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Effects of coffee ring via inkjet printing seed layers on field emission properties of patterned ZnO nanorods

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ABSTRACT

Inkjet printing, a fast, simple, efficient graphical deposition technology, is first applied to achieve high-quality emission arrays. Patterned arrays of ZnO nanorods have been successfully synthesized via hydrothermal method after inkjet printing the ZnO seed layer. During printing, different substrate temperatures were found to affect the morphology, microstructure and field emission (FE) properties of ZnO arrays. The results showed that the FE performance was improved when the coffee ring effect was eliminated by raising the substrate temperature due to higher aspect ratio of the nanorods. Both the compensating flow characteristics inside the droplets and the mechanism of regulating the rheological behavior of the solution during inkjet printing were analyzed to inhibit the effect of coffee ring, which played an important role in the later patterning electrode construction of emission arrays. The selective growth of the emitter material can be easily realized by introducing the direct patterning technology of inkjet printing in the preparation of field emission electron source.

1. Introduction

As is known, the patterned array of emission materials can improve the emission performance of electron source and facilitate the large-scale integration of electron source devices. There are many problems in traditional electronic source patterning preparation processes, such as microfabrication and vacuum deposition. These processes are complex, polluted and impurities are introduced during processing, which may destroy the material properties, resulting in emission current instability. In order to find a lower cost, more simple manufacturing process, we count on the direct pattern of technology, i.e. inkjet printing [1–4]. Inkjet printing [5], an additive process, compared to the traditional semiconductor material processing technology, can make the cost of large-scale process more acceptable. Because of its full data-driven and maskless process, it is more versatile than other direct printing methods. The material can be deposited on the substrate in a carrier solution by piezoelectric driving. This solution process also makes the selection of deposited materials and substrates more flexible [6]. Patterned printing can be applied to any types of substrates (e.g. flexible polymer [7]) and used in large quantities of production or roll-to-roll processing of large substrates. Since inkjet printing can directly achieve patterned processing on the flexible and large area of the substrate, the substrate is not selective and the process is pollution-free. It has attracted wide interests in low-cost flexible electronics. Therefore, this paper is devoted to the application of inkjet printing to the preparation of field emission electron source. With the help of this technology, the patterning electrode construction of electron source and the selective growth of the emitter material can be easily achieved.

ZnO one-dimensional nanomaterials [8], which have a low turn-on field and high emission current density due to their wide band gap about 3.37 eV and high exciton binding energy around 60 meV, have become one of the most promising materials for field emitters. The traditional patterned self-assembling of ZnO is commonly performed by photolithography [9] or electron beam lithography [10] followed by selective etching by sputter deposition of zinc metal [11] or by chemical vapor deposition [12]. However, these technologies are complex and may introduce impurities during processing, which may destroy the field emission properties. In recent years, other methods of realizing the patterned ZnO seed layer have been reported, such as self-assembly monolayer by hydrophobic/hydrophilic interaction [13,14], micro-contact printing [15], atomic layer epitaxy (ALE) lithography [16]. The seed layers are subsequently grown to form the patterned ZnO nanoarrays in the processes of thermal oxidation [17], thermal evaporation [18] or hydrothermal reaction [9,11,19]. Nevertheless, these methods have many common shortcomings, including complicated steps, very time-consuming, high cost, low yield, strict requirements for preparation conditions (high temperature and pressure) and so on. Some methods are also subjected to practical limitations, such as the

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need for photolithography photomask or the mold for contact printing. And the lithography cannot be applied to plastic substrate which is heat sensitive or corrosive chemical sensitive. Therefore, the development of a fast, simple and efficient graphical deposition technology with accurate positioning is of great significance to achieve ZnO emission arrays with high-performance.

Inkjet printing has opened up a new field of research for the selective growth of nanomaterials because it can directly pattern the nanomaterials in the predetermined area to obtain the controlled morphology of the nanoparticles [4,20] and nanowires [21,22]. Besides, the growing position of ZnO nanoarrays may be easily changed during printing. Recently, Ko [23] has reported the formation of ZnO nanowires in direct local regions by inkjet printing of ZnO nanoparticles as seed layers. However, direct inkjet printing of nanoparticles or nanowires has a common drawback, that is, nozzle clogging, and the choice of ink in terms of concentration and viscosity is limited. In this regard, Kwon [24] proposed inkjet printing of zinc acetate precursor to get ink patterning instead of printing ZnO nanoparticles, followed by local hydrothermal growth of ZnO nanowires, which not only avoids the traditional method of multi- process, but also eliminates the frequent nozzle clogging.

In this paper, we reported the rapid patterning method of ZnO emitter arrays in the specific location of the field emission electron source device assisted by the precise deposition of ZnO seed layer on the cathode by inkjet printing. The effects of the coffee ring during printing the seed layers on the filed emission properties of patterned ZnO arrays were further studied. Meanwhile the presented method may break through the unstable emission problems caused by impurity in the traditional manufacturing process of electronic source and is expected to be applied to flexible substrates and large-scale industrial production.

2. Experimental methods

According to the schematic diagram in Fig. 1, the patterning process of ZnO nanorods mainly includes two simple steps: the deposition of the seed layer by inkjet printing and the selective growth of ZnO nanorods by hydrothermal reaction. The whole preparation process is delineated in Fig. 2(c) and the detailed steps are as follows.

2.1. Deposition of seed layer by inkjet printing

The sol-gel precursor ink, with a concentration of 10 mM, was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) in ethanol. After 30 min' sonication, the ink was filtered through a 0.2 μL syringe filter to make sure that no ZnO nanoparticles existed inside the ink, thus avoid the problem of nozzle clogging. By utilizing the inkjet printer integrated with the CAD system, the zinc acetate ink seed layer of the desired pattern was printed on the ITO substrate. The inkjet printing system, as shown in Fig. 1(a), generally includes MicroFab Co.'s piezo-type inkjet nozzles, pulse generation systems, high-speed cameras for taking images, illumination sources for back-illuminating as well as coaxial lighting. The print head with a 30 pL volume was employed, and the droplet size and dot pitch were varied by modifying the print parameters and substrate heating conditions, as depicted in Fig. 1(b). Detailed inkjet system settings and jetting parameters were set as follows: first rise time 3 μs, dwell time 5 μs, fall time 3 μs, echo time 10 μs, second rise time 5 μs, idle voltage 0 V, dwell voltage 30 V and echo voltage −30 V. The heating temperature of the substrate, playing a significant role in the morphology of patterned seed layer, was adjusted from room temperature to 80 °C during printing. Once the printing was completed, the sample was then dried in an oven and annealed at 400 °C for 1 h under atmospheric conditions to ensure that the zinc acetate would decompose into ZnO seed layer and the seed particles tightly adhere to the substrate.

2.2. Selective growth of ZnO nanorods

A crystallized dish was filled with a growth fluid for the hydrothermal reaction. The reaction solution consisted of 50 mM zinc acetate dihydrate and HMTA with the molar ratio of 1:1 in deionized water. The substrate was immersed upside down in the above solution. The thin coverslips were placed on a substrate with a 2 mm spacer to control and suppress the growth of the natural convection along with subsequent nanorods on the unseeded adjacent substrate regions. The mixture was uniformly dissolved by a magnetic stirrer, and then kept in a preheat oven at 90 °C about 2 h to grow ZnO nanorod arrays on the patterned areas. The sample was finally rinsed with deionized water and dried on a heating platform.

2.3. Characterization of patterned arrays

The morphology and structural characteristics of the samples were tested by field emission scanning electron microscopy (SEM, Hitachi, S3000N), optical microscope (Olympus BX51M), atomic force microscopy (AFM, Bruker MultimodeV system), X-ray diffraction (XRD, X'Pert Pro MPD). Field emission (FE) measurements were carried out in a vacuum chamber (high vacuum up to 5.0×10^{-4} Pa). The 2 cm (W) × 3 cm(L) sample was used as a field emission cathode and an ITO glass sheet with a phosphor was printed as an anode. The cathode was separated from the anode by a spacer with a height of 0.1 cm. The results came out from more than 5 times of reproducible measurements.

3. Results and discussion

3.1. Synthesis of ZnO nanorods

It is known that zinc acetate is decomposed to form basic zinc acetate by losing the acetic anhydride at a temperature around 200 °C [25]. The acetic acid is formed after acetic anhydride hydrolyzes, then zinc acetate is further hydrolyzed to get ZnO microcrystals in the existence of residual water vapor. After the printed zinc acetate precursors are annealed at 300 °C for 1 h, the basic zinc acetate is decarboxylated and decomposed into ZnO nanoparticles with average size around 4–7 nm as ZnO seed layer. The nucleation sites are then growing into ZnO nanorods in the following hydrothermal process. The whole reaction is given by Eqs. (1)–(4).

$$4Zn(CH_3COO)_2 \xrightarrow{200\,^{\circ}C} Zn_4O(CH_3COO)_6 + (CH_3CO)_2O \tag{1}$$

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH \tag{2}$$

$$Zn_4O(CH_3COO)_6 + 3H_2O \rightarrow 4ZnO + 6CH_3COOH \tag{3}$$

$$Zn_4O(CH_3COO)_6 \xrightarrow{300\,^{\circ}C} 4ZnO + 3CH_3COCH_3 + 3CO_2 \tag{4}$$

3.2. Morphological characteristics

Fig. 2 shows the morphological characteristics of the printed ZnO seed layer with 0.5 M inks at different heating temperatures of 20 °C, 40 °C, 60 °C by the optical microscope. It can be seen that the substrate temperature has a great impact on the uniformity of the patterned grains during inkjet printing. The coffee ring effect on the seed layer of the zinc acetate precursor is severe at room temperature of 20 °C in Fig. 2(a) and (e), whereas this effect is reduced as the substrate temperature increases, thus it is basically eliminated at about 60 °C as is shown in Fig. 2(c) and (g). The corresponding surface profiles of the films in Fig. 2(d) was obtained by depth profiler (BRUKER, DektakXT), in which the surface tends to be flatter and the height difference between the peak and the valley becomes smaller with the rise of temperature. To further study how the coffee rings affect the field emission