PROCEEDINGS OF THE INTERNATIONAL DISPLAY WORKSHOPS, VOL.29, 2022

Formation of Nano-Sized Crystals of Organic Phosphor on Substrate with Fine-Hole Structure

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Keywords: Nano-sized crystal, Solution process, Organic phosphor, Surface wettability

ABSTRACT

To obtain nano-sized crystals of organic phosphor for high efficiency and narrow band emission, we proposed fine-hole structure and wettability pattern control. As a result, we found that we can control the crystal growth field by wettability control. We also succeeded in making nano-size organic phosphor crystals.

1 Introduction

Phosphors are widely used as light emitting devices and wavelength conversion materials due to their ability to absorb incident light and emit it at different wavelengths [1]. In the future, there is a need for more flexible excitation and fluorescence wavelengths and narrow-band emission to improve light utilization efficiency, color purity, and color rendering. On the other hand, in recent years, organic dyes and semiconductors with carbon as their molecular backbone have remarkably improved their luminescence efficiency and electrification transfer properties by improving their molecular structures and molecular packing according to the progress of OLED displays. Therefore, organic phosphors have attracted much attention. However, there is a problem of concentration quenching (Fig. 1), in which an increase in fluorescence concentration causes nonradiative inactivation, in which excitation energy is converted to thermal vibration or other energy, resulting in a decrease in fluorescence intensity[2]. To solve this problem, there is a method of reducing the size of the phosphors to nano-sized body. Nanosized organic phosphor crystals are not affected by concentration quenching due to their own size. In addition, narrowing of the emission spectrum (quantum dots) can be expected (Fig. 2). Nano-sized organic phosphor crystals are expected to be applied to wavelength conversion devices and OLEDs because of their luminescence efficiency and narrow bandwidth [3][4]. However, it is difficult to form nano-sized crystals on a substrate with a flat surface because the deposition position of crystal nuclei cannot be controlled.

To solve this problem, this study attempted to grow organic phosphor crystals using a substrate with fine-hole structure with a limited crystal growth field for the fabrication of nano-sized organic phosphor crystals.

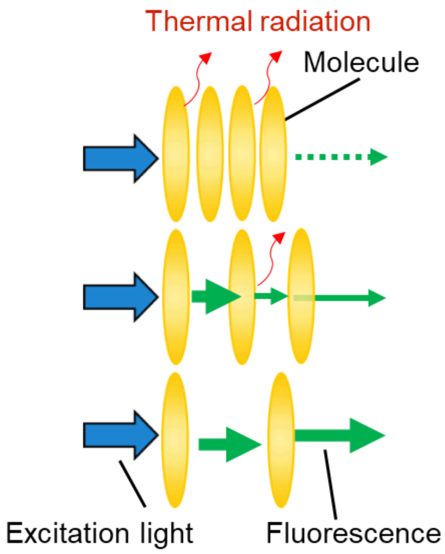

Fig. 1 Efficiency by concentration optimization

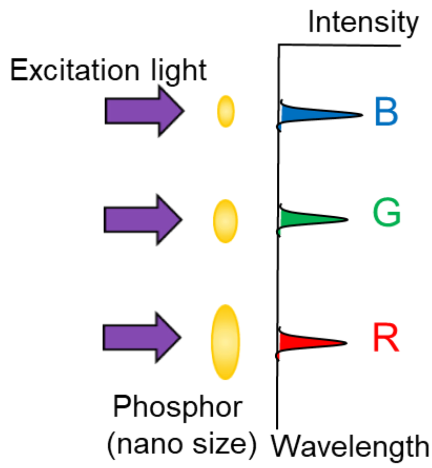

Fig. 2 Narrow band emission by quantum dots effect

2 Principle of fabrication method of nano-sized organic phosphor crystals using fine-hole structure

In this study, we proposed the method shown in Figure 3 for the fabrication of organic phosphor nano-sized crystals. First, we make a microfabricated substrate to limit the crystal growth field to a small area. By confining the organic phosphor solution to those micro regions, crystals of uniform size are generated. To ensure that the volume of solution injected into each micropore is uniform, the wettability of the substrate surface is controlled. For example, as shown in Figure 4, a mechanism is expected to efficiently accumulate the solution in the holes by reducing the wettability of the substrate surface. Next, the solution is applied using a miniaturization technique so that the solution penetrates into the micromoles. The substrate surface is then flattened with a blade to make the amount of solution in each hole uniform. At the bottom of each hole, crystals grow due to recrystallization associated with the volatilization of the solvent.

The structure of the nano-hole substrate used in this study is shown in Figure 2. Holes of 1 µm in both diameter and depth were fabricated by photolithography at 1 µm intervals, 10 mm in length and 5 mm in width (the substrate is supplied from Dai Nippon Printing Co.,ltd). The substrate material is quartz.

Wettability control and solution miniaturization are discussed in the next chapter.

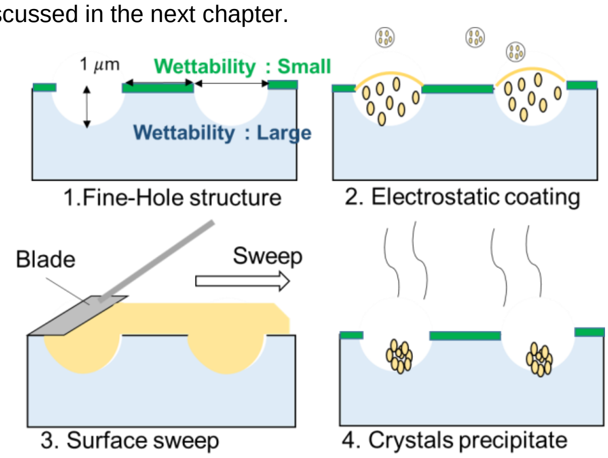

Fig. 3 Manufacturing principle

3 fabrication of nano-sized organic phosphor crystals using a wettability-controlled and electrostatic coating system

In this chapter, we proposed a method making nano-sized crystals composed of organic phosphor using a wettability-controlled and electrostatic coating system.

3.1 Substrate design and fabrication

The target crystal size is approximately several nanometers to several tens of nanometers. To fabricate the crystals, we defined the size of the fine-hole as several hundred nanometers to several microns. We fabricate the fine-hole structure in quartz glass by lithography method using electron beam. We fabricated several types of holes using this method. Among them, we use 1 µm holes in this experiment.

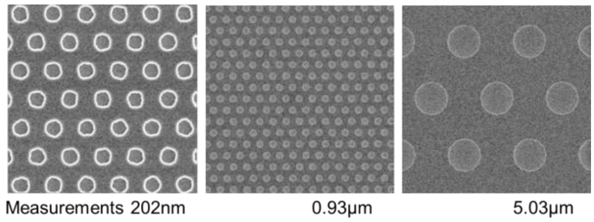

Fig. 4 Photographs of fine-hole structure

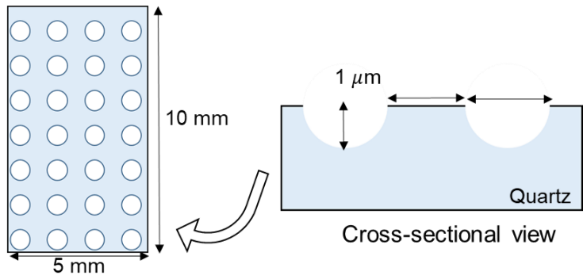

Fig. 4 Schema of fine-hole structure

3.2 Solution Considerations

In order to fabricate nano-sized crystals, organic phosphors are selected based on the following two conditions. First, the phosphors must be soluble. Second, the molecular structure of the phosphor must be known. The reason is that it reveals the properties of the substance. Considering these factors, we selected coumarin 6 as the organic phosphor. Next, the solvent was selected based on the following two conditions. First, the solvent must be sufficiently soluble in coumarin 6. The first is that the solvent must be sufficiently soluble in coumarin 6, since performing solution applications. Second, the volatilization speed must be relatively slow. The second reason is that the volatilization rate is relatively slow, because if the volatilization rate is fast, the material does not crystallize and becomes amorphous. Considering these factors, we selected chlorobenzene as the solvent. After examining various solvents, we found that coumarin 6 is soluble in chlorobenzene. Therefore, we selected chlorobenzene as the solvent. It is mixed and used at a concentration of 0.3 wt%.

3.3 Wettability Control by Friction Transfer Method

When crystals are fabricated on the proposed substrate, it is expected that non-uniform crystals will be generated if phosphor solution remains on the flat surface of the substrate surface. Therefore, it is necessary to control the solution so that no solution remains on the substrate surface, but only in the holes. It has been shown that the difference in wettability can be used to limit the crystal growth field [5][6]. Therefore, wettability control is performed by imparting water repellency only to the substrate surface. As a method, we propose the friction transfer method.

We selected a fluoropolymer CYTOP (CTL-809A, AGC) as the water-repellent material. First, it is applied by spin-coating method on bare glass and heated on a hot plate at 100°C for 7 minutes (Fig. 5). Then, the CYTOP coated bare glass is friction-transferred onto the mold substrate. For friction transfer, the bare glass is placed on the nano-hole substrate and pressed down hard by hand and rubbed for 30 seconds. Then, the film is baked in an oven at 200°C for 1 hour to create a water-repellent film.

We performed contact angle measurements to confirm whether the CYTOP was transferred to the wetting control substrate produced by this method [7]. The contact angle is the angle formed by the tangent line between the substrate surface and the droplet edge. A large contact angle indicates low wettability (easy to repel), while a small contact angle indicates high wettability (easy to wet). To measure the contact angle, a few μ L droplet is photographed from the side with a camera, and the contact angle is calculated by analyzing the contour shape of the droplet from the image. The solution to be dropped is chlorobenzene, which is used as a solvent for coumarin 6. Photographs of the measured contact angles are shown in Figures 5 and 6. The contact angle of the substrate before transfer was 5.18° and that of the substrate after transfer was 39.25°. Thus, friction transfer of the water-repellent film is effective.

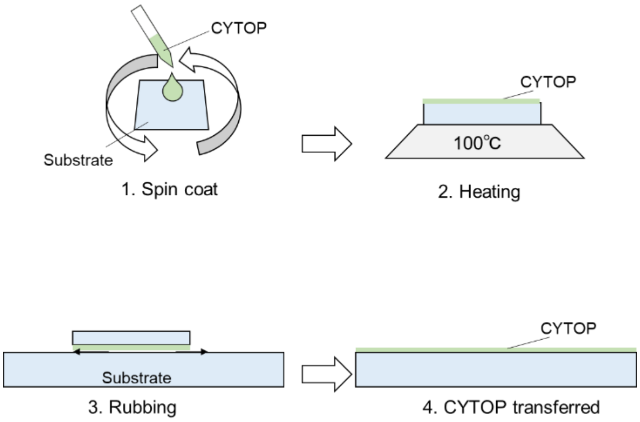

Fig. 5 Friction transfer

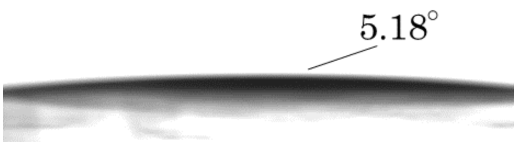

Fig. 5 Before friction transfer

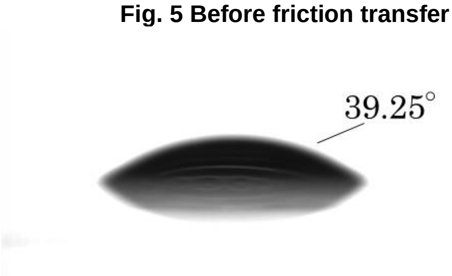

Fig. 6 After friction transfer

3.4 Micronized spraying by electrostatic coating

Electrostatic coating was used as a method of droplet miniaturization. Electrostatic coating is a method in which an electric field is applied to the surface of the liquid dripping from the nozzle tip to split it into fine droplets [8]. The principle diagram is shown in Figure 3 and the actual photograph in Figure 4. Positively charged droplets repel each other inside themselves and repeatedly break up. As a result, the droplet is broken up exponentially and becomes finer. Since the droplets can be applied at a few microns, they can easily penetrate into holes.

The conditions for electrostatic coating are a voltage of 10 kV and a coating volume of 0.01 ml/min. After a certain amount of solution has been dropped, the solution is removed by using a water-repellent spatula to scrape off the solution on the substrate surface. The substrate is then left for 1 hour to allow the solvent to fully volatilize.

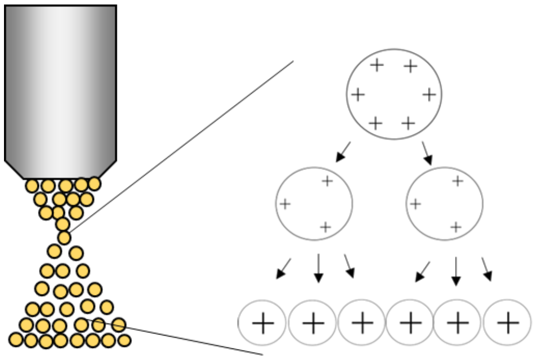

Fig. 7 Principle of electrostatic coating

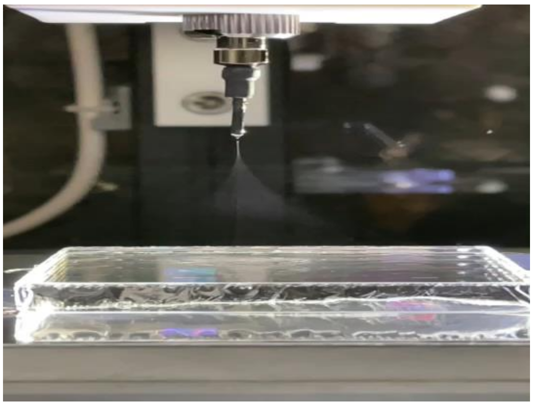

Fig. 8 Photo of electrostatic coating

4 Crystal fabrication results

We performed electrostatic coating method on the substrate after wettability control by the proposed method. The results of observation of the substrate with a polarizing microscope are shown in Figure 9 and Figure 10. It can be seen that phosphors are deposited on the surface of the substrate without wettability control. On the other hand, the substrate with water wettability control shows that the phosphors are deposited only in the holes. In addition, comparing Figure 11~13 observed by polarizing microscope under crossed Nichol, the extinction position can be confirmed. From this, we concluded that phosphors are crystallized. Further fine-hole miniaturization will reduce agglomeration of crystals. In addition, single crystallization will also be possible.

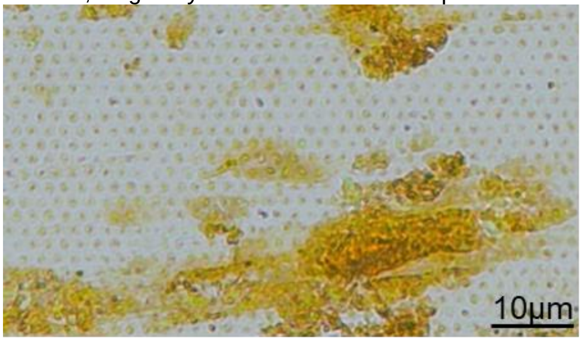

Fig. 9 Electrostatic coating with untreated substrate

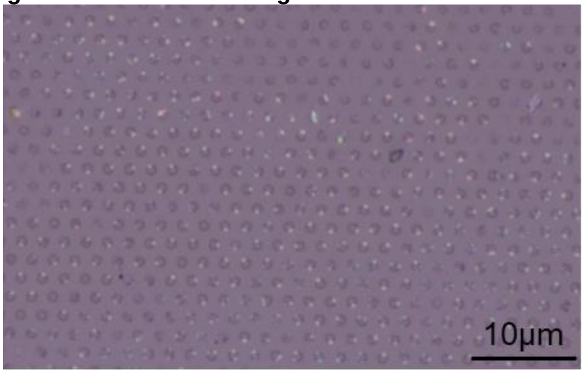

Fig. 10 Electrostatic coating with wettability control substrate

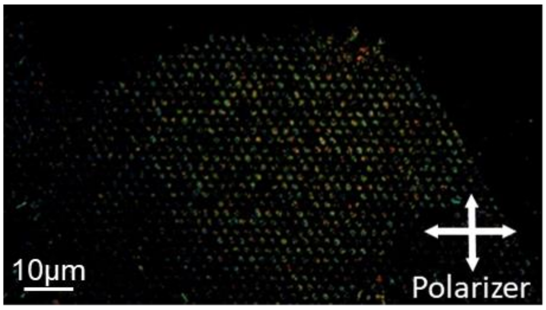

Fig. 11 Polarizing microscope

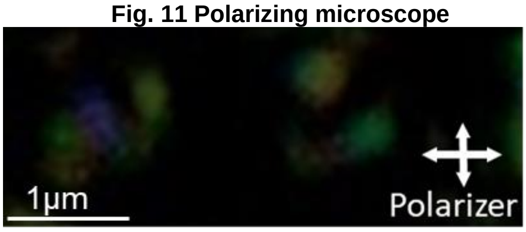

Fig. 12 Enlarged view (0°)

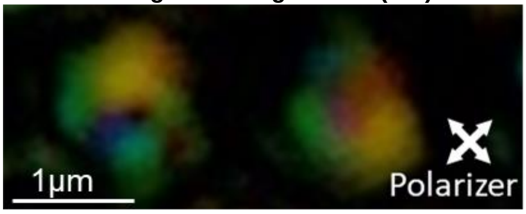

Fig. 13 Enlarged view (45°)

5 Conclusions

In this study, in order to realize nano-sized crystal formation of organic phosphors based on nano-hole substrates, wettability control and electrostatic coating system were evaluated. As a result, it was clarified that the crystal growth field can be limited by wettability control substrate. Furthermore, it was clarified that nano-sized crystals of organic phosphors can be fabricated by using nano-hole substrates.

These results indicate that it is possible to fabricate crystals of arbitrary size by changing the size of the holes.

ACKOWLEDGEMENT

This work was supported by JSPS KAKENHI (grant number: 20H00232).

Fine-hole patterned substrates were supplied from Dai Nippon Printing Co,ltd.

References

[1] T. Murase, "Development of a New Type of High-Brightness Phosphor - Expectations for Applications in Lighting and Displays," *AIST Today*, pp. 7–9, 2003.

[2] S. Kato, "Research on quenching action on organic phosphorescent substances." Japanese Journal of Chemistry. vol. 74, no.10, pp. 865–871,1952.

[3] S. Takeshita, "Size-Controlled Synthesis of Inorganic Nanoparticle Phosphors," pp. 106–110, 2015.

[4] M. Iwasaki, "Preparation of nanosized red phosphor and its fluorescent properties *," *Min. Mater. Process. Inst. Japan*, vol. 120, pp. 446–450, 2004.

[5] K. NOGI and K. OGINO, "Control of wettability between metals and ceramics.," *Journal of the Japan Society for Composite Materials*, vol. 16, no. 3. pp. 85–92, 1990.

[6] N. Takayama, "Attempt to control wettability by surface texture," Precision Engineering Society Spring Conference Academic Lecture. p. 102, 2003,

[7] H. Takao, H. Hasegawa, T. Tsukada, K. I. Yamada, and M. Yamashita, "Development of Wettability Evaluation Technique Using Contact Angle Measuring Equipment in Soldering," *J. Japan Inst. Electron. Packag.*, vol. 6, no. 6, pp. 488–495, 2003.

[8] T. Suzuki, "Photoluminescence Spectrum for Organic Deposited by Electrospray Deposition Method," *Inst. Image Inf. Telev. Eng.*, pp. 77–80, 2009.