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Random lasing films from multifunctional charged optical silica particles

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ABSTRACT

Multifunctional SiO_2 particles with charged and fluorescent properties were synthesized and their films with different thickness were prepared using electrophoretic deposition for random lasing. In case of 50-μm-thick film, when the excitation energy density increases above 25 μJ/cm^2, spectral narrowing and nonlinear increasing of intensity were observed. To get more information on lasing, single-shot spectrum was measured. Finally, the dependence of the lasing behavior, including the recognition of the existence of a threshold on the film thickness was demonstrated.

1. Introduction

Nowadays, the investigation of hybrid organic–inorganic materials is the subject of a large number of research works [1–4]. For example, fluorescent SiO_2 particles have attracted a great attention due to their considerable advantages with respect to conventional molecular dyes for fluorescent labels, tracers, sensors and so on [5–9]. Because of the encapsulation of a large number of dyes into the small volume of a single SiO_2 particle and the large variety of available fluorescent dyes, it is plausible to expect the expansion of the application area of fluorescent SiO_2 particles. Here, we have used the fluorescent SiO_2 particles for random lasing system since they have higher concentration of dye and scatters [10] itself.

Since the first observation of lasing-like emission in disordered media [11], random lasing has been demonstrated in a variety of systems, such as semiconductor nanocrystalline powder and film [12–17], nanostructured semiconductor thin films [18], laser dye solutions and polymer films with scattering particles [19–23], and porous alumina membrane filled with hybrid polymer nanowires [24].

In this study, we report on random lasing occurrence in the films which are electro-fabricated with charged fluorescent SiO_2 particles for the first time. To prepare a film with a homogeneous thickness, we have used electrostatically charged fluorescent SiO_2 particles (multifunctional SiO_2 particles) because electrophoretic deposition method is an advantageous method to prepare smooth coatings and a desired pattern. The thickness of the film can be systematically controlled by adjusting the deposition time. Finally, it is demonstrated that the existence of lasing behavior implies a threshold in the film thickness. This is important for potential applications, since we were able to determine the minimum thickness required for the construction of multifunctional SiO_2 particles film laser.

2. Experimental

SiO_2 particles were synthesized by following the recipe of Stöber method [25]. Briefly, 13.5 g of tetraethyl orthosilicate (Aldrich) was slowly added to a mixture of NH_3 (33% in water), ethanol, and water of the following composition (4.3 mL/65.7 mL/1.2 mL). This mixture was heated to 40 °C under vigorous stirring for 3 h.

To get the functionalization of silica particles, 1 mL of 3-aminopropyltriethoxysilane (Aldrich) was dissolved into 10 mL of dichloromethane at room temperature. Then 80 mg of Rhodamine B isocyanate (RBI, Aldrich) was added and the reaction was continued for 15 min [26]. After reaction, this solution was added without purification to the above mixture. It was stirred overnight, and then the multifunctional SiO_2 particles were centrifuged and repetitively washed with ethanol 3 times.

Prior to electrophoretic depositions, the multifunctional SiO_2 particles were once again washed by centrifugation for 30 min with ethanol. It was confirmed that there was no dye leakage from the SiO_2 particles. Two ITO-coated glasses as electrodes were cut into 3.0 cm × 10.0 cm and then the electrode surface was cleaned using isopropyl alcohol before use. To prevent aggregation of multifunctional SiO_2 particles, particles dispersed in ethanol were treated with ultrasonication for 30 min. As shown in Scheme 1, two ITO-coated glasses were immersed in a small glass cell containing the multifunctional SiO_2 particles (20 mg) in ethanol (60 ml). The distance between the two electrodes was 2 cm. A 50 V DC voltage was applied constantly. The deposition time varied from 15 to 60 min according to the desired film thicknesses. After the electrophoretic deposition was complete, the films were dried at room temperature.

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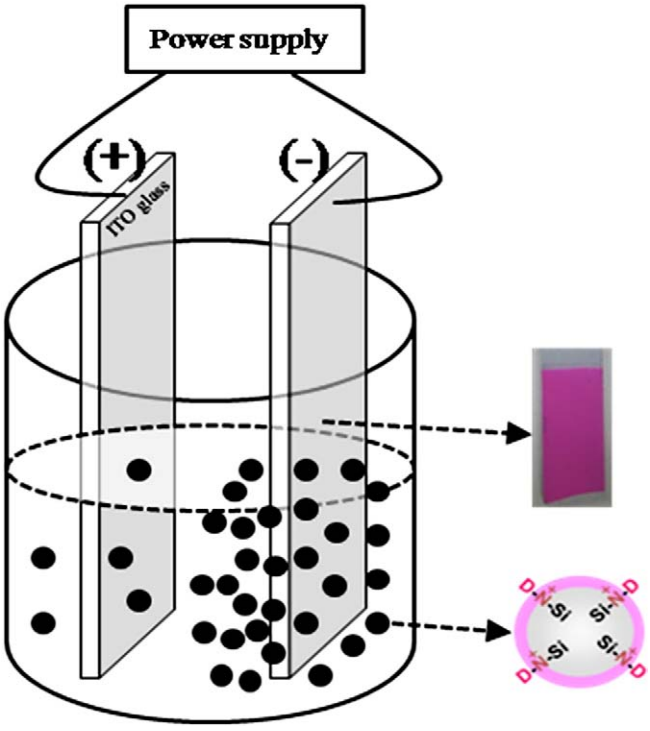

Scheme 1. Fabrication of random lasing film by electrochemical coating.

The experimental setup to investigate the lasing behaviors was the same as described in Ref. [24]. The frequency-doubled output (532 nm) of mode-locked Nd-YAG laser (Continuum Leopard D-10, 25 ps pulse width, 10 Hz) was used as a pump pulse which was focused to a spot on the surface of the films. Emission light was collected using a fiber-coupled spectrometer equipped with a thermoelectrically cooled charge-coupled detector (Andor, DU401-BV). The angle between the fiber and the plane of films was 45°. Pulse energy was controlled by a set of neutral density filter and residual pump light was eliminated by a cut-off filter prior to the detector. The overall spectral resolution of the detection system was estimated to be 0.3 nm from the calibration with a Hg lamp (CVI).

For SEM pictures a field emission scanning electron microscope (FE-SEM, Jeol, JSM-6700F) was used.

3. Results and discussions

SEM images of the multifunctional SiO_2 particles and its film are shown in Fig. 1. It can be seen that the film consists of spherical particles with a mean diameter of about 800 nm. In addition, cross-sectional views of the film (Fig. 1(c)–(d)) indicate that the thickness is 50 μm with a small surface roughness of ±3 μm.

Fig. 2(a) shows the evolution of the photoluminescence (PL) spectra from 50-μm-thick film with excitation energy densities ranging from 4 to 66 μJ/cm^2. The accumulation number was 50 laser pulses for each spectrum. At low excitation energy densities, the PL spectra exhibit a broad spontaneous emission with a full width at half-maximum (FWHM) of 50 nm. When the excitation energy density

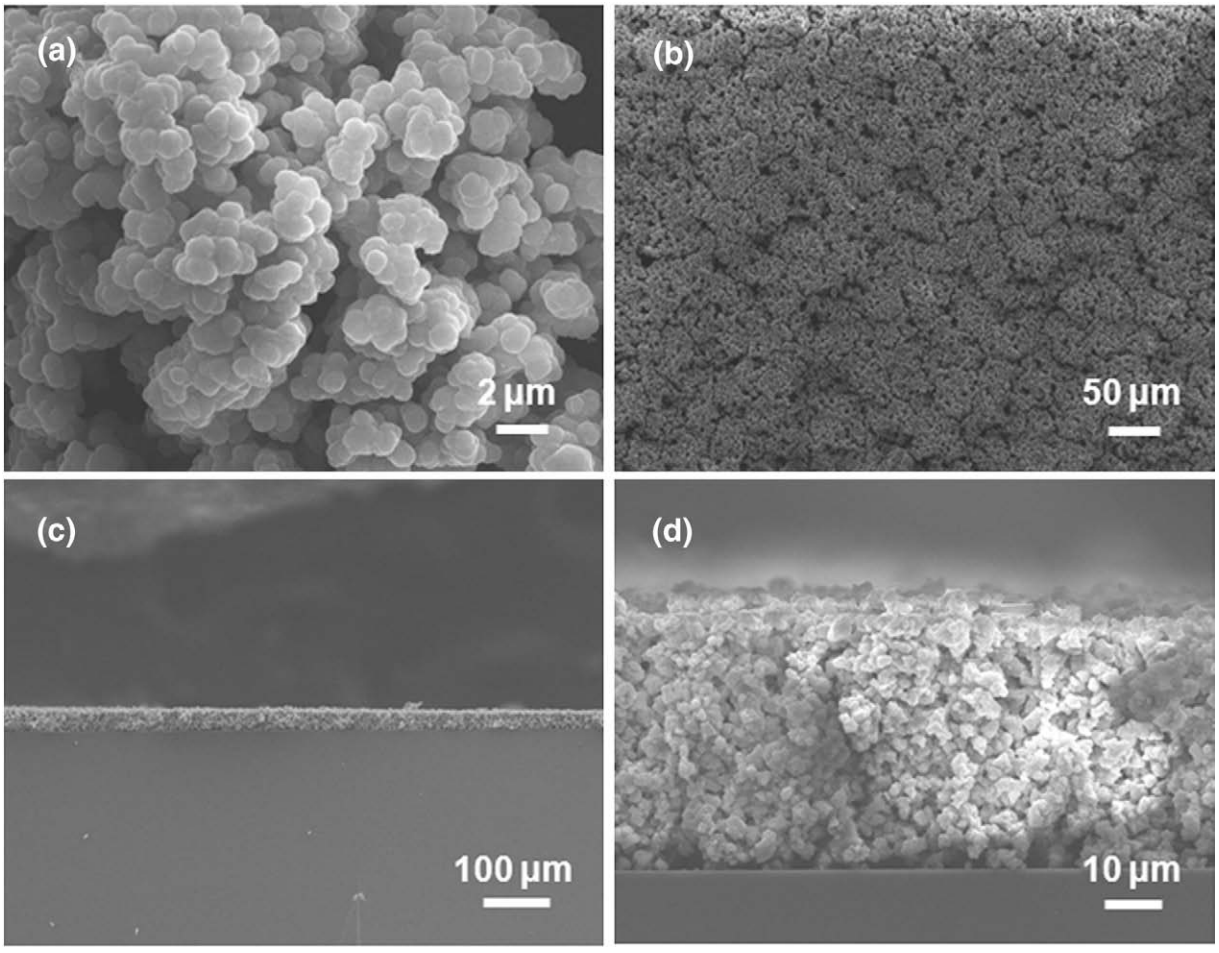

Fig. 1. FE-SEM images of (a) multifunctional SiO_2 particles, (b) top and (c)–(d) cross-sectional views of 50-μm thick multifunctional SiO_2 film.

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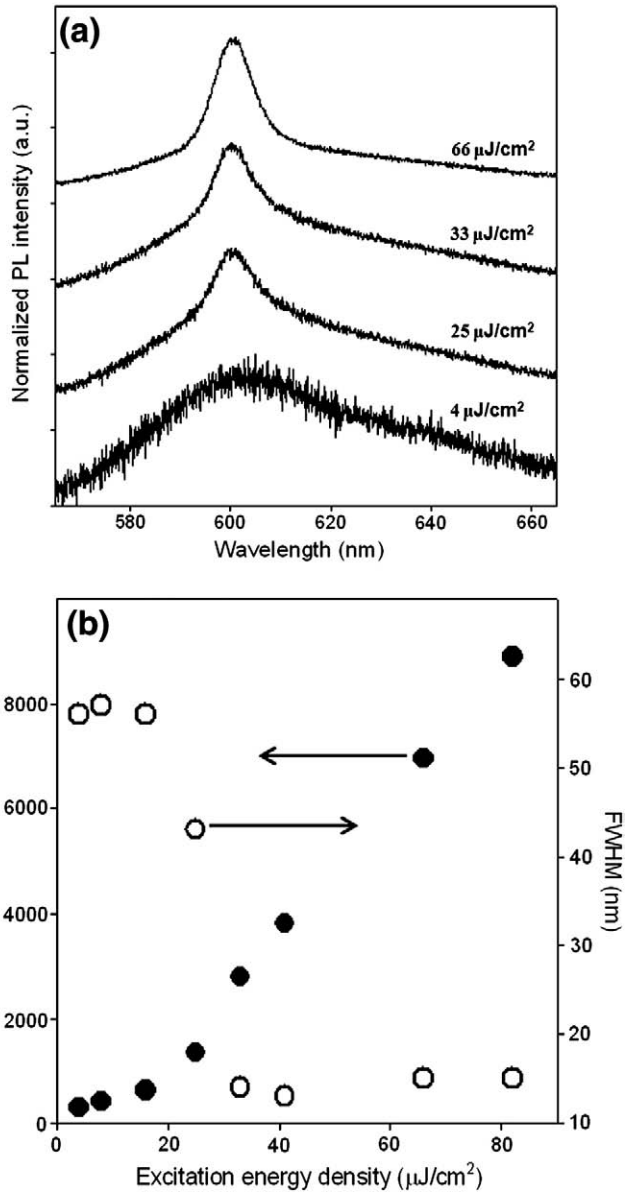

Fig. 2. (a) PL spectra of a 50-μm thick multifunctional SiO_2 film with different excitation energy densities. The accumulation number was 50 laser pulses for each spectrum. (b) Spectral bandwidth (empty circles) and peak intensity (filled circles) as functions of excitation energy density.

increases above 25 μJ/cm^2, the PL intensity increases much more rapidly and the FWHM of the PL spectrum narrows down to 13 nm simultaneously. As shown in Fig. 2(b), the intensity and FWHM of the PL band versus excitation energy density indicate a clear threshold.

Such spectral narrowing associated with a nonlinear intensity variation is indeed characteristic of an amplified spontaneous emission (ASE), but not necessarily random lasing [20,21,27]. According to our previous study of random lasing within a porous alumina membrane [24], it is necessary to obtain spectrally sharp peaks to assess the occurrence of random lasing. However, it should be mentioned that close-packed SiO_2 particles within pumped volume provides many lasing modes above the threshold, which leads to a more complicated lasing behavior. Especially, since the measured PL spectra represent the collective emission during the accumulation, it could be possible that the superposition of lasing modes turns a series of sharp peaks into a seemingly ASE band of 13 nm at FWHM [28,29].

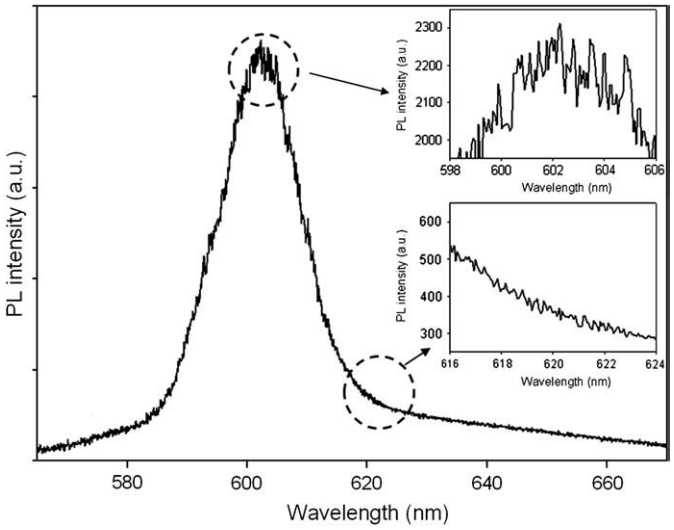

Fig. 3. Single-shot PL spectrum from 50-μm thick multifunctional SiO_2 film with excitation energy density of 66 μJ/cm^2. The inset shows a magnified spectrum.

To confirm this assumption, we captured a series of single-pulse spectra upon excitation of the same spot. Fig. 3 shows single-shot PL spectrum from a 50-μm thick film with an excitation energy density of

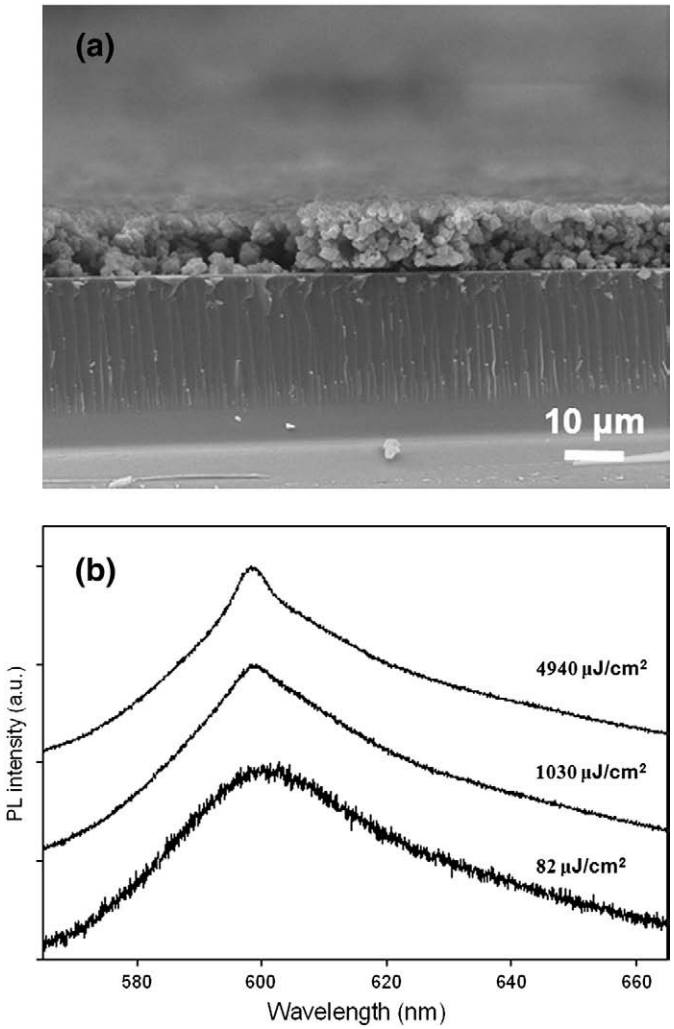

Fig. 4. (a) FE-SEM image of the cross-sectional view of a 12-μm thick multifunctional SiO_2 film. (b) PL spectra with different excitation energy densities for the same film. The accumulation number was 50 laser shots for each spectrum.

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66 μJ/cm^2. As shown in the insets of Fig. 3, a number of sharp emission peaks were seen with a reasonable signal-to-noise ratio although no individual lasing mode was clearly resolved. In order to confirm that the peaks were not the noise but the random lasing, statistical standard deviation calculation was done in two typical ranges of the signal where one was considered to be the noise range and the other range was possibly from the lasing peaks. As expected from the visual observation of the data in insets of Fig. 3, the lasing peaks to be expected indicate a 52.32 value of the standard deviation from the best polynomial fitting, whereas the signal in the noise expected range yields 5.97 value of the standard deviation from the same fitting routine. Therefore such a large difference of 10 times in the standard deviation implies that the peaks in the range of signal expected are to be due to the multimode random lasing. In addition, the PL spectrum including the peak positions changed from pulse to pulse in a random manner on the same spot. Therefore, it is understandable that there are too many lasing modes within one given pumped volume to be separated into individual modes.

In order to verify that the lasing behavior also depends on the thickness, the power dependant PL measurements of films with various thicknesses were performed. Fig. 4(b) shows the PL spectral evolution pattern of 12-μm thick film (cross-sectional view shown on Fig. 4(a)). The evolution was similar to that of the 50-μm thick film; however the 1030 μJ/cm^2 lasing threshold was much higher than the one of the 50-μm thick film (25 μJ/cm^2).

Fig. 5(a)–(e) presents the spectral FWHM and the peak intensity of the PL band as a function of the excitation energy density. Clearly the figures indicate film thickness dependence of the threshold value of excitation energy density. Fig. 5(f) summarizes the film thickness dependence of the threshold. Although there is no significant difference in the lasing spectra between films with different thickness from 10 to 50 μm, the lasing threshold is increased while the thickness decreases. It is noteworthy that, in case of thinner film less than 10 μm, we could not observe any lasing behavior even at the damage threshold of ~6 mJ/cm^2. It is because the volume of this film is not enough for forming the closed loops.

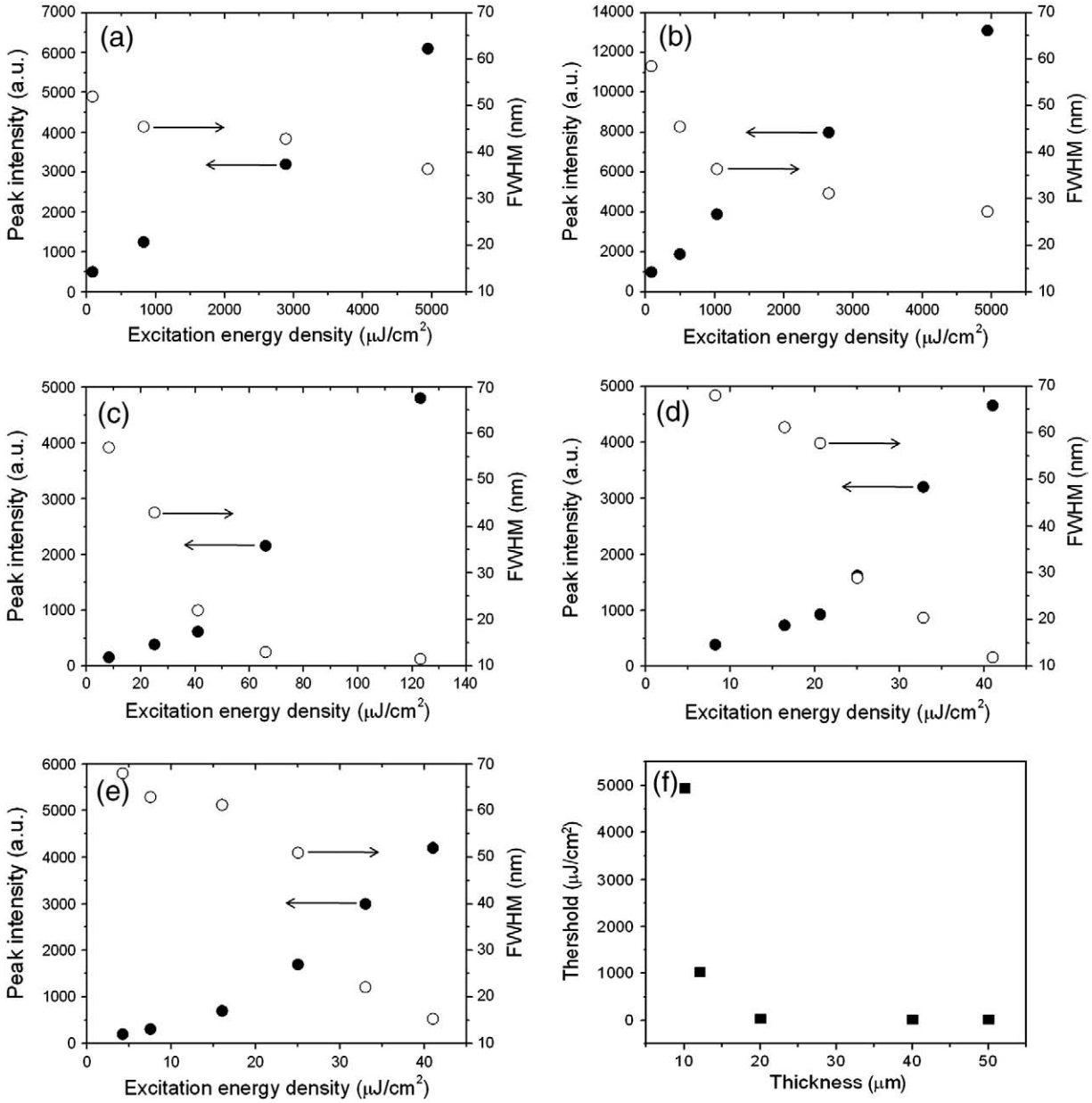

Fig. 5. Spectral bandwidth (empty circles) and peak intensity (filled circles) as functions of excitation energy density at multifunctional SiO_2 films of various thicknesses: (a) 10 μm, (b) 12 μm, (c) 20 μm, (d) 40 μm and (e) 50 μm. Variation of lasing threshold with thickness of the multifunctional SiO_2 film (f).

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4. Conclusions

It was demonstrated that random lasing in multifunctional SiO_2 particle films could be achieved within films featuring various thicknesses. The thickness could be precisely controlled by adjusting the electrophoretic deposition time. From the single-pulse PL spectrum, it was revealed that several lasing modes were generated and superimposed each other within a pumped volume above the threshold. From the relation between the thickness and lasing threshold, it can be estimated that a thickness of 20 μm is close to an optimum for random lasing.

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