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Emission from Organized Molecular Systems with the Order of Emissive Wavelength

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Emissive behaviors from the systems with the sizes of the order of visible wavelength are described. Control of electrically-pumped emission from thin-film electroluminescent devices by use of one-dimensional planer cavities is demonstrated. Photoluminescence behaviors from organic dielectric stacks with buried emissive centers prepared by vacuum-vapor deposition were examined. Photoluminescence from self-organized three-dimensional ordered arrays of polystyrene small particles with luminescent dyes is also studied. In both systems, inhibition of spontaneous emission due to photonic gaps were observed.

Keywords: spontaneous emission, microcavity, photonic bandgap, molecular organized system

INTRODUCTION

Thin-film electroluminescence (EL) displays made of organic compounds are now very close to commercialization. This means that electrically-pumped emission from organic thin films, which is one of the first successful examples of the fabrication of artificial light-source made of organic compounds by the modern technologies, has manifested excellent stability and reliability[1]. Now we can say that we have big opportunities for using organic compounds not only for electronics but also basic researches related with production of excited states in various classes of molecular systems.

We have learned two important issues through the research and development of organic EL devices in these ten years: First, surprisingly large amounts of electronic charges, comparable with the cases in conventional

semiconductors, are easily introduced into organic solids, and they are converted to photons with quite high quantum efficiency. The second point is that high density of excited states are able to be produced within organic solids by electric excitation processes and thus local high density excitations of molecules or chromophores may be selectively created in organic solid films. Thus we expect that a new research field in photochemistry and photophysics related with the behaviors of excited states in organic solids, such as excited states production, energy transfer and luminescence, is to be open.

Fascinating feature of organic EL devices, in another aspect, is the extremely small size of organic films used. The total thickness of organic layers in EL devices is about 100 nm, which is less than the wavelengths of emissive light. Thus the quantum optical effects due the confinement of electromagnetic field in small space are expected to appear. In the frame work of classical photochemistry, a spontaneous emission process, for example, has been assumed to be an irreversible process, which reflect intrinsic nature of excited molecules. When one deals with optical behaviors on macroscopic scale systems, the above treatment gives reasonable scientific basis. When the sizes of the systems are reduced to the order of the wavelength of visible light, all optical phenomena must be treated in the frame work of quantum optics[2]. Behaviors of excited states of molecules should be understood in connection with electromagnetic radiation fields which surround them. For example, a spontaneous emission should be understand as a consequence of the coupling between excited molecules and radiation field. The use of microcavity structures with the dimension of the wavelength of visible light is one of the promising ways towards the manifestation of the quantum optical effects; mutual interaction of excited molecules and radiation field. Using optical microcavity structures which has the sizes of emissive wavelength, one can control emission properties of materials placed inside the cavities.

In 1991, we proposed the introduction of microcavity structures in thin-film EL devices, because the thicknesses of organic layers were less than a quarter of an emissive wavelength and a pair of electrodes may play the roles of reflective mirrors[3]. We reported one of the first studies on the emission

produced by electric pumping from microcavities made of organic dye film[4]. Both spectral narrowing and a large alteration in the spatial distribution of intensity of emitted light were actually observed in organic EL devices with a Fabry-Perot microcavity structure. We also demonstrated that EL devices with sharply directed emission were fabricated[5],[6]. The Fabry-Perot type microcavity structures provide one-dimensional cavities and the confinement of emissive photons within cavities was imperfect. If two or three dimensional cavities are available for the EL devices, one finds a possibility to observe novel quantum optical phenomena based on perfect confinement of excited states.

Construction of three-dimensionally confined systems by means of the modern technology such as vacuum-vapor deposition and lithography is highly difficult. Self-organization of molecules is expected to provide one of the best solutions for the attainment of sophisticated three dimensional structures with the order of wavelength of visible light. Two or three dimensional periodic structures are expected to be easier to construct compared with the cases of two or three dimensional microcavities. Thus we focused our attention on the periodic structures made of organic molecules, in other words, so-called photonic crystals.

Photonic crystals recently have been attracted great attention from both on theoretical and experimental aspects[7]. When three dimensional periodic dielectric structures were introduced, for example, propagation of photons is expected to be perfectly forbidden in a certain range of energies at all directions (known as photonic band gap). When emissive centers are regularly arranged in a periodic lattice with the order of visible wavelength, emissive behaviors specific to regular arrays may be observed. Thus we have started the study on the construction of periodic structures using organic emissive materials and tried to examine spontaneous emission properties in the periodic structures which have the sizes of emissive wavelengths. In this article, two systems were examined: one is one-dimensional structures of stacked dielectric layers with buried emissive centers, and the other is self-organized array of polystyrene (PS) microspheres with doped fluorescent molecules.

EL DEVICES WITH OPTICAL MICROCAVITIES

Electrically-pumped emission from EL devices were successfully controlled by use of a simple Fabry-Perot type microcavity. Although the enhancement and suppression of spontaneous emission rates were not possible due to imperfection in mode confinement, both sharpening of emission spectra and large alteration of spatial emission patterns are attained even in simple planer microcavities introduced in thin-film EL devices. Here we will show a typical example of the control of emissive behaviors, sharply-directed emission from thin-film EL devices with a microcavity structure.

Figure 1 shows the device structure of the EL device with microcavity and the molecular structures of materials used. The device consists of a dielectric reflector/ITO layer/HTL/EML/ETL/MgAg mirror, in which HTL , EML and ETL represent hole-transporting, emissive and electron-transporting layers, respectively. A Fabry-Perot cavity sandwiched between the metal mirror and the dielectric reflector consists of the three organic layers.

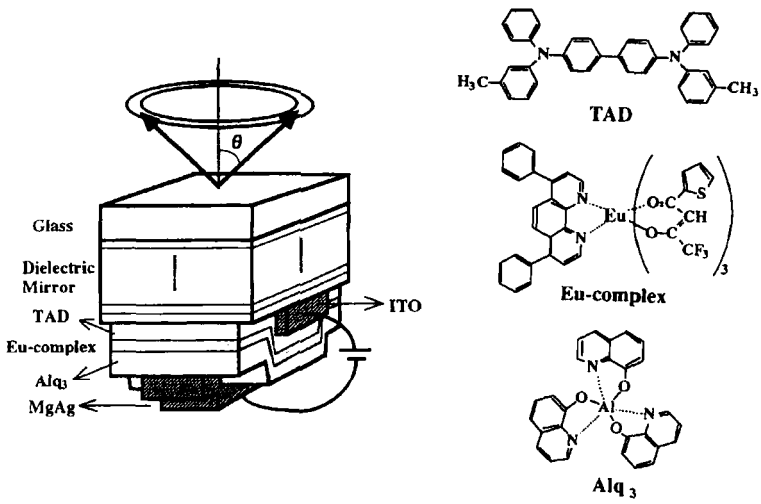

FIGURE 1. The device structure of microcavity EL device and the structures of materials used.

The EL devices with a microcavity structure were fabricated on a glass substrate with a dielectric reflector coated with an ITO conductive layer. The reflectance of the substrate at around 617 nm was 85 %. On a substrate with a patterned ITO electrode, a TAD layer for HTL, a 12-nm-thick Eu-complex layer for EML, an Alq layer for ETL, and a top MgAg alloy cathode (150 nm) were formed. The thicknesses of HTL and ETL were varied from 35 nm to 65nm. The EL devices were driven by dc voltage as large as 15 V, and sharp red emission was observed in every device. The intensity of emitted light was proportional to the input current. Observed emission from the EL device was sharply directed along fixed outer emission angles which form cone surfaces. The angles which define the emissive direction were dependent on the total thicknesses of organic layers, in another expression, the length of optical cavities. Figure 2 shows the emission pattern of the device with total organic layer thickness of 87nm. In this device, the sharply directed emission vertical to the emissive surface was observed.

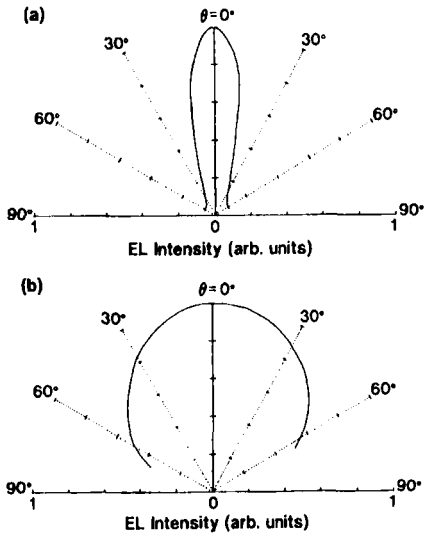

FIGURE 2 Spatial distribution of emission intensities in EL devices with (a) and without (b) microcavity.

In the same figure, the emission pattern of the conventional device without microcavity with the same organic layer thickness was shown. The latter device showed uniform spatial distribution nearly Lambertian.

Figure 3 compares the EL emission spectra between the devices with and without a microcavity structure. The EL spectrum from the device without cavity contained several small peaks characteristic to the emission from an Eu ion in free space. These small peaks perfectly disappeared in the device with microcavity. This is another clear evidence that the microcavity structure is surely effective in attaining the single resonance in a cavity.

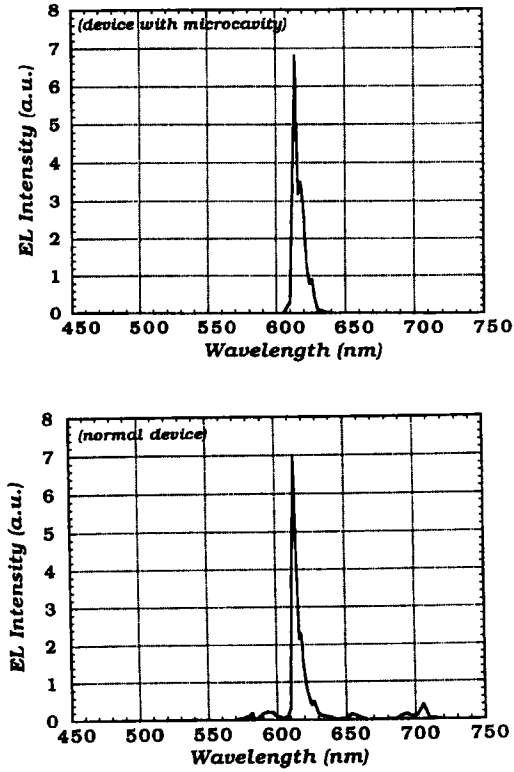

FIGURE 3 Comparison of emission spectra in EL devices with and without microcavity.

CONTROL OF EMISSION IN PERIODIC STRUCTURES WITH THE ORDER OF OPTICAL WAVELENGTH

One-dimensional periodic array made of vacuum-deposited organic layers

As a simple extension of the microcavity EL devices, we fabricated a periodic stack of thin emissive layers with transparent inert separating layers. For the thin emissive layer, a, typical emissive dye, tris(8-hydroxyquino)aluminum (Alq) with the thickness of 16 nm was used. The peak wavelength of emission was at 520 nm and refractive index of the Alq at 500 nm was 1.76. Plasma-polymerized thin layers of hexamethyldisiloxane (PHDS), which was transparent between 350 and 800 nm were adopted for optically inert spacer layers. The refractive index of PHDS was 1.51 at around 500 nm. Thirty pairs of Alq/PHDS stacks were prepared by successive vapor-phase deposition. When the thickness of PHDS was fixed to be 168 nm, effective optical path length of the Alq/PHDS pair corresponds with the half of photoluminescence wavelength from the Alq layer. Transmission spectra and photoluminescence spectra excited at 350 nm for the 30 pairs were observed as a function of an observation angle. Figure 4 represents emission spectra as a function of the observation angle as well as transmission spectra. The vertical direction to the film surfaces was referred to be zero in both emission and transmission spectra.

Dips which shifted to lower wavelengths with the change of observation angle were clearly observed in the photoluminescence spectra. Apparent absorption peaks which were due to selective reflections by stacked layers with two different refractive indices were detected at the same wavelength of the emission dips. These observations suggest that suppression of emission due to so-called photonic-gaps can be observed in a quite simple one-dimensional systems. One should note, however, that only a specified optical mode was actually influenced in those partially confined systems.

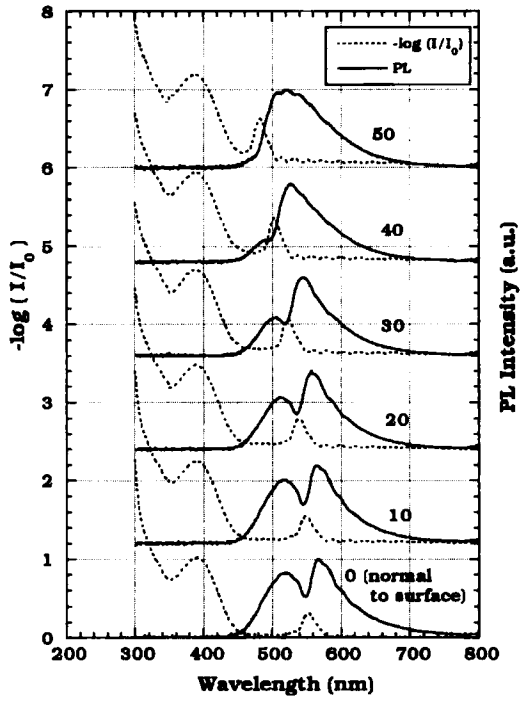

FIGURE 4 Transmission and photoluminescence spectra of the 30 layer stack of Alq/PHDS pairs. The numerals in the figure represent observation angle.

Self-organized ordered array of polystyrene microspheres

Polystyrene (PS) microspheres have been known to form highly ordered self-assembled ordered arrays under certain conditions. Although a perfect photonic-gap is not achieved by using that class of periodic dielectric structures due to small dielectric constant difference between the PS spheres and surrounding medium, the periodic structures made of PS particles is expected to be useful for the model study of one- or two-dimensional photonic crystals.

PS microspheres with the diameter of 200 nm including fluorescent molecules, Fluoresbrite YG microspheres purchased from Polyscience Inc. were used. By controlling temperature and humidity during casting processes, we have succeeded in preparing highly ordered thin films which are composed of densely packed PS microspheres. From optical microscope and AFM observations of the surfaces of the prepared films, we confirmed that the films were composed of the aggregates of microcrystals with specified orientations. Photoluminescence spectra from the structures which have the size of visible wavelength were measured by using the system shown in Figure 5.

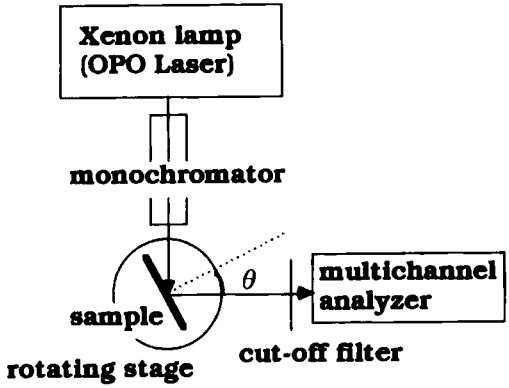

FIGURE 5 Setup for the measurement of angular dependence of photoluminescence spectra.

The alternation in the emission spectrum, which depended on an observation angle, by the periodic structures were observed as shown in Figure 6. Deep dips at around 530 nm were appeared in the photoluminescence spectrum. With increasing the observation angle, the dip shifted toward the shorter wavelength. The dips in the spectrum is explained as the partial suppression of radiation modes in the periodic dielectric structures.

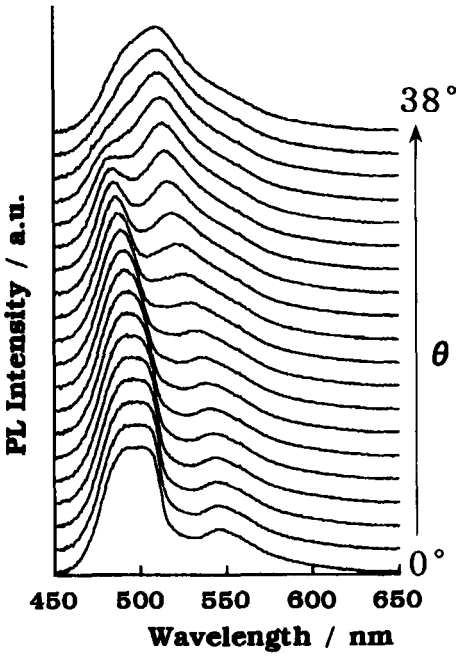

FIGURE 6 Photoluminescence spectrum from PS ordered array as a function of observation angle.

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References

[1.] T. Tsutsui, *MRS Bulletin*, **22**, 39 (1997).
[2.] Y. Yamamoto and R. E. Slusher, *Physics Today*, **46**, 66 (1993).
[3.] T. Tsutsui, C. Adachi and S. Saito, *in Phtochemical Processes in Organized Molecular Systems*, edited by K. Honda (Elsevier Sci. Pub. B.V., Amsterdam, 1991), p. 437.
[4.] N. Takada, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, **63**, 594 (1993).
[5.] T. Tsutsui, N. Takada, S. Saito and E. Ogino, *Appl. Phys. Lett.*, **65**, 1868 (1994).
[6.] T. Tsutsui, N. Takada and S. Saito, *Synthetic Metals*, **71**, 2001 (1995).
[7.] J. D. Joannopoulos, P. R. Villeneuve and S. Fan, *Nature*, **386**, 143 (1997).