論文の内容の要旨

論文題目

A Study on Electrostatic Deposition Method using
Nanoparticles Generated by Atomizer
（霧化器により形成されたナノ粒子を用いた静電成膜法の研究）

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Thin film formation methods for organic materials, biomaterials and polymers are becoming important for organic light emitting diode (OLED) display, organic semiconductors, bio-chips and biosensors. Concerning those thin film formation technology, not only pattern resolution, but also thin film quality such as thickness uniformity, controllability, costs and speed are the key issues.

In case of inorganic materials, using established process based on the photolithography combined with thermal deposition, sputtering and CVD (Chemical Vapor Deposition) and so on, it is possible to make a high resolution thin film pattern with high quality. However, these processes require high temperatures, high vacuum process and/or chemical treatment such as etching and development, which are not compatible with organic materials, biomaterials nor polymers.

For these reasons, direct patterning methods such as ink-jet printing, spin coating, micro spotting and micro contact printing have been proposed. In these methods, samples are patterned or deposited directly on the substrate without thermal and chemical process. These methods are low damage process, however these are wet process, which may cause non-uniform film thickness by ring stain effect upon drying.

To cope with these problems, dry-direct patterning methods combined with electrostatic collection such as electrospray deposition (ESD) and surface acoustic wave atomizer and electrostatic deposition (SAW-ED) have been proposed in 1999 and 2005 respectively. Concepts of these methods are as follows: (1) sample is atomized in tiny droplets and charged by high voltage, (2) tiny droplets are quickly dried up to be nano-sized particles (3) charged nanoparticles are deposited or patterned on the substrate by electrostatic force.

Advantages of dry patterning/deposition methods are that it is performed under atmospheric pressure and room temperature, and that it does not require any thermal or chemical processes that may damage target material. Moreover, size of dried particles can be controlled by concentration of liquid samples. Thus, not only high uniformity, but also high resolution patterning is possible at the same time. Furthermore, thick film or multi-layered structure can be also fabricated. Dry-direct pattering methods have a lot of merits, compared with other wet patterning methods. They will be important techniques for thin film fabrication of micro/nano patterns of bioactive/organic materials.

The purpose of this research is to increase the deposition speed keeping the quality of the deposition and to expand the application fields of dry patterning method.

In order to increase deposition quality, smaller nanoparticles are required. Particle size is mainly determined by the size of atomized drop and concentration of sample. One of the simple methods to obtain small nanoparticles is to reduce concentration of sample, however sample quantity and deposition time are drastically increased with lowered concentration. For this reason, balanced condition between particle size and deposition time must be compromised. To increase deposition speed keeping particle size, small drop size and high atomization speed should be simultaneously achieved.

Quality of the deposition can be evaluated by particle size as well as formation of particles making a thin film. As mentioned in the previous paragraph, it is possible to reduce particle size by control of drop size or sample concentration. In the case of particle formation, it is not easy to fabricate film with regular thickness using dry direct pattering. Since charged nanoparticles are deposited by the electrostatic force, their flight paths as well as deposition characteristics strongly depend on the electrostatic fields. Electrostatic fields are fluctuated during deposition process since charged nanoparticles lead to variation of boundary conditions on target electrodes. For this reason, pin hole or non-regular thickness film is easily generated. For the purpose of electronic functional layers, generation of pin hole is critical demerits, which may cause break down and malfunction of devices.

Finally, to expand the application fields of dry patterning method, some of drawback needs to be solved. The most distinctive demerit is that it is hard to deposit on the non-conductive substrate. Conductive substrate is required for attracting charged nanoparticles by electrostatic force. Deposition on the non-conductive substrate is necessary for variety of applications. For example, it may require to pattern on the non-conductive substrate, such as insulator layer of glass/plastics for micro total analysis system (microTAS) and electronic devices. In addition, many applications like OLED, electrode arrays are composed of conductive and non-conductive substrate. Thus, advanced deposition method is required for deposition on the non-conductive substrate.

To verify above mentioned purpose, performances of the dry direct pattering according to the atomizer are compared since performance of atomizer is the most important parameter which determines size of nanoparticles. Three types of atomizers, electrospray, surface acoustic wave (SAW) atomizer, and mesh type nebulizer, are compared in terms of particle size, collection efficiency and atomizing speed. As the results, average diameters of deposited particles are 0.1 (ESD), 0.11 (SAW-ED) and 0.25 (Nebulizer-ED) micrometers by using 0.5 mg/ml protein solution. Size of initial atomized droplet can be estimated from deposited particles. Mean diameters of initial atomized droplets are 1.3 (ESD), 1.4 (SAW-ED) and 3.2 (Nebulizer-ED) micrometer, respectively. Collection efficiency is 26 % (ESD), 2.2 % (SAW-ED), and 0.8 % (Nebulizer-ED). Atomization speed is 0.01 (ESD), 0.3 (SAW-ED) and, 7 (Nebulizer-ED) microliter per second, respectively. In case of ESD method, it is possible to atomize tiny and uniform size droplets compared with other methods, collecting efficiency is much higher, but atomizing speed was slower than others. In case of SAW-ED method, mean diameter of deposited particle is a little bit larger than ESD. However, atomizing speed is higher

approximately 30 times than ESD. And, collection efficiency is lower than ESD. In case of nebulizer-ED, it showed higher atomizing speed than ESD and SAW-ED, but, particle size is largest and collecting efficiency is lowest.

Atomization speed of SAW atomizer is faster than ESD, however particle size is larger than ESD as well as experimental formula proposed by Lang. Main reason of differences between theoretical estimation and performance was that second peak on the larger diameter in the size distribution was generated. To investigate the reason of second peak generation, a new standing wave type SAW atomizer was proposed. Driving circuits was also improved, which is possible to apply not only intermittent burst driving, but also continuous driving. Then, the earlier progressive wave and the proposed new type are compared by means of vibration mode, atomization speed, and electrostatic deposition tests. In case of vibration mode and atomization speed test, standing wave type showed higher Standing Wave Ratio (SWR) and slower atomization speed than progressive wave type. In the electrostatic deposition test, liquid sample is atomized by two type of SAW atomizers combined with two different driving modes, which are continuous and intermittent drive. And then, deposited dry particles are measured by field-emission type scanning electron microscopy (FE-SEM) and its sizes are calculated by image processing software. Among them, only standing wave with continuous drive showed no second peak within size distribution.

Proposed standing wave type SAW atomizer showed high performance on the regular size distribution. However, it is still larger than mean drop size by ESD. For this reason, high frequency type of SAW atomizer is proposed. Based on the theory of ultrasonic atomization, drop size is reduced according to the frequency rise. SAW atomizers which excitation frequency ranging from 50 to 95 MHz type were constructed and evaluated by atomization speed and SAW-ED methods. On the atomization speed test, the minimum power required for atomization was approximately 4 W (50 MHz), 11 W (75 MHz) and 24 W (95 MHz). In this power, atomization speed was 0.06 (50 MHz), 0.04 (75 MHz) and 0.01 (95 MHz) microliter per second. Finally, the estimated mean diameter of atomized droplets was 5.7 (50 MHz), 4.4 (75 MHz) and 2.7 (95 MHz) micrometer, respectively. Drop size and atomization speed were reduced by the increasing frequency, however the required power for atomization is increased.

Not only drop size and atomization speed, applicability is also important. In the dry direct patterning, conductive substrate is requited for the generation of high intensity electrostatic fields. For the deposition on the non-conductive substrate, a new deposition method combined with corona discharge and SAW-ED was proposed. Process is composed of two steps: The first is patterning of the electric charges on the substrate using a corona discharge; The second is deposition of the dried nanoparticles on the pre-charged area using SAW-ED method. To generate charge pattern by corona discharge, a high voltage of 4.5 kV was applied between thin metal wire and conductive base plate in a distance of 3-4 cm. Then, 5 microliter of 5 mg/ml Bovine Serum Albumin (BSA) solution was deposited on the charge-patterned substrate by SAW-ED process. A high voltage of 5 kV is applied between conductive base plate and thin conductive wires placed just above the atomizer. The distance between atomizer and conductive base plate is approximately 15 cm. Corona discharge is applied for 10 minutes and atomization time was 20 seconds. As a result, approximately 200 micrometer width lines are deposited successfully.

To expand the application fields of dry patterning method, film quality need to be improved. For this reason, a new fabrication method for thin film for OLED was proposed. The basic concept of the proposed method is that nanoparticles are deposited on the target substrate just before they become completely dry. This is done by mixing in an additional solvent which has an evaporation speed that is relatively lower than that of the original solution. To investigate the morphology of the deposited layer, different concentrations of poly(2-methoxy-5-(2-ethylhexoxy)-1, 4-phenylenevinylene (MEH-PPV) solutions were sprayed on and then measured using field-emission scanning electron microscopy (FE-SEM) and a white-light interferometer. In the morphology test, some of sample shows good average surface roughness under the 1 nanometer. Based on these results, a small OLED pixel was fabricated, and current-voltage curve and luminescence characteristics were measured. Distinctive merit of proposed method is that it is possible to fabricate thin and regular-thickness films without pin hole.

Dry direct patterning using electrically charged nanoparticles generated by atomizer has proved to have many merits. First, performances of ordinary atomizers as a dry direct patterning were compared. In this test, SAW atomizer showed high atomization speed, but particle size was larger than ESD. To reduce particle size, standing wave type SAW atomizer which is possible to atomize tiny and regular drops was proposed. High frequency SAW atomizers were also utilized and tested. Then, new patterning method for deposition on the non-conductive substrate was proposed by combination of SAW-ED and corona discharge. Finally, OLED film was successfully fabricated by controlling drying speed using additional solvent. In conclusion, this study has proved that dry direct patterning using electrically charged nanoparticles generated by atomizers has many advantages over conventional methods and that it can be applied to various thin/thick film deposition including biomaterials, polymers and organic semiconductors/ electroluminescent materials.