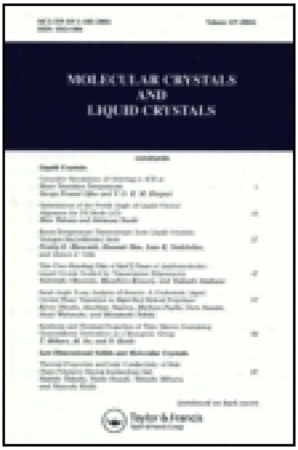

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Vacuum Spray Method for Semiconductor Polymer Thin Film Preparation

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Semiconductor polymers poly(3-dodecylthiophene-2,5-diyl), regioregular (PDDT) and poly[2,5-bis(octyloxy)-1,4-phenylenevinylene] (BO-PPV) are prepared by thin films by a spray method under vacuum. The formation process and properties of these polymer thin films are described. The dilute solution was used to prepare thin film by this method; annealing the semiconductor polymer thin film under vacuum would highly increase their surface smoothness.

Keywords: semiconductor polymer; spray method; thin film; vacuum

INTRODUCTION

These years, polymer opto-electric devices have been widely researched such as electroluminescence devices [1], solar cells [2], transistors [3], and so on. Compared to other inorganic or small organic molecular devices, they have some special merits: easy preparing, flexible, low cost. Most important material in these devices is semiconductor polymer. To meet the requirements of the devices, a

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lot of semiconductor polymers were synthesized. Some methods were also developed to prepare polymer to thin films. Most popular methods are spin-coating, screen-printing [4], ink-jet printing [5], doctor-blading [6]. In these methods, one requirement for the polymer materials is that they should easily be dissolved in some solvent with high concentration (>1%). Although there are thousands of semiconductor polymers, some of them are hard to find suitable solvents to dissolve them, or the solvents are deleterious, that is why the solvents such as benzene, toluene, tetrahydrofuran (THF) often appeared in the reported papers. Because of decomposition under high temperature, unlike inorganic or small molecule organic materials, polymers cannot been prepared by normal physical vapor deposition (PVD) which was concerned as the best choice for the thin film preparation. Usually the polymer thin film was prepared under atmospheric condition, therefore the gas and dust residues in the thin film are very hard to remove. That may reduce the performance of final opto-electric device. Spray method [7,8], is a new method to prepare semiconductor polymer thin films. One advantage of this method is low-concentration solution requirement. So the polymer opto-electric device fabrication has more polymers to choose, and less deleterious solvents can be used.

A spray method which can be performed under vacuum is developed [9–12]. It has the advantages of both normal spray method and PVD. Figure 1 shows the system schematic of vacuum spray method. The system has a 20 μm pinhole nozzle to introduce polymer solution into the vacuum chamber. And the liquid nitrogen cold traps are used catch solvent in order to prevent oil damage from of the vacuum pump. The substrate can be heated from front and back by halogen lamps to

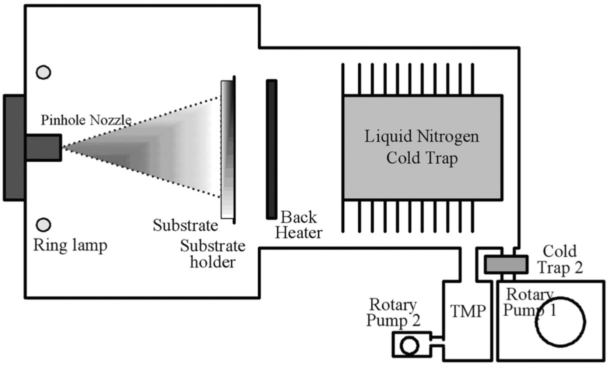

FIGURE 1 System schematic of vacuum spray method.

evaporate the solvent in the polymer solution quickly. When the polymer solution was introduced into vacuum chamber by a high pressure liquid pump, the solvent in solution mists began evaporate due to vacuum and the heat lamps. After the mists reached to the substrate, there still had some solvent in the mists, the heaters made the solvent continue evaporate quickly and prevented the substrate temperature decrease too quickly due to the evaporation. After some time, a uniform polymer thin film would form on the substrate.

EXPERIMENTAL

The semiconductor polymers poly(3-dodecylthiophene-2,5-diyl) regioregular (PDDT; Aldrich Chemical Co., Inc.), poly[2,5-bis(octyloxy)-1,4-phenylenevinylene] (BO-PPV; Aldrich Chemical Co., Inc.) are used in thin films preparation by the vacuum spray method.

The polymer thin film formation progress was studied by preparing PDDT thin films in different spray time, then their surface images were observed by a microscope. The experiment conditions are described below: The concentration of the PDDT solution was 300 ppm in chloroform; the introduced pressure was 120 kg/cm^2; the substrate was heated to about 440 K; the chamber was prepumped to about 1×10^{-3} Pa with a turbo molecule pump; during spray only a powerful rotary pump evacuated the chamber. Another PDDT thin film used to check the difference before and after annealing was prepared with 100 kg/cm^2 introduced pressure, 350 K substrate temperature during spray. The annealing temperature was 450 K, annealing time was 20 minutes.

The BO-PPV thin film was prepared to prove that less soluble semiconductor polymer could be prepared as thin film by the vacuum spray method. The BO-PPV was dissolved in chloroform at the concentration of 200 ppm, the introduced pressure was about 80 kg/cm^2; the substrate was heated to about 420 K; the vacuum chamber was prepumped to about $\acute{1}10^{-5}$ Pa, during spray, the vacuum pressure decreased to about 10 Pa, due to the evaporation of chloroform. After 2 minutes later, the red color BO-PPV thin film was found on the substrate.

RESULTS AND DISCUSSION

Figure 2 shows the formation of small polymer (PDDT) particles on the glass substrate on the beginning of spray process in vacuum. The PDDT solution (50 ppm) in chloroform was introduced into the chamber in 120 kg/cm^2. In this figure, some cycle patterns can be found. That showed that when the solution mists reached the substrate, there

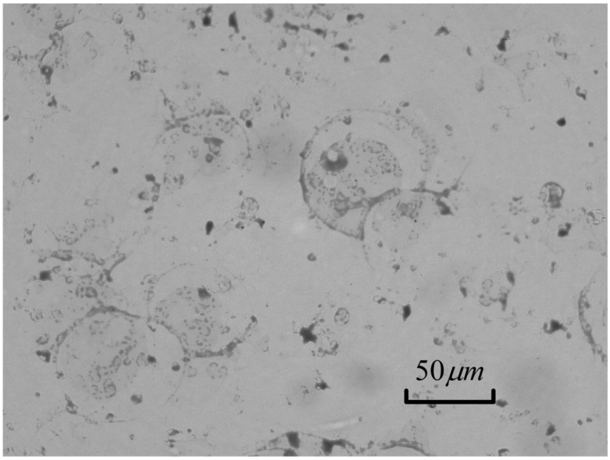

FIGURE 2 Microscope image of small particles formed by the vacuum spray method.

were still a lot of solvent inside them, on the substrate, solvent continue to evaporate to the vacuum; after the solvent ran out, only polymer left on the substrate, and formed a lot of small polymer particles.

The formation process of polymer thin film by vacuum spray method is similar as that thin film formation in PVD process [13]. Figure 3 showed the PDDT thin film formation process by vacuum

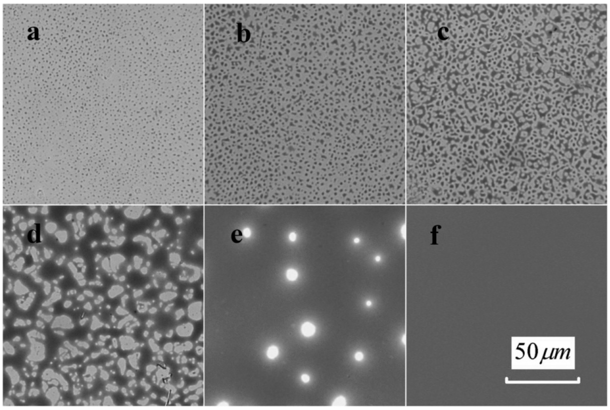

FIGURE 3 Microscope images of PDDT thin film formation (a → f show the steps of formation progress: particles, growth of particles, coalescence, channels, holes, homogeneous film).

spray method. First as described above, small polymer particles was formed on the substrate (a), then the particles grew bigger as islands (b), as the spray continued, these islands became coalesce (c), after that the channels could found in the figure (e), then only holes (f), at last holes disappeared, the homogeneous film (f) was formed on the substrate. The difference between the vacuum spray method and PVD is the particles generated by the vacuum spray method are much bigger than that of PVD method. This is also a problem of vacuum spray method: it is a little difficult to prepare very thin films by the vacuum spray method. Unlike the other “wet” process, they can prepare very thin film because the molecule has more mobility energy in the solution. But in other word, the solvent in the solution was evaporate very quickly, so maybe less solvent would left in the thin film at last.

BO-PPV is a semiconductor polymer which is hard to be found suitable solvent to be prepared as thin film by normal method. Its solubility in chloroform is less than 0.1 wt% in our experiment. A thin film prepared by spin-coating with its saturated chloroform solution on glass substrate was tried. On the condition of 500 rpm, 30 s, the thickness of thin film was only about 2–3 nm measured by a KLA-Tencor profiler. For opto-electric device application, it was too thin. To make thicker BO-PPV thin film, vacuum spray method was used. Figure 4 shows the BO-PPV thin film prepared by vacuum spray method. The thin film seemed uniform; under microscope, the film was not so smooth, but for some opto-electric device application, the

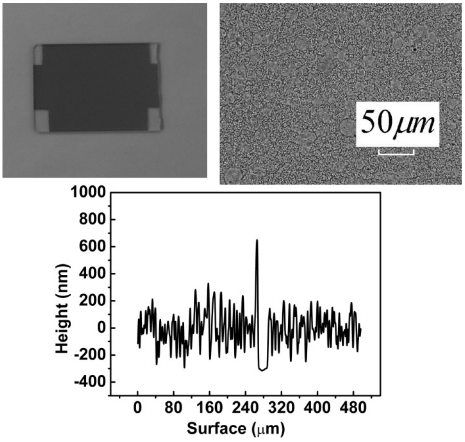

FIGURE 4 BO-PPV thin film prepared by vacuum spray method.

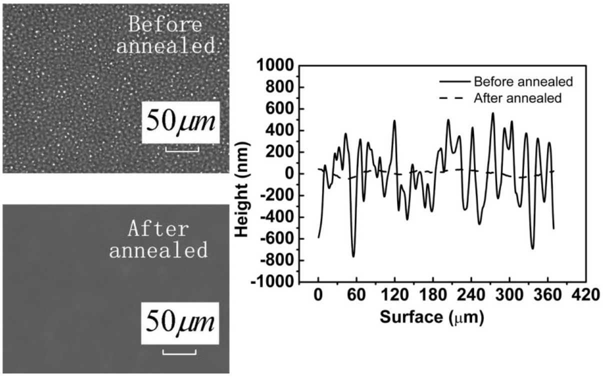

FIGURE 5 Annealing effect of PDDT thin films.

polymer thin film is not need very smooth, this may increase the interface area which is better for the efficiency increasing. The average thickness of this film measured by the profiler was about 200 nm. Vacuum spray method is a better choice for low solubility semiconductor polymer thin film preparation. If it is needed, thick films also can be prepared by this method, even thick as 100 mm polymer film was already been prepared.

As described above, the polymer particles formed on the substrate was somewhat bigger, so the very smooth film is hard to get by the vacuum spray method. It was found that when the substrate was heated to higher than the glass transition temperature (T_g) or melting point (T_m) of the polymer, the smoothness of the polymer thin film would greatly increased. Figure 5 shows a PDDT thin film smoothness change before and after annealing in the vacuum. Before annealing, the PDDT thin film was very rough, the roughness was about several hundreds nanometers, under microscope, the surface was consisted by a lot of grains in the size of several micrometers, after annealing 20 minutes under vacuum, the surface profile showed that the roughness of the thin film decrease to about 30 nm, in the microscope image, the film became more uniform. The T_g and T_m of PDDT are 313 K and 443 K [14], when the temperature is high than that, the molecular mobility in film greatly increase, this much improve the smoothness of the polymer thin film.

CONCLUSION

Vacuum spray method was used for semiconductor polymer thin film preparation. The thin film formation process is different from the normal polymer thin film preparation methods; it is more like the process of PVD, also has particles, growth of particles, coalescence, channels, holes, homogeneous film steps during formation process. Annealing the polymer thin film under vacuum higher than its T_g or T_m will improve the smoothness of the film. Dilute polymer solutions can be used in this method, so many less soluble semiconductor polymers can be prepared as thin film, also dye-dispersed or multi-layers polymer thin films can be easily achieved. Since the thin film preparation process is carried out under vacuum conditions, no dusts and gas will be left in the film, due to the high evaporation speed, solvent is almost free in the polymer thin films. Polymer EL device and solar cells were also tried to be fabricated with the vacuum spray method; it proved that this method can be a new candidate method in opto-electric device fabrication.

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