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Novel formation method of opto-electric devices by using vacuum process

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A new technique for coprecipitation of organic dye with polymer using high vacuum (HV) conditions has been developed. Rapid evaporation of solvents from a solution of dye dissolved polymer under HV is essential for making a thin film with low residual solvent in the solidified polymer matrices in contrast to a slow evaporation method under atmospheric conditions. Another advantage of the method is easy way to form a thin multi layer of different dye/polymer system with same solvent. A clear and transparent thin polymer film with dissolved organic compound is obtained. Conditions of thin film formation are mainly determined by substrate temperature and size of the mist which is controlled by injection pressure of the solution. Properties of the obtained film will be discussed.
Key words: polymer, thin film, spray method, vacuum

1. INTRODUCTION

Recently, opto-electric devices made by organic materials such as optical switches[1], light-emitting diodes[2], thin film transistors[3] and solar cells[4] have been heavily studied because the properties of lightweight, flexible and inexpensive. Now more polymer materials are also have potential to make opto-electric devices. Dye-dispersed polymer films have some special properties in devices fabrication. Many methods of organic thin film preparation are brought out. The conventional methods are dip-coating, spin-coating and vacuum deposition. But most of the organic materials especially polymers can not been prepared as thin film using vacuum deposition, because they would decomposed in high temperature. And recently a lot of functional polymer were found and synthesized for opto-electric devices of next generation. But some of them can not find the proper solvent to get high concentration solution in order to preparing thin film using dip-coating, spin-coating and ink-jet printing. Even the polymers that can be solved, the solvent they used is maybe deleterious or dangerous. Except vacuum deposition, other methods have another disadvantage of solvent and dust residue even these methods can be preceded under nitrogen or inert atmosphere, because the slow evaporation of solvent during the film preparation. These solvent and dust are harmful to the properties of opto-electric devices.

The problems described above can be solved by a novel method for organic/polymer thin film preparation. That is spray deposition under vacuum[5-7]. Spray method has already been used in polymer thin film preparation, but mostly it is used under atmosphere[8]. In vacuum, during deposition, solvent would evaporate very quickly, and vacuum also can provide most clean condition which means less dust and solvent residue in the polymer film. For high performance optical or electrical devices fabrication, that is very important. Using spray method, dye can be solved with polymer in the same solvent, so it is very easy to get dye-dispersed polymer thin film. Also this method does not need high concentration in the solution. So most of the polymer thin films can be achieved using safe and nontoxic solvent with low concentration solution. Since this method is under vacuum circumstance, so it is easy to combine with other vacuum deposition methods, and to fabricate devices without broken vacuum.

We tried to prepare dye-disperse polymer thin film using spray method under vacuum previously, but it seems it is hard to get the clear and transparent thin films, although the films seems uniformly. Under the microscope, these films were rough; a lot of islands can be seen. The reason of that is the mists which generated during spray were too big. Now the smooth dye-dispersed polymer thin films can be achieved using spray method under vacuum combined with samples annealing. And with the ratio of the dye/polymer changed, the clear and transparent polymer thin film even can be got without annealing.

2. INSTRUMENTAL

The popular dye and polymer are chosen for experiment. N-[9-(2-carboxyphenyl)-6-(diethylamino)-3H-xanthen-3-ylidene]-N-ethylethanaminium chloride (Rhodamine B; EASTMAN KODAK Co.,) is used as the dye; and poly(methyl methacrylate) (PMMA; Aldrich Chemical Co., Inc., Mw: 15,000) is used as polymer matrix.

The instrument used to do spray method experiment is similar to conventional high vacuum (HV) system. It includes the aluminum chamber and vacuum pumps and gauges. For spray experiment, it has a pinhole nozzle and liquid nitrogen trap. (Fig.1). A special designed rotary pump with liquid nitrogen trap was used during spray to prevent turbo molecule pump (TMP) from evaporated organic solvents. A $\Phi 20\mu m$ pinhole nozzle was used for generation of small mists. Substrates were set on a hold with mechanic moving system. A ring lamp was located in the front of the substrate holder as a substrate heater. The temperature of substrates was measured by an infrared temperature monitor through a CaF_2 window. Solutions with dye introduced into the nozzle were injected into the vacuum chamber using a pressure difference from atmospheric pressure to high vacuum.

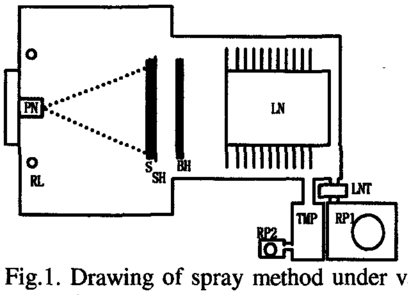

Fig.1. Drawing of spray method under vacuum system: PN: pinhole nozzle, RL: ring lamp for front heat, S: sample, SH: sample holder, BH: back heat, LN: liquid nitrogen trap, TMP: turbo molecular pump, RP1, RP2: rotary pump, LNT: liquid nitrogen trap for protect rotary pump.

3. EXPERIMENT and RESULTS

The chamber was first pumped to high vacuum about 1×10^{-4}Pa using TMP and rotary pump in order to get the clean circumstance. During spray, the TMP was separated from the main chamber from the pollution of solvent. Mists with a droplet diameter smaller than 100μm were obtained by injection of the solution. Solutions of Rhodamine B dissolved in acetone with PMMA at concentration of 0.1(wt)% in acetone injected into the vacuum chamber with pressure at 100kg/cm^2, normally, the higher pressure results in more fine mists. The temperature of substrate before spray was set above 373K for quick evaporation of volatile acetone on the substrate. A thin film was formed on a cover glass (18mm square, 140μm thick) at a working pressure of 30Pa. When the ejected mists ran into vacuum, the solvent became evaporated from the mists; for the high pressure, the speed of the mists are very high, and the distance between the nozzle and substrate was not long enough, so there was still much solvent in the mists when they reached the surface of substrate; since the substrate was heated by ring lamp and back heater, acetone would evaporate rapidly within 1 second. After spray the solution into the vacuum for several seconds to several minutes, the uniform dye-dispersed Rhodamine B/PMMA thin film was formed on the substrate in different thickness.

First the 1×10^{-4}mol/l concentration of Rhodamine B in acetone was used. The substrate temperature was set at 393K before spray. During spray, because the pinhole size of nozzle is still too big, a large amount of the acetone reached the substrate at the same time, due to the heat capacity of the substrate and solvent evaporation, the temperature of the substrate decreases very quickly, even it would below 303K, it was much lower than T_g of PMMA, after 20 seconds, the uniform thin film was achieved. But the film was not clear and transparent. Because the film was formed by a lot of polymer islands which were formed during spray under low temperature of the substrate.

Although some opto-electric devices do not need very smooth film, the smooth dye-dispersed thin film has more wide application. So the thin film achieved above was kept in vacuum and increase the temperature of substrate to 423K, then the condition was kept for 1-2 hours. Then the Rhodamine B/PMMA thin film became clear and transparent. The roughness of the film was measured by a KLA-Tencor profiler P.15. In Fig.2. We can found that before annealing, the roughness of the film is about 400nm, and the total thickness of the film is only 700nm (the dump in the curve which was formed by scratching the film). After the thin film was annealed, the roughness of the film decreased to about 20nm, and the thickness change was not very sharp. Microscope is also used to check the property of the film (Fig.3). Before annealing, a lot of small islands can be found on the film surface. After annealing, the film seems very uniform under microscope.

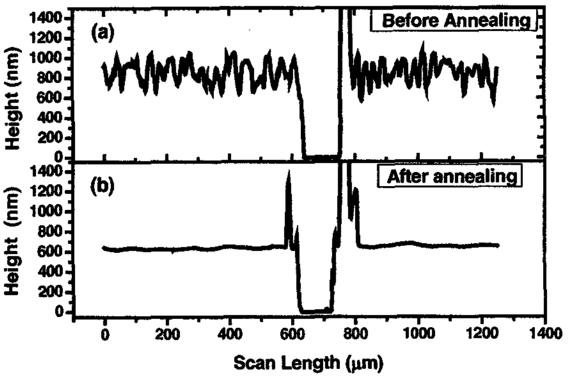

Fig.2. Profiles of the Rhodamine B/PMMA surface. (a) before annealing; (b) after annealing.

The clear and transparent dye-dispersed thin film can be achieved by spray method under vacuum with annealing. But it seems the dye concentration in the solvent can greatly influent the polymer thin film.

When the concentration of Rhodamine B/acetone increases to 1×10^{-3}mol/l, the PMMA/acetone concentration and the injection pressure keep without change, the temperature of substrate was set on 403K, after about 5 minutes spray, the clear and transparent thin film was found formed on the substrate without more annealing. Fig.4. shows the surface profile of the thin film. Although the thickness of the film is about 9μm, the roughness of the film is less than 150nm, and the thickness of the film changes very smoothly. Maybe the more Rhodamine B in the PMMA greatly changes the physical property of the polymer such as T_g. This experiment also shows that the thick dye-dispersed polymer film can be achieved by spray method under vacuum. Those thick films can be used as holographic optical memory, and other opto-electrical devices.

Fig.5 is the absorption spectra of the Rhodamine B/PMMA thin film and Rhodamine B in Acetone. They have peaks in same wavelength. And their baselines are almost same. So there is no scattering in the Rhodamine B/PMMA thin film. Rhodamine B in the PMMA thin film may keeps its original properties and has not been broken. It is good to keep the original state of the dye in the polymer.

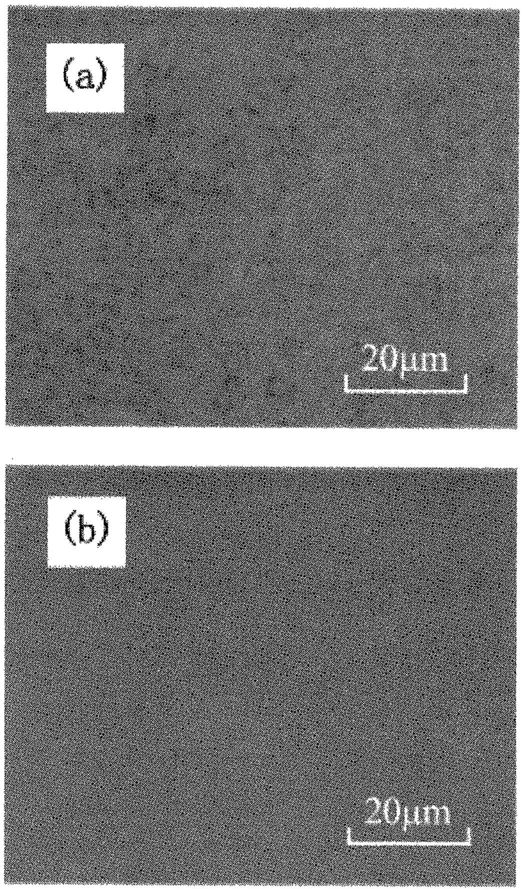

Fig.3. Photographs of the Rhodamine B/PMMA film. (a) before annealing; (b) after annealing

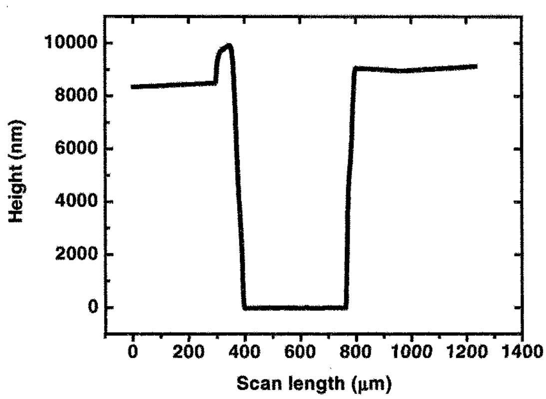

Fig.4. Profiles of the Rhodamine B/PMMA surface (the original concentration of Rhodamine B/acetone is about 1×10^{-3}mol/l)

4. CONCLUTION

Novel dye-dispersed polymer thin film preparation method has been developed. Rapid evaporation of solvents from a solution of dye dissolved polymer under HV is essential for making a thin film with low residual solvent in the solidified polymer matrices in contrast to a slow evaporation method under atmospheric conditions. Another advantage of the method is easy to form a thin multi layer of different dye/polymer system with same solvent. A clear and transparent thin polymer film with dissolved organic compound is obtained. The smooth film can be formed by annealing or increase the dye/polymer concentration. The thickness of the polymer thin film can be controlled easily by control the spray time of experiment, and thicker film (even thicker than 10μm) can be achieved than that prepared by spin-coating or dip-coating. Unlike spin-coating and dip-coating, this method does not need high concentration of polymer in solution (even lower than 1×10^{-4}wt%), so most polymers can be prepared as thin film. It also can be combined with other vacuum methods easily. This method is expected to be used in fabrication of high quality opto-electric polymer devices. Indeed we have succeeded in fabricating the electroluminescence (EL) and solar cell devices using this method.

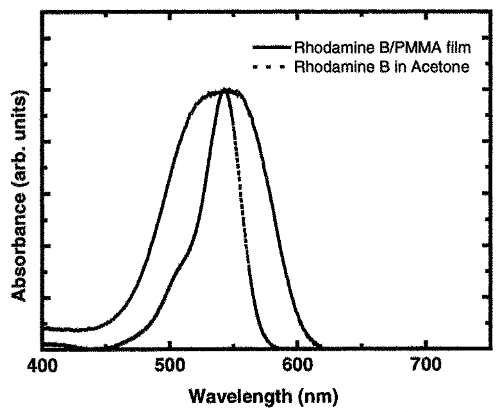

Fig.5. Absorbance spectra of the Rhodamine B/PMMA film and Rhodamine B in Acetone.

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