Field Emission from Single-Walled Carbon Nanotubes Aligned on a Gold Plate using Self-Assembly Monolayer

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Abstract

Field emission from single-walled carbon nanotubes (SWNTs) aligned on a patterned gold surface is reported. The SWNTs emitters were prepared at room temperature by a self-assembly monolayer technique. SWNTs were cut into sub-micron length by sonication in an acidic solution. Cut SWNTs were attached on the gold surface by the reaction between the thiol groups and the gold surface. The field emission measurement showed that the turn-on field was 4.8 V/μm at the emission current density of 10 μA/cm^2. The current density was 0.5 mA/cm^2 at 6.6 V/μm. This approach provides a novel route for fabricating CNT-based field emission displays.

1. Introduction

Carbon nanotubes (CNTs) have drawn much attention because of their unique physical properties and wide variety of applications [1,2]. One potential application is the field emitter tip [3,4]. The advantages of using CNTs as field emitter tips include a small radius of curvature, a high aspect ratio, high chemical inertness and mechanical strength. Although a variety of ideas have been proposed as CNT-based field emission displays (CNT-FED), few devices have actually been produced [5]. There are still problems to be solved to fabricate a practical CNT-FED device. One of the outstanding problems is the high processing temperature, which significantly limits the choice of substrate materials and fabrication processes. In this context, the establishment of a reliable method to fabricate CNT-based FED at low temperature is considered to be a breakthrough in the production of commercial CNT-FED devices. Recently, several investigators reported that SWNTs could be attached on a substrate using the self-assembly monolayer (SAM) of thiol-based chemicals on a gold surface [6,7]. However, there has been no report for the application of these SWNTs to a field emitter. In this letter, the field emission properties of SWNTs attached by SAM on a patterned gold surface, which is highly desirable to practical devices, are investigated. Our work shows the potential for CNT-based field emission arrays to be fabricated at room temperature. This method removes a major limitation for the choice of substrate materials and fabrication processes. It also allows the possibility of a flexible display based on a CNT field emitter.

2. Experimental

Purified SWNTs were supplied by Iljin Nanotech Co.. First, SWNT bundles were chopped, as described previously [8]. 0.1 g of purified SWNTs were dissolved in a 120 ml mixture of 98 % H$_2$SO$_4$ and 70 % HNO$_3$ (volumetric ratio - 3:1). The beaker containing this solution was partially dipped into the sonicator. Ultrasonic waves with a frequency of 40 kHz were applied to the solution at 40 °C for 8 h. After sonication, the solution was diluted with deionized water to 500 ml and laid aside overnight. After supernatant liquid had been poured out, 50 ml of deionized water was added to the solution and kept for one day. The floating water was again decanted and 25 ml of deionized water was added to the solution. Then, the chopped SWNTs in the remaining solution were filtered with a track-etched membrane made of polycarbonate. After filtration, the membrane was washed with deionized water several times to remove the residual acid. The membrane was dipped into a basic solution of pH 11. SWNTs were dispersed in this basic solution by sonication for a few seconds.

The emitter was constructed on a p-type Si (110) wafer. An oxide layer of SiO$_2$ with 300 nm thickness was formed by thermal oxidation. A Cr layer with a thickness of 20 nm was first sputtered, then a gold layer with the thickness of 30 nm followed. This gold layer was lithographically patterned into circles with 140 μm diameter. The circles were located at even intervals of 200 μm. The number of circles was 2500 (an array of 50 by 50) and the circles were regularly spread on the area of 1 cm by 1 cm. After patterning, the total area of gold surfaces was 0.385 cm^2. Fig. 1 shows the optical microscopy image and the schematic diagram of the substrate after the patterning of the gold.

(a)

Au ——
Cr ——

(b)

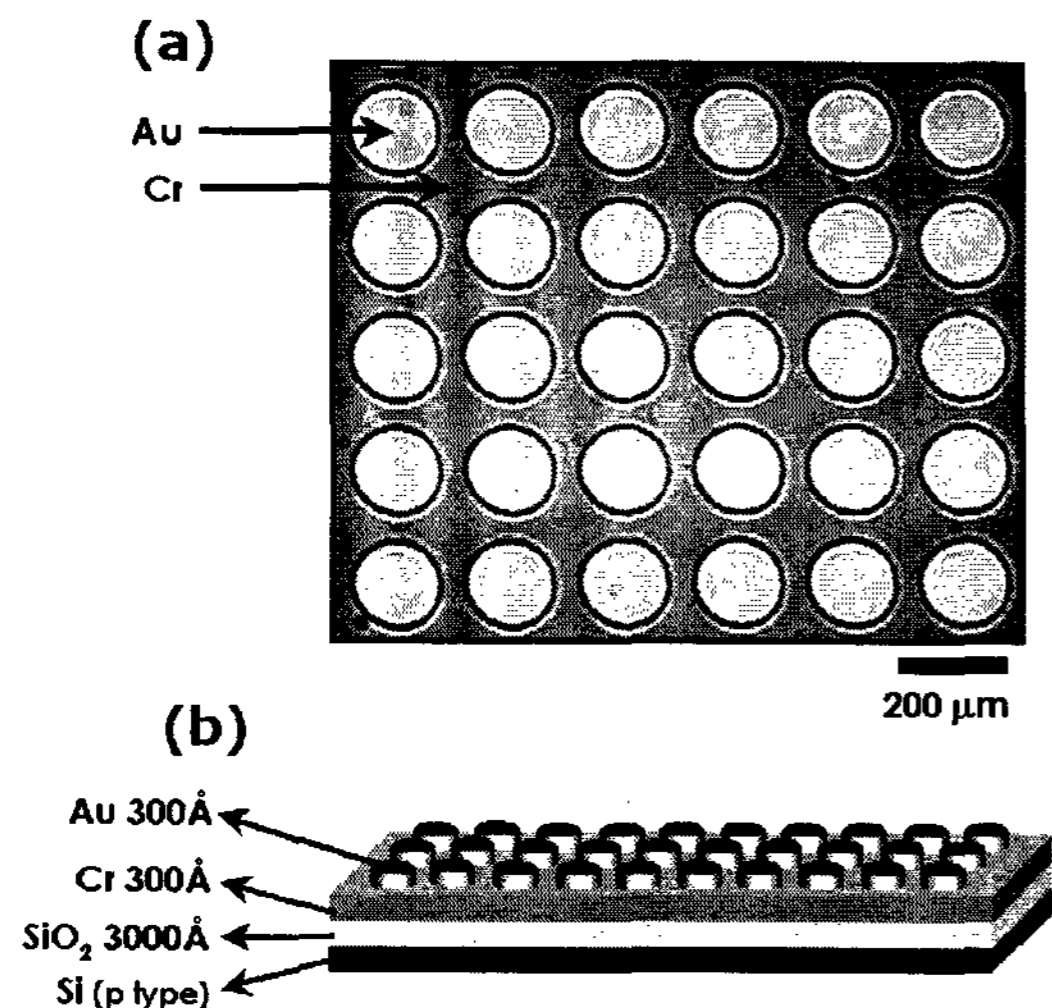Au 300Å ◄
Cr 300Å ◄
SiO₂ 3000Å ◄
Si (p type) ◄

200 µm

Fig. 1 Images of the substrate after patterning of gold.

(a) Optical microscopy image of the substrate patterned by photolithographic technique (top view), (b) Schematic diagram of the substrate

To remove organic matter from the gold surface after patterning, patterned gold substrate was dipped into a solution of 51 % H_2SO_4 and 30 % H_2O_2 (volumetric ratio - 3:1) for 5 min at 90°C. After cleaning, residual acidic solution on the substrate was washed with deionized water and then with ethanol. The cleaned substrate was immersed into a 1mM ethanol solution of 11-mercaptoundecanoic acid [HS-(CH₂)₁₀-COOH] for 4 h to form the SAM on the gold surface. Then, the substrate was rinsed with ethanol and deionized water, then dried with a stream of inert gas. The thiolized gold substrate was dipped into a saturated solution of $ZnSO_4$ for 5 min. The gold substrate was then washed with deionized water and dried with a stream of inert gas. Finally, the substrate was dipped into the basic solution (pH 11) containing SWNTs for 1 h.

To confirm the SWNTs attached to the gold surface, atomic force microscopy (AFM, DME, Rasterscope 5000) with a non-contact mode and Raman Spectroscope (Renishaw, Raman System 3000) were used. The field emission current from the SWNTs attached to the patterned gold substrate was measured as follows. The Cr layer located between the Au and silicon oxide layer was employed as the cathode. A glass coated with an indium-tin-oxide (ITO) layer was used as the anode. The space from the gold surface to the anode was 270 um. Measurement of the field emission was performed at a pressure of 5×10^{-6} torr.

3. Results and discussion

3.1. Reactions between gold surface and SWNTs

Three different reactions are involved in the attachment of SWNTs on a gold surface. One is the reaction between the gold surface and the thiol group in 11-mercaptoundecanoic acid. Another is the reaction between the carboxyl group at the end of 11-mercaptoundecanoic acid and the Zn ion in the $ZnSO_4$ saturated solution. The last is the reaction between the carboxyl groups at the end of a SWNT and the Zn ion attached to the 11-mercaptoundecanoic acid.

The formation of the chemical bonds between Zn and SWNTs is affected by the pH of the solution. During the chopping of SWNTs in acidic conditions, edge sites of the graphene layers of SWNTs were functionalized with carboxyl groups. In the reaction between Zn and SWNTs, some of the bonds between Zn and the oxygen of the carboxyl group at the end of 11-mercaptoundecanoic acid or the hydroxyl group of the aqueous solution were broken, and the Zn connected with the carboxyl groups of SWNTs. In Fig 2, the change in the carboxyl groups at the end of SWNTs with different pH is schematically shown. At low pH, the carboxyl groups at the end of SWNTs exist as a form of COOH. On the other hand, the carboxyl groups have a form of COO⁻ at high pH. Zn linked with 11-mercaptoundecanoic acid was connected to the hydroxyl groups in the basic solution. In this atmosphere, the bonds between Zn and hydroxyl groups are readily broken and new bonds between Zn and carboxyl groups of SWNTs form. Therefore, more SWNTs are expected to be attached (thus, more stable emission) in a solution of high pH.
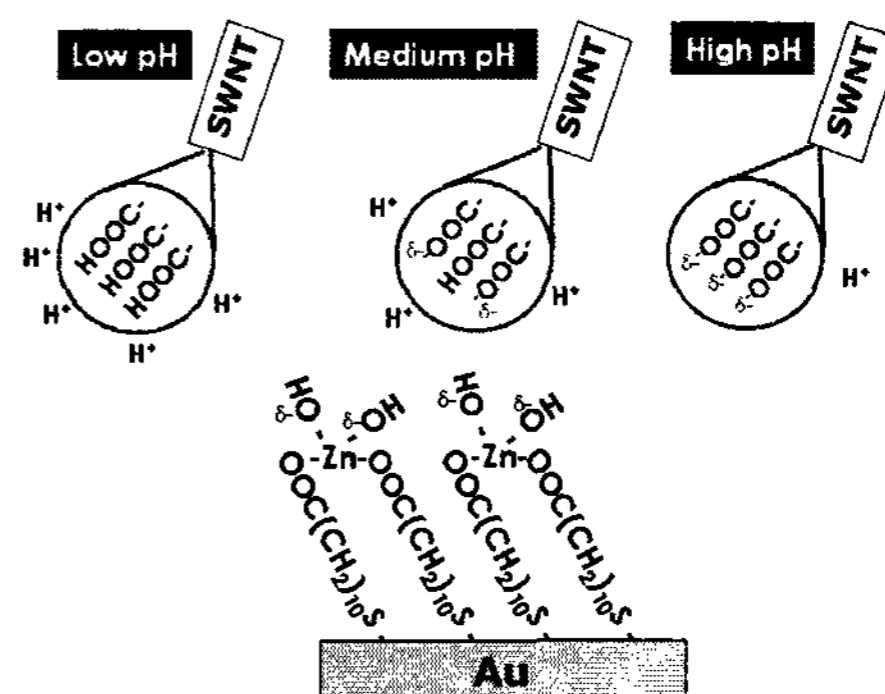

Fig. 2. Effect of pH on the functional groups at the end of SWNTs

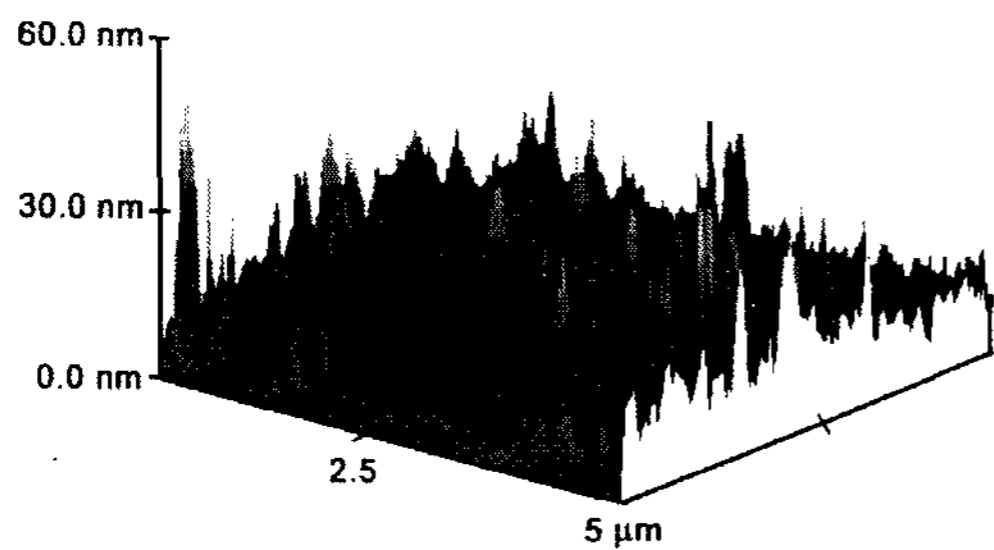## 3.2. Characterization of the gold substrate after SWNT attachment

Fig. 3. AFM image of SWNTs attached on the gold surface

Fig. 3 is an AFM image of the attached SWNTs on the gold surface. Sharp tip-like features are interpreted as the SWNTs standing perpendicularly on the gold surface. The aspect ratio is large, as is obvious in this figure, so that they are appropriate as field emitters. It should be noted that the diameters of peaks in Fig. 3 are much larger than the diameter of individual SWNTs. This is mainly because the diameter of the AFM tip is much larger than both the diameter of a SWNT and the distance between standing SWNTs. There is also a possibility that some SWNT bundles are not dispersed into individual SWNTs even after sonication.
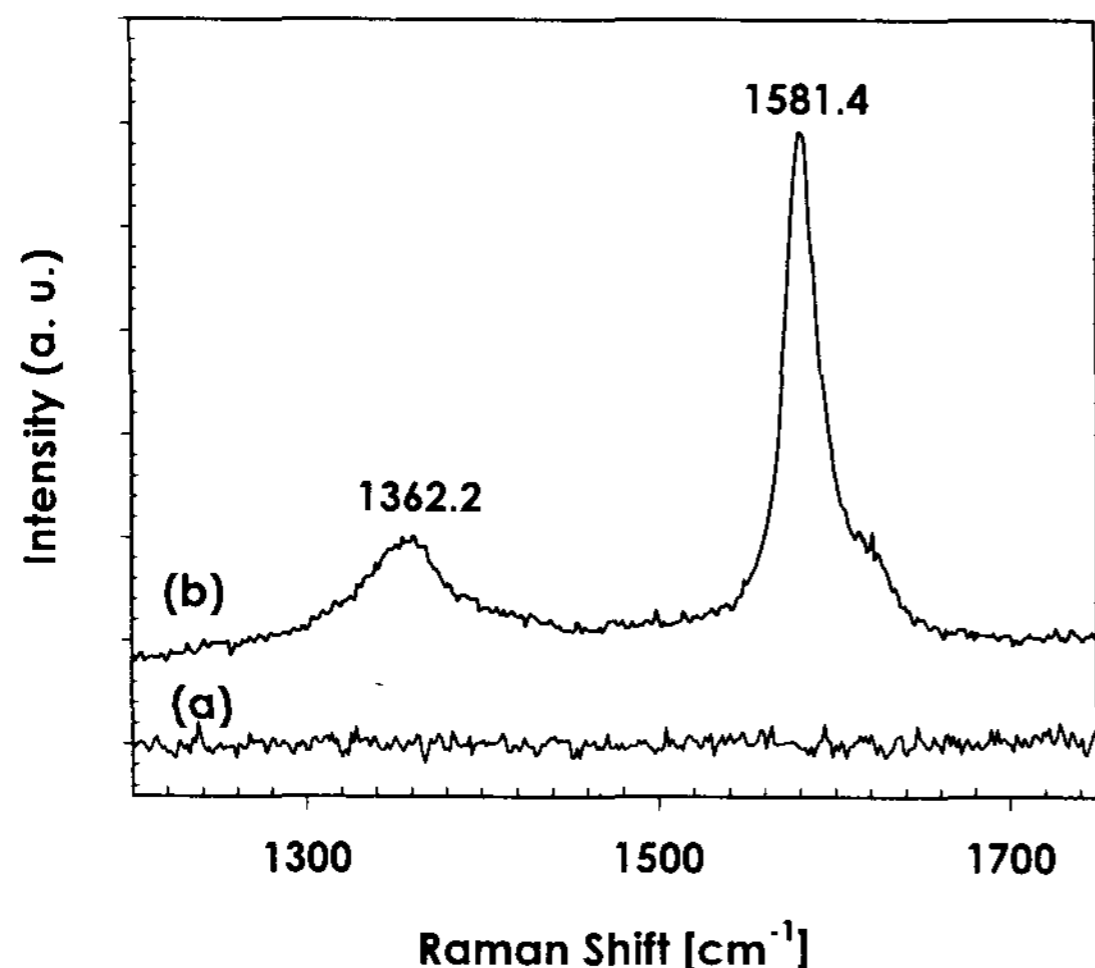

Fig. 4. Raman Spectra of the gold surfaces on the Si wafer.

(a) Raman spectrum of the bare gold surface, (b) Raman spectrum of the gold surface after the attachment of SWNTs

Fig. 4 is the Raman spectra for the gold surfaces before and after the attachment of SWNTs. The wavelength and size of an incident Ar-ion beam were 514.5 nm and 2

μm, respectively. No distinctive peak was observed in the spectrum of the bare gold surface. On the other hand, the spectrum of dipped Si wafer clearly showed two characteristic peaks of CNTs, verifying the attachment of SWNTs on the gold surface. A single crystal of graphite can be certified by two E_{2g} modes, which appear in the Raman band at 1581 cm^{-1} and in a low-frequency neutron scattering at 47 cm^{-1} [9]. The peak at 1581 cm^{-1} is assigned to the G-band, which is a feature of graphite crystal. The D-band at 1362 cm-1 is due to the defects of the graphene layer and tube ends.

3.3. Field Emission Properties of SWNTs aligned on the gold surface

Emission current from the SWNTs aligned on the gold surface appears in Fig. 5. This current-voltage (I-V) curve was obtained after sweeping the voltage from 30 V to 1800 V several times. The emission current density was 0.5 mA at 6.6 V/um, which is a rather large value considering the distance between the cathode and the anode. The E_{to}(turn-on field) at the field emission current density of 10 $\mu A/cm^2$ was 4.8 V/μm. This value is higher than those previously reported with SWNTs emitters [10].
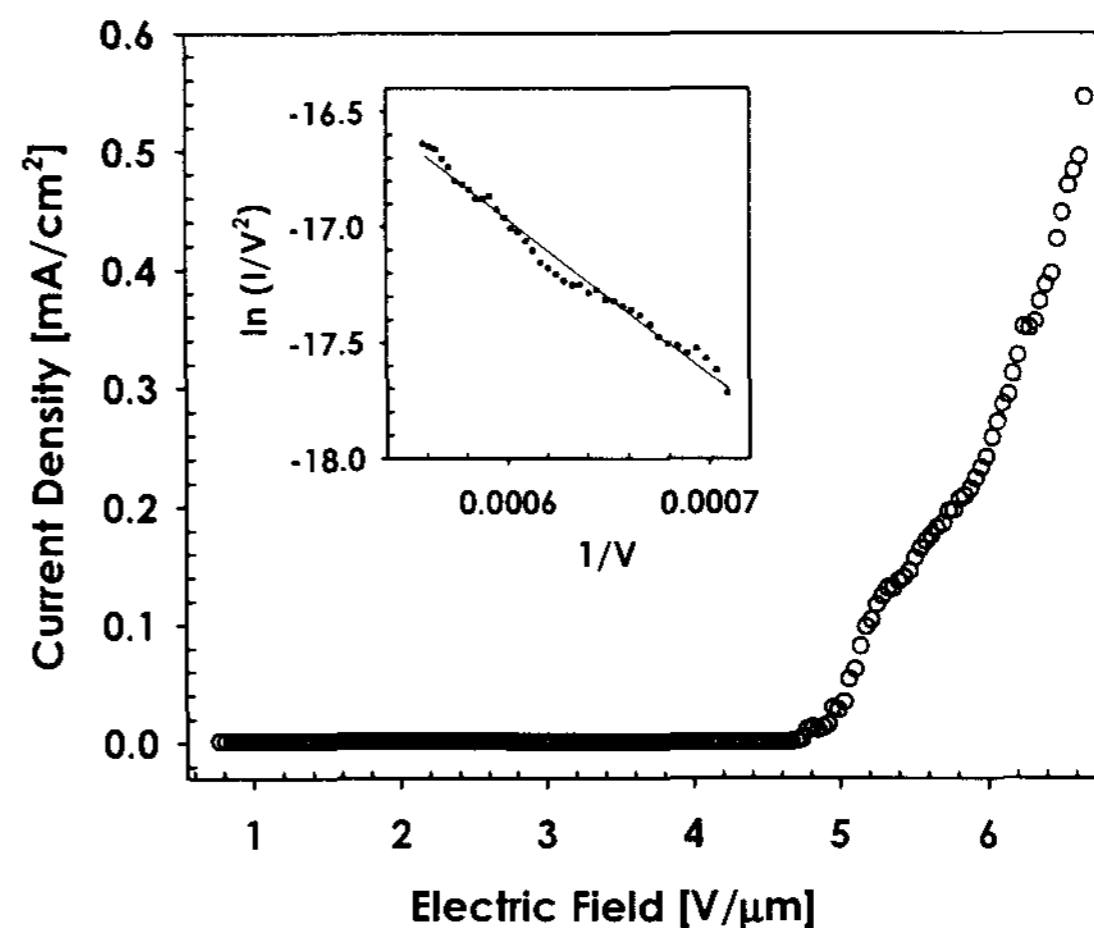

Fig. 5. Emission current density vs. electric field for the SWNTs emitter. (Inset) Fowler- Nordheim plot.

The structure of our emitter resembles the metal-insulator-metal emitter system. The gold layer and SWNTs are located on the side of cathode and of vacuum, respectively. The insulating layer including the SAM of 11-mercaptoundecanoic acid lies between these two layers. Once an electric field is applied to the sample, the energy band is inclined opposite to the direction of the field and electrons are transported from gold surface to the SWNTs via insulating SAM. Later, these electrons are emitted from the SWNTs to the vacuum. Tunneling of electrons is affected by dc conductance of the insulating layer, which

decreases exponentially with the thickness according to the Bethe's equation [11]. A resistive layer beneath the emitter tips is beneficial to a stable emission at the cost of high emission current and low E_{to} [12]. As the thickness of SAM is reduced, the E_{to} might have a lower value and the emission current increase. Therefore, the field emission property can be controlled by the thickness of the SAM – the length of alkyl group in the thiol-contained chemical. In a specific system of CNT-FED, there is an optimal length of SAM with a low E_{to} and a uniform field emission of electrons. Extensive research would be needed to clearly elucidate the relationship of the nature of the field emission with the thickness of insulator located between cathode and field emitters.

The Fowler-Nordheim (FN) plot was employed to analyze the field emission current [13]. As shown in the inset of Fig. 5, the I-V curve agrees with the FN model, confirming that the emission current in Fig. 5 is indeed from the cold electron emission. We calculated the field enhancement factor β from the FN plot. The slope of the linear correlation is given by $B\phi^{3/2}d/\beta$, with $B = 6.87 \times 10^9$ [V eV$^{-3/2}$m^{-1}], ϕ the work function and d the distance between the gold plate and the anode [14]. The work function of SWNTs of the sample was assumed to be that of graphite (= 5 eV). The field enhancement factor, β estimated from the slope of the FN plot is about 3000. This value agrees with those reported previously by other groups [15].

4. Conclusion

A Field emitter composed of SWNTs attached onto a gold surface using the SAM technique can be fabricated using well-known sulfur chemistry. This emitter is fully functional with a high field enhancement factor. This approach shows the potential for CNT-based field emission array to be fabricated at room temperature. It removes a major limitation for the choice of substrate materials and fabrication processes. It also allows the possibility of a flexible display based on a CNT field emitter.

5. References

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