Applied Surface Science 257 (2011) 2250–2253

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Effects on the field emission properties by variation in surface morphology of patterned photosensitive carbon nanotube paste using organic solvent

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ARTICLE INFO

Article history:
Received 7 April 2010
Received in revised form 24 August 2010
Accepted 27 September 2010
Available online 7 October 2010

Keywords:
Field emission
Carbon nanotubes
Multi-walled carbon nanotube
Organic binder

ABSTRACT

Photosensitive carbon nanotube (CNT) paste was prepared by 3-roll milling of multi-walled carbon nanotubes (MWNTs), UV-sensitive binder solution, and Ag as filler additives. Arrays of MWNT dots with a diode structure were fabricated by a combination of screen printing method and photolithography using these paste, and acetone utilized as the developer. The MWNT dots were well-defined and the organic binder materials in the dots were partially removed. The MWNT film without a heat treatment showed a high current density of 1.35 mA/cm^2 at 3.25 V/μm and low turn-on field of 2.2 V/μm at 100 μA/cm^2. Acetone can be used as an efficient developer to form patterns and to remove the organic residues in patterns, simultaneously.

1. Introduction

Carbon nanotubes (CNTs) as a form of carbon have attracted much attention in recent years because of their remarkable mechanical and electronic properties [1,2]. CNTs as field emitter have high aspect ratios and small radii of curvature leading to large electric field-enhancement at their tips and resulting in low operating voltages for electron emission [1,3]. These require that the CNTs to be patterned at selective positions with large-scale control for location and orientation. Pervious methods for assembly and integration of CNTs on substrates include direct growth by chemical vapor deposition (CVD) [4], self-assembling techniques [5], electrophoresis [6], and screen-printing [7]. The direct-growth method can be used to fabrication well-defined CNT patterns by growing CNTs on pre-patterned metal catalyst [4]. However, this method has some limitations in large-scale applications because of the high temperatures required and inefficient processing. The electrophoresis and self-assembly methods have been used for CNT patterning, and have proven to be especially powerful for patterning at low temperature; however, these processes are too complicated to use for large-scale production. By contrast, the screen printing method is a more effective technology for large-scale production, and it has the advantage of low cost and a simple process [7,8]. Although this approach has a low resolution limit because of the inherent paste rheology, well-defined patterns can be fabricated by the use of photosensitive CNT paste in conjunction with a photolithographic process [9,10].

Most photosensitive CNT pastes are composed of CNTs along with an organic binder such as ethyl cellulose or acrylic polymer, a photoinitiator, and an inorganic binder such as metal and glass powders. The photosensitive organic binder in photosensitive CNT paste is photopolymerized by ultraviolet (UV) exposure in order to produce a negative pattern through the developing process [10]. However, these photosensitive pastes must be fired at high temperature of above 450 °C to remove the organic additives, which minimize undesirable effects caused by out-gassing form the residual organic vehicles in their application such as the emitter for field emission devices. (The high temperature processing and the residue of organic vehicles in fired CNT pattern limit the glass substrate, and the firing process may cause substrate deformation.)

To get around these issues, we suggest using an alternative strategy involving acetone as the developer for screen printing method using the photosensitive multi-walled CNT (MWNT) paste. The organic solvent could be removed the organic binder in the printed MWNT paste [11]. Such an advantage enabled us to obtain the well-defined MWNT patterns that effectively remove the residue of organic vehicles at low temperature.

Here, we report the fabrication of a cathode with well-defined CNT patterns by the use of the photosensitive CNT paste and acetone as its developer, shown in Fig. 1, and invest their surface morphologies and field emission properties.

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doi:10.1016/j.apsusc.2010.09.082

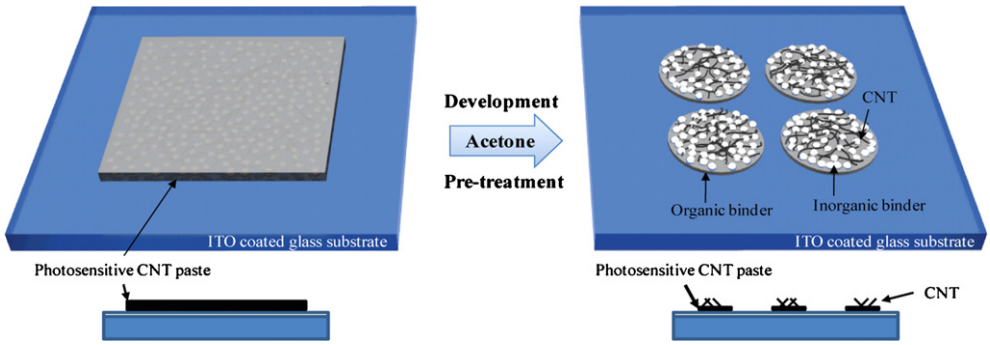

Fig. 1. Schematic diagram of the photosensitive CNT paste developed by organic solvent such as acetone.

2. Experimental

CNT powders consisting of 90 wt% multi-walled CNTs (MWNTs) grown by thermal CVD were obtained in purified form from Hanhwa Nanotech Inc. The MWNTs and acryl based organic solution were used as an electron emission source and organic binder, respectively. To form a photosensitive organic binder, ethyl cellulose was dissolved in α-terpineol and mixed with a photosensitive monomer, photosensitive oligomer, and photoinitiator which are sensed to an I-line (365 nm). The CNT powder, photosensitive organic binder, and Ag powder, as an inorganic binder, with diameters of few micrometers were pre-mixed. Then the 3 roll milling process was carried out for mixing and dispersion of CNTs in the organic binder as polymer matrix.

The size of an indium tin oxide (ITO) coated glass substrate and the screen printing area were 3 cm × 6 cm and 1 cm × 1 cm, respectively. The mechanically well-dispersed CNT paste was printed onto the substrate through a metal mesh and subsequently dried at 90°C for 15 min in a conventional oven. To check the chemical reaction between the printed paste and acetone, the samples were immersed for several seconds in acetone and dried at 95 °C for 30 min. Other samples were exposed to UV light by backside exposure process [9] and then were etched away by a dipping process using acetone. In order to perfectly remove the residual of organic vehicle on the surface of MWNTs and melt the Ag particles in the MWNT patterns, the patterned samples were heated at 380 °C for 30 min in nitrogen atmosphere.

The printed CNT films generally require a special surface activation such as laser irradiation [12], viscous elastomeric solidification [13], and surface rubbing with adhesive tape [14] to achieve a high emission current density and uniform emission sites through the protrusion of CNTs. The surface activation was performed using the adhesive taping method [14]. The field emission properties of samples were measured in a vacuum chamber with a parallel diode-type configuration at a pressure of less than 10^{-6} Torr using a high voltage power supply. An anode, using a printed green phosphor on the ITO coated glass substrate, and a cathode were kept apart by spacers with a thickness of 240 μm. The surface morphologies of the CNT films were observed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4300).

3. Results and discussion

Fig. 2 shows the FE-SEM images of the printed paste on the ITO glass substrate before and after the treatment using acetone. The surface morphology of as-printed paste seemed to be densely packed with the organic materials such as the binder, and not protruded from the surface of the paste [see Fig. 2(a)]. After the treatment using acetone, the MWNTs and Ag particles were protruded from the surface of the printed paste due to the organic binders being partially removed by acetone [see Fig. 2(b)]. As a result, acetone could partially remove the organic materials between MWNTs and Ag particles before the heat treatment at high temperature (>400 °C) and was thus used as a liquid pretreatment.

Fig. 3 shows the measured field emission current densities as a function of the applied field for the paste shown in Fig. 2(b) before and after the surface activation. The turn-on electric fields, at which the emission current density reaches 100 μA/cm^2, were 2 and 1.3 V/μm before and after the surface activation, respectively. A current density of 1 mA/cm^2 is required for flat panel display; [3], where samples with and without the surface activation exhibited a current density of this value at applied fields of approximately 2.7 and 1.7 V/μm, respectively.

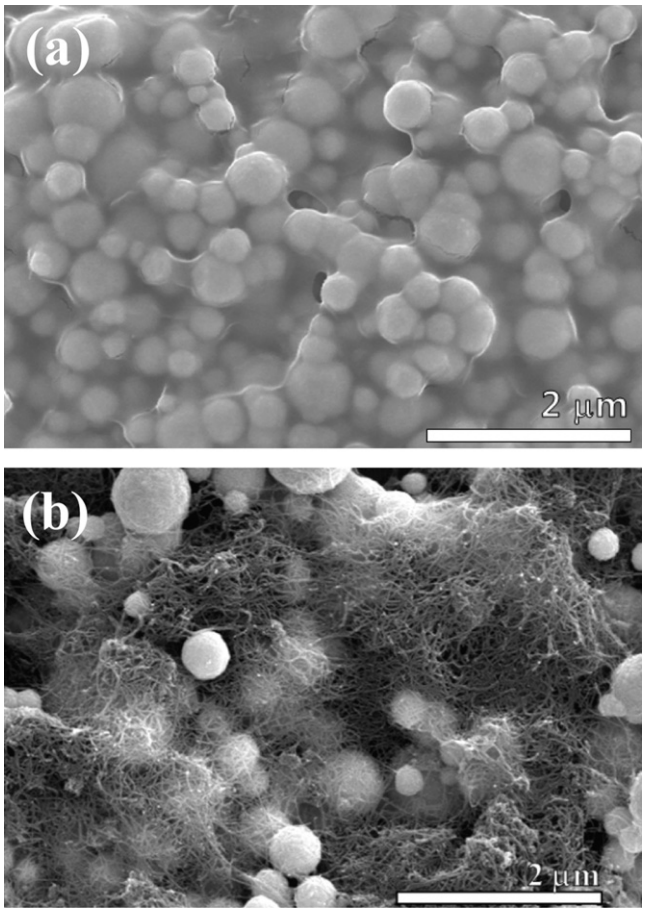

Fig. 2. FE-SEM images of the MWNT paste printed on ITO glass substrate (a) before and (b) after treatment using acetone.

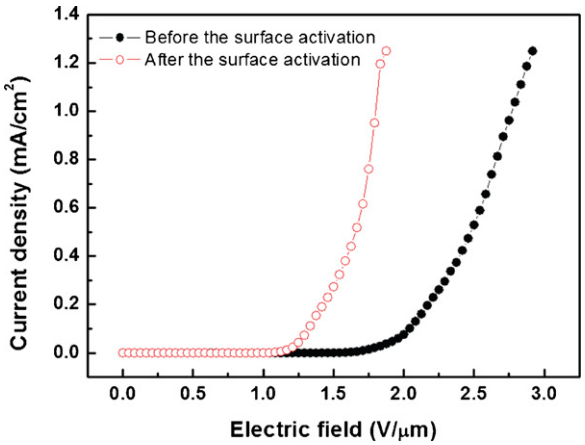

Fig. 3. Current density vs. electric field properties for the printed paste shown in Fig. 2(b) before and after adhesive taping used for surface activation.

Fig. 4(a)–(e) shows the FE-SEM images of the patterned MWNT film on the ITO glass substrate before (sample 1) and after (sample 2) the heat treatment. For all samples, the surface activation was preformed. The diameter of the film, which was patterned in the shape of a dot, was 400 μm, and its patterns were well defined. The area and the number of the dot array are 0.264 cm^2 and 14×14, respectively. In sample 1, the MWNTs and Ag particles could be observed on the surface of the pattern, as shown in Fig. 4(b). Although the observed MWNTs had an entangled morphology because the organic binders still remained, a considerable amount of MWNTs were protruded from the surface of the dot [see Fig. 4(d)]. In case of sample 2, the organic binder surrounding MWNTs were almost removed and the free standing MWNTs were highly aligned from the surface of the dot [see Fig. 4(e)], but the density of MWNTs was decreased because a portion of MWNTs were probably covered with the melted Ag, thermally damaged, and oxidized [see Fig. 4(c)]. It is found that acetone can not only form the MWNT pattern, but also remove the organic materials in the patterned MWNT photosensitive paste with aryl resin because of the difference in the chemical reaction rate of acetone between UV exposed and unexposed regions.

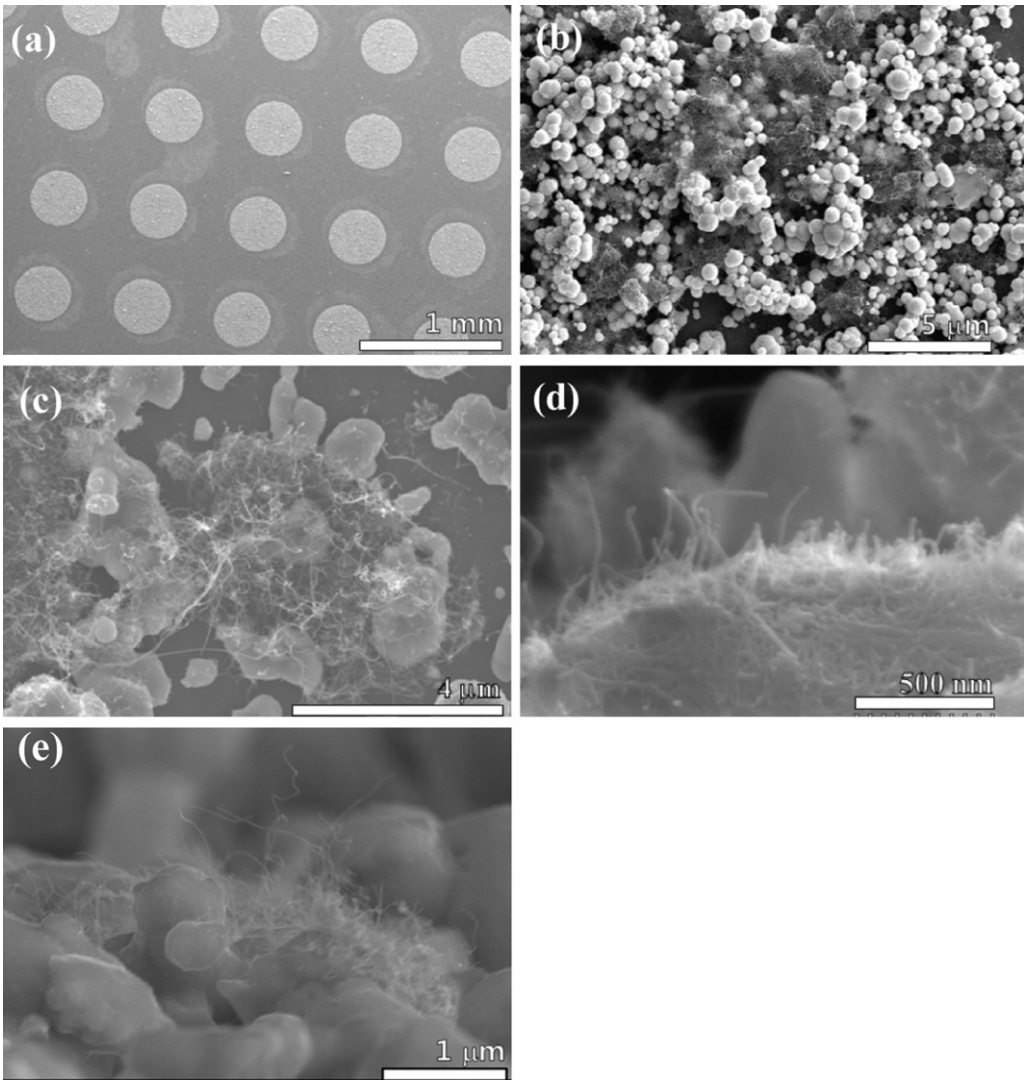

Fig. 4. FE-SEM images of the MWNT film patterned on the ITO glass substrate with the surface activation using the adhesive taping method before and after the heat treatment at 380°C for 15 min in nitrogen ambient: (a) the MWNT pattern array, top view of the MWNT film, (b) before and (c) after the heat treatment, and Cross sectional view of the MWNT film (d) before and (e) after the heat treatment.

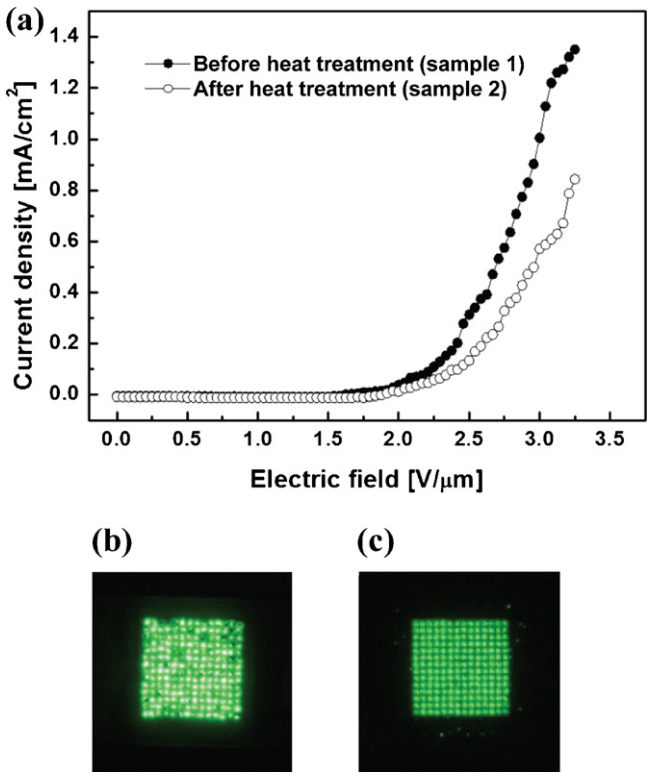

Fig. 5. (a) Current density vs. electric field properties for the patterned MWNT film with the surface activation using the adhesive taping method before (sample 1) and after (sample 2) heat treatment. Emission images from the MWNT film (b) before and (c) after the heat treatment as the electric field of 3.5 V/μm.

Fig. 5(a) shows the current density-electric field curves for the patterned MWNT films in Fig. 4(d) and (e). The measured current density reached its highest value of approximately 1.4 mA/cm^2 at an applied field of 3.5 V/μm. In sample 1, the turn-on field was about 2.2 V/μm, while the turn-on field in sample 2 was 2.4 V/μm. The samples display an emission image all over the dot patterns as shown in Fig. 5(b) and (c), where sample 2 showed a more uniform emission sites than sample 1. The resulting uniformity of sample 1 suggests that a high current can be extracted from the rough film surface containing the spherical Ag particles, more completely contacted by an adhesive tape, and such extraction has caused emission uniformity problems, called "hot spots". Therefore, sample 1 needed to be heat-treated under an N_2 atmosphere to improve its emission sites, but the heating temperature for sample 1 can be dropped to less than 380 °C with regard to the melting temperature of the inorganic binder.

4. Conclusions

To investigate the effects of acetone (organic solvent) as a developer, the photosensitive MWNT paste was prepared and the MWNT patterns were formed on the ITO glass substrate by the screen printing method and photolithography technique. The well-defined MWNT patterns were obtained through the difference in the chemical reaction rate of acetone between the UV exposed and unexposed regions. Simultaneously, acetone effectively removed the organic binder materials from the patterns. The patterned MWNT film without the heat treatment showed a high current density and low turn-on field. After the heat treatment, the patterned MWNT films display a more uniform emission image all over the patterns. Thus, it is confirmed that acetone can be used an efficient developer for photosensitive CNT pastes.

Acknowledgments

This work was supported by Industrial Strategic Technology Development Program (No. 10037394) funded by the Ministry of Knowledge Economy (MKE, Korea), Korea Research Foundation Grant funded by Korea Government (MOEHRD) (KRF-2006-331-D00213), and Seoul Metropolitan Government though Seoul Research and Business Development (Grant No. CR0700540).

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