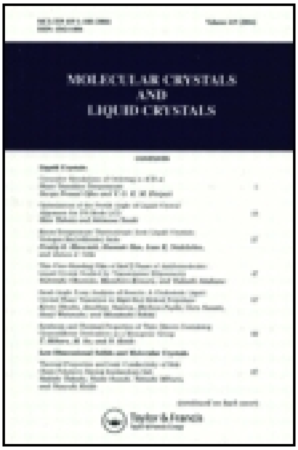

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Local Defective Structures in C_{60} Composite Films and their Light Emission Properties: Photoluminescence and Electroluminescence

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Local Defective Structures in C_{60} Composite Films and their Light Emission Properties: Photoluminescence and Electroluminescence

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Intense white photoluminescence from C_{60} composite films observed under green laser irradiation is found to be closely connected with local defective structures incidentally formed during the film fabrication process. On the basis of the finding, we succeeded in introducing such emissive structures by intentional mechanical scratching. White electroluminescence was also observed at such modified structures. A possible mechanism of such unusual light emission is discussed.

Keywords: fullerene; C_{60}; composite film; defect; photoluminescence; electroluminescence

INTRODUCTION

Because of their rich π-electron conjugation surrounding the quasi-spherical molecular surface, fullerenes show promise as a completely new class of photonic materials. Due to the high molecular symmetry, however, the HOMO-LUMO transition is dipole forbidden, exhibiting only very weak luminescence in the near infrared region. As a result, they cannot be considered as attractive materials for light emission applications. Measures to overcome this restriction may include lowering the high symmetry by the introduction of heterogeneous structures into fullerene solids, thus relaxing the optical forbiddenness. Following this strategy, we fabricated C_{60}/Si composite films by the alternate deposition of C_{60} and Si that turned out to demonstrate

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intense white light emission under green laser irradiation[1]. By extending the measurement wavelength range to the mid infrared (up to 4.5 μm), we have discovered that the spectrum of the white light emission almost perfectly fit Planck distribution for black-body radiation, giving the surprisingly high effective black-body temperatures of 1200-1600K[2].

In the present study, we observed the morphology of the C_{60}/Si composite films using a microscopic CCD camera. We also characterized the emissive spots in the films by microscopic Vis-NIR spectroscopy. On the basis of the careful inspection of the emissive spots that were incidentally formed during the fabrication process, we tried to introduce such structures by intentional mechanical scratching. This resulted in the successful formation of a similar kind of emissive spots in the composite films. Furthermore, defective structures formed in a similar way exhibited white electroluminescence that could be well described again by black-body radiation.

EXPERIMENTAL

Composite films were fabricated by alternate deposition of C_{60} and Si layers on fused quartz plates; the former by vapor deposition and the latter by RF sputtering using a chamber in an Ar atmosphere of 10^{-3} Torr. The thickness of each layer was 30-50 nm for C_{60} and 0.2-0.6 nm for Si, and the deposition was repeated 60-100 times, resulting in the total film thickness of 2-5 μm.

For the measurements of photoluminescence, a CW Ar ion laser was used as an excitation source operating at 514.5 nm with the power of 8-28 mW focused into a beam size of approximately 0.2 mm^2, the power density being 4-14 W/cm^2 on the sample surface. The emission from the samples was collimated with a CaF_2 lens and fed into a FT-IR spectrophotometer (Jasco Model FT/IR-800) equipped with a liquid nitrogen cooled InSb detector. Spectral calibration of the detection system was done using a halogen lamp operating at 3400K. The samples were kept in a vacuum cryostat at room temperature unless otherwise specified. For the analysis and observation of the emissive spots, we used a microscope Vis-NIR spectrophotometer (Zeiss Model UMSP-80) as well as a conventional microscopic CCD camera system.

RESULTS AND DISCUSSION

The spectra of the white photoluminescence at four different excitation intensities at 514.5 nm are shown in Fig. 1. They are quite broad and featureless in the range 0.6-4.5 μm and the peak shifts to the shorter wavelength as the excitation intensity increases. It is striking that the experimental plots give an excellent fit to the solid curves that represent Planck's formula for black-body radiation. Note that the deviation from the theory at >2.5 μm is due to the absorption by the envelope of the halogen lamp used for the spectral calibration. By curve fitting, we obtained the effective black-body temperatures of 1200-1600K as indicated in Fig. 1. They are surprisingly high considering that the sample was kept at room temperature.

Figure 2 shows a microscopic photograph of a composite film under laser irradiation taken with the CCD camera. The laser spot is approximately 0.7 × 0.35 mm in elliptical shape. The film is rather inhomogeneous, consisting of black islands scattered over the grayish background whose actual color was reddish. Remarkably, it is these black islands that emit intense white light under laser irradiation as demonstrated in Fig. 2. Moreover, we found that these black islands were formed instantly by laser irradiation itself.

Figure 3 shows the Vis-NIR spectra of the non-emissive (reddish back ground) and emissive (black island) spots measured by the microscope spectrophotometer. The samples were at room temperature in air in this case. As shown in Fig. 3(a), the visible absorption spectrum of the reddish background is similar to that of pristine C_{60} thin films, which is reasonable because the Si content in the composite films should be very small (< 1%). Figure 3(b) and (c) depict the near infrared transmission spectra of the reddish background and a black island, respectively, showing a great difference in transmittance. This implies some chemical modification of C_{60} in black islands. Such a possibility is corroborated by the results of preliminary measurements of microscopic FT-IR and Raman spectra that indicated partial disintegration of the C_{60} cage.

By carefully examining microscopic images of a number of composite films like shown in Fig. 2, we noticed that most of such emissive structures

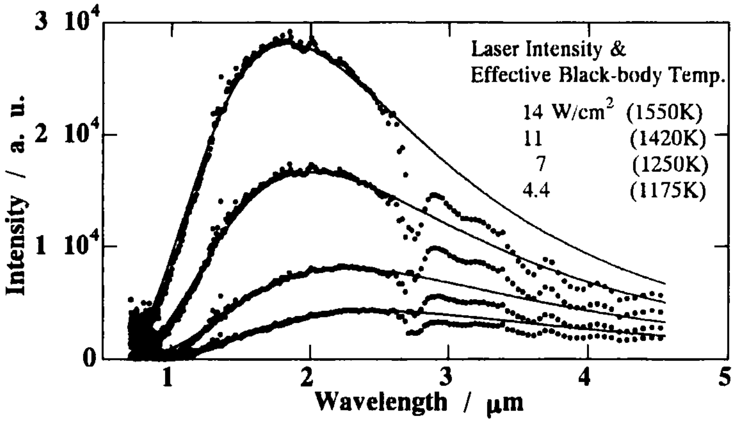
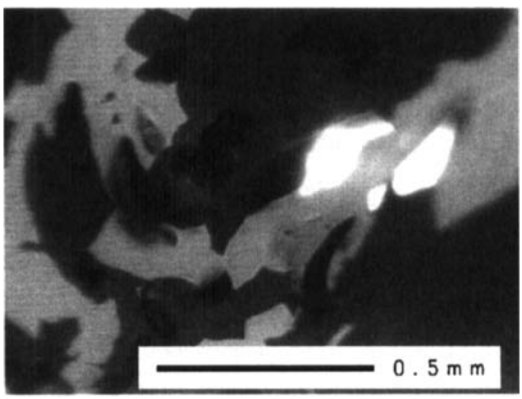


Fig. 1 Emission spectra of C60/Si composite film under Ar ion laser irradiation (514.5 nm). Solid curves are the best fits based on the Planck distribution, giving the effective black-body temperatures as indicated.

Fig. 2 Microphotographic image of a C_{60}/Si composite film under laser irradiation.



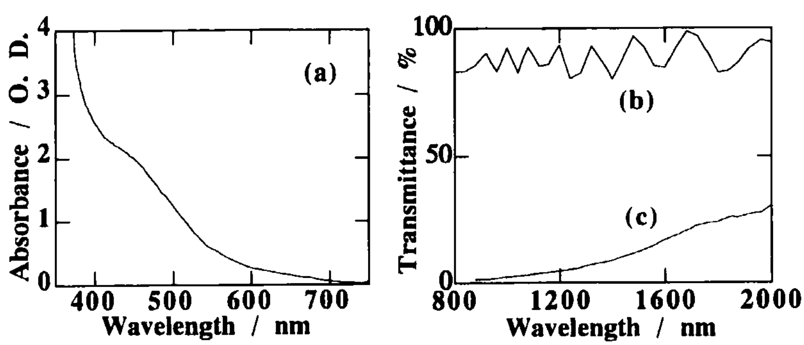


Fig. 3 Microscopic visible absorption spectrum of the reddish background (a) and NIR transmission spectra of the reddish background (b) and a black island (c).

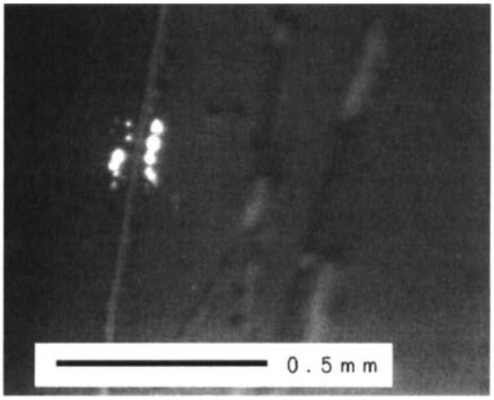


Fig. 4 Microphotographic image of a C_{60}/Si composite film with intentionally created scratches. Laser was irradiated in a similar way as Fig. 2.

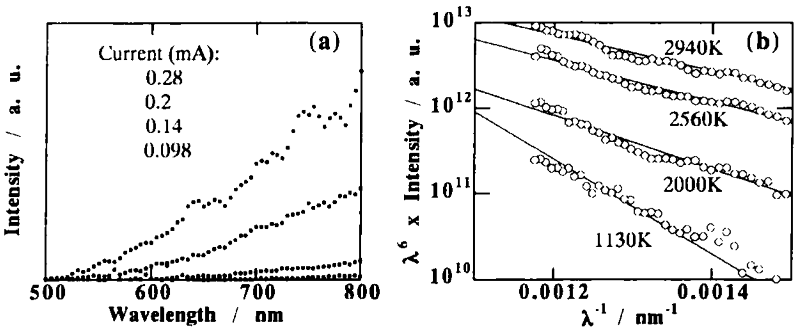


Fig. 5 Emission spectra of electroluminescence from a composite film at four different currents (a) and curve fitting (b), giving effective black-body temperatures for each case. See ref. [1] for the fitting procedure.

are located near cracks that were formed during the film fabrication process. This lead us to suspect that the white light emission is connected to some defective morphology in composite films. Thus we intentionally introduced cracks into a composite film by mechanical scratching using a sharp metal tip and then irradiated that spot. The result is striking as shown in Fig. 4. Spots that were non-emissive before the scratching started to emit white light under laser irradiation and those spots are located along the crack just created. These observations have established that the white photoluminescence has its origin in some defective structures in C_{60}/Si composite films. Probably, the laser induced darkening mentioned above can occur only at such structural disorders, and the concomitant enhancement of light absorption causes drastic increase in local temperatures leading to intense black-body radiation. More details of such a process are now under investigation.

With the intention of developing these findings into electroluminescent applications, we deposited a pair of aluminum electrodes over a composite film that was previously scratched many times. We applied voltage up to 1000 V between the electrodes to see if any light emission occurred by the current flow. While most of the trials were unsuccessful, a few spots all near the scratches were found to emit white light by the application of voltage. We measured the emission spectra in the visible range and found them very broad and their intensity critically dependent on the magnitude of the current (Fig. 5(a)). It was also shown by the same procedure as that in our previous publication[1] that these spectral curves gave good fit to Planck's formula, yielding effective black-body temperatures of 1130-2900K (Fig. 5(b)). The current necessary for this emission to occur ranged 0.1-0.3 mA, while the voltage was very high. This is supposed to be due to the film's very high series resistance in the lateral direction. While its confirmation should await more detailed studies, the common involvement of scratching in both photoluminescence and electroluminescence strongly suggests their common origin. We also feel that the electroluminescence observed here is essentially the same as those reported by Werner et al.[3] and Palstra et al.[4], and our results provide some new implications about the mechanism by which such phenomena emerge in C_{60} solids.

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