in organic solvent, which will be convenient for its spinning into the pores of PS so as to stabilize PS. Besides its easy solution, the good electroluminescent behavior and high stability of MEH-PPV was thus expected to associate with PS for light emission.

2. Experiment

Using an HF/C2H5OH mixture (1:2 in volume ratio) as an electrolyte, PS layers were produced by electrochemical anodic etching on n-type (100) silicon wafers (2–6 Ω cm). The current density was set at 10 mA cm−2 with a back-illumination (50 W), and the pores of PS were about
1–2 μm in diameter. Then the 0.5 ml MEH-PPV dissolved in trichloromethane with concentrations 1.2, 2.5, 5, 10 and 15 mg/ml was spanned on the PS. The composites were annealed in a vacuum drying oven at 60 °C for half an hour. Absorption of the PS and MEH-PPV was carried out on a PE Lambda 20 spectrometer. The PL was carried out on a Hitachi F-4500 spectrometer with the excited wavelength of 330 nm.

3. Results and discussion

Fig. 1 shows the normalized spectra of UV–vis absorbance of the MEH-PPV and photoluminescence of PS, while Fig. 2 shows the normalized spectra of UV–vis absorbance of PS and photoluminescence of MEH-PPV. The PS presented an emission peak centered at 613 nm (Fig. 1) while the MEH-PPV emitted light at 578 nm (Fig. 2). It is evident that the PS had negligible absorption in the main MEH-PPV excited wavelength range (Fig. 2). On the other hand, the low-energy absorption band of the MEH-PPV had an overlapping at 586 nm with the high-energy luminescence band of the PS, which means that the MEH-PPV could absorb the excited light from the PS (Fig. 1), i.e. the energy transfer from PS to MEH-PPV may take place.

Fig. 1. Normalized spectrum of UV–vis absorbance of the MEH-PPV (solid line) and photoluminescence of PS (dash–dot line).

Fig. 2. Normalized spectrum of UV–vis absorbance of the PS (solid line) and photoluminescence of MEH-PPV (dash–dot line).

Fig. 3 shows the PL spectrum of MEH-PPV and the composites consisted by PS and MEH-PPV with the concentration of 2.5, 10 and 15 mg/ml, and the inset shows the de-convoluted Gaussian curves of the composite of the PS and MEH-PPV in the composite (with 2.5 mg/ml concentration of MEH-PPV).

As for the increase in PL intensity with the increase in capped MEH-PPV's concentration, it was ascribed to two matters. Firstly, the existence of \(1.2–10\) mg/ml. However, when the concentration was higher than 10 mg/ml, the PL intensity decreased, as shown in Figs. 3 and 4. Furthermore, the center of the composites’ PL peak was found red shift compared with the PL peak of MEH-PPV. With the increase in the concentration of MEH-PPV, the PL peak was found red shift 2 nm at a concentration of 2.5 mg/ml. There was a maximum of about 10 nm red shift from the lowest to the highest concentration of MEH-PPV as shown in Fig. 3.

As for the increase in PL intensity with the increase in capped MEH-PPV’s concentration, it was ascribed to two matters. Firstly, the existence of \(\pi\) conjugation of MEH-PPV and its increase caused the enlarged PL intensity. Due to the pores of PS, the MEH-PPV molecules were separated, which not only decreased the collision of MEH-PPV but also increased the conjugation of molecules. The decrease of col-
collison between molecules of MEH-PPV would depress the quench of luminescence while the increase of conjugation could enhance the emission of MEH-PPV. Thus, both of them increased the luminescence of MEH-PPV. Secondly, the exciton transfer from PS to MEH-PPV seemed to be another reason. It is well known that the luminescence of PS was contributed to not only quantum confinement [1] but also surface states [19], which are the traps of carriers. Besides the traps of carriers, surface states can also act as intermediate energy levels for the charge transfer between interfaces. Therefore, after PS capped by MEH-PPV, the emission of PS was strongly affected by the reaction between the surface states and MEH-PPV molecules. The capped MEH-PPV firstly led to the decrease in combination efficiency of irradiated centers formed by surface states. On the other hand, the reaction between the surface states and MEH-PPV molecules provided a route of non-radiative recombination that then transferred a part of excitation energy of PS to MEH-PPV. Under illumination, the excited carriers in PS would transfer to the conduction band of MEH-PPV. The transfer process may be as following: (1) the excited carriers with an energy higher than the conduction band of MEH-PPV injected directly into the MEH-PPV; (2) the excited energy firstly transferred to the surface states of PS from which carriers were injected into MEH-PPV; (3) Exciton induced by hot carrier in PS could also transfer to MEH-PPV by the ballistic mechanism [20,21]. Thus, the excitation transfer made the composite emission intensity enhanced.

Furthermore, with the increase in the MEH-PPV concentration, the amount of excitation transfer would also increase, which also enhanced the PL intensity. However, when the capped MEH-PPV concentration was higher than 10 mg/ml, both the interaction between MEH-PPV molecules and decreasing efficiency for carrier tunnelling caused the quenching of luminescence of the composites. Moreover, once the MEH-PPV absorbed the exciton of PS, emission peak would red shift correspondingly.

4. Conclusion

By spin coating, the MEH-PPV was capped onto the PS. The heterostructure possessed the combined properties of both the components. The emission light intensity of the composites of PS and MEH-PPV was enhanced with the increase in MEH-PPV concentration while the position shifted red. It was the exciton transfer from PS to MEH-PPV and the pore structure of PS, which decreased the collision and increased conjugation of MEH-PPV molecules that caused the enhanced luminescence of the composites. Also, the red shift of composite’s emission was considered to be the transfer of excitation of PS to MEH-PPV.

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References