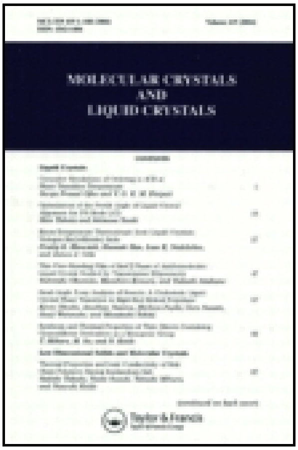

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Olaf Karthaus [a], Chihaya Adachi [a], Shiho Arakaki [a], Ayataka Endo [a] & Toshihiro Wada [a]
[a] Chitose Institute of Science and Technology, Chitose, Japan

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Preparation of Micropatterned Organic Light Emitting Diodes by Self-Organization

Olaf Karthaus
Chihaya Adachi
Shiho Arakaki
Ayataka Endo
Toshihiro Wada
Chitose Institute of Science and Technology, Chitose, Japan

A dewetting process of an evaporating solution is used to form micrometer-sized amorphous droplets, or domes, of the low molar mass solute on substrates such as silicon, mica, glass, and indium-tin-oxide. Using dewetting, the organic hole transporting material of organic light emitting diodes was patterened into micrometer-sized domes on an indium-tin-oxide electrode. Annealing led to a structural change of the domes, which was investigated by optical and electron microscopes. The dewetted dome samples were then coated with electron transport material and top electrode to give functioning organic light emitting diodes devices.

Keywords: dewetting; hole transport material; light-emitting microdomes; microdroplet; OLED; organic light emitting diode

INTRODUCTION

Organic light emitting diodes (OLEDs) have attracted increasing interest over the past few years. Organic electroluminescence was first described in molecular crystals in the 1960s [1,2]. Groundbreaking work has been done by Tang and Slyke [3] who used vacuum evaporated thin films, and by Friend *et al.* [4] who used a wet spin coating process to produce OLEDs from emitting and conducting polymers. Both techniques allow the preparation of patterned devices. Evaporation through a shadow mask, screen-printing, or ink-jet printing

Address correspondence to Olaf Karthaus, Chitose Institute of Science and Technology, Bibi 758-65, Chitose 066-8655, Japan. E-mail: Karthaus@phton.chitose.ac.jp

are commonly used to prepare patterns of organic materials with dimensions down to a few ten micrometer.

We have recently reported on the self-organization of hole transporting materials into micrometer-sized droplets, or "domes" on substrates. Preparation of OLEDs from these dewetted structures gave light emitting spots with one micrometer in diameter [5]. Thus not only the engineering approach of surface patterning through masks, etc. is successful to prepare patterned films, but also the self-organization of organic materials into micron-sized aggregates can be utilized to form patterned OLEDs. Advantages of the self-assembly are low cost, ease of fabrication, speed, no need for shadow masks or ultra-high vacuum, preparation of large areas, etc.

Another advantage of restricting the compound in micrometer-sized domes is the control of aggregation state. Low molar mass compounds are known to crystallize if the absolute value of the enthalpy of crystallization is larger than the loss in entropy upon crystallization. Thus the amorphous state of a low molar mass compound is often thermodynamically unstable, and crystallization takes place. This process then leads to the destruction of the OLED device, since the crystallization of a thin film gives rise to polycrystalline films where energy or electron trapping at grain boundaries occurs.

We have found that crystallization of organic compounds can be controlled [6–10], and even be suppressed [5] by fabrication of the material into microdomes. Depending on the annealing conditions, each microdome crystallizes into a single crystal, or as polycrystals.

Here, we report on the formation of yet another aggregation state (besides amorphous, single crystalline and polycrystalline) of tetraphenylbenzidine (TPB), a hole transport material for OLEDs, and on the electroluminescent characteristics of OLED devices patterned into microdomes.

MATERIALS AND EXPERIMENTAL METHODS

N,N,N′,N′-Tetraphenylbenzidine (TPB) was used as purchased from TCI; Japan. Indium-Tin-oxide-covered glass (Sanyo Vacuum Industry Co. Ltd., Japan) was cleaned in an UV/ozone cleaner (Nippon Laser + Electronics, NL-UV 253 S) for 30 minutes. Poly(ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT/PPS) (Baytron, Germany) was spin cast from dilute solution to give an approx. 25 nm thin film on the ITO electrode. This coating of the ITO electrode gives a very smooth and hydrophilic surface, which is desirable for effcient dewetting of the organic solution [5]. Furthermore, it facilitates hole injection into the organic compound. TPB was dissolved in chloroform (Merck, Germany) to form a 0.1 wt% solution. This was cast onto the PEDOT/PSS coated ITO electrode with the help of a roller having a gap of ca. 1 mm between ITO substrate and roller. The roller was moved with a constant speed of 5 mm/min over the substrate, and the dewetted TPB domes prepared by this method had a diameter of a 3–7 μm. The sample was then annealed in an oven in ambient atmosphere at 120°C–160°C for 24 h. Optical microscopy (Olympus BX-51, Japan) and electron microscopy (Hitachi S3500N) was performed to check the morphology of the samples. For OLED devices, the annealed samples were coated with the electron transport material, tris-quinolato aluminum (Alq3) and top electrode (Mg/Ag and Ag) by conventional vacuum deposition. The device was driven at 6 V and the luminescence image was taken by an inverted microscope (Olympus IX-70, Japan), equipped with a high-resolution CCD camera (Hamamatsu Photonics C 4880, Japan).

Film Morphology

TPB microdomes directly after dewetting on the PEDOT/PSS-coated ITO are spherical and transparent. They show a narrow size distribution of 3–7 μm and an inter-dome distance of approximately 4 times their diameter. Figure 1 shows a reflection micrograph of sample after annealing at 120°C for 24 hrs. In the lower left part a few remaining spherical domes can be seen. The reflection micrograph shows concentric interference patterns, which are a proof for the spherical shape. Some of the domes in the upper part of the picture are crystalline, and connected by crystalline fibers. These fibers grow out of crystallizing domes, as described earlier [6]. Both features, amorphous and crystalline, can also be observed in the transmission micrograph of the sample. But the round features in the central part of the reflection micrograph (indicated by the arrows) are not reproduced in the transmission mode. The shape and distance from the crystals and amorphous domes suggest that they are remnants of amorphous domes. But the height of the features is too small to give a contrast in the transmission micrograph. The reflectivity of the features is only slightly different from the substrate itself, so it can be concluded that they have to be very thin disk-like aggregates of TPB. Since some of them are in direct contact with crystal needles, it also can be said that they are not amorphous [6]. Because the disk state is very thin, polarizing microscopy did not show any birefringence, so there is no direct proof for crystallinity. Since the underlying PEDOT/PSS film is fluorescent, fluorescent microscopy cannot be used either to elucidate on the aggregation state (shift of fluorescence wavelength, polarized emission, etc).

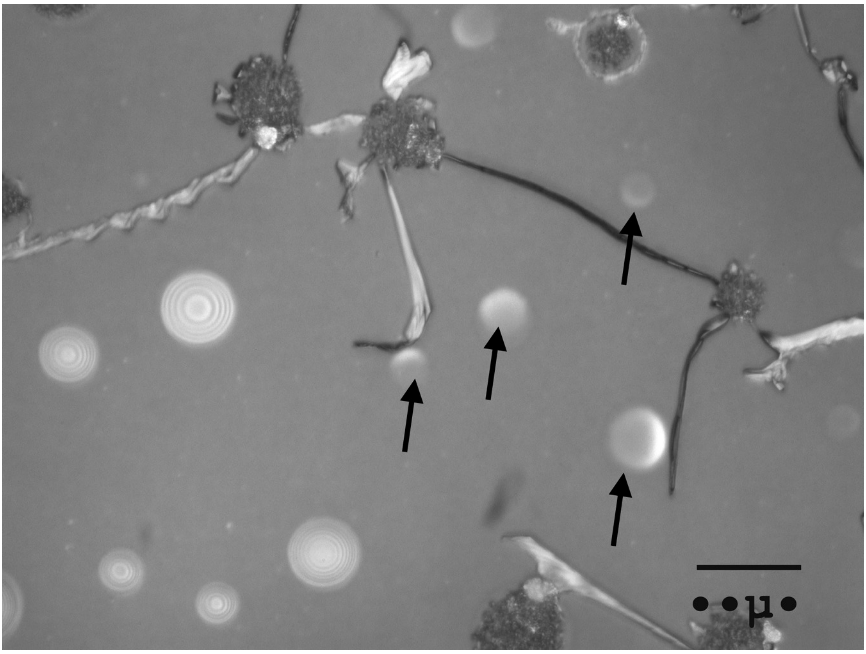

FIGURE 1 Reflection micrograph of a dewetted sample of TPB on a PEDOT/PSS-coated ITO electrode after annealing for 24 h at 120°C. The arrows indicate disk-shaped aggregates of TPB (details in the text).

Thus there is no direct evidence for the aggregation state of the TPB molecules in the disks.

Scanning electron micrographs of a similar sample after annealing are shown in Figure 2. It shows the same three morphologies: amorphous domes, polycrystalline needles and disk-like aggregates. Some of the disks protrude from the PEDOT/PSS film, while others look like a depression in the film.

Even though there is clear evidence for a third aggregation state for TPB, it is still unclear what aggregation state it is. Annealing at elevated temperature might have led to the diffusion of the TPB into the underlying PEDOT/PSS film, maybe facilitated by residual solvent in the initially amorphous microdome of TPB.

Electroluminescence

One of the annealed samples, which showed polycrystalline and disk-like features, was used to prepare an OLED. An electron-conducting

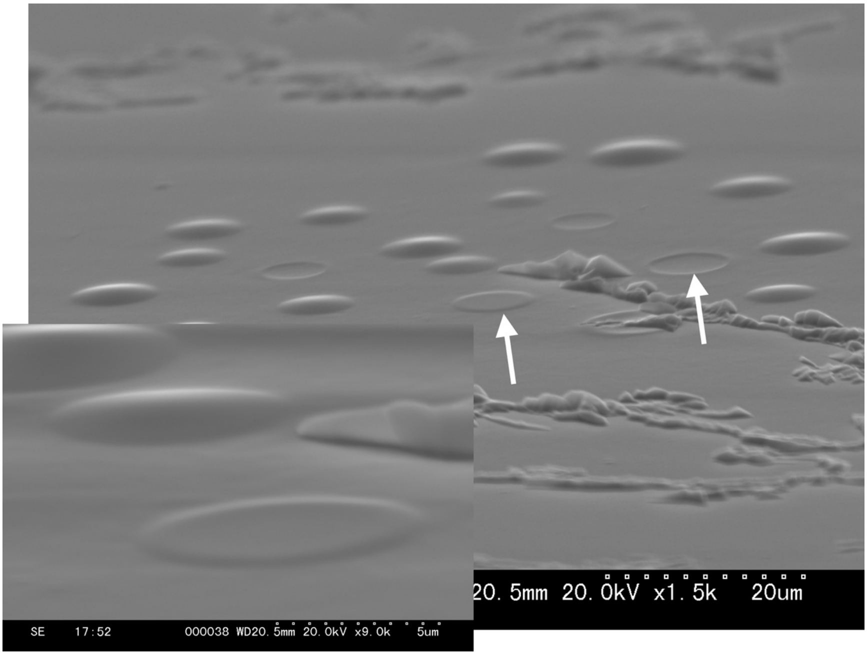

FIGURE 2 Scanning electron micrograph of a TPB sample annealed at 120°C for 24 h. The white arrows indicate two disk-like structures, one protruding from the film (on the left) and one embedded in the film (on the right). The inset shows a larger resolution of the protruding disk.

layer of Alq3 and a Mg/Ag top electrode were vacuum evaporated on top of the partially crystalline hole transport layer. The OLED was placed upon an inverted microscope, which allowed the contact of the metal electrode from above, while the electroluminescence was collected by a 10× lens below the transparent ITO electrode. Figure 3 shows the electroluminescence image of a device operated at 10 V. The driving voltage of 10 V was chosen, because a device made of amorphous TPD microdomes showed stable electroluminescence at this voltage [5]. This previously reported "amorphous" device showed linear relation between driving voltage and current in the double-logarithmic plot [5], and an external quantum yield of ca. 0.1% between 4 and 10 V.

The polycrystalline domes and the connecting crystal fibers do not luminesce at all. This was expected, since polycrystalline samples have grain boundaries, defects and other type of sites that can act as trap sites for charge carriers. Crystallization leads to a change in

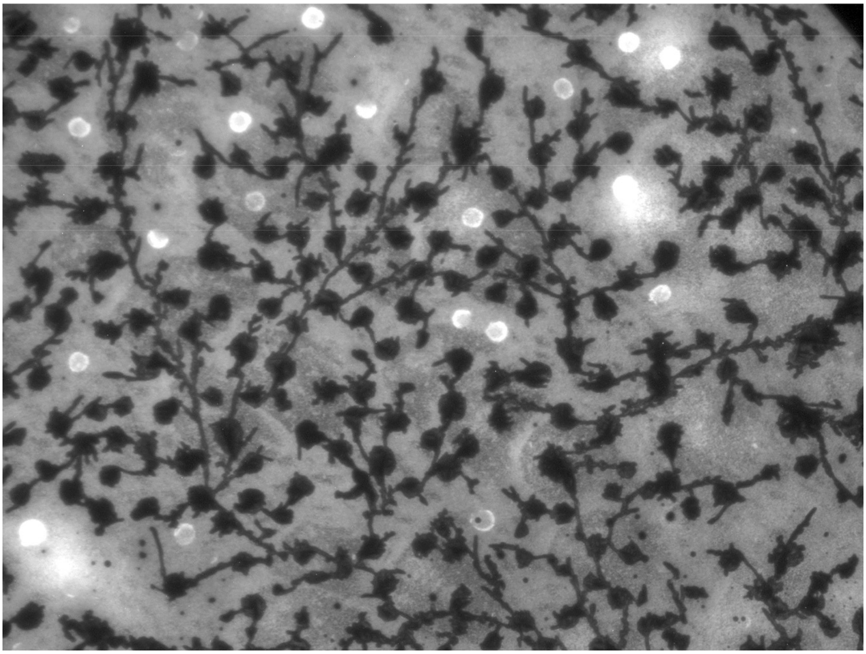

FIGURE 3 Electroluminescence micrograph of a partially crystallized sample of TPB coated with Alq3 and Mg/Ag top electrodes. The picture width is 240 μm.

dome morphology that might also disrupt the electric contact with the electrodes, so it is not surprising that the polycrystalline parts remain dark. PEDOT/PSS facilitates the carrier injection into the hole-transporting layer while it acts as a blocking layer for electrons. Thus the Alq3, which is in direct contact with PEDOT/PSS in-between the TPB crystals, is expected to emit light with low intensity. This explains the light gray background of the image. Surprisingly, there are a few very bright spots in the film. From the position of the bright spots in respect to the crystals and also from the spot density, we can conclude that the bright spots correspond to the disk-like features in the reflection micrographs and electron micrographs. Detailed inspection found that some of the disks are circular with homogeneous brightness, while others show a brighter rim, or are non-spherical. A few of the bright spots are also in direct contact with crystal fibers, so that it can be concluded that they are not amorphous. Compared with the amorphous device [5], this heterogeneous device is less stable. Shortcuts occur after a few minutes of operation at 10 V and the device breaks down. This can be explained by the presence of polycrystalline parts. These polycrystals can have a height in the micrometer-range and thus it can be expected that the evaporation of the Alq3 and metal top electrodes leads to inhomogeneous coverage and pinholes.

Annealing a freshly dewetted sample of amorphous TPB at higher temperatures (160°C) for a shorter time (12 h) succeeded in the preparation of large areas (up to several mm^2) of microdisk arrays without any evidence for crystallization. The OLED of such a sample was prepared as described above and the electroluminescence microscopic image is shown in Figure 4.

Bright electroluminescent disks with a diameter of about 10 µm can be seen. Besides this, amorphous domes still remain on the substrate, but their luminescence is much weaker. A line through five of the disks reveals that the disks are approximately five times brighter than the amorphous state (200 counts vs. 40 counts per pixel of the CCD camera). The brightness of the disks and amorphous domes, respectively, is similar throughout the sample. This shows that there is a distinct difference between the electroluminescence properties of amorphous and disk state and that the disk state is superior in brightness. The increase in brightness may stem from a facilitated carrier injection from the PEDOT/PSS coated ITO electrode, or due to increased carrier transport in the disk state. The former reason may be the result of a shift in work function of the TPB, which diffused into the PEDOT/PSS, PSS, while the latter may the result of molecular aggregation of TPB

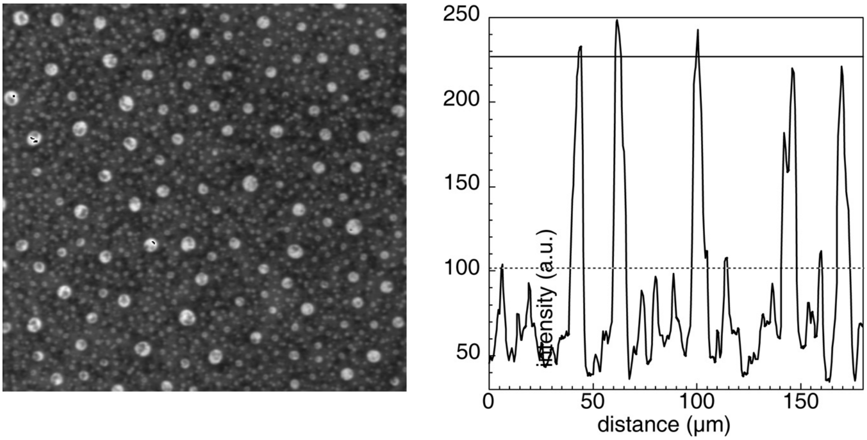

FIGURE 4 Electroluminescence image of a TPB sample annealed at 160°C for 12 h (left). The picture width is 200 µm. Intensity profile through five of the disks (right). The lines show the brightness levels of the disk state (solid line) and amorphous domes (dotted line), respectively.

and the formation of ordered arrays within the disks on top of the PEDOT/PSS film. The lifetime of the device was not measured, but the non-encapsulated display can be driven at 6 V for several minutes without measurable decay of brightness.

CONCLUSIONS

We could show that tetraphenylbenzidine, TPB, can be used as a hole transport material for organic light emitting diodes. TPB de-wets from PEDOT/PSS coated ITO electrodes and forms micrometer-sized dome structures. These initially amorphous domes can transform into crystals or a not yet well understood "disk state," which is confirmed by optical and electron microscopy. Annealing temperature and duration can control the ratio of crystal and disk state. The disk state shows superior luminescence properties. Since the disk state is the result of a thermal treatment, the disk state should also be thermodynamically more stable than the amorphous state, and thus should prolong the lifetime of the OLED devices.

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