Field Emission Characteristics of Dot-patterned Photosensitive CNT paste

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Abstract

Fabrication of dot-patterned carbon nanotube (CNT) emitters with excellent field emission properties using photo-sensitive CNT paste is described. The photosensitive CNT paste showed good photo-patternability, which led us to easily form 10-μm-diameter dot arrays. We presented a parametric study on formulating the photo-sensitive paste and their resultant field emission characteristics.

1. Introduction

Carbon nanotubes (CNTs) have recently attracted much attention because of their unique characteristics such as diverse electrical properties, high mechanical strength, and chemical stability, together with hollowness and high aspect ratios of extremely small diameters to great lengths [1]~[4]. Such superior genetic natures of CNTs enable them to be highlighted as one of the best materials ever for field emitters. Many approaches have been attempted to form CNT field emitters, such as screen printing of CNT paste [5], spaying or spin coating of CNT solution, direct growth of CNTs onto substrates, etc, among which the screen printing method has been most widely used for practical applications to CNT-field emission displays or CNT-backlights of thin film transistor liquid crystal displays. In this paper, we present the fabrication processes and the field emission characteristics of a photosensitive CNT paste and of 10-μm-diameter dot arrays on glass substrates formed by using screen printing and backside exposure of UV light.

In the screen-printing method, problematic are the weak adhesion of CNTs to the substrate and the non-uniformity of electron emission. The fillers are added to the CNT paste to improve the adhesion as well as to regulate the distance between CNT emitters in the dot-patterned arrays for more emission. This study carried out a parametric approach to formulate the photo-sensitive paste by changing the amounts of fillers in the range of 5~15% and the powder sizes of fillers by high-energy milling.

2. Experimental

We used the thin multi-walled CNTs produced by catalytic CVD to fabricate the CNT paste, whose morphologies and Raman spectrum are given in Fig. 1. Their diameters measured by TEM and I_G/I_D ratio are 7~10 nm and ~1.34, respectively. The photosensitive CNT paste was fabricated by mechanical stirring CNT powders, photo-initiator, photo-sensitizer, acryl binder, and frit fillers in solvent, then followed by repeated three-roll milling for more complete mixing and dispersion of ingredients in the polymer vehicle. In this study, we added different amounts of SnO_2 fillers in the range of 5~15% and the powder sizes of fillers by high-energy milling.

Fig. 2 schematically shows the fabrication processes of dot-patterned CNT emitter arrays by using the photosensitive CNT paste. A Cr layer, which serves as a cathode electrode and later as a mask for the backside exposure of photosensitive CNT paste, was first patterned by conventional photolithography of photoresist and by wet etching. Following the screen printing of the CNT paste, the backside exposure of UV light and its subsequent development enabled us to form the dot arrays of CNT paste.

Field emission properties were measured in a diode configuration at a vacuum level lower than ~5x10^{-7} torr at room temperature. A gap of 300 μm was kept between an anode plate of bare indium-tin-oxide glass or phosphor-coated one and a CNT cathode plate. Square-pulse high voltages with the 1% duty and 100

Hz frequency were applied to the anode while the cathode was grounded. Field emission currents were measured between the cathode and the ground.

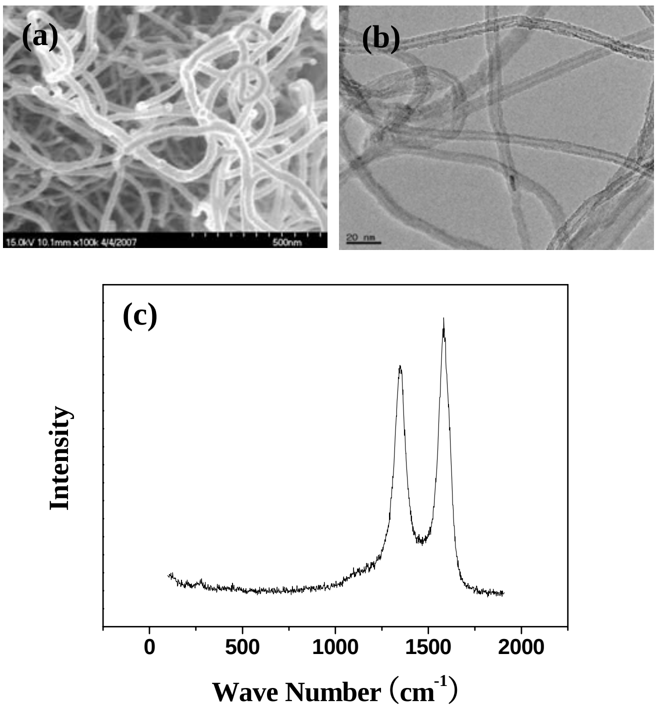

Fig. 1. (a) SEM and (b) TEM images and (c) Raman spectrum of CNTs used to fabricate the CNT paste.

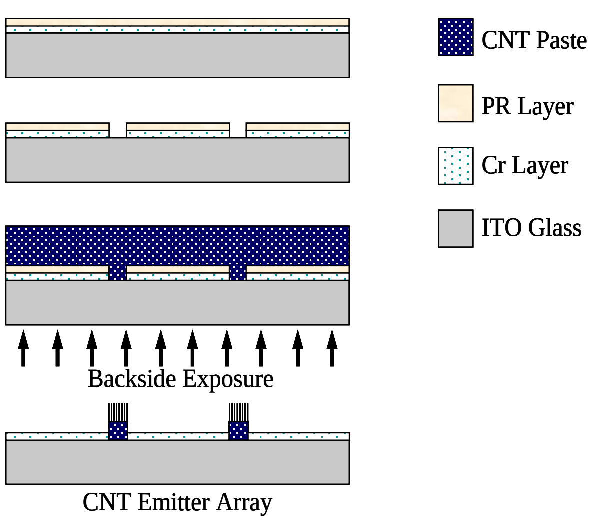

Fig. 2. Schematic fabrication processes of dot-patterned CNT emitter arrays by using photosensitive CNT paste.

3. Results and discussion

We fabricated field emitter arrays of 10-μm-diameter dots with their pitch of 300 μm by using the photosensitive CNT paste. As shown in Fig. 3(a), the CNT paste dots were successfully formed all over an area. A CNT paste dot shows a bulged shape just after developing [Fig. 3(b)]. Subject to firing at 420 °C in air, the dot shrinks considerably by burning out the polymer vehicles [Fig. 3(c)]. After the tape activation process, the CNTs are revealed above the surface by peeling off the topmost surface layer which is mostly filler materials [Fig. 3(d)]. An application of high electric fields to the long and crooked CNTs can make them stand up straight along the fields [Fig. 3(e)].

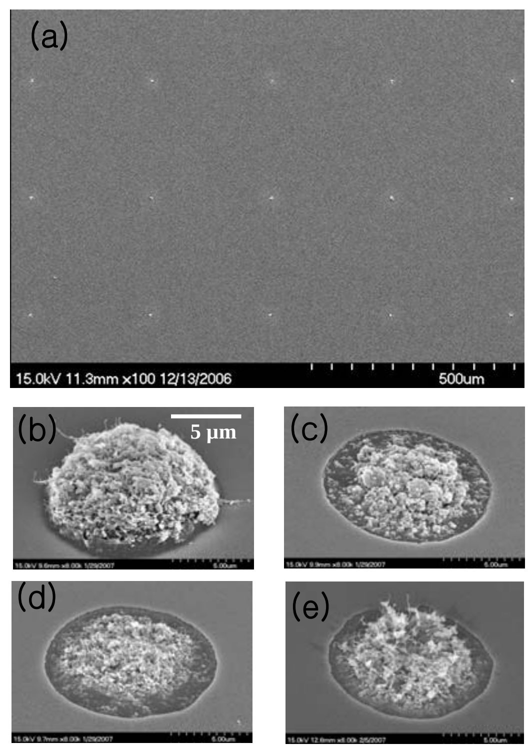

Fig. 3. SEM images of 10-μm-diameter dot arrays patterned by using the photo-sensitive CNT paste: (a) an array of CNT paste dots, (b) a dot after developing, (c) a dot after firing, (d) a dot after tape activation, and (e) a dot after measuring field emission.

Fig. 4 shows an SEM image of nano-scale SnO_2 powders added as fillers to the CNT paste. The particles are 10 ~ 20 nm in size, but severely agglomerated. We prepared the photosensitive CNT

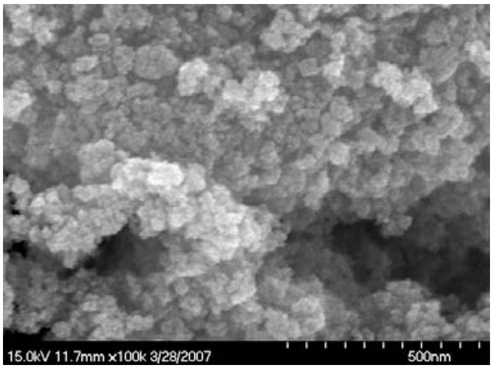

Fig. 4. SEM image of SnO_2 fillers used to fabricate the CNT paste.

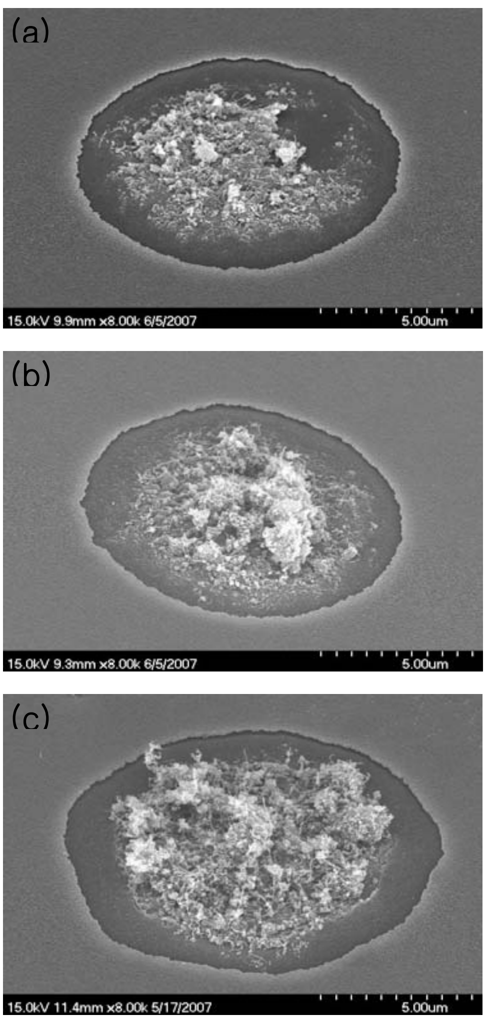

Fig. 5. SEM images of a CNT emitter dot formed by printing the CNT pastes with different amounts of SnO_2 fillers: (a) 5, (b) 7.5, and (c) 12.5%. All samples were subject to firing and tape activation.

paste with different amounts of the SnO_2 fillers 5, 7.5, and 12.5%. Fig 5 gives SEM image of the CNT emitter dots fabricated using these CNT pastes. At 5% fillers [Fig.5 (a)], most paste is detached by a tape activation that few CNTs remain in the dot. At 7.5 and 12.5% fillers [Fig.5 (b) and (c)], more and more paste is left. At 12.5%, many CNTs are protruded on the surface. It is noted that the SnO_2 nano-scale powders serve well as the fillers to provide a good adhesion between the paste and the substrate and thus to control the CNT density on the surface.

Fig. 6 presents field-emission current densities (J) as a function of electric fields (E) and their Fowler-Nordheim plots, measured from the CNT emitter dot arrays prepared with CNT pastes having 5, 7.5, and 12.5 % SnO_2 fillers. The J-E curves indicate that the

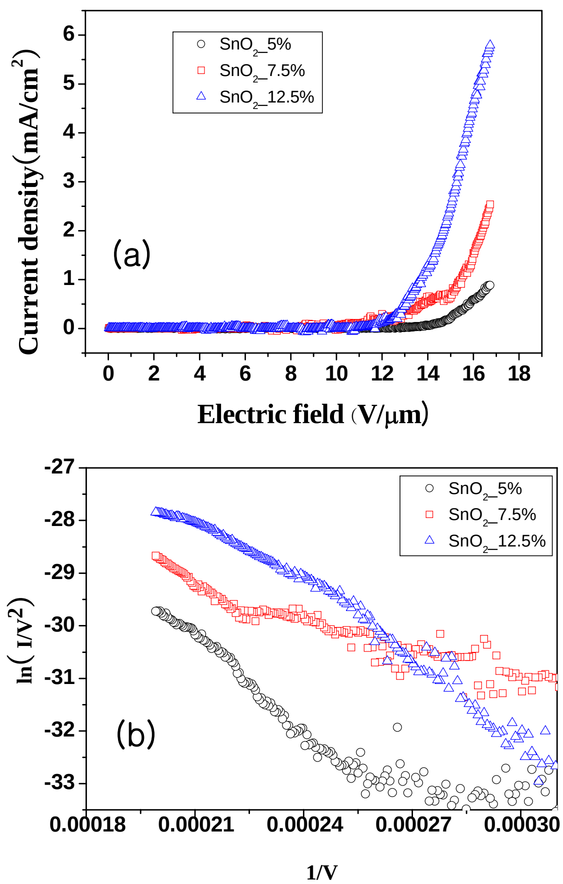

Fig. 6. (a) Field emission J-E curves of the CNT emitter dot arrays containing different amounts of SnO_2 fillers 5, 7.5, and 12.5% and (b) their Fowler-Nordheim plots. Note that the duty ratio of the field emission measurement is 1%.

dot arrays with higher contents of SnO_2 fillers gives better field emission characteristics. The F-N plots are quite linear, implying that the electrons occur by field emission. Currently, we have optimized further the photosensitive CNT paste in terms of rheological and emission characteristics.

4. Summary

We successfully formulated the photosensitive CNT paste and fabricated the CNT field emitter arrays with the 10-μm-diameter dots. Addition of larger amounts of SnO_2 fillers to the CNT paste resultantly gave rise to a considerable improvement of their field emission characteristics, probably due to better adhesion of the paste to the substrate. This technology is expected to contribute to the development of CNT-FEDs and CNT- backlights of TFT-LCDs.

5. References

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