We are IntechOpen,
the world's leading publisher of Open Access books
Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

6

Research and Application of CNT Composite Electroplating

Guifu Ding, Yan Wang, Min Deng, Xuemei Cui,
Huiqing Wu and Lida Zhu
National Key Laboratory of Nano/Micro Fabrication Technology
Key laboratory for thin film and microfabrication of Ministry of Education
Institute of Micro and Nano Science and Technology
Shanghai Jiao Tong University
P. R. China

1. Introduction

Carbon nanotubes (CNTs)[1] are one of the most exciting new materials, which possess excellent mechanical properties as well as thermal and electrical characteristics. The Young's modules of CNTs have an order of 1TPa [2, 3], which is much higher than that of the glass fibers (70GP) and most of the other material. Direct measurement on individual nanotubes using atomic force microscopy shows that CNTs can accommodate extreme deformation without fracture [4]. Besides, CNTs are excellent conductors and possess high thermal conductivity.

Many of the remarkable properties of CNTs are established well now [5-8], and their exploitation in a wide range of applications forms a major part of current research and development efforts[9,10]. One of the challenges is to tackle the problem of manipulating CNTs, individually or collectively, to produce a particular arrangement needed for a given application. Moreover, if CNTs are be combined with metal materials to form composites, it is generally important to develop processing methods that disperses the CNTs homogeneously in the metallic matrix

However, it is difficult to make CNTs dispersed uniformly in the metal-matrix. According to Dujardin's report [11], the pure metals would not easily wet the surface of CNTs for their surface tension out of a cut-off limit between 100 and 200mN/m. Therefore, traditional techniques such as powder metallurgic process would bring formidable technical hurdles to prepare high quality metal matrix CNTs composites, which ascribed to the low strength interfacial adhesion [12, 13].

CNT composite electroplating (CCE) is one of the most important techniques for preparing CNT composite films, because no melting and solidification of metal matrix are induced.

The interest in the CCE is driven not only by its applicability to a great variety of metal materials but also by its simplicity. CCE is a cost-effective method usually requiring simple equipment as well as being amenable to scaling-up to large dimensions. In addition, the CCE can be integrated with the micro-electro-mechanical systems (MEMS) [14]. The metal matrix CNTs composite films can be processed to be various micro-scale structures for MEMS devices such as field emission cathodes and electronic contacts [15].

In this study, we consider the following contents including preparation of metal/CNT composite using CCE (Section 2), Fabrication of Ni-matrix CNT field emitters using CCE (Section3), Cu/ CNT contact material prepared by CCE (Section 4) and CNT field emission micro-cathode arrays fabrication (Section 5). Finally, the potential applications of the resulting CNT structures and the scope for future work are highlighted in Sections6 and 7.

2. Preparation of metal/CNT composite using CCE

The most critical problem in preparation of excellent metal/CNT composite film is achievement of a homogenous stable dispersion of CNTs in the plating bath [16].
The influences of cathode-current density plating PH value CNTs concentration in plating bath and agitation mode on the dispersion of CNTs in the metal matrix are discussed in this chapter.
As-produced CNTs are intrinsically inert, often aggregated or entangled, and may contain impurities such as amorphous carbon or catalytic metal particles [17–19]. The amorphous carbon or catalytic metal and all other impurity particles coated on the CNTs will influence the dispersion interface bonding and other electrical, mechanical properties of CNTs in the composite.
Fig.1 shows the schematic diagram of CCE.In the CCE process, adequate CNTs must be conveyed to the cathode surface and embedded in metals through diffusion layer in order to obtain composite coating with moderate CNT content. In the meantime, if CNTs are embedded in the form of aggregation, which will hamper the complement of metal cationic and metal deposition process because of the small clearances formed among CNTs. These will also cause the organization osteoporosis of coating structure and deteriorate the performances. Therefore, adequate amounts of CNTs must be added in the plating for good dispersion degree.
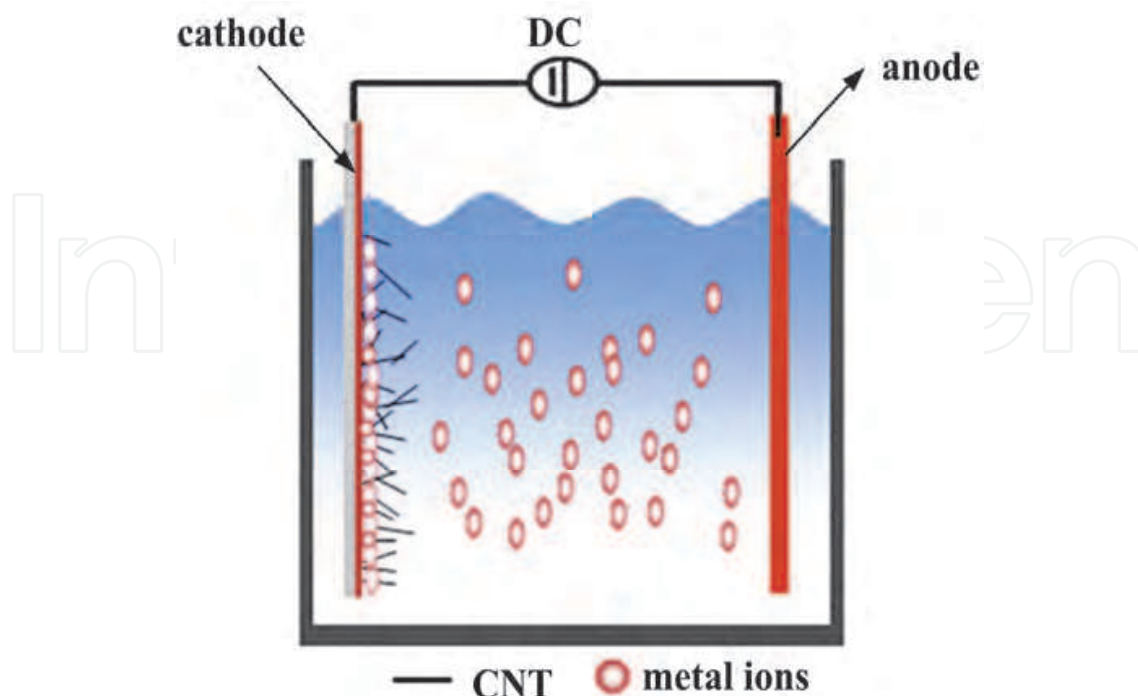

Fig. 1. Schematic diagram of CCE.

In this study, it mainly utilize the mechanical ball mill oxidation processing adding additive and ultrasonic agitation processing to improve suspension stability of CNTs in the electroplating bath.

Long CNTs are more easily aggregated or entangled than shorter CNTs. Mechanical ball mill are often utilized to cut and disperse aggregated CNTs. Fig.2 shows the SEM images of the CNTs composite coatings with the CNTs before (Fig.2A) and after (Fig.2B) ball milling treatment . As can be seen from the images, the mechanical ball milling can effectively improve the dispersibility of the CNTs in the matrix.
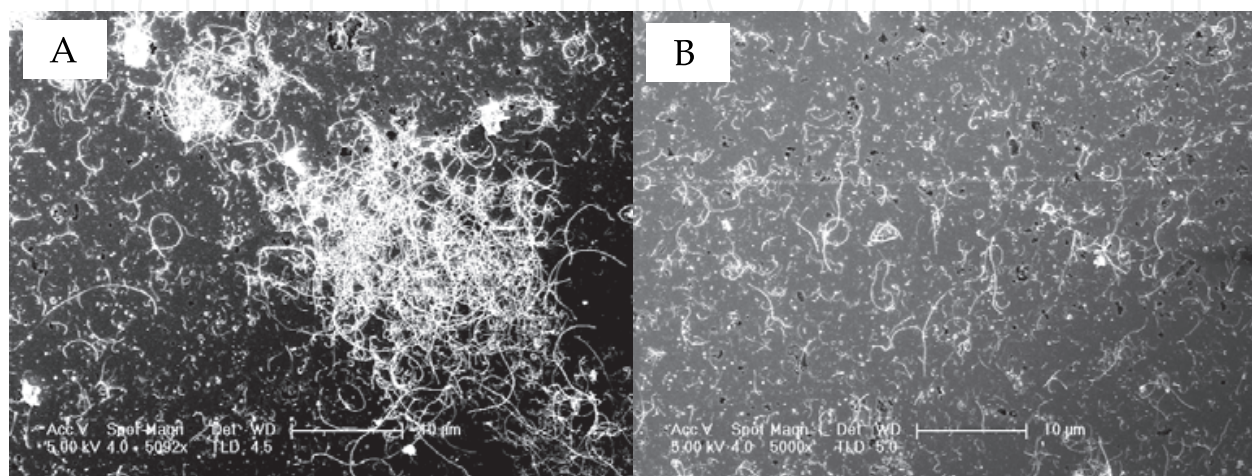

Fig. 2. SEM image of the CNTs composite coatings with the CNTs before (Fig.2A) and after (Fig.2B) ball milling treatment

The purification processes that have been investigated usually utilise the differences in the aspect ratio [20] and oxidation rate between CNTs and impurities [21, 22]. A typical strategy is to use thermal oxidation, then acid reflux in concentrated HCl, and finally a thermal annealing treatment to purify the raw material; a surfactant can subsequently be used to disperse CNTs using sonication [23]. In this study, the CNTs were used after being boiled in potassium hydroxide molten for 5 h and concentrated sulfuric acid for 21h. The CNTs were oxidated in concentrated acid in purification, which reduces the aggregation of the CNTs and enhances their chemical stability in solution. The chemical processing after the CNTs surface defective parts are grafted the hydroxyl and carboxyl group. These ion dissociation increases the negative charge of the CNT surface and strengthens the stability of CNTs suspension.

Fig.3 shows the images of the CNTs before and after being treated by concentrated sulfuric acid. As can be seen from the image, Severe aggregation and tangling exist in the original CNTs (Fig.3A,B) compared with the treated CNTs (Fig.3C,D). In order to validate the existence of the functional groups on the CNTs after being handled by concentrated sulfuric acid, we tried to graft Fe_3O_4 particles on the CTNs by the covalent bond linked. In high resolution electron microscopy, we can see that Fe_3O_4 particles are successfully grafted and uniform disperse on the CNTs (Fig3.D). It is confirmed that there are abundant covalent bond functional groups on the pretreated CNTs.

Besides the chemical pretreatment, adding additive such as ethanol[24], Polyacrylic acid(PA5000), n-pentanol [25], Dodecyl sulfonic acid sodium, tetrahydrofuran (THF) [26–28], dimethly formamide (DMF) [29,30] and deionised water with pyrrole [46,47] is an
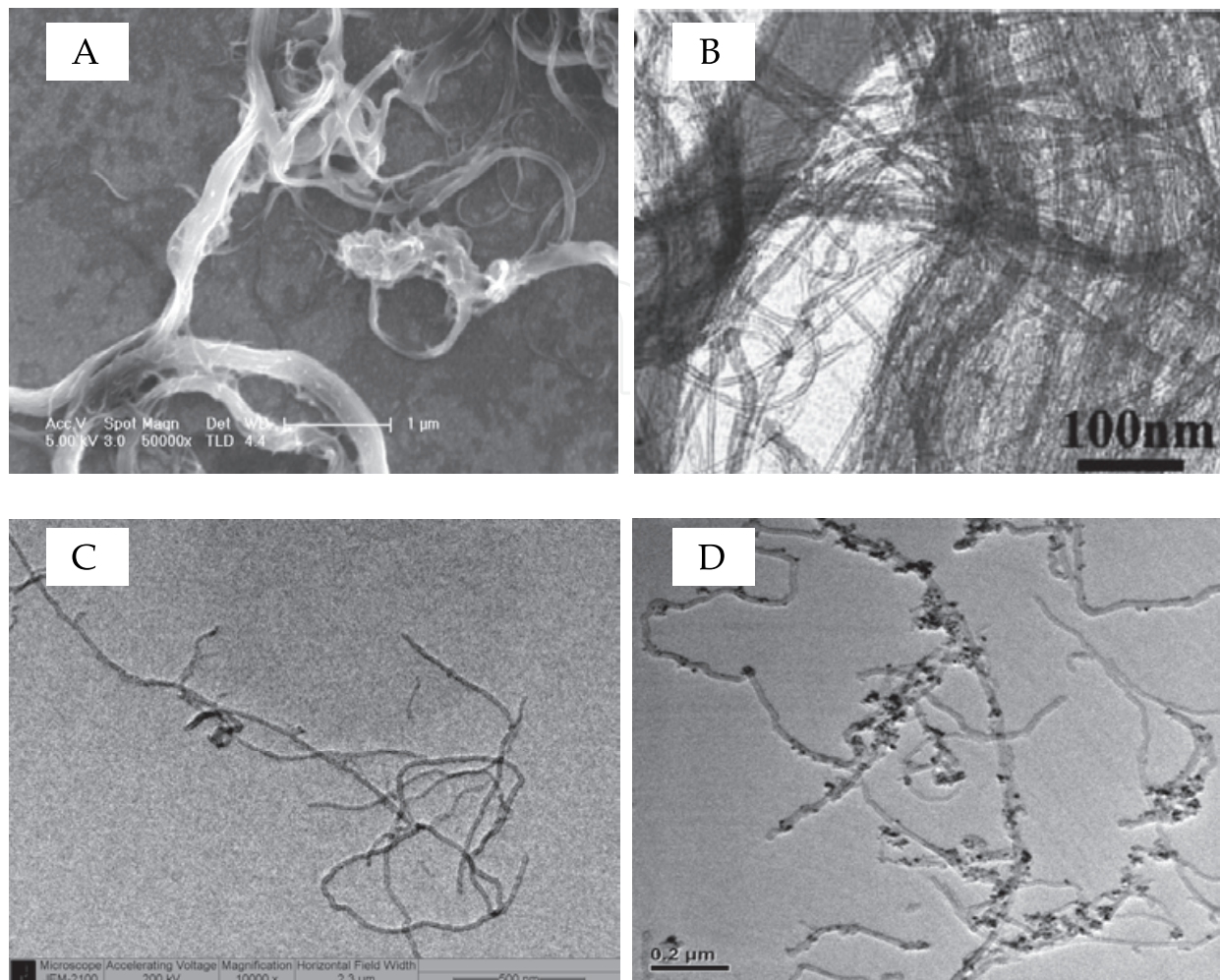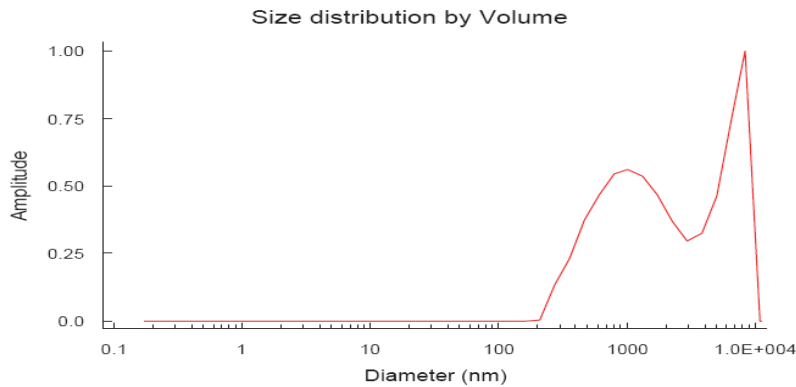
Fig. 3. The SEM (A) and TEM (B) images of the original CNTs and the SEM images of the CNTs after treatment of purification (C) and grafting of Fe_3O_4 (D)
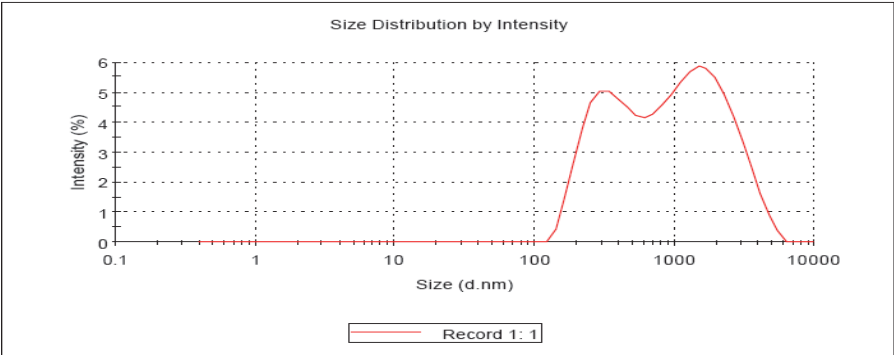
another effective way to raise the CNT dispersion degree in plating bath. In this study, As a conventional bright additive, the molecular weight of 5,000 polyacrylic acid (PA) was added to disperse the CNTs. Though polycyclic acid is a high-performance polymer surfactant, dispersion effect of this low molecular surfactant is small because of its simple molecular structure and small molecular weight. Therefore, in order to achieve the ideal dispersion, increasing the dosage of the low molecular surfactant would be an effective way. The dispersiveability polymer surfactant is better than the low molecular surfactant due to long high molecular chain big molecular weightmore kiss water-based and dredging water-based.

The dispersity of the CNTs in water-based solution is determined using the HPPS nanometer particle size analyzer. Figure 4 shows that the untreated CNTs disperse poorly in the water-based solution. The sizes of the reunion things are in the range from 990nm to 5800nm. After being treated, the sizes of the reunion things fell to the range from 360nm to 1750nm. The dispersity of the CNTs in the water-based solution was impoved.

In addition, ultrasonic agitation processing was utilized in the CCE progress to improve the dispersity of the CNTs in the composite film. Figure 5 shows the growth processes of the metal/CNT composite films prepared by CCE with ultrasonic agitation. The growth mechanism of the metal/CNT film will be changed when the ultrasonic agitation is applied.

Results

Z-Average size (nm): **895.6**	Peak 1 mean: 990.11	% by Volume:	58.4
Polydispersity index: **0.461**	Peak 2 mean: 5885.33	% by Volume:	41.6
	Peak 3 mean: –	% by Volume:	

Size distribution by Volume

Results

		Diam. (nm)	% Intensity	Width (nm)
Z-Average (d.nm): 617	Peak 1:	1750	61.1	997
Pdl: 0.448	Peak 2:	364	38.9	135
Intercept: 0.479	Peak 3:	0.00	0.0	0.00

Size Distribution by Intensity

Record 1: 1

Results

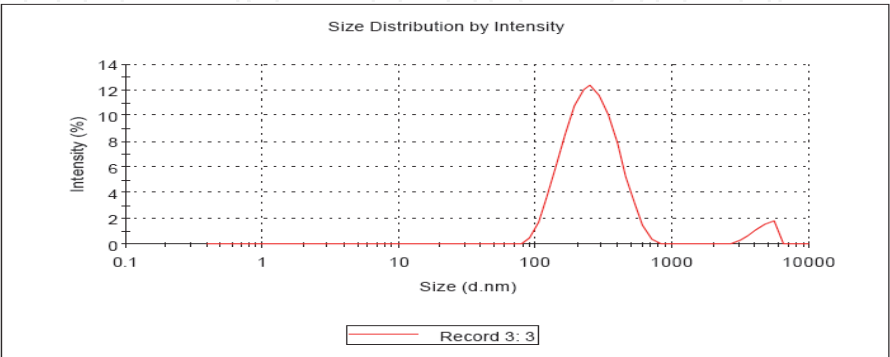|		Diam. (nm)	% Intensity	Width (nm)
Z-Average (d.nm): 242	Peak 1:	273	94.8	115
Pdl: 0.285	Peak 2:	4690	5.2	784
Intercept: 0.843	Peak 3:	0.00	0.0	0.00

Size Distribution by Intensity

Record 3: 3

Fig. 4. The granularity dispersion curves of the CNTs in the water-based solution, (a) original CNT; (b) CNT after being treated; (b) after being added bright additive.

Initially, because the CNT aggregates with bigger size will suffer larger impulse force from the electroplate liquid; the CNT aggregates with bigger size are more difficult to be absorbed on the cathode compared with the single CNTs. When the CNT aggregates absorbed on the cathode are washed off, the single CNTs which combine firmly with the substrate would be left on the surface of the composite film. As illustrated in Fig.5(b), the diffusion layer is compressed under the effect of ultrasonic agitation, the agitation further prevent the aggregates from being captured by the cathode and embedded into the composite coating. Moreover, the relatively long single CNTs which metal grains deposit on them may also be pulled out from the metal matrix because of their bigger size and heavier weight compared with other CNTs. For the same reason, the bigger metal grains will be pulled off from the surface of the CNTs too when the combination between the metal grains and the CNT are not enough firm. Finally, the single CNTs are embedded into the metal matrix with the deposit of metal on the cathode and a compact and smooth metal/CNT composite is obtained as a result.
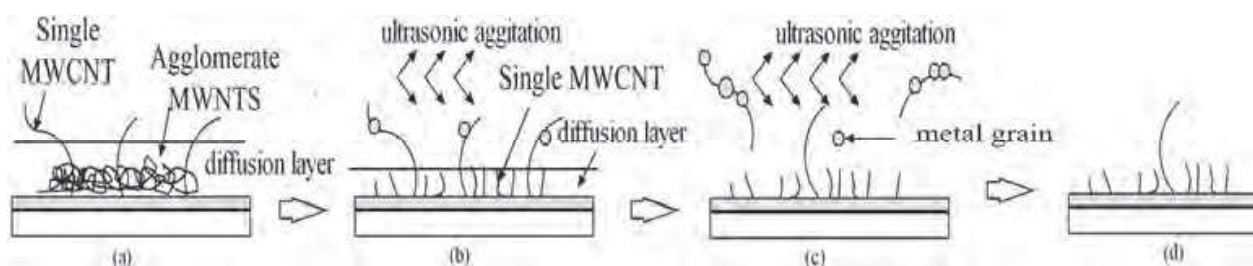

Fig. 5. The growth process of metal/CNT composite films prepared by CCE with ultrasonic agitation. (a) CNT aggregates are absorbed on the substrate. (b) Desorption of the CNT aggregates under ultrasonic agitation. (c) CNTs with metal particles deposited on them are pulled off from the composite film. (d) Single CNT is embedded into the CCE.

Figure 6 shows the SEM images of Ni/CNT composite films prepared by CCE and CCE with ultrasonic agitation. Figure 6 (a) shows the SEM image of Ni/CNT composite films prepared by CCE with electromagnetic stirring and their higher magnification are shown in Fig.6 (b) and(c). It is easy to find that there are a lot of spherical Ni grains are deposited on the CNTs with a diameter from several nanometers to about 700nm.The CNTs accumulate on the cathode, and most of them incorporated into the composite films in the form of aggregates. The CNT aggregates are wrapped by numberless Ni grains. A rough and uneven composite film is formed. Figure 6 (d) shows the SEM image of Ni/CNT composite films prepared by CCE with ultrasonic agitation and their higher magnification SEM images are shown in Fig.6 (e) and (f). From these SEM images, we see that a compact and smooth Ni/CNT composite film has been obtained by CCE with ultrasonic agitation. The CNTs are dispersed homogeneously in the Ni matrix, and most of CNTs incorporated into the composite film in the form of single CNTs without beads-shaped structure is observed.

3. Fabrication of Ni-matrix CNT field emitters by CCE

Electron field emitters based on CNTs are currently being investigated as next-generation cold cathode materials [33–35]. Compared with other field emitters such as spindt-type and silicon field emitter arrays, CNTs possess the advantages of very high aspect ratio, small radius of curvature, lack of vacuum-arcing, low sputter yield, chemical inertness, thermal
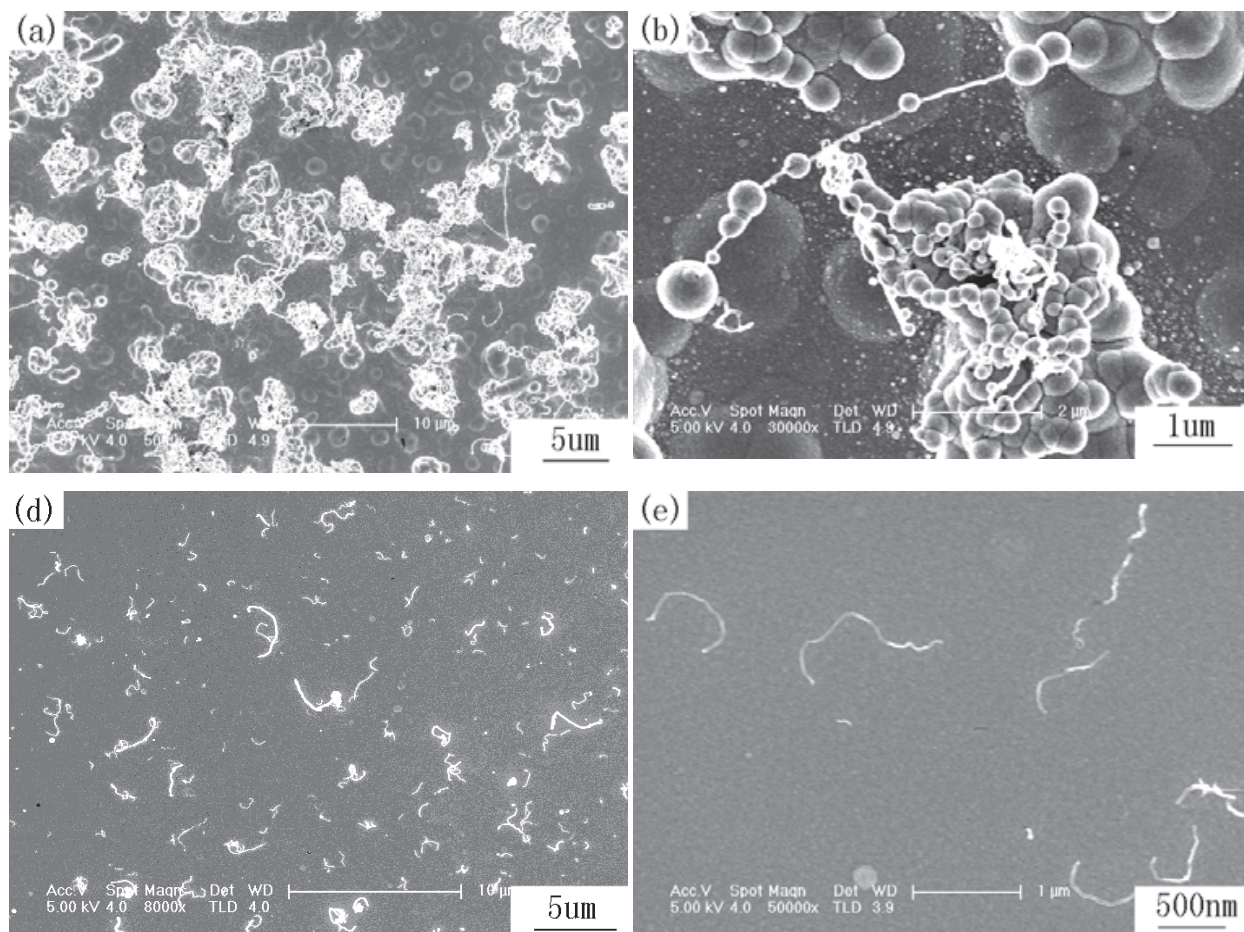
Fig. 6. The SEM images of Ni/CNT composite films prepared with CCE: (a) Ni/CNT composite film prepared without using ultrasonic agitation, (b) is the enlarge image corresponding to (a);(d) Ni/CNT composite film prepared with ultrasonic agitation ;(c)are the enlarge images corresponding to (d).

stability and low work function of electron tunneling [36]. CNT field emission cold cathodes have a potential to be applied to emission devices which include flat panel field emission displays, cathode ray tubes, backlights for liquid crystal displays, outdoor displays and traffic signals [37–40].In order to function as good field emitters, CNTs should have good crystallinity, a clean surface, and good electrical contact with the substrate. Considerable effort has been made to develop various methods in fabricating CNT field emitters [41–47].These methods can be categorized into two fundamental types – direct growth and the screen-printing. Each method has certain advantages and disadvantages. For example, the direct growth is of high efficiency for controlling the CNT alignment, density, and length. However, the preparing method has the following three disadvantages: (1) Due to the self-assembling nature of the CNT synthesis process, it is still difficult to control the length of CNT. Therefore, the distance between the CNT tips and the gate may not be accurately controlled; (2) The adhesion of the CNTs which are catalytically grown on the substrates is often not strong enough to survive the mechanical shaking involved in the fabrication processes;(3) The high temperature condition (800~1000 ℃) which may damage some glass substrates is obligatory for this method. In the screen printing, large area field emitters can be fabricated in lower cost. However, for such emitters, the density and heights of CNTs

Table 1 shows several succefully plating bath composition and process conditions for CCE in our present research.

Metal matixs	Solution components	Content	Electroplating conditions
Cu	$CuSO_4 \cdot 5H_2O$	30g/L	Operating temperature：20±1℃; PH:4.5 Cathode-current density：0.1～1A/dm² ; Ultrasonic agitation ; Anode: pure Cu plate
	H_2SO_4(98%)	76g/L	
	MHT	1ml/L	
	PA5000	3ml/L	
	MWCNTs	4g/L	
Zn	ZnSO4 ·7H2O	110g/L	Operating temperature：20±1; PH：5.0 ; Cathode-current density：0.9～1.2A/dm2 ; Ultrasonic agitation ; Anode: pure Zn plate
	Na2 SO4	21g/L	
	CH3COONa	20mL/L	
	MWCNTs	2g/L	
Ag	KAg(CN)2:H	80g/L	Operating temperature：25±1℃ ; PH：4.8 Cathode-current density :0.5～1A/dm2 ; Ultrasonic agitation ; Anode: Pt plate
	30KCNS	150～250g/L	
	KCl	25 g/ L	
	MWCNTs	4g/L	
Ni	Amino-sulfonic nickel	400 g/L	Operating temperature：25±1℃ ; PH：4.46 ; Cathode-current density :1A/dm² ; Ultrasonic agitation ; Anode: pure Ni plate
	Chlorinated nickel	10 g/L	
	Boric acid	15 g/L	
	Dodecyl sulfonic acid sodium	0.05 g/L	
	MHT	4 ml/L	
	Dodecyl sulfonic acid sodium	0.05 g/L	
	Polyacrylic acid （PA5000）	6～8 ml/L	
	MWCNTs	2g/L	

Table 1. Several succefully plating bath composition for CCE in our present research

were random and the turn-on voltage may not be a characteristic of average CNTs but of early igniting CNTs instead. In addition, direct growth and screen printing may cause the tubes be contaminated with some impurities, like metallic catalyst particles, amorphous carbon or organic residues which can introduce further defects into the CNTs during their removal [48, 49]. If all the advantages in both methods are combined and all disadvantages are eliminated, a CNT field emitter with good properties can be fabricated.

In this study, we propose a novel method of fabricating a Ni-matrix CNT (NMCNT) field emitters using CCE and micromachining (CEMM) at room temperature. Pretreated multi-walled CNT and Ni are deposited onto a Cr/Cu conducting layer by CCE; subsequently, protruding tips of CNTs are obtained by etching away a layer of Ni as emitters, followed by emitter pixels being formed by micromachining. This method is not only relatively simple in fabrication process, but also combine advantages of direct growth and screen printing. The NMCNT field emitters we fabricated shows relatively good field-emission properties and stability. It is believed that this is the first report of NMCNT field emitters fabricated by CEMM and the investigation may be helpful to CNT cathodes wide application for industry.

3.1 Experiment

Referring to Fig.7, the fabrication process is described as follows:

1. Cr/Cu (30/50 nm) is deposited on a glass substrate as the conducting layer by sputtering.
2. Photoresist spin coating and photolithography are per-formed to form emitter pixels.
3. The CNT and Ni composite film is deposited on Cr/Cu conducting layer by CCE (the reason for choosing Ni as the basement is its resistance to corrosion). Initially, the multi-walled CNTs with tube diameters ranging from 20 to 40 nm are boiled in potassium hydroxide molten for 5 h and concentrated sulfuric acid for 21 h in order to obtain pure and dispersed emitting materials. Then, the pretreated CNTs are added into Ni electroplating solution, and the solution is sonicated at 21 kHz for 3 h to produce a homogeneous suspension. Finally, the CNT and Ni composite films are deposited on the Cr/Cu conducting layer by composite electroplating using the CNT suspension.
4. The CNT and Ni composite film is polished by polisher to form a flat surface (roughness Ra < 0.2 lm).
5. A layer of Ni is etched away from the CNT and Ni composite film with a flat surface to obtain protruding tips of CNTs as emitters by wet chemical etching, the etching depth is carefully controlled by etching time in order to keep the roots of CNTs still remain in the metal matrix.
6. Photoresist spin coating and photolithography are performed to protect those CNT arrays used as field emitters in the process of reactive ion etching (RIE).
7. Removing the photoresist after RIE of CNTs not used as field emitters.

All experimental steps stated above in (1)–(7) are completed at room temperature. A scanning electron microscope (SEM, JSM-6700F of JEOL Company) is used to analyze the surface morphology of NMCNT field emitters.

3.2 Results and discussion

Figure 8 shows a series of SEM images of NMCNT emitters with different amplified factor. It can be seen that the cathodes with a flat surface were covered with dispersed CNTs (see
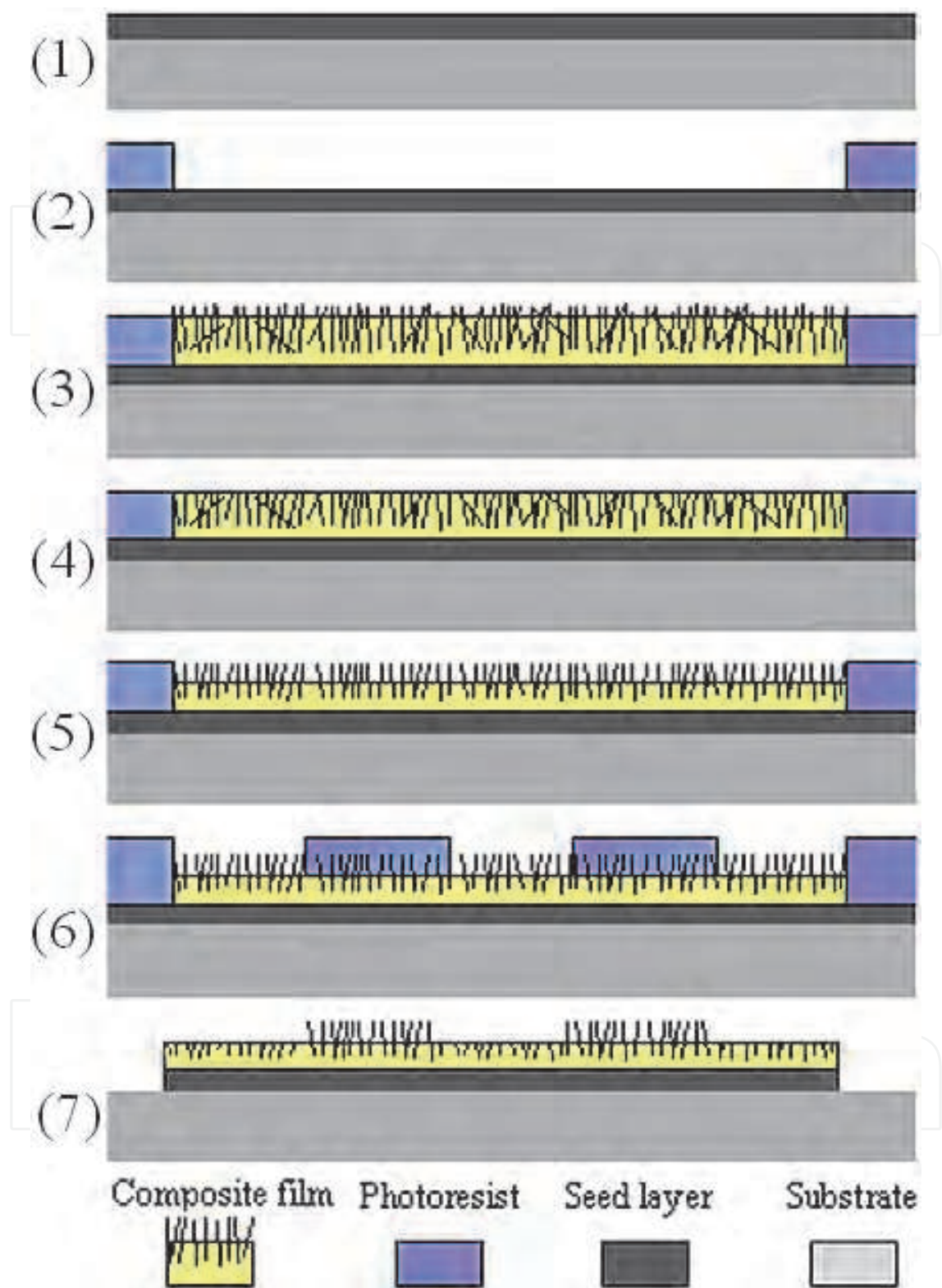
Fig. 7. The fabrication process of NMCNT emitters:(1) sputtering Cr/Cu (30/50nm) conducting layer on a glass substrate, (2) photolithography of NMCNT emitter pixels, (3) CCE of the CNT and Ni composite film, (4) polishing of the surface of CNT and Ni composite film, (5) wet chemical etching of Ni layer, (6) photolithography of NMCNT emitter arrays, (7) removing the photoresist after RIE of CNTs not used as field emitters.

Fig.8a and b), the roots of CNTs were firmly embedded in the cathode and no contamination was induced (see Fig.8c and d). In addition, the distribution and heights of CNTs have been well controlled by the etching time and operation condition of CCE. In conventional CNT emitters, both by screen printed and chemical vapor deposition synthesized, the distribution and height of CNTs were random. In such emitters, the turn-on voltage may not be characteristic of average CNTs but of early igniting CNTs. The early emission from some particular tubes can reveal the apparently low turn-on voltage, which is usually defined by the voltage at a given reference current intensity.
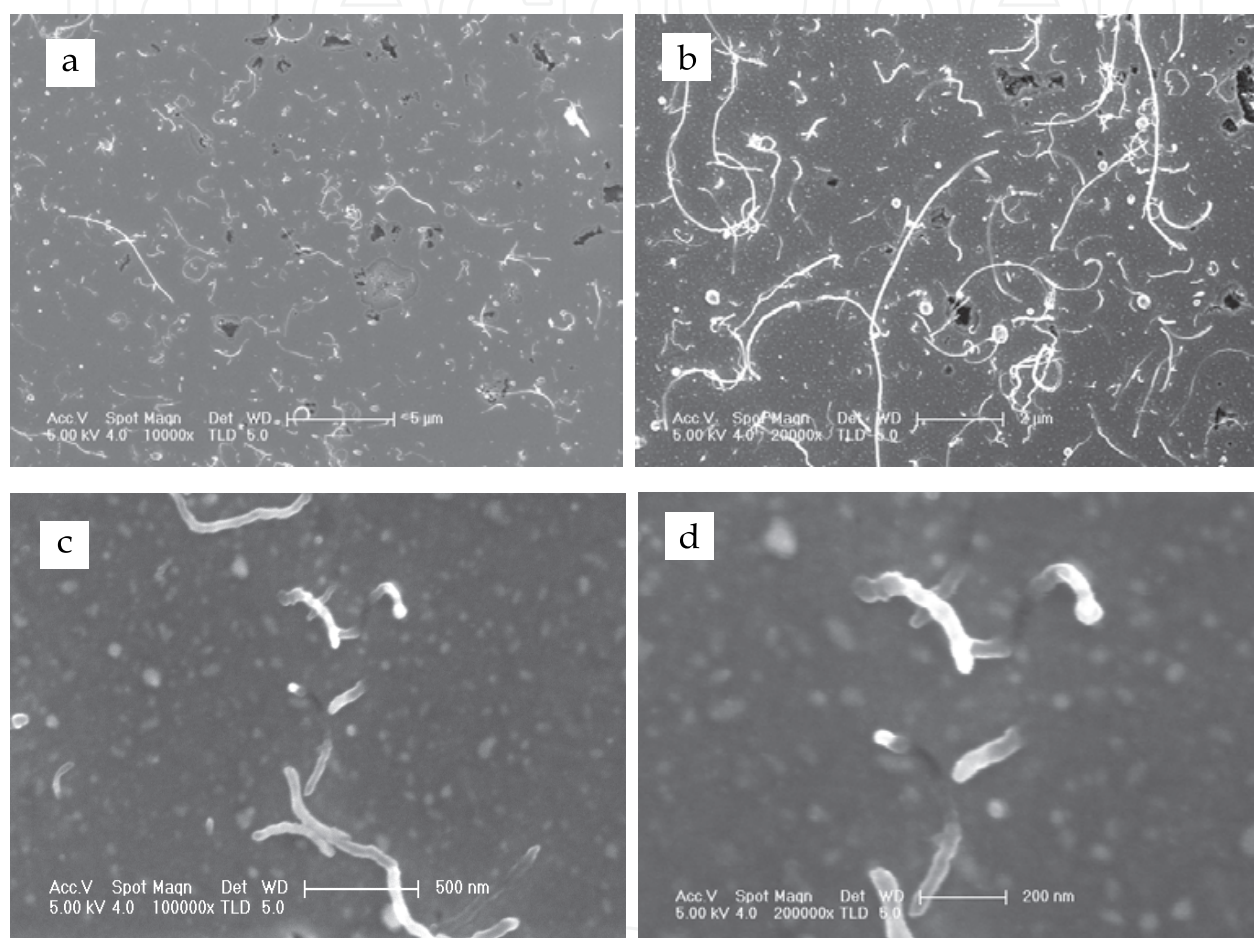

Fig. 8. The SEM images of NMCNT field emitters with different amplified times:(a)10000X, (b)20000X,(c)100000X,(d)200000X.

The SEM image of NMCNT emitter pixels fabricated by CEMM is shown in Fig.9 (a) and their higher magnification SEM image is shown in Fig.9 (b). The spacing between pixels shouldn't be too small, small emitter pixel spacing would induce the field screening effect between adjacent emitters. However, large emitter pixel spacing would decrease the display effect of field emitters. In the fabrication process of NMCNT emitters, it is convenient to adjust the size of emitter pixels by masking and photolithography. The optimized distance between NMCNT emitter pixels was 60um and the area of emitter pixel was 625μm^2 in the present study.

The electron field-emission properties of NMCNT field emitters with a diode structure were measured in a vacuum chamber at a pressure of 1.7×10^{-5}Pa. The distance between the cathode and the anode was 170μm, and the electric field referring to the value of the applied
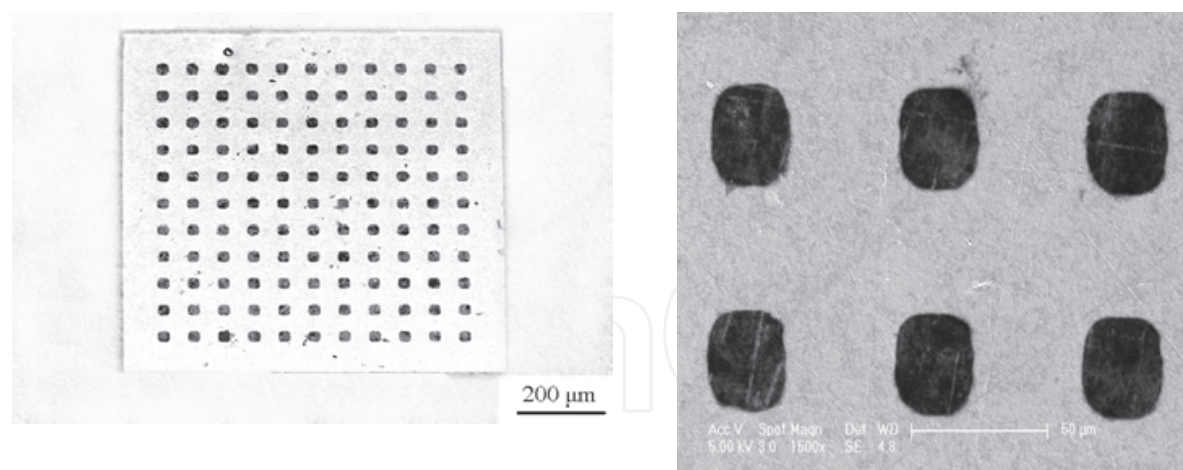
Fig. 9. The SEM images of (a) CNT emitter pixels, (b) a magnified view of pixels.

voltage mentioned in the following descriptions is divided by the electrode distance. In contrast to the distance between electrodes, the surface of the test sample is very flat (roughness Ra < 0.2µm), we consider that field emission has actually occurred from the all NMCNT pixels on the test sample in the same applied field. The actual emission area of NMCNT field emitters is $1600 \times 0.000625 cm^2$ (1600 is the number of pixels on the test sample). Figure 10 shows a plot of the field-emission current density (ECD) versus the applied electric field, and the corresponding filed emission curve is shown in the inset. It is easy to find that all dots on the filed emission curve fit a single straight line well, which indicates the Fower-Nordheim-type field-emission behavior. The ECD of NMCNT emitters increases monotonically with the applied field, and the shape of the curve in Fig.5 is relatively smooth. When the applied electric field is enough high, the current gets saturated and remains constant. The highest current density was about 13mA·cm⁻² at an applied electric field of 3.4Vµm⁻¹ and the measured turn-on field to extract a current density of 10µA·cm⁻² was 0.53 V µm⁻¹. Considering the fact that the emission area of NMCNT emitters was 1cm², this should be a rather strong filed emission performance in carbon-related cathodes. CNT films grown on various well treated or fabricated planar substrates with an ECD higher than 1mA·cm⁻² were also reported, although it is of an actual emission area which is only several square millimeters. For example, ECD of~6A·cm⁻² (at 7.4V µm⁻¹)and~25mA·cm⁻² (at 4V µm⁻¹) were demonstrated by CNT films grown on Fe/Al/TiN/Si and Ti substrates, with the emission areas being 10⁻⁴ and 0.04 cm², [50, 51].However, when the actual emission area reaches the magnitude of square centimeters, the ECD will drastically drop down to a scale from several tens to several hundreds of microamperes. For example, for CNT films grown on SiO_2/Si (0.8 cm²), indium tin oxide coated soda lime glass (64cm²) and glass modified by organic functional groups (1cm²), the corresponding ECDs were only 42 µA·cm⁻² (at 6 V µm⁻¹), 62 µA·cm⁻² (at 2 V µm⁻¹) and 160µA·cm⁻² (at 4.8 V µm⁻¹) [52-54]. Based on these comparisons, it was concluded that the field electron emission from NMCNT field emitters was greatly enhanced, and the technical parameters, such as turn-on field and ECD, had almost satisfied the typical technical requirements for flat panel display operation [55]. The enhancement factor β was derived from the slope of the graph by assuming that the work function of CNTs was the same as that of graphite (5eV).The enhancement factor for the NMCNT-field-emitter was 27735. Such a β value is much higher than typical values reported for CNT cathodes, such as 400~1200

for CNTs on silicon and glass substrates, and 2600~3500 for highly ordered CNT arrays on porous aluminum oxide [56, 57]. Therefore, considering the actual emission area, the obtained turn-on field, current density, and the calculated field enhancement factor, the NMCNT emitters fabricated by CEMM is an ideal candidate cathode.
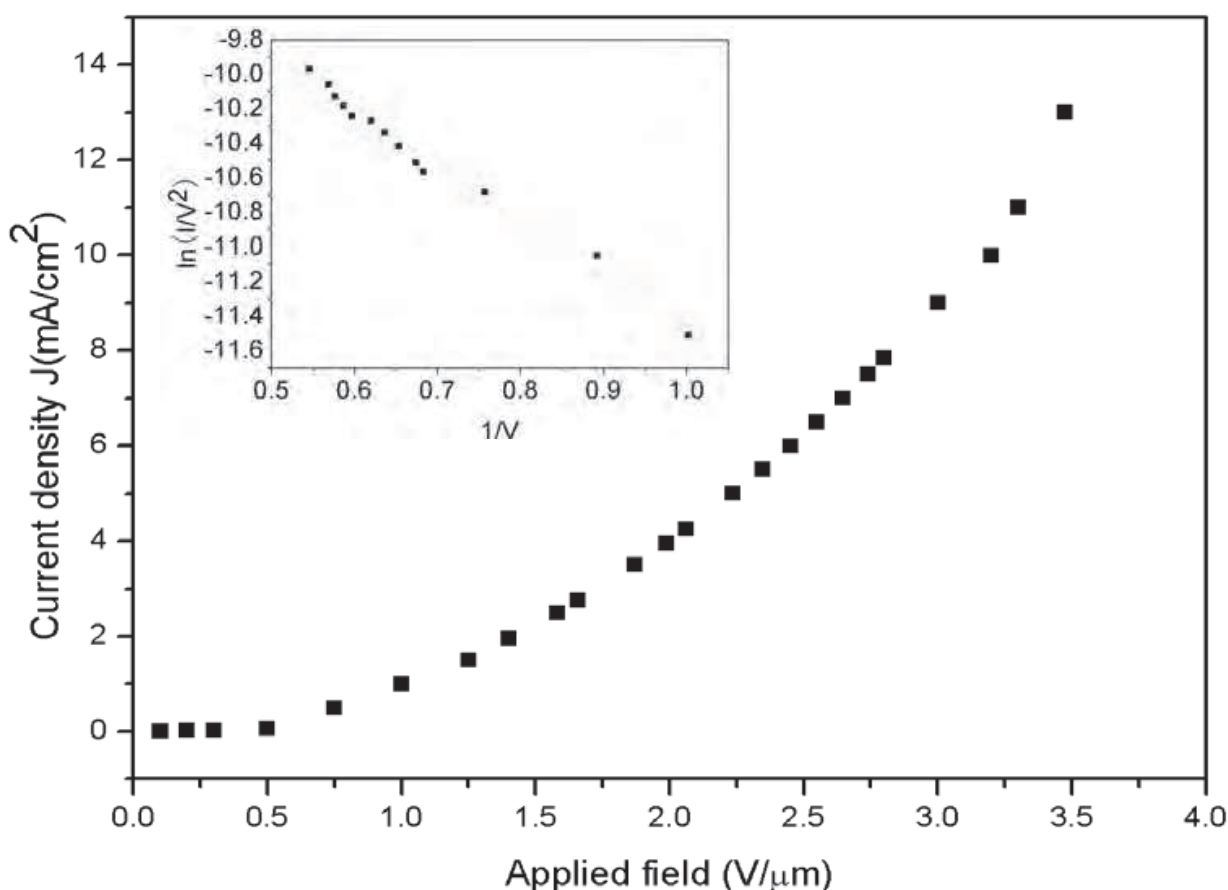

Fig. 10. ECD versus the applied electric field for the NMCNT field emitters fabricated by CEMM. Inset shows the Fowler–Nordheim plot.

3.3 Conclusions

In conclusion, we have fabricated large area NMCNT field emitters by CEMM at room temperature. Pretreated multi-walled CNT and Ni are deposited onto a Cr/Cu conducting layer by CCE; subsequently, protruding tips of CNTs are obtained by etching away a layer of Ni as emitters, followed by emitter pixels being formed by micromachining. Through the process of CEMM, CNTs with a clean surface are vertically embedded in the flat Ni substrate. Our field emitter shows relatively good field-emission properties such as high current density (13mA·cm^{-2} at an applied electric field of 3.4 V μm^{-1}), low turn-on field (0.53 V μm^{-1}), and good stability (110 h for 10% degradation of current density from 400μA·cm^{-2}). This excellent field emission performance is attributed to the uniform distribution of CNTs on the cathode, the strong adhesion of CNTs to Ni matrix and the flat surface of NMCNT field emitters. This method is not only simple in fabrication process, but also combine advantages of direct growth and screen printing. Above all, no further treatment is needed

to initiate or augment field emission. The NWCNT field emitters can obtain practical applications such as backlight units of liquid crystal displays and cathode ray tubes.

4. Cu/CNT contact material prepared by CCE

The damage of electrical contact is a vital factor for the invalidation of integral electrical appliances [57–59], so materials used as electrical contacts in these applications must have a good combination of electrical conductivity, wearing qualities, and resistance to erosion and welding [60, 61]. Otherwise, the contacts will be eroded, which causes poor contact and arcing. Arcing takes place when contacts are in the process of establishing a current flow or interrupting the flow of current. Arc is characterized by high temperature and a high current density in the arc column. Because of the high temperature and mass flow, the contact material surface is severely corroded and eroded, which results in erratic contact resistance and material loss. Therefore, an electrical contact material should have high electrical and thermal conductivity, high melting point and high resistance to the environmental reaction, as well as high arc erosion to maintain contact integrity [62–65]. Cu is a good candidate material due to its high thermal and electrical conductivity, but it has a high coefficient of thermal expansion (CTE). Materials with low CTE and high thermal conductivity, such as Cu/CorCu/W composites, have improved the reliability of electronic devices [66, 67]. However, these composites are often too expensive for many applications. In addition, their machinability and the elaboration of thin sheets remain very difficult.

The CNTs reinforced Cu-matrix composites offer a good compromise between thermo-mechanical properties and thermal conductivity. Their advantages are :(i) lower density than copper, (ii) excellent thermal conductivity, (iii) low coefficient of thermal expansion and (iv) good machinability. Other advantages of Cu/CNT composites are adaptive thermal properties, which can be adjusted [68–70]. However, it is difficult to make CNTs disperse uniformly and combine well in the metal matrix [71], traditional techniques such as the powder metallurgic process would bring for midable technical hurdles to prepare high-quality metal- matrix CNT composites, which is ascribed to the low-strength interfacial adhesion [72]. As no melting and solidification of the matrix would be induced, CCE is one of the most important techniques for preparing high-quality-metal-matrix CNT composite. In addition, the CCE is compatible with the micro-electro-mechanical systems (MEMS) technology. The metal-matrix CNT composite films can be processed to various small volume and high-performance electric contacts by MEMS technology.

In this study, the CNT Cu-matrix composite films are prepared by CCE. SEM images show that the CNTs are dispersed uniformly and combined well in the Cu matrix. The Cu/CNT contact material displays good resistance to electric arc. We believe that the investigation should be helpful to the Cu/CNT contacts wide application for industry.

4.1 Experimental details
4.1.1 Preparation of Cu/CNT composite films

The pretreated CNTs ($1gL^{-1}$, $2gL^{-1}$, $3gL^{-1}$, $4gL^{-1}$, $5gL^{-1}$, $6gL^{-1}$) were added to the Cu electroplating baths, and six different plating baths were prepared for making a comparison. Then, these solutions having different concentrations were sonicated at 21 kHz for 3 h to produce homogeneous suspensions. The CNT Cu-matrix composite films were prepared by CCE using these CNT suspensions; the optimum plating baths are chosen by the quality

comparison of these CNT composite films. All chemicals are chemically pure. A Cu plate with a purity of 99.98% is used as the anode.

4.2 Results and discussion
4.2.1 The choice of Cu electroplating baths and the combined state of CNT with the Cu matrix
Through the quality comparison of different CNT composite films fabricated by the six electroplating baths, we found that the CNT composite films have the best quality when the concentration of the CNTs in the Cu electroplating baths reaches 4 g L^{-1}. So this electrolyte concentration is chosen as the optimum plating bath for preparing the CNT Cu composite films. Figure11 shows the SEM images of the Cu–CNT composite films; it can be seen that the CNTs dispersed uniformly and combined well in the Cu matrix, the enhancements have not increased the porosity rate of composite films, and the surfaces of composite films are homogeneous.
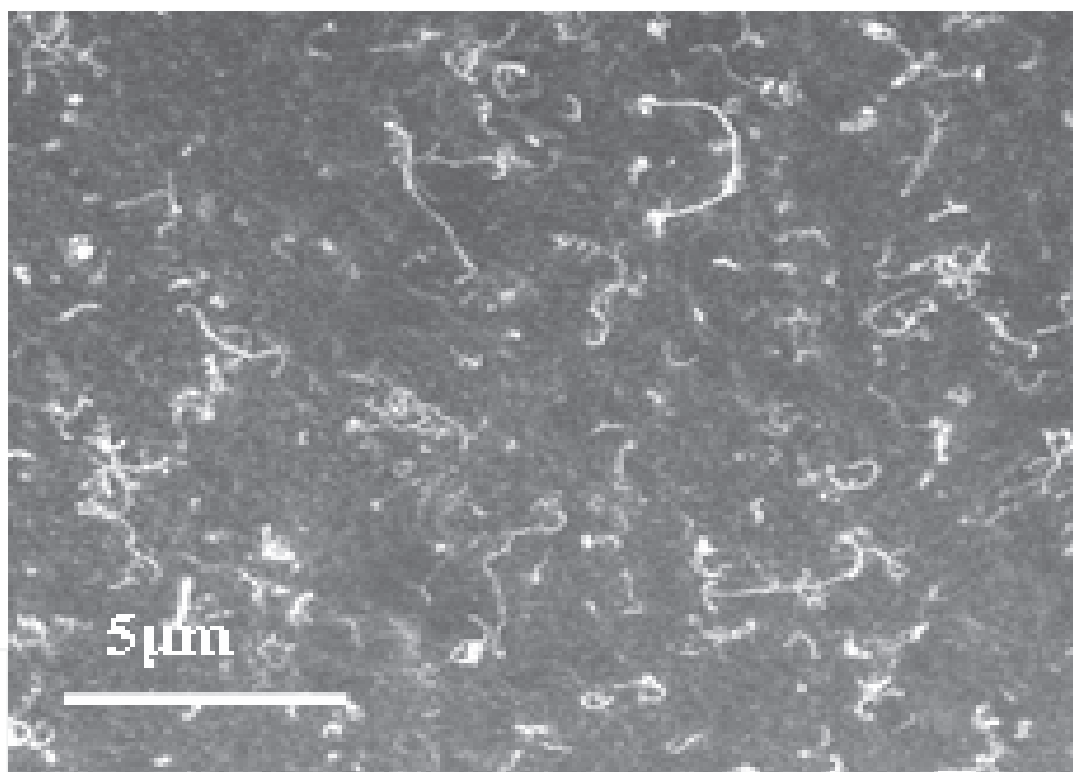

Fig. 11. The SEM images of CNT composite films

4.2.2 Mechanical properties of the Cu/CNT composite plating film
The hardness of the Cu–CNT composite films and a Cu film was tested by digital-micrographic hard-meter (model number: HXD-1000 TMB/LCD). Figure 12 shows the hardness change of the CNTs (a) (b) Cu composite films with the concentration variation of CNTs in the plating baths. From the graph, we found that the hardness of the CNF composite film was enhanced significantly with the increase of the CNTs in the plating baths, but for the CNT composite film it has not obviously been changed with the increase of the CNTs in the plating baths. The hardnesses of the CNT Cu composite films reach the maximum of 156 HV and 207 HV with the concentration of the CNTs of 4gL^{-1} and the

concentration of the CNFs of 4 g L^{-1}in the plating baths, and about 13.9% and 51.1% higher than that of the pure copper plating film (137 HV). This result indicates that the CNTs/CNFs have significant effect on promoting the hardness of the Cu-matrix composite film, especially for the CNFs.
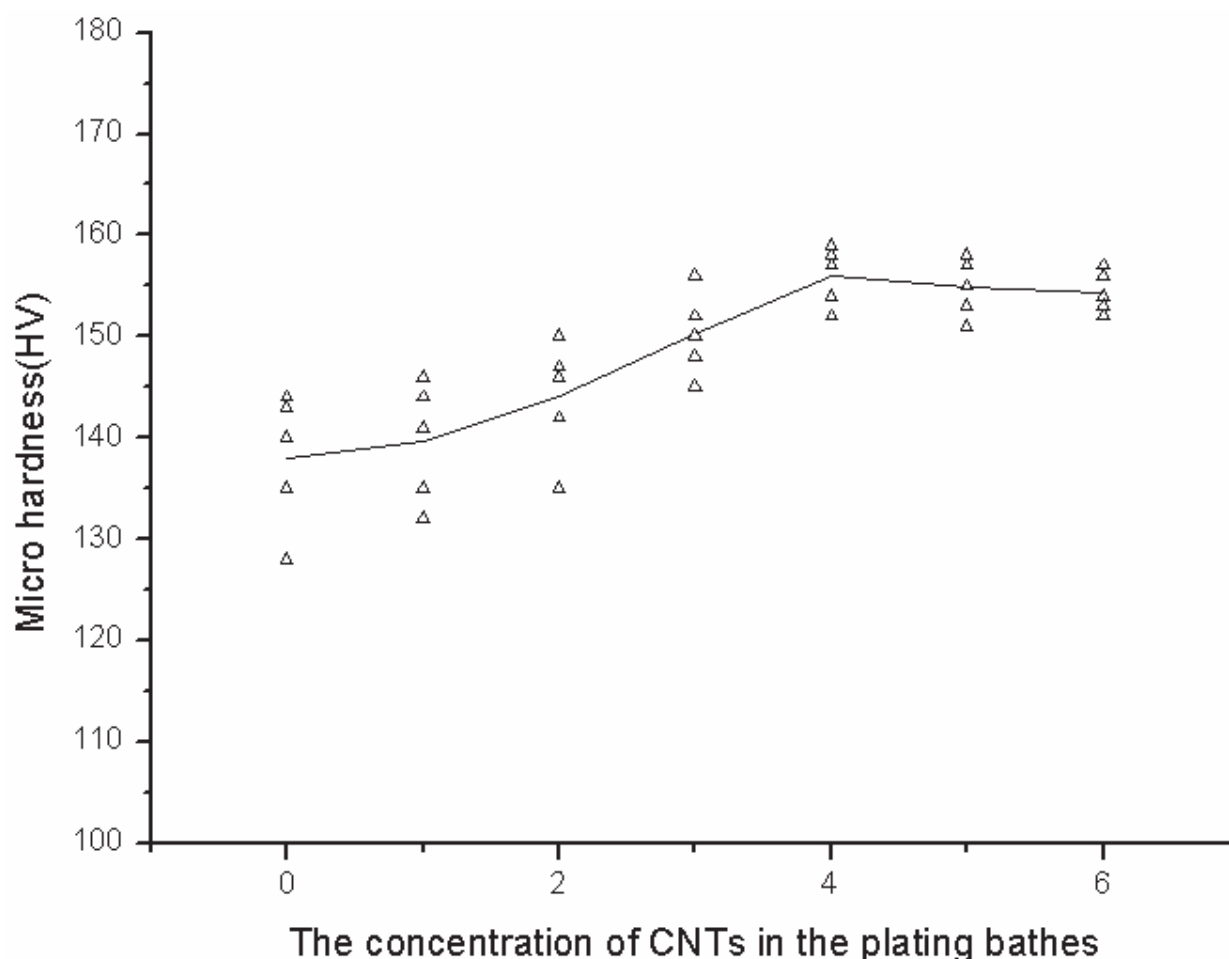

Fig. 12. The hardness change of CNT Cu composite films with the concentration variation of CNTs in the plating baths.

4.2.3 The electrical properties of the Cu/CNT composite films

The CNT composite films are tested by a contourgraph and semiconductor parameter analyser. The resistivity of the film can be expressed as $\rho= R.S/L,$ where R is the electrical resistance, S and L are the cross–sectional area and the length of the composite plating films. The resistivities of the two different plating films are listed in table.2; it shows that the resistivities of the Cu/CNT composite plating films and Cu film are 2. 656 ×10^{-6}Ω cm , 1.745 ×10^{-6}Ω cm. The resistivity of the Cu/CNT composite plating film is higher than that of pure Cu film ,but lower than those of other Cu–matrix composites such as CuW 4. 35 ×10^{-6}Ω cm、CuMo 3. 571 ×10^{-6}Ω cm.Theoretically, the Cu/CNT composite plating films should have better conductivity performance than that of pure Cu film. According to O. HJORTSTAM's report [73], it is possible that the room-temperature resistivity of CNT–metal composite is 50% lower than that of Cu when the CNT filling in the range of 50%–60% of the composite. The ultra-low resistivity is possible because the ballistic conducting CNTs have

an electron mean free path several orders of magnitude longer than metals like Cu and Ag. The reason of the resistivity of CNT/Cu composite plating films fabricated by our method is higher than that of pure Cu film may be that the relatively low composite density of CNT in the Cu–matrix composite films limits the overall conductivity of CNT composite films [74].It needs our further research to resolve the problem and prepare ultra-low resistivity Cu/CNT composite.

species	resistance (Ω)	length of linetype film（cm）	cross–sectional area of linetype film（cm^2）	resistivity（$\Omega \cdot$cm）
pure Cu films	10.50	53.25	8.850×10^{-6}	1.745×10^{-6}
Cu/CNTs composite plating films	15.80	53.25	8.950×10^{-6}	2.656×10^{-6}

Table 2. Resistivity of two different plating films

The thickness of the Cu/CNT composite films are controlled in the size rang of 1-10um by adjusting the process parameters of CCE and the same properties of composite films can be held; the CNT composite films are processed to various size films and employed for micro-relay by MEMS technology. Because of the stable processing technique and the compatibility of CCE with MEMS technology, the micro special contacts are directly integrated on the surface of the contact of MEMS micro relay.

In the process of arc erosion test, the closing force of contact is 1N, breaking force is 0.75N, circuit voltage is 1.5V, current is 1A and the frequency of breaking is 6000. There exists apparent electric spark when the contact was broken. Figure 13 shows the micrographs of electric contact samples before (a) and after the arc erosion test. The result shows that the arc erosion of the Cu/CNT contact is 2.7mg, and 22.9% lower than that of pure Cu (3.5mg).This implies that the CNTs can effectively improve the arc erosion of micro special contact.
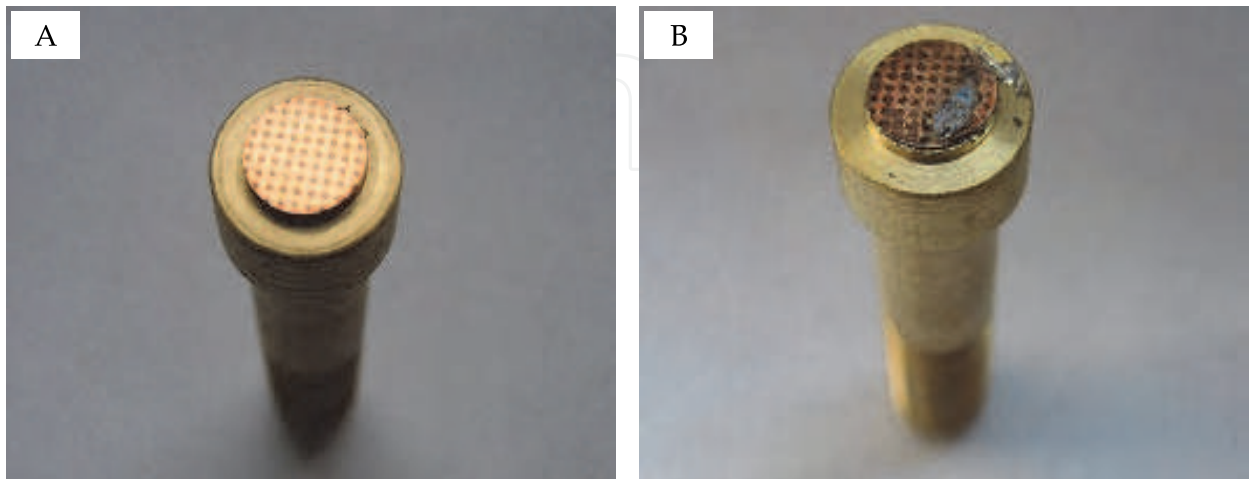

Fig. 13. The micrographs of electric contact samples before arc erosion being tested (A) and after arc erosion being tested (B)

4.3 Concluson

In the present research, the Cu/CNT matrix composite films are prepared by CCE. SEM images show that the CNTs dispersed uniformly in the Cu–matrix. Furthermore, the Cu–CNT composite films show relatively good physical properties such as the hardness of 156 HV, and about 13.9% higher than that of pure Cu plating film (137HV); the resistivity of the CNT composite plating films is $2.656 \times 10^{-6} \Omega \cdot cm$, and lower than those of other Cu–matrix composites such as CuW ($4.35 \times 10^{-6} \Omega \cdot cm$) and CuMo ($3.571 \times 10^{-6} \Omega \cdot cm$). In addition, the arc erosion behavior of the Cu/CNT contact has been examined on an electric arc erosion apparatus. The result shows that the arc erosion loss of the Cu/CNT contacts is 2.7mg, and 22.9% lower than that of pure Cu (3.5mg) under the same conditions. We believe that the investigation should be helpful to the Cu/CNT wide application for industry.

5. CNT field emission micro-cathode arrays fabricated using CCE followed by micro-machining

On the basis of preparing the CNT emitters above, we propose a novel design of CNT field emission micro-cathode arrays. The 3D structure drawing is shown in Fig. 14, compared with previously reported CNT field emission micro-cathodes [33-36], this structure have relatively complete functional units, including bottom electrode down-lead current-limiting resistance CNT emitters supporting wall insulator layer suspension grid and focusing electrode. In this design, each structure layer is fabricated by using layer by layer lithography alignment process. All experiments are executed at room temperature.

5.1 Experimental details

The flow of the fabrication process for the triode-type CNT field emission micro cathode arrays is drawn in Fig.14 and the detail process is described as follows:

1. First, a patterned Au layer (1μm) is deposited on the Cr/Cu (10/40nm) seed layer as bottom electrode by photolithography and electroplating (Fig.14.a).
2. Then, a Al_2O_3 film (50nm) is sputtered on the Au electrodes as resistor layer, and then, the fabrication of the patterned CNT field emitters is preformed(Fig.14.b,c).
3. Afterward, a 5μm patterned Ni supporting wall (the reason for choosing Ni is its resistance to corrosion) is deposited by photolithography and electroplating (Fig.14.d).
4. Then a polysilicon insulator layer is deposited on the supporting wall to suppress the leakage current by sputtering (Fig.14.e).
5. Subsequently, patterned Ni gate electrode (1μm) electroplating is performed (Fig.14.f and g).
6. Finally, patterned focusing electrode is formed by electroplating with photolithography (Fig.14.h).

5.2 Results and discussion

The optical images of the integrated devices are shown in Fig.15 (A), (B) and their higher magnifications are shown in Fig.15(C), (D) and (E). It can be seen that the integrated CNT field emission micro-cathode arrays have uniform structure and good repeatability. The gate pores' diameter is ~1 μm and the height between the Ni metal gate and the CNT pattern edge is ~5 μm (Fig.15D).The pore density is about 1.2×10^5 /cm². The inset map in Fig.14E is a magnified view of a CNT emitter pixel; the CNTs are uniformly embedded in the pixel as shown in the inset map. The emitter pixel spacing shouldn't be too small,

small emitter pixel spacing would induce the field-screening effect between adjacent emitters. However, big emitter pixel spacing would decrease the resolution of field emitters. In the fabrication process of the integrated devices, it is convenient to adjust the size of the emitter pixels by masking and photolithography. The optimized distance between the every two adjacent CNT emitter pixels is 2.5um and the area of emitter pixel is 9 μm^2 in the present study.
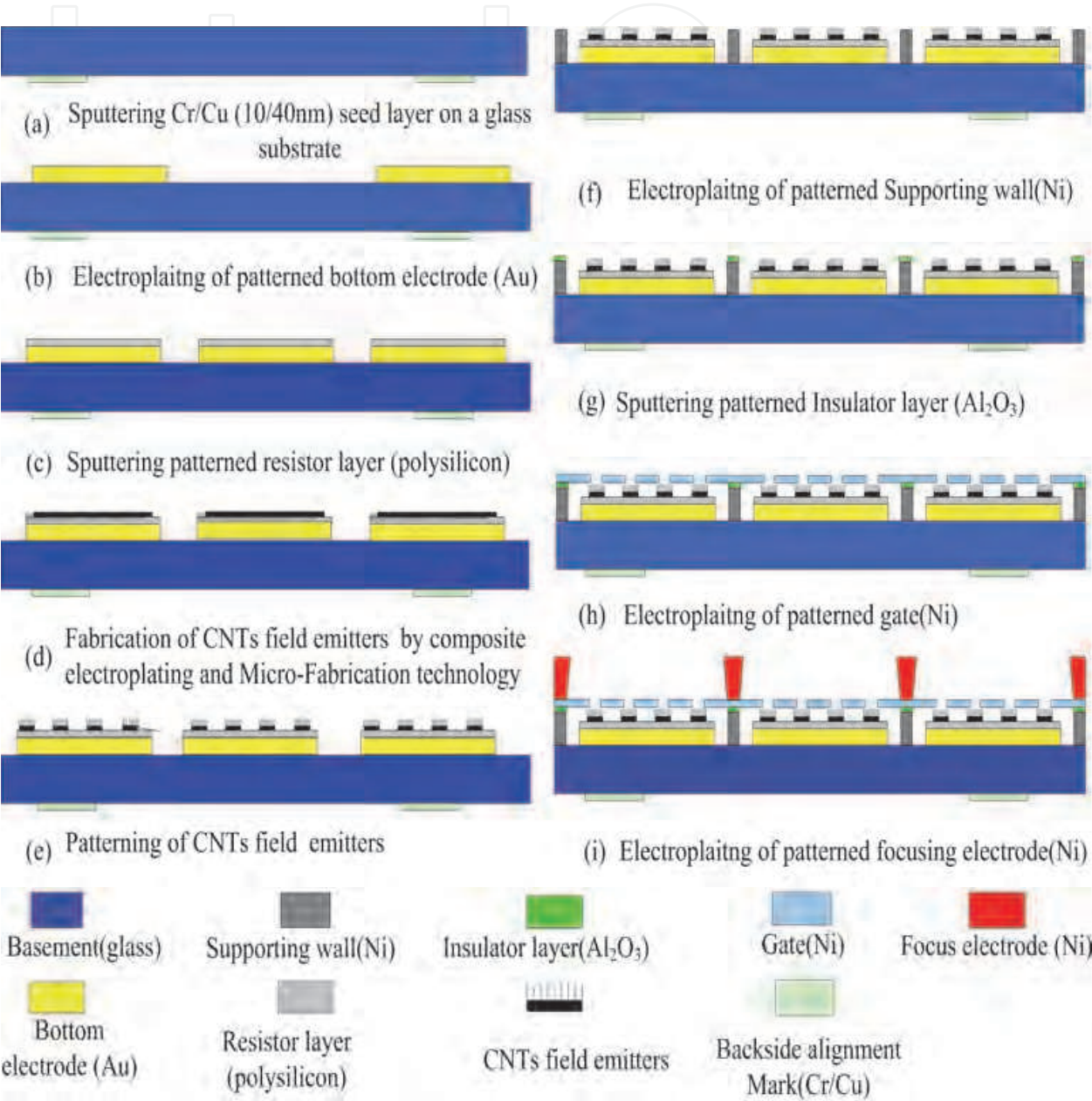

Fig. 14. Schematic diagrams of the fabrication process for the triode-type micro-gated CNT emitter arrays :(a)Patterned bottom electrode (Au) is deposited on basement by electroplating, (b) Resistor layer (Al_2O_3) is deposited on bottom electrode by sputtering, (c)Patterned CNT emitters are fabricated by electrochemical micromachining, (d) Electroplating of patterned Supporting wall (Ni),(e) Patterned insulator layer (polysilicon) is deposited on the supporting wall by sputtering, (f)(g) Gate(Ni) is fabricated by photolithography and electroplating, (h) The electroplating of Ni focusing electrode.
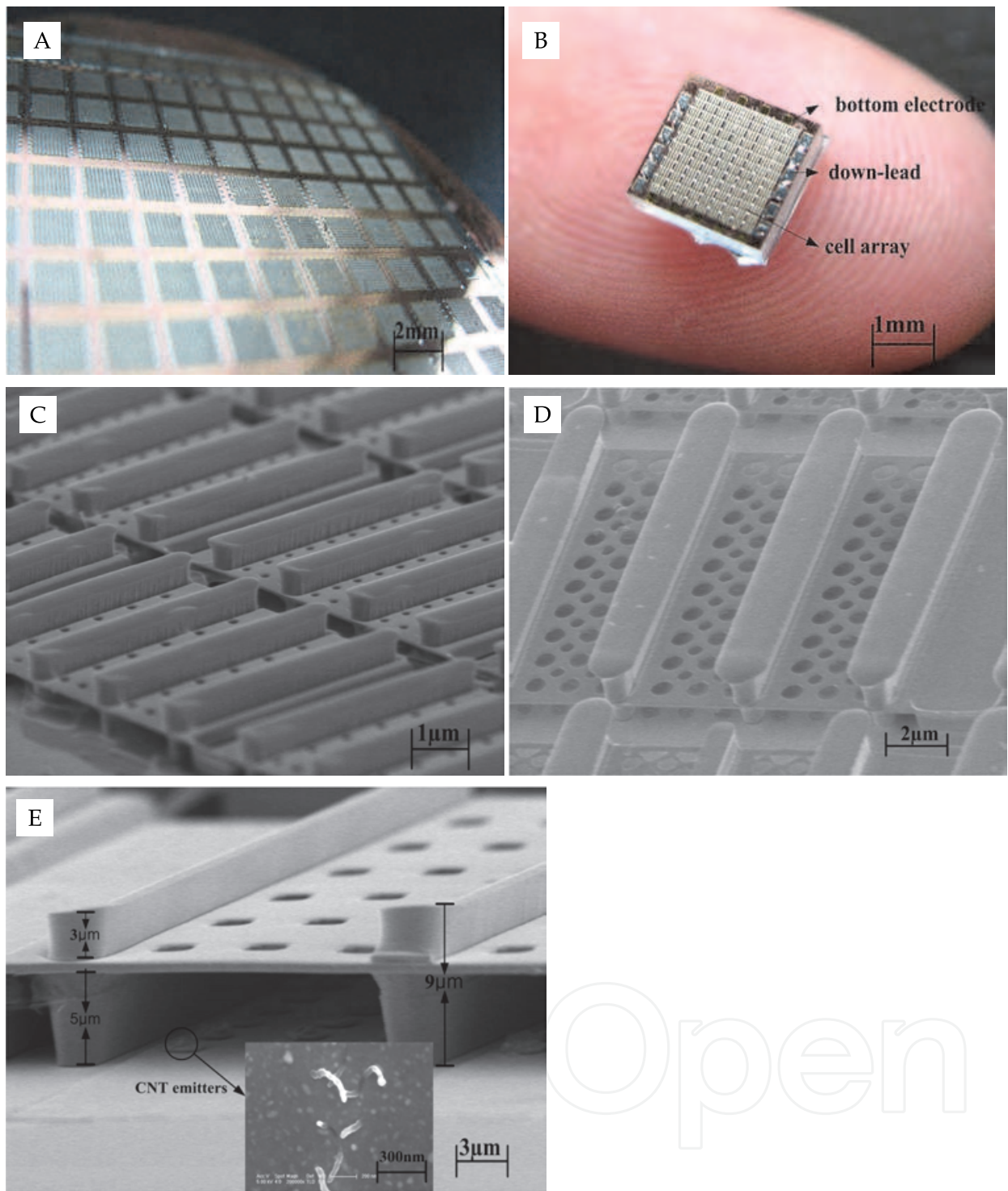
Fig. 15. The optical images of integrated devices (A, B) and their higher magnifications (C, D and E). The inset map in Fig.15E is a magnified view of a CNT emitter pixel.

Figure 16 shows a plot of the device field-emission current density (ECD) versus the applied electric field, and the corresponding field emission curve is shown in the inset. It is easy to find that all dots on the field emission curve fit a single straight line well, which indicates the Fower-Nordheim-type field-emission behavior. The ECD of the emitters increases monotonically with the applied field. When the applied electric field is high, the gate current

gets saturated and remains constant. The highest gate current density is about 15.7mA·cm^{-2} at an applied electric field of 12V/µm and the measured turn-on field to extract a current density of 10µA·cm^{-2} is 2.4V·µm^{-1}. The device characteristics are compared with those in other CNT emitter structures, although they are all fabricated by different structures and processes [79]. Pirio et al [80] observed turn-on voltages of 9–15 V, defined at 0.1 nA·cm^{-2}. The low turn-on voltage was obtained with a sub-micrometer gate-to-tip distance realized using a self alignment process. However, the turn-on field remained at relatively high values of 18–30 V·cm^{-1}. In Hu et al [81], a structure fabricated by screen-printed CNTs with a turn-on voltage of 40–45 V was obtained with ~ 5 µm gate-to-tip distance. Jang et al [82] obtained a turn-on voltage of 20 V (turn-on field ~ 1 V·µm^{-1}) at ~10 nA·cm^{-2} with pasted CNTs. They all report, at most, mA·cm^{-2} range values for the maximum current density. On the other hand, Uh [83] obtained an exceptionally high current density of 275mA·cm^{-2} with a turn-on voltage of 38 V using catalytically grown CNTs. In summary, the triode emitter structure fabricated on a glass template using CCE and micromachining shows a very low turn-on voltage and a high current density, which are better than or, at least, compatible with those of other triode structures. The field enhancement factor (β) for the CNT emitters is derived from the slope of the graph by assuming that the work function of CNTs is found to be 2.4×10^6 cm^{-1} under the assumption of the work function to be the same as that of graphite (4.5eV), which is calculated from the following equation: $\beta = 2.84 \times 10^7\, \varnothing^{3/2}\, /S$, where Ø and S represent the work function of CNTs and the absolute value of the slope of the F–N plot. The field enhancement factor extracted from triode-type configuration is approximately two orders of magnitude higher than that of diode-type configuration fabricated by using the same method and also much higher than typical values reported for CNT cathodes, such as 400~1200 for CNTs on silicon and glass substrates, and 2600~3500 for highly ordered CNT arrays on porous aluminum oxide [84, 85]. The very high field enhancement factor confirms the high efficiency of the triode structure in electron extraction. The structure shows good field-emission properties, but the challenge of fabricating an applied device still remains including the further optimization of integral construction and preparation technology.

5.3 Conclusions

A new CNT field emission micro cathode array structure fabricated by CCE and micromachining is achieved. The relevant processing technology is also developed. Integrated CNT field emission micro-cathodes have intact structure and good repeatability. The structure revealed a very efficient performance as indicated by the high field enhancement factor and current density, low turn-on voltage and good emission stability. The micro-cathodes can obtain practical applications such as backlight units of liquid crystal displays and cathode ray tubes .This study laid a foundation on the device integration and cost-effective mass production, but it requires further optimization in the device configuration and processing.

6. The potential applications of CNT films prepared by CCE

Metal/CNT composite films produced by CCE are suitable for a wide range of applications; suggestions to date include field emission devices, biomedical sensors, contact materials and coatings as well as large surface area electrodes for fuel cells, capacitors and gas sensors. So far, the development of CNT-based devices from CNT films produced by the CCE method

has been focused mainly on the field emission properties. It is well known that CNTs are promising candidates for field emission devices, due to their high aspect ratio, small size, structural and chemical stability and thermal conductivity; these features are responsible for a low emission threshold and high emission current densities compared to other alternatives.
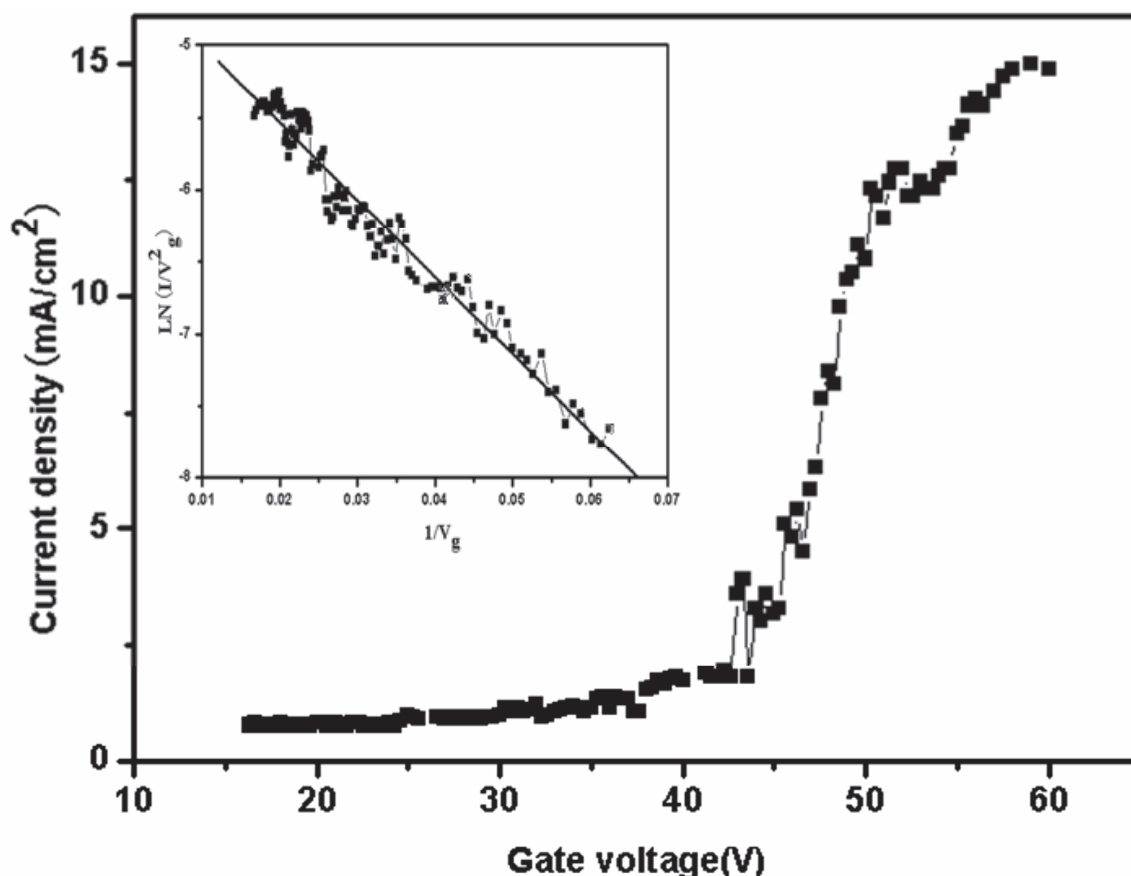

Fig. 16. The ECD versus the applied electric field for the CNT field emission micro-cathodes. Inset shows the Fowler–Nordheim plot.

6.1 The potential application in the displays

CNT field emission displays (CNT-FEDs) are promising for a range of situations including flat panel displays, cathode-ray tubes, and backlights for liquid crystal displays. CNT-FEDs have the potential to provide high quality moving images with low power consumption.

The technical parameters of field emission cathodes prepared by CCE in our present research, such as turn-on field and field emission current density, had almost satisfied the typical technical requirements for flat panel display operation. This suggests that CCE is a useful technique to obtain an electron source with minimal out-gassing and to make triode-type CNT field emission displays. Through the process of fabrication of Ni-matrix CNT field emitters using CCE in chapter 3, CNTs are vertically embedded in the flat Ni substrate. No further treatment is needed to initiate or augment field emission and the field emitters exhibit good field-emission properties such as high current density (13mA cm-2 at an applied electric field of 3.4 V μm−1), low turn-on field (0.53 V μm−1), and good stability (110 h for 10% degradation of current density from 400μA cm-2). In addition, we have

successfully developed an effective fabrication method at room temperature for the mass production of triode-type CNT field emission micro cathode arrays. This technique combines CCE and micromachining, avoids the direct growth and screen-printing procedures conventionally used to fabricate such structures. Due to low cost and room temperature process, the technique is proven to be advantageous in mass production. Results of field emission testing show that the micro cathodes have perfect field-emission properties, such as high current density (15.7mA cm^{-2}), low turn-on field (2.5V μm^{-1}), and good stability (109 h for 10% degradation of current density from 400μA cm^{-2}). In addition, in the structure the leakage current of the gate has been reduced to near zero by coating the Al_2O_3 on the gate.

In addition, for CNT-FEDs and related devices, vertically aligned CNTs are preferred because they provide a low turn-on field as well as a uniform and stable electron emission. The CCE method has the potential to produce highly efficient CNT-based FED devices due to its ability to fabricate large, vertically aligned, and patterned nanotube arrays at low temperature.

CNT arrays by CVD; thermal CVD involves high processing temperatures so that glass or polymer substrates cannot be used. Although plasma-enhanced CVD can be used at lower temperatures, there are still difficulties in fabricating large area field emitter arrays.

6.2 The potential application in the modified electrode

In the area of electrochemistry, the combination of high aspect ratio, nanometer-sized dimensions, good electrical conductivity and low capacitance in the pristine state dictates that CNTs have the capability to make excellent electrodes. CNT film electrodes were first introduced for voltammetric analysis by Liu and his coworkers. Following this report, the electrocatalytic properties of CNT- modified electrodes became a hot topic. The basic electrode configuration of randomly dispersed, purified CNTs on the surface of a conducting support macroelectrode was used extensively for the electrochemical detection of a multitude of redox – active molecules in solution. The preparation of CNTs-modified electrodes has many problems. CNTs are insoluble in many solvents due to the large inter tube attraction energy. The CNTs dispersed by volatile solvents are often randomly dispersed on the surface. The conventional ways of CNT dispersion and the performances of interface are difficult to control. However, CNTs successfully dispersed in metallic matrixs are easily controlled by CCE. If CCE is utilized to prepare CNT modified electrode, it has several advantages which help improve the interface performance of the composite film. First, CNT can be homogeneously dispersed in the metallic matrixs; Secondly, metallic matrixs can be controllable etched by specific reagent, and make part of CNTs exposed on the surface of the metal/CNT composite without pollution; Thirdly, the density of CNTs in metal can be controlled by changing the density of CNTs in the plating bath and plating current density. Fourthly, the firm connection between CNT and metal matrix can be achieved and ensure a good electrical conductivity. In addition, the CCE is compatible with the MEMS technology. The micromachining technology helps us efficiently choose which area of the electrodes will be modified, thus making CNTs implantation technique feasible, controllable and reliable.

6.3 The potential application in the electrical contact.

As previously analysis in chapter 4, materials used as electrical contacts in electronic devices must have a good combination of electrical conductivity, wearing qualities, and resistance to erosion and welding. Otherwise, the contacts would be eroded to cause poor contact and

arcing. Arcing takes place when contacts are in the process of establishing a current flow or interrupting the flow of current. Arc is characterized by high temperature and a high current density in the arc column. Because of the high temperature and mass flow, the contact material surface is severely corroded and eroded, which results in erratic contact resistance and material loss. Therefore, an electrical contact material should have high electrical and thermal conductivity, high melting point and high resistance to the environmental reaction, as well as high arc erosion to maintain contact integrity. Metals with high thermal and electrical conductivity are good candidate material, but they usually have high coefficient of thermal expansion (CTE). Materials with low CTE and high thermal conductivity, such as Cu/CorCu/W composites, have improved the reliability of electronic devices. However, these composites are often too expensive for many applications. In addition, their machinability and the elaboration of thin sheets still remain very difficult.

Furthermore, the metal/CNT composite films show relatively good physical properties. The hardness of the Cu/CNT composite film prepared by CCE is 156 HV and about 13.9% higher than that of pure copper plating film (137HV). The resistivity of the CNT/CNF composite plating film is 2. 656 ×10$^{-6}\Omega$·cm, and lower than those of other Cu–matrix composites such as CuW 4. 35 ×10$^{-6}\Omega$ ·cm CuMo 3.571 ×10$^{-6}\Omega$·cm. In addition, Cu/CNT micro special electric contact has been designed and successfully fabricated by MEMS technology. The arc erosion behaviors of the Cu/CNT contacts have been examined on an electric arc erosion apparatus. The result shows that the arc erosion loss of the Cu/CNT contact is only 2.7mg, and 22.9% lower than that of pure Cu (3.5mg) under the same conditions. The Cu/CNT matrix specific contact can be fabricated with high yield and good reproducibility. High producing rate of finished products can effectively reduce the manufacturing cost of micro special electric contact and make them achieve practicable application. The thickness of the CNT/ Cu composite film are controlled in the rang of 1-10μm by adjusting the process parameters of CCE; The CNT composite films are processed to various films with different thickness and employed for micro-relay by MEMS technology. Because of the stable processing technique and the compatibility of composite electroplating with MEMS technology, the micro special contacts can be directly integrated on the surface of the contact of MEMS micro relay.

Exploitation of CCE in these and other applications will frequently rely on the attachment of functional groups or other nanostructures to the CNT surfaces. The combination of CNTs and nanocrystalline particles should have applications in field emission displays, nanoelectronic devices, drug delivery systems, antibacterial films, biosensors, photocatalytic nanostructures and other functional composites. We anticipate that CCE and combinations of CCE and other colloidal processing methods will play a significant role in the development of such metal/CNT composite nanostructures.

7. Conclusions

In this study, we considered the preparation of the metal/CNT composite using CCE method. The effects of pretreatments of the CNTs, such as purification activation and mechanical ball milling on the metal /CNT composite film were discussed. A detailed study of the Ni-matrix CNTs field emitter fabrication by CCE was presented. The CCE fabrication processes of the Cu/ CNT contact material and the CNT field emission micro-cathode arrays were followed. The potential applications of the resulting CNT structures and the scope for the future work are highlighted. Further developments of the CCE processes will allow the

reliable fabrication of three dimensionally controlled nanostructures and nanocomposites either in the form of dense materials or with a required porosity; graded, aligned, and patterned features may also be incorporated as desired. It is believed that the investigation may be helpful to metal/CNT composite functional material and devices prepared by CCE wide application for industry.

8. References

[1] Iijima S. Helical microtubules of graphitic carbon. Nature 1991;354:56–8.

[2] Belin T, Epron F. Characterization methods of CNTs: a review. Mater Sci Eng B 2005;119:105–18.

[3] Gooding JJ. Nanostructuring electrodes with CNTs: a review on electrochemistry and applications for sensing. Electrochim Acta 2005;50(15):3049–60. Sp Iss.

[4] Iijima S. CNTs: past, present and future. Physica B 2002;323:1–5.

[5] Y. Qin, M. Hu, Field emission properties of electrophoretic deposition carbon nanotubes film, Appl. Surf. Sci. 255 (2009) 7618–7622.

[6] D.O. Kim,M.H. Lee, J.H. Lee, T.W. Lee, K.J. Kim, Y.K. Lee, Transparent flexible conductor of poly (methyl methacrylate) containing highly-dispersed multi-walled carbon nanotube, Org. Electron. 9 (2008)1–13.

[7] Berber S, Kwon YK, Tomanek D. Unusually high thermal conductivity of CNTs. Phys Rev Lett 2000;84(20):4613–6.

[8] Krishnan A, Dujardin E, Ebbesen TW, Yianilos PN, Treacy MMJ.Young's modulus of single-walled nanotubes. Phys Rev B1998;58(20):14013–9.

[9] Yan Chena, Fanli Menga, Minqiang Li，Novel capacitive sensor: Fabrication from carbon nanotube arrays and sensing property characterization.Sensors and Actuators B 140 (2009) 396–401

[10] M. Penza,R.Rossi,M.Alvisi, M.A. Signore, E.Serra, R. Paolesse, Metalloporphyrins-modified carbon nanotubes networked films-based chemical sensors for enhanced gas sensitivity. Sensors and Actuators B 144 (2010) 387–394.

[11] E. Dujardin, T. W. Ebbesen, H. Hiura, K. Tanigaki, "Wetting andnanocapillarity of CNTs," Science, 1994, vol. 265(5180), pp.1850-1852

[12] W. X. Chen, W. L. Chen, Z. D. Xu, Z. J. Liu, J. P. Tu, X. B. Zhang, et.al. "Characteristics of CNTs and High-quality Composite,"Acta Materiae Compositae Sinica, 2001, vol. 18(4), pp. 1-5

[13] W. F. Zhang, D. Zhu, "Electrodeposited nanocomposites: Research advances and applications," Materials Review, 2003, vol. 17, pp. 57-60

[14] Min Deng, Guifu Ding , Yan Wang, Huiqing Wu, Yuanjin Yao, Lida Zhu, Fabrication of Ni-matrix CNT field emitters using CCE and micromachining. CARBON 47 (2009) 3466 – 3471

[15] Min Deng, Guifu Ding, Yan Wang, YuchaoWang, HongWang and Shi Fu, MEMS-based CNT and carbon nanofiber Cu micro special electric contact. J. Micromech. Microeng. 19 (2009) 065001 (8pp)

[16] S. Khabazian, S. Sanjabi, The effect of multi-walled CNT pretreatments on the electrodeposition of Ni–MWCNTs coatings. Applied Surface Science xxx (2011) xxx–xxx)

[17] Singh C, Shaffer MS, Windle AH. Production of controlled architectures of aligned carbon nanotubes by an injection chemical vapourdeposition method. Carbon 2003;41(2):359–68.

[18] Andrews R, Jacques D, Qian DL, Rantell T. Multiwall carbon nanotubes: synthesis and applications. Accounts Chem Res2002;35(12):1008–17.

[19] Murakami Y, Chiashi S, Miyauchi Y, Hu MH, Ogura M, Okubo T,et al. Growth of vertically aligned single-walled carbon nanotubefilms on quartz substrates and their optical anisotropy.Chem PhysLett 2004;385(12):298–303.

[20] Shelimov KB, Esenaliev RO, Rinzler AG, Human CB, Smalley RE.Purification of single-wall carbon nanotubes by ultrasonically assistedfiltration. Chem Phys Lett 1998;282:429–34.

[21] Peng-Xiang Hou, Chang Liu, Hui-Ming Cheng, Purification of carbon nanotubes. CARBON 46 (2008) 2003 – 2025

[22] S.Costa,C.Tripisciano, E. Borowiak-Palen, R.J. Kalenczuk,Comparative study on purity evaluation of singlewall carbon nanotubes. Energy Conversion and Management 49 (2008) 2490–2493

[23].Orazio Vittorio, MSc, Vittoria Raff, Alfred Cuschieri, Influence of purity and surface oxidation on cytotoxicity of multiwalled carbon nanotubes with human neuroblastoma cells. Nanomedicine: Nanotechnology, Biology, and Medicine 5 (2009) 424–431

[24] Du CS, Heldebrant D, Pan N. Preparation of carbon nanotubes composite sheet using electrophoretic deposition process. J Mater SciLett 2002;21(7):565–8.

[25] Yu K, Zhu Z, Li Q, Lu W. Electronic properties and field emission ofcarbon nanotube films treated by hydrogen plasma. Appl Phys A2003;77:811–7

[26] Girishkumar G, Vinodgopal K, Kamat PV. Carbon nanostructures in portable fuel cells: single-walled carbon nanotube electrodes for methanol oxidation and oxygen reduction. J Phys Chem B 2004;108(52):19960–6.

[27] Girishkumar G, Rettker M, Underhile R, Binz D, Vinodgopal K,McGinn P, Kamat P. Single-wall carbon nanotube-based protonexchange membrane assembly for hydrogen fuel cells. Langmuir2005;21(18):8487–94.

[28] Barazzouk S, Hotchandani S, Vinodgopal K, Kamat P. Single-wall carbon nanotube films for photocurrent generation. A prompt response to visible light irradiation. J Phys Chem B 2004;108:17015–8.

[29] Kamat P, Thomas K, Barazzouk S, Girishkumar G, Vinodgopal K,Meisel D. Self-assembled linear bundles of single wall carbon nanotubes and their alignment and deposition as a film in a dc field.J Am Chem Soc 2004;126:10757–62.

[30] Lee CY, Chuang HM, Li SY, Lin P, Tseng TY. Characteristics and electrochemical performance of supercapacitors with manganese oxide-carbon nanotube nanocomposite electrode. J Electrochem Soc2005;152(4):A716–20.

[31] Jin YW, Jung JE, Park YJ, Choi JH, Jung DS, Lee HW, et al.Triode-type field emission array using carbon nanotubes and a conducting polymer composite prepared by electrochemical polymer-ization. J Appl Phys 2002;92(2):1065–8.

[32] Chen GZ, ShafferMSP, Coleby D, Dixon G, ZhouW, Fray DJ, et al.Carbon nanotube and polypyrrole composites: coating and doping.Adv Mater 2000;12(7):522–6.

[33] Jung MS, Jung HY, Suh JS. Horizontally aligned carbon nanotube field emitters having a long term stability. Carbon 2007; 45(15): 2917-2921

[34] Zhu L, Sun Y, Hess DW, Wong CP. Well-aligned open-ended carbon nanotube architectures: an approach for device assembly. Nano Lett 2006; 6(2):243–7

[35]Klinke C, Delvigne E, Barth JV, Kern K. Enhanced field emission from multiwall carbon nanotube films by secondary growth. J Phys Chem B 2005; 109(46):21677–80

[36] Wong YM, Kang WP, Davidson JL, Choi BK, Hofmeister W, Huang JH. Fabrication of aligned convex CNT field emission triode by MPCVD. Diam Relat Mater 2005; 14 (11): 2069 – 2073

[37] Nishuang Liu, Guojia Fang, Xiaoxia Yang, Wei Zeng, Chun Li, Mingjun Wang , Jun Lia, Xingzhong Zhao, Synthesis of patterned carbon nanotube arrays for field emission using a two layer Sn/Ni catalyst in an ethanol flame。Diamond & Related Materials 18 (2009) 1375–1380

[38] Nguyen Van Quy, Nguyen Duc Hoa,Wan Jun Yu, You Suk Cho,Gyu SeokChoi and Dojin Kim, The use of anodic aluminium oxide templates for triode-type carbon nanotube field emission structures toward mass-production technology. Nanotechnology 17 (2007) 2156–2160

[39] A.Mathur, S.S. Roy , Kiran S. Hazra , D.S. Misra , J.A. McLaughlin, Growth of carbon nanotube arrays using nanosphere lithography and their application in field emission devices. Diamond & Related Materials 19 (2010) 914–917.

[40] Do-Hyung Kim , Chang-Duk Kim, Hyeong Rag Leea , Effects of the ion irradiation of screen-printed carbon nanotubes for use in field emission display applications. Carbon 42 (2004) 1807–1812。

[41] Fan-Guang Zeng, Chang-Chun Zhu, Weihua Liu, Xinghui Liu, The fabrication and operation of fully printed Carbon nanotube field emission displays. Microelectronics Journal 37 (2006) 495–499.

[42] Milnoux E, Groening O, Teo KBK, Dalal S, Ganggloff L, Schnell JP, et al. Achieving high-current carbon nanotube emitters. Nano Lett 2005; 5(11):2135–8

[43] Kang DW, Suh JS. Fabrication temperature effect of the field emission from closed and open tip carbon nanotube arrays fabricated on anodic aluminum oxide films. J Appl Phys 2004; 96(9):5234–8

[44] Min Qian, Tao Feng*, KaiWang, Hui Ding, Yiwei Chen, Zhuo Sun，A comparative study of field emission properties of carbon nanotube films prepared by vacuum filtration and screen-printing。Applied Surface Science 256 (2010) 4642–4646.

[45] Rujia Zou, Guannan Zou , Chunrui Wan, Shaolin Xue, Jian Liu , Guangping Ren , Improving the emission characteristics of a carbon nanotube film in NaCl electrolyte. Microelectronics Journal 40 (2009) 115– 119.

[46] Uh HS, Ko SW, Lee JD. Growth and field emission properties of carbon nanotubes on rapid thermal annealed Ni catalyst using PECVD. Diam Relat Mater2005; 14(7): 850-854

[47] Wang SC, Huang BC. Field emission properties of Ag/SiO2/carbon nanotube films by pulsed voltage co-electrophoretic deposition.Thin solid films2008; 26(11):436–9

[48] Fang-HsingWang, Tzu-Ching Lina,b, Shien-Der Tzeng, Field emission properties of carbon nanotube cathodes produced using composite plating Applied Surface Science 256 (2010) 7600–7605

[49] Kai Wang, Hui Ding, Yiwei Chen, Qiong Li, Zhuo Sun, Field emission of carbon nanotube films fabricated by vacuum filtration Min Qian, Tao Feng. Physica E 43 (2010) 462–465

[50] Chen Z, Engelsen D, Bachmann P K, Elsbergen V, Koehler I, Merikhi et al. High emission current density microwave-plasma-grown carbon nanotube arrays by postdepositional radio-frequency oxygen plasma treatment.Appl.Phys.Lett2005; 87(24): 3104-87

[51] Hahn J, Jung SM, Jung HY, Heo SB, Shin JH, Suh JS. Fabrication of clean carbon nanotube field emitters . Appl.Phys.Lett2006; 88(11): 3101-76

[52] Uh HS, Ko SW, Lee JD. Growth and field emission properties of carbon nanotubes on rapid thermal annealed Ni catalyst using PECVD. Diam Relat Mater2005; 14(7): 850-854

[53] Lee HJ, Lee YD, Cho WS, Ju BK, Lee YH, Han JH, et al. Field-emission enhancement from change of printed carbon nanotube morphology by an elastomer. Appl.Phys.Lett2005; 14(3): 850-854

[54] Jung MS, Ko YK, Jung DH, Choi DH, Jung HT, Heo JN et al. Electrical and field-emission properties of chemically anchored single-walled carbon nanotube patterns. Appl.Phys.Lett 2005; 87(1): 3114-80

[55] Amaratunga GAJ, Silva SRP. Nitrogen containing hydrogenated amorphous carbon for thin-film field emission cathodes.Appl.Phys.Lett2005; 68(18): 2529-7

[56] Xu X, Brandes GR. A method for fabricating large-area, patterned, carbon nanotube field emitters. Appl.Phys.Lett1999; 74(17): 2529-2

[57] ZHANGJ H, CHANYC, Research on the Contact Resistance, Reliability and Degradation Mechanisms of Anisotropically Conductive Film Interconnection for Flip-chip-on-flex Applications [J]. Journal of Electronic Materials, 2003, 32 (4) : 228~234.

[58] K.-C. Liao, C.-C. Chang, Applications of damage models to durability investigations for electronic connectors. Materials & Design, Volume 30, Issue 1, January 2009, Pages 194-199

[59] J. Das, S. M. Sivakumar, An evaluation of multiaxial fatigue life assessment methods for engineering components .International Journal of Pressure Vessels and Piping,Volume 76, Issue 10,August 1999, Pages 741-746

[60] Tadeusz Hejwowski, Erosive and abrasive wear resistance of overlay coatings. Vacuum,Volume 83, Issue 1, 4 September 2008, Pages 166-170 Chung, I.T. Han, A.Y. Cao, X.F. Zhang, X. Xiao, M.Q. Ding, D.M. Zhuang, C.L. Xu, B.Q. Wei, J. Liang, D.H. Wu, Materials Letters, 51, 2001,371–374

[61] E.Bousser, M.Benkahoul,L. Martinu, J.E. Klemberg-Sapieha, Effect of microstructure on the erosion resistance of Cr–Si–N coatings Surface and Coatings Technology.In Press, Corrected Proof,Available online 13 August 2008

[62] Phaedon Avouris, Carbon nanotube electronics. Chemical Physics, Volume 281, Issues 2-3, 1 August 2002, Pages 429-445

[63] R.C. Batra, W. Jiang, Analytical solution of the contact problem of a rigid indenter and an anisotropic linear elastic layer. International Journal of Solids and Structures, Volume 45, Issues 22-23,November 2008, Pages 5814-5830

[64] W. Wayne Chen, Q. Jane Wang, A numerical model for the point contact of dissimilar materials considering tangential tractions Mechanics of Materials,Volume 40, Issue 11,November 2008, Pages 936-948

[65] Riaz A. Mufti, Adrian Jefferies, Novel method of measuring tappet rotation and the effect of lubricant rheology. Tribology International,Volume 41, Issue 11, November 2008, Pages 1039-1048

[66] Xiaohong Yang, Shuhua Liang, Xianhui Wang, Peng Xiao, Zhikang Fan, Effect of WC and CeO2 on microstructure and properties of W–Cu electrical contact material. Journal of Refractory Metals & Hard Materials 28 (2010) 305–311

[67] Pierre-Marie Geffroy, Thierry Chartier, Jean-François Silvain, Preparation by tape casting and hot pressing of copper carbon composites films. Journal of the European Ceramic Society, Volume 27, Issue 1, 2007, Pages 291-299

[68] Korb, G., Buchgrader, W. and Schubert, T., Thermophysical properties and microstructure of short carbon fibre reinforced Cu-matrix composites made by electroless copper coating or powder metallurgical route respectively, IEEE/CPMT Berlin, Int'l Electronics Manufacturing Technology Symposium,27–28 April, 1998

[69] Praksan, K., Palaniappan, S. and Seshan, S, Thermal expansion characteristics of cast Cu based metal matrix composites. Composites Part A, 1997,28, 1019–1022.

[70] Kor´ab, J., Stef´anik, P., Kaveck´y, S., Sebo, P. and Korb, G., Thermal expansion of cross-ply and woven carbon fibre-copper matrix composites. Composites Part A, 2002, 33, 133–136.

[71] Huiqing Wu, Guifu Ding, Yuchao Wang, Ying Cao, Hong Wang, Chunsheng Yang, Composite Electrodeposition of Zinc and Carbon Nanotubes, IEEE Review On Advances In Micro/Nano And Molecular System (2006) Vol. 1, 211-212

[72] R.H.Baughman,A.A.Zakhidov,W.A.deHeer,Carbon nanotubes:the route toward application.Science,2002,vol.

297 (2),pp.787-792

[73] O. Hjortstam, P. Isberg ,S. S Oderholm ,H. Dai,Can we achieve ultra-low resistivityin carbon nanotube-based metal composites?Appl.Phys.A 78,1175-1179(2004)

[74] O.Chauvet,J.M.Benoit,B.Corraze,Electrical,magneto-transportandlocalization of charge carriers in nanocomposites based on carbon nanotubes.Carbon, Volume 42, Issues 5-6,2004, Pages 949-952

[75] Wu JF, Wyse M, McClain D, Thomas N, Jun J. Fabrication and Field Emission Properties of Triode-Type Carbon Nanotube Emitter Arrays. Nano Lett 2009; 9 (2): 595-600

[76] Nguyen VQ, Nguyen DH, Wan JY, Cho YS, Gyu SC, Kim DJ. The use of anodic aluminium oxide templates for triode-type carbon nanotube field emission structures toward mass-production technology. Nanotechnology2006; 17 (5):2156–2160

[77] Hahn J, Jung SM, Jung HY, Heo SB, Shin JH, Suh JS. Fabrication of clean carbon nanotube field emitters.Appl.Phys.Lett2006; 88(11): 3101-76

[78] Nguyen VQ, Nguyen DH, An MC, Cho YS, Kim DJ. A high-performance triode-type carbon nanotube field emitter for mass production. Nanotechnology2007; 18 (6): 345–361

[79] Nguyen VQ, Nguyen DH, An MC, Cho YS, Kim DJ. A high-performance triode-type carbon nanotube field emitter for mass production. Nanotechnology2007; 18 (6): 345-361

[80] Pirio G, Legagneux P, Pribat D, Teo BK, Chhowalla M, Amaratunga G A J, et al. Fabrication and electrical characteristics of carbon nanotube field emission

microcathodes with an integrated gate electrode. Nanotechnology2002; 13 (4): 143-147

[81] Hu WC, Yuan LM, Chen Z, Gong DW, Saito K. Fabrication and Characterization of Vertically Aligned Carbon Nanotubes on Silicon Substrates Using Porous Alumina Nanotemplates. J. Nanosci. and Nanotechnol 2002; 2(7): 203-207

[82] Jang Y T, Choi C H, Ju B K, Ahn J H , Lee Y H .Suppression of leakage current via formation of a sidewall protector in the microgated carbon nanotube emitter. Nanotechnology 2003; 14 (5):14-497

[83] Uh H S. Low Turn-On Voltage Field Emission Triodes with Selectively Grown Carbon Nanotube Emitters. J. Korean Phys Soc 2004; 45(5):1343 -1343

[84] Xu X, Brandes GR. A method for fabricating large-area, patterned, carbon nanotube field emitters. Appl.Phys.Lett1999; 74(17): 2529-2

[85] Wan JY, Cho YS, Choi GS, Do J. Patterned carbon nanotube field emitter using the regular array of an anodic aluminum oxide template. Nanotechnology 2005; 16 (5): 291–295

Carbon Nanotubes - From Research to Applications

Edited by Dr. Stefano Bianco

ISBN 978-953-307-500-6

Hard cover, 358 pages

Publisher InTech

Published online 20, July, 2011

Published in print edition July, 2011

Since their discovery in 1991, carbon nanotubes have been considered as one of the most promising materials for a wide range of applications, in virtue of their outstanding properties. During the last two decades, both single-walled and multi-walled CNTs probably represented the hottest research topic concerning materials science, equally from a fundamental and from an applicative point of view. There is a prevailing opinion among the research community that CNTs are now ready for application in everyday world. This book provides an (obviously not exhaustive) overview on some of the amazing possible applications of CNT-based materials in the near future.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Yan Wang, Min Deng, Xuemei Cui, Huiqing Wu, Lida Zhu and Guifu Ding (2011). Research and Application of CNT Composite Electroplating, Carbon Nanotubes - From Research to Applications, Dr. Stefano Bianco (Ed.), ISBN: 978-953-307-500-6, InTech, Available from: http://www.intechopen.com/books/carbon-nanotubes-from-research-to-applications/research-and-application-of-cnt-composite-electroplating

INTECH
open science | open minds